NATIONAL BUREAU OF STANDARDS REPORT

8186

Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds

(Supplement to NBS Reports 6297, 6484, 6645, 6928, 7093,
7192, 7437, 7587, 7796, and 8033)

1 January 1964

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

0300-11-03419
0302-11-03426
0307-11-03471
0505-11-05496
0903-11-09430
1302-11-13423
1501-11-15513
1504-11-15442

1 January 1964

NBS REPORT

8186

Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds

(Supplement to NBS Reports 6297, 6484, 6645, 6928, 7093,
7192, 7437, 7587, 7796, and 8033)

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

Reference: ARPA Order No. 20

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

ABSTRACT

This is the eleventh semiannual report on the current experimental, theoretical, and evaluative program, at the National Bureau of Standards, on the thermodynamic properties of selected light-element compounds of primary interest in high-temperature research. Presented in detail are the results of new experimental measurements at the Bureau on a number of such compounds, a coverage of recent literature in several areas, and examination of certain data for thermodynamic consistency.

New NBS heat measurements on solids and liquids have yielded the standard heat of formation of $A\ell_4C_3$, as well as the heat capacity of $BeA\ell_2O_4$ (0°-1200°K), Li_2BeF_4 (300°-900°K), and $Li_3A\ell F_6$ (300°-1000°K). Three special mechanical devices resistant at high temperatures to fluorides such as BeF_2 were developed and are described. The rates of evaporation of liquid $A\ell_2O_3$ were measured, and, presumably owing to chemical interaction, were found to be four times as great in water vapor as in argon under comparable conditions. Revised molecular constants of the $A\ell_2O$ molecule based on unpublished matrix spectroscopy are given. A new gas species Be_2OF_2 was detected mass-spectrometrically; its molecular constants were estimated, and led to a value for its heat of formation agreeing within a few kcal/mole with that derived from the temperature variation of its equilibrium data (1550°-2150°K).

A comprehensive bibliography of the past year's publications on the heats of formation of fluorine compounds of selected elements is given. Also given are brief resumes of recent publications on solid oxides and hydroxides of certain light metals, on a comprehensive correlation of the high-temperature thermodynamic properties of solid unsaturated zirconium hydrides, and on new spectroscopic and equilibrium studies of three gaseous oxides of lithium. Smooth adjusted values of low- and high-temperature heat capacities are given for eight alkali halides and borohydrides based on the published data, and for solid and liquid BeF_2 based on recent unpublished data determined by the U. S. Bureau of Mines. The latter data are important in the establishment of a thermodynamic inconsistency for BeF_2 which ought to be resolved. The recent precise NBS thermal data on $A\ell_4C_3$ (heat-of-reaction and heat-capacity) permitted calculation of the equilibrium constants of several high-temperature reactions, and criticism of the published directly measured equilibria. Described briefly is a new program being developed at NBS, under sponsorship of the U. S. Air Force, for computing real-gas thermodynamic properties of hydrogen up to high pressures and elevated temperatures.

Twenty-four new tables of thermodynamic functions, covering nearly all of the substances enumerated above, are given.

Thomas B. Douglas

Thomas B. Douglas
Project Leader

Chas W Beckett

Charles W. Beckett
Assistant Division Chief for Thermodynamics
Heat Division

TABLE OF CONTENTS

Page

Abstract

Chap. 1. THE HEAT OF COMBUSTION AND HEAT OF FORMATION OF ALUMINUM CARBIDE
(by R. C. King and G. T. Armstrong) 1

1.0 Introduction 1
2.0 Experimental Procedure 4
  2.1 Materials 4
    Table 1. Analyses of $A\ell_4C_3$ Sample . . 5
  2.2 Combustion Experiments 6
    Table 2. Calibration Experiments . . 8
  2.3 Examination of the Products of the Combustion 8
    Fig. 1. Train for Analyses of Bomb Gases 9
  2.4 Identification of Solid Product . . . 11
    Table 3. X-ray Data for Finely Divided Aluminum Oxide Formed 12
3.0 Results 13
  3.1 Heat Measurements 13
    Table 4. Heat Measurements on Aluminum Carbide Samples 13
    Table 5. Corrections to Combustion Data on Aluminum Carbide 13
    Table 6. Heat of Combustion of $A\ell_4C_3$. 15
  3.2 Heat of Formation of Aluminum Carbide . 16
Acknowledgements 16
    Fig. 2. Heat of Combustion of $A\ell_4C_3$ as a Function of Fraction δ-$A\ell_2O_3$ . . 17
4. References 18

Chap. 2. HEAT CAPACITY AND ENTHALPY MEASUREMENTS ON ALUMINUM CARBIDE ($A\ell_4C_3$) FROM 15° to 1173°K. THERMODYNAMIC PROPERTIES FROM 0° to 2000°K
(by George T. Furukawa, Thomas B. Douglas, William G. Saba, and Andrew C. Victor) . . 21

Abstract 21
1. Introduction 21
2. Sample 22
3. Low-Temperature Calorimetry 23
  3.1 Apparatus and Method 23
  3.2 Results 24

TABLE OF CONTENTS (Continued)

Page

4. High-Temperature Relative-Enthalpy Measurements 26
 4.1 Method and Apparatus 26
 4.2 Results 26
5. Correlation of the Low and High Temperature Heat Data with the Vapor-Pressure Data . 27
6. Acknowledgements 32
7. References 33
 Table 1. Spectrochemical Analysis of the Sample of Al_4C_3 35
 Table 2. Chemical Analyses of the Sample of Al_4C_3 36
 Table 3. Observed Heat Capacity of Aluminum Carbide 37
 Table 4. High-Temperature Enthalpy Measurements on Al_4C_3 38
 Table 5. Comparison of the Entropy of Al_4C_3 at 1800°K Calculated from Vapor-Pressure Data . . 39
 Table 6. Thermodynamic Functions for Al_4C_3 40
 Table 7. Thermodynamics of the Dissociation of Al_4C_3 42
 Table 8. Thermodynamics of the Reaction of AlN with Carbon 43
 Table 9. Thermodynamics of the Reaction of Al_2O_3 with Carbon 44
 Fig. 1. Deviations of the Heat-Capacity Measurements on Sample Plus Calorimeter Vessel 45
 Fig. 2. Deviations of the Heat-Capacity Measurements on the Empty Vessel 46
 Fig. 3. Observed Values of the Molal Heat Capacity of Al_4C_3 . . . 47
 Fig. 4. Comparison of the Final Selected Values of Heat Capacity of Al_4C_3 with the Observed Low-Temperature and Smoothed High-Temperature Values 48
 Fig. 5. Comparison of Vapor Pressures Calculated from Heat-of-Formation and Thermodynamic Data with Published Values Obtained in High-Temperature Equilibrium Measurements 49

TABLE OF CONTENTS (Continued)

Page

Chap. 3. BERYLLIUM ALUMINATE (CHRYSOBERYL), $BeO \cdot Al_2O_3$. MEASUREMENTS OF THE HEAT CAPACITY FROM 16° to 380°K (by George T. Furukawa and William G. Saba) 50

1. Introduction 50
2. Sample 50
    Table 1. Spectrochemical Analysis of the $BeO \cdot Al_2O_3$ Sample 51
    Table 2. Chemical Analysis of the $BeO \cdot Al_2O_3$ Samples 52
3. Apparatus and Method 52
4. Heat-Capacity Measurements and Results . . 53
    Fig. 1. Deviations of the Heat Capacity Measurements on the Calorimeter Vessel Plus $BeO \cdot Al_2O_3$ Sample 54
    Fig. 2. Deviations of the Heat Capacity Measurements on the Empty Calorimeter Vessel Used with the $BeO \cdot Al_2O_3$ 55
    Table 3. Observed Heat Capacity of $BeO \cdot Al_2O_3$ 56
    Fig. 3. Observed Values of the Molal Heat Capacity of $BeO \cdot Al_2O_3$. 57
    Table 4. Thermodynamic Functions for $BeO \cdot Al_2O_3$ 58
5. Thermodynamic Functions 59
    Fig. 4. Comparison of the Heat Capacity of $BeO \cdot Al_2O_3$ with that of an Equimolar Mixture of BeO and Al_2O_3 60
6. References 61

Chap. 4. $BeO \cdot Al_2O_3$: MEASUREMENTS AT THE NATIONAL BUREAU OF STANDARDS OF ITS RELATIVE ENTHALPY FROM 273° to 1173°K (by Thomas B. Douglas and William H. Payne) . 62

    Table 1. Enthalpy Measurements on $BeO \cdot Al_2O_3$ 64
    Table 2. Deviations of the Smoothed High-Temperature Heat Capacity of $BeO \cdot Al_2O_3$ from Additivity . 66

References 67

TABLE OF CONTENTS (Continued)

Page

Chap. 5. SOLID $Li_3A\ell F_6$: THERMODYNAMIC FUNCTIONS FROM 298° TO 1000°K BASED ON RECENT MEASUREMENTS OF ITS RELATIVE ENTHALPY AT THE NATIONAL BUREAU OF STANDARDS
(by Thomas B. Douglas and John E. Neufer) . . 68

Table 1. Chemical Analysis of the Dried Sample 69
Table 2. Enthalpy Measurements on $Li_3A\ell F_6$(solid) 71
Table 3. Deviation from Additivity of the Heat Capacity of Solid $Li_3A\ell F_6$ 74

References 74

Chap. 6. Li_2BeF_4: RECENT MEASUREMENTS AT THE NATIONAL BUREAU OF STANDARDS OF ITS HIGH-TEMPERATURE ENTHALPY; RESULTING THERMODYNAMIC FUNCTIONS
(by Thomas B. Douglas and William H. Payne) 75

Introduction 75
Preparation of the Sample and Choice of Its Container 75
Composition of the Sample 75
Table 1. Chemical Analysis of the Sample 76
Calorimetric Method 76
Table 2. Assumed Chemical Composition of the Sample . . . 77
Data Obtained 77
Corrections for Impurities; Smoothed Results 77
Table 3. Enthalpy Measurements on Li_2BeF_4 78

References 82

Chap. 7. A COMPUTER PROGRAM FOR THE ESTIMATION OF THERMODYNAMIC PROPERTIES OF MOLECULAR HYDROGEN (REAL GAS)
(by Harold W. Woolley) 83

TABLE OF CONTENTS (Continued)

Page

Chap. 8. APPARATUS DEVELOPMENTS FOR PURIFICATIONS AND ANALYSES (THERMAL) TO 1000°C
(by Augustus R. Glasgow, Jr.) 84

High-Temperature Valve 84
Fig. 1. High-Temperature Valve . . 85
Fig. 2. Ultra-High Vacuum Coupling 85
Trap for Fluorides 86
Rupture-Disc Ampoule 86
Fig. 3. Nickel-Monel Trap for Fluorides 87
Fig. 4. Rupture-Disc Ampoule . . 88

Chap. 9. THERMODYNAMIC PROPERTIES OF SOME SELECTED COMPOUNDS OF ALKALI METALS
(by G. T. Furukawa and M. L. Reilly) . . . 89

$LiBH_4$, NaF 89
NaCℓ, $NaBH_4$, KF 90
KCℓ, KBr 91
KBH_4 92
References 93

Chap. 10. HIGH-TEMPERATURE THERMODYNAMIC FUNCTIONS FOR ZIRCONIUM AND UNSATURATED ZIRCONIUM HYDRIDES
(by Thomas B. Douglas) 94

Fig. 1. Phase Diagram (Partial) of the Zr-H System . . . 95
References 96

Chap. 11. RECENT PUBLICATIONS ON OXIDES AND HYDROXIDES OF THE LIGHT METALS
(by Thomas W. Mears) 98

References 98

Chap. 12. HIGH TEMPERATURE STUDIES ON $A\ell_2O_3$
(by J. J. Diamond and A. L. Dragoo) . . . 99

I. Automatic Pyrometer 99
II. Rate of Vaporization in Argon and Water Vapor 99
Table: Results Obtained in Ar and H_2O 101
References 102

TABLE OF CONTENTS (Continued)

Page

Chap. 13. MASS SPECTROMETRIC STUDY OF THE BeO-BeF_2 SYSTEM AT HIGH TEMPERATURES (by J. Efimenko) 103

Experimental 103
Results 104
Discussion 104
References 106
Fig. 1. Formation of $Be_2OF_2(g)$ between 1300° and 1600°C . . 107
Fig. 2. Formation of $Be_2OF_2(g)$ between 1600° and 1900°C . . 108
Table 1. Mass Spectrometric Temperature-Intensity Data . 109
Table 2. Mass Spectrometric Temperature-Intensity Data . 110
Table 3. Correction of Experimental Heat of Reaction to Absolute Zero 111
Table 4. Corrections for Free Energy Functions of BeF_2 111
Table 5. Heat of Reaction, ΔH_0^o, Using Corrected Free Energy Functions for $BeF_2(g)$ 112
Table 6. Auxiliary Data for Computations 112

Chap. 14. BERYLLIUM FLUORIDE, BeF_2: COMPARISON OF HEAT-CAPACITY AND RELATIVE-ENTHALPY DATA WITH VAPOR-PRESSURE DATA (By G. T. Furukawa and M. L. Reilly) 113

References 115
Fig. 1. Observed Molal Heat Capacity of BeF_2 (U. S. Bureau of Mines, Tuscaloosa Metallurgy Research Center) . 116
Fig. 2. Relative Enthalpy (H_T-$H_{273.15}$) of BeF_2 (U. S. Bureau of Mines, Tuscaloosa Metallurgy Research Center) 117

TABLE OF CONTENTS (Continued)

Page

Chap. 15. HIGH-TEMPERATURE MATRIX SPECTROSCOPY (by D. E. Mann) 118

1. Oxides of Lithium: Li_2O, LiO, and Li_2O_2 . 118
2. Al_2O: Aluminum Suboxide 119
3. Estimates of the Structure and Spectra of Be_2OF_2 119
4. Thermodynamic Functions 120

Chap. 16. NEW LITERATURE RELATING TO HEATS OF FORMATION OF FLUORINE COMPOUNDS OF SELECTED LIGHT ELEMENTS (by M. C. Bracken and G. T. Armstrong) . . 122

Introduction 122
Table 1. Recent Contributions to the Thermochemistry of Selected Fluorine Containing Substances . . . 124
Table 2. Some Substances for which Thermodynamic and Thermochemical Data are Given, in References [41] and [42] 135
References 136

APPENDIX A. IDEAL-GAS THERMODYNAMIC FUNCTIONS 143

Table	Formula	Temperature Range (°K)	
A-57 REVISED	Al_2O	0-6000	144
A-86	Be_2OF_2	0-6000	146
A-87	Li_2O	0-6000	148
A-88	Li_2O_2	0-6000	150

TABLE OF CONTENTS (Continued)

Page

APPENDIX B. THERMODYNAMIC FUNCTIONS FOR SOLIDS AND LIQUIDS . 153

Table	Formula	Phases	Temperature (Range (°K)	
B-46 REVISED	Zr	solid (α,β)	298.15-1200	154
B-47 REVISED	$ZrH_{0.25}$	solid ($\alpha+\delta,\alpha+\beta,\beta$)	"	154
B-48 REVISED	$ZrH_{0.50}$	solid ($\alpha+\delta,\alpha+\beta,\beta$)	"	155
B-48a	$ZrH_{0.57}$	solid ($\alpha+\delta,\beta$)	"	155
B-49 REVISED	$ZrH_{0.75}$	solid ($\alpha+\delta,\beta+\delta,\beta$)	"	156
B-50 REVISED	$ZrH_{1.00}$	solid ($\alpha+\delta,\beta+\delta,\beta$)	"	156
B-51 REVISED	$ZrH_{1.25}$	solid ($\alpha+\delta,\beta+\delta$)	"	157
A-82 ADAPTED	H_2	Ideal gas	"	157
B-58 REVISED	BeF_2	solid (Quartz 1, Quartz 2), liquid	0-1200	158
B-83 REVISED	$BeO \cdot A\ell_2O_3$	solid	0-2150	160
B-106	$Li_3A\ell F_6$	solid (α,β)	298.15-1000	162
B-107	Li_2BeF_4	solid, liquid	298.15-1500	163
B-108	$LiBH_4$	solid	0-300	164
B-109	NaF	solid, liquid	0-1900	165
B-110	$NaC\ell$	solid, liquid	0-1700	167
B-111	$NaBH_4$	solid	0-700	169
B-112	KF	solid, liquid	0-1800	171
B-113	$KC\ell$	solid, liquid	0-1500	173
B-114	KBr	solid	0-1000	175
B-115	KBH_4	solid	0-700	177

Chapter 1

THE HEAT OF COMBUSTION AND HEAT OF FORMATION OF ALUMINUM CARBIDE

by R. C. King and G. T. Armstrong

1.0 Introduction

Although several thermodynamic studies have been made on $A\ell_4C_3$, which is a very stable refractory compound, there exist very little data on the heat of formation. We have, therefore, determined the heat of combustion in oxygen (reaction 1), and have derived the heat of formation.

$$A\ell_4C_3(s) + 6O_2(g) = 2A\ell_2O_3(s) + 3CO_2(g) \qquad (1)$$

We believe that the most reliable previous study was that of Meichsner and Roth [1], who also determined the heat of combustion in oxygen by bomb calorimetry. For reaction (1) they reported $\Delta H_{293} = -1047.6 \pm 3$ kcal mole^{-1}. In a parallel series of experiments they determined the heat of combustion of aluminum, for which they reported $\Delta H_{293} = -392.4 \pm 0.4$ kcal mole^{-1}. They calculated ΔHf°_{293} $[A\ell_4C_3] = -20 \pm 3$ kcal mole^{-1}.

The heat of combustion of aluminum is very important in establishing the heat of formation of $A\ell_4C_3$ by this method, because of the presence of aluminum oxide in the products. In the work of Meichsner and Roth it is given added weight by the fact that the latter authors mixed their $A\ell_4C_3$ with aluminum powder in order to obtain complete combustion. A significant fraction of the total heat they observed was due to the combustion of the free aluminum. The value of the heat of formation of $A\ell_4C_3$ calculated from their work is therefore very sensitive to the value selected for the heat of formation of $A\ell_2O_3$.

As a result of later work on the combustion of aluminum, Roth [2] modified the calculations of Meichsner and Roth and obtained -40 kcal mole^{-1} for the heat of formation of $A\ell_4C_3$. If one assumes that the aluminum oxide in their product was corundum (α-$A\ell_2O_3$), and if a recent value for its heat of formation, -400.4 ± 0.3 kcal mole^{-1} [3], is used in recalculating their data, a value of -48.6 kcal mole^{-1} is obtained for ΔHf°_{298} $[A\ell_4C_3]$. However, because Meichsner and Roth determined the heat of combustion of aluminum under nearly the same conditions as those under which they determined the heat of combustion of aluminum carbide, it now seems to us that little can be done to improve the calculation they made in their original publication. The principal difficulty in the way of making any further refinement of their original data now seems to be the lack of any detail about the form of $A\ell_2O_3$ found in the product. They assumed the $A\ell_2O_3$ to be corundum, but mention no test of their assumption. Because of the presence of a carbonaceous promoter in their reactions, the presence of another form must now be assumed on the basis of the findings described in this paper.

Our work differs from that of Meichsner and Roth in (1) the exclusion of carbonaceous combustion aids from the reaction, (2) the absence of elemental aluminum as a combustion promoter, (3) the absence of water in the combustion bomb, (4) the unambiguous determination of the amount of reaction by measurement of the mass of CO_2 formed, and (5) the identification of the crystal forms of the solid combustion product.

Before the work of Meichsner and Roth, the heat of combustion of aluminum carbide had been measured, and the heat of formation calculated by Berthelot [4], Wöhler and Hofer [5], and Kameyama and Yoshida [6]. The values they reported for the heat of reaction (1) and the heat of formation of $A\ell_4C_3$ which we have recalculated on the basis of the recent value for $A\ell_2O_3$ were, respectively, in kcal mole^{-1}: Berthelot, -824, -258.9; Wöhler and Hofer, -825.1, -257.8; Kameyama and Yoshida, -991.8, -91.2. These measurements were all made on aluminum carbide samples of relatively low purity. Because of this their work is not considered further, although Kameyama and Yoshida used great care in documenting their measurements.

In addition to the calorimetric measurements, several high temperature equilibrium studies involving aluminum carbide have been made, from which the heat of formation can be calculated. In each case the original calculations required estimates of the values of the thermal functions used for $A\ell_4C_3$ and in some cases other compounds as well. Recent measurements of the heat capacity by Saba and Furukawa [7], and by Victor, Thurber, and Douglas [8], permit calculations now to be made using functions based on measurements over much of the temperature ranges of interest for $A\ell_4C_3$. In general, we consider the equilibrium studies to be less reliable than the best combustion measurements for calculating the heat of formation. The measured heat of formation and heat capacities can be used to correlate the equilibrium studies. Inconsistencies in the equilibrium data can possibly be used to detect errors of technique or interpretation of the equilibrium measurements. Such a study is presented elsewhere in this report by Furukawa, Douglas, Saba, and Victor [9].

The equilibrium studies will be briefly mentioned. Campbell [10] measured the activity of aluminum in $A\ell_4C_3$ at 920°C, from which he calculated the free energy of formation of aluminum carbide, $\Delta Gf^{\circ}_{1193} = -35.8$ kcal mole^{-1}. Using thermodynamic data for $A\ell_4C_3$ based on the heat capacity measurements of Saba and Furukawa [7], and of Victor, Thurber, and Douglas [8], and recent tabulations of thermal functions of $A\ell(g)$ and $C(s)$ [11] we calculated $\Delta Hf^{\circ}_{298}\ [A\ell_4C_3] = -51.2$ kcal mole^{-1} from Campbell's free energy of formation.

The vapor pressure of aluminum carbide has been measured approximately by Ruff [12] between 1500 and 2300°K, by Chupka, et al. [13] at 2100°K, and by Meschi and Searcy [14] over the range 1500 to 1800°K. In the measurement of Ruff the species in the vapor do not appear to be well defined and his pressures are much too high when compared with those of Chupka and of Meschi and Searcy. Chupka, et al. found $p = 6\text{x}10^{-4}$ atm from which we can calculate $\Delta Hf^{\circ}_{298}\ [A\ell_4C_3] = -91.5$ kcal mole^{-1}, assuming the only vapor species present to be $A\ell(g)$. Taking from Meschi and Searcy the average vapor pressure, $p = 4.2\text{x}10^{-6}$ atm at 1600°K, and assuming that vaporization occurred according to reaction (2) we calculate

$$A\ell_4C_3(s) = 4A\ell(g) + 3C(s) \qquad (2)$$

$\Delta H_{1600} = 366.3$ kcal mole^{-1} and $\Delta Hf^{\circ}_{298}\ [A\ell_4C_3] = -63.5$ kcal mole^{-1}.

Equilibria in the system $A\ell_4C_3$-N_2 were studied by Prescott and Hincke [15]. They assumed that the equilibrium was represented by eq. (3).

$$A\ell_4C_3(s) + 2N_2(g) = 4A\ell N(s) + 3C(s) \qquad (3)$$

Stackelberg, et al. [16,17] pointed out that the more probable reactions were reaction (4) in the nitrogen rich mixture and reaction (5) in the nitrogen lean mixtures and that a distinction could be drawn between these, which would lead to the energy of reaction (6).

$$A\ell_5C_3N + 2N_2 = 5A\ell N + 3C \qquad (4)$$

$$5A\ell_4C_3 + 2N_2 = 4A\ell_5C_3N + 3C \qquad (5)$$

$$A\ell_4C_3 + A\ell N = A\ell_5C_3N \qquad (6)$$

This manner of treating the data has been discussed by Satoh [18] and by Efimenko, et al. [19].

If we use the results of the analysis by Efimenko, et al., which gives $\Delta H_{298} = 263.2$ kcal mole^{-1} for the enthalpy change of reaction (3) and apply ΔHf°_{298} (AℓN) = -76.0 kcal mole^{-1} recommended by Armstrong and Krieger [20], we find ΔHf°_{298} ($A\ell_4C_3$) = -40.8 kcal mole^{-1}.

Herstad [21] reports a measurement of equilibrium pressures of Mg vapor in reaction (7) near 1400°K, and calculation of the free energy of formation of aluminum carbide from solid carbon and liquid aluminum at 1400°K; $\Delta Gf^{\circ}_{1400} = -220 \pm 1.5$ kcal mole^{-1}. Using this value and free energy functions for $A\ell_4C_3$, Aℓ, and C [7,11], we calculate ΔHf°_{298} ($A\ell_4C_3$) = -58.5 kcal mole^{-1}.

$$8MgO(s) + A\ell_4C_3(s) = 2MgA\ell_2O_4(s) + 3C(s) + 6Mg(g) \qquad (7)$$

Equilibria in the system Aℓ-O-C were studied at high temperatures and the vapor pressures of CO in this system were measured by Prescott and Hincke [22], Brunner [23], and Treadwell and Gyger [24]. These equilibrium studies were used to calculate the heat of formation of $A\ell_4C_3$ by various workers, before it was realized that the equilibria are complicated by the occurrence of aluminum oxycarbides [25]. More recent equilibrium studies by Cox and Pidgeon [26], by Motzfeldt [27], and by Frank [28] take into account the formation of $A\ell_4O_4C$ and $A\ell_2OC$. However, no thermodynamic data have been measured for these compounds. The calculation of the heat of formation of $A\ell_4C_3$ from the observed equilibrium data requires estimates of the thermal functions of $A\ell_4O_4C$ and $A\ell_2OC$, and therefore, we do not consider these equilibria further in this paper.

2.0 Experimental Procedure

2.1 Materials

The aluminum carbide sample was supplied by the Aluminum Company of America Research Laboratories. It was prepared by heating a stoichiometric mixture of aluminum and lampblack in an argon atmosphere at 1800°C. Prior to the present work, this sample had been used for high- and low-temperature heat capacity measurements at the National Bureau of Standards [7,8]. Specimens from the original sample were spectrochemically and chemically analyzed. After the heat capacity measurements, specimens were again chemically analyzed. The results from the analyses are given in Table 1.

Table 1

(a) Qualitative Spectrochemical Analysis of Aluminum Carbide Sample

Element	Percent	Element	Percent
Ag	?	Mn	0.0001-0.001
Aℓ	> 10	Ni	0.001 -0.01
Ca	0.0001-0.001	Si	0.01 -0.1
Cr	0.001 -0.01(?)	Ti	0.001 -0.01
Cu	0.001 -0.01	V	0.01 -0.1
Fe	0.1 -1.0	Zr	0.001 -0.01
Mg	0.001 -0.01		
Total metal other than Fe and Aℓ 0.0262 - 0.262%			

(b) Quantitative Chemical Analyses of Aluminum Carbide Sample

Component	Percent by Weight					
	1	2	3	4	5	6
$A\ell_4C_3$	94.9	94.8	94.61	94.8	94.46	
Free Aℓ	1.2	1.3	1.25	1.0	1.00	
Free C	0.9	0.7	0.8	1.0	1.00	
AℓN	1.4	1.3	1.35	1.3	1.29	
$A\ell_2O_3$	2.0	2.0	1.99	2.2	2.19	
Fe	-		-	0.06	0.06	
Total	100.4	100.1	100.00	100.36	100.00	
Total C	24.65	24.43	24.48	24.73	24.64	24.57

The spectrochemical analysis was performed in the Spectrochemical Section at the National Bureau of Standards. The quantitative analyses 1, 2, 4, and 6 were made by R. A. Paulson using methods previously described [8]. Analyses 1 and 2 were made on two specimens before any heat capacity measurements were made. Analyses 4 and 6 were made on two specimens after the sample had been used for high temperature and low temperature heat capacity studies. The fact that the chemical analyses total slightly more than 100 percent may be caused by uncertainties in the analytical methods and small inhomogeneities in the sample. Analysis 3 is the average of analyses 1 and 2, normalized to 100 percent. Analysis 5 is the same as analysis 4, normalized to 100 percent. Analysis 6 was an independent measurement of total carbon, made by combustion of the sample and collection of carbon dioxide as for an organic compound. It was carried out because total carbon dioxide in the product gases was to be used as a measure of the amount of reaction occurring in the calorimetric experiments. The total carbon as listed in column 6 is in excellent agreement with the average of the total carbon in the normalized analyses, columns 3 and 5, but is less than the total carbon calculated from the actual results of these analyses.

The oxygen used in these experiments was of high purity, specified by the manufacturer to contain impurities, not exceeding 0.005 percent. Although further purification was probably not necessary for this gas, the oxygen was passed over copper oxide heated to 500°C to oxidize combustible impurities and through successive columns of ascarite and magnesium perchlorate to remove carbon dioxide and moisture.

2.2 Combustion Experiments

The samples were burned in a Dickinson-type calorimeter [29]. The combustion bomb was a commercial calorimeter bomb made of type 20 corrosion resistant alloy steel and equipped with platinum-iridium inlet tube and electrodes. A platinum-iridium support loop, approximately one inch in diameter, was attached to the lower end of the inlet tube.

The combustions were conducted under 30 atmospheres of oxygen. In order to remove the air, the bomb was filled with 10-15 atmospheres of oxygen for three times before being filled to the final pressure. The samples were ignited with a fuse wire for which the ignition energy amounted to 22 joules.

The definition, 1 calorie = 4.184 joules, was used for expressing the results in calories. All atomic weights were taken from the 1961 Table of Atomic Weights based on Carbon-12, adopted by the International Union of Pure and Applied Chemistry [30].

The calorimeter was calibrated with benzoic acid, National Bureau of Standards sample 39i, which has a certified heat of combustion of 26,434 j g^{-1} (weight in vacuo).

We found it necessary to use different supports for the samples in the calibration experiments and in the aluminum carbide combustions. The benzoic acid pellets were weighed and burned in a small platinum crucible (about 7.5 grams). The powdered aluminum carbide samples were weighed in small platinum pans, made from 0.004 in. thick foil. The samples were burned in these containers on aluminum oxide discs, 1/16 in. thick by 1 1/4 in. diameter. In the bomb the discs were supported on the platinum-iridium loop described above. It was found that a platinum support with a low enough heat capacity to allow complete combustion of benzoic acid melts when aluminum carbide burns on it. On the other hand, incomplete combustion of the benzoic acid occurs if the support is massive enough to prevent melting during the aluminum carbide combustions. The difference is attributed to the fact that most of the heat from a benzoic acid combustion is carried away from the reaction zone by the products of combustion, which are all gases. On the other hand, in the aluminum carbide combustions some of the solid product, aluminum oxide, is in contact with the sample support and retains a large amount of the heat in this location. In all cases the combustion of the carbide was greater than 99.5 percent complete.

The alumina disc container was weighed before and after each aluminum carbide combustion experiment. During the experiment, the disc cracked but remained on the supporting loop. As an extra precaution, the base of the combustion bomb was covered with alumina discs so that the bomb could be cleaned easily if the container disc had shattered during the combustion.

A preliminary test of the behavior of the $A\ell_4C_3$ sample on exposure to air showed that a gain in weight occurred, which was very gradual at first, and then became increasingly rapid. On the other hand, a sample kept in a desiccator showed no weight change in the same interval of time. This test, which extended over an interval of two months, showed that if, after opening the sealed vial, it was stored in a desiccator, the aluminum carbide could be handled in air for the short time necessary to weigh the combustion sample, and prepare the bomb for a heat measurement, without detriment to the sample. In another preliminary experiment the aluminum carbide was tested for possible reaction in the bomb prior to ignition. A weighed sample was placed in the bomb and all process steps were conducted up to the point of ignition. After four hours, the sample was reweighed. No significant weight increase was observed.

The standard calorimeter for the calibration experiments consisted of the calorimeter vessel with stirrer and water, the platinum resistance thermometer, and the combustion bomb with its electrical connections, fuse, platinum crucible, an alumina disc sample support for aluminum carbide, 30 atmospheres of oxygen, one ml. water, and five alumina discs covering base of the bomb. The water and calorimeter vessel, not including lid, weighed 3670 g. The results for seven calibration experiments are given in Table 2.

Table 2

Calibration Experiments

Experiment No.	m_s	ΔR_c	f	q	Δe_i	E_s
	g	ohms	$x10^6$	j	j ohm^{-1}	j ohm^{-1}
6	1.002313	.191495	-134.25	22.24	15.5	138441.0
8	1.000229	.191044	-129.73	22.30	16.3	138479.5
9	1.001456	.191300	-129.13	22.30	16.4	138464.4
15	1.000091	.191031	-143.38	23.20	14.1	138474.1
17	1.001660	.191317	-134.58	22.30	15.5	138480.3
21	1.001504	.191374	-140.98	22.30	14.5	138417.7
22	1.000912	.191257	-139.41	22.30	14.7	138420.5

The calibration experiments were interspersed with measurements on aluminum carbide. In Table 2 the columns listed beginning on the left, give the experiment number: the mass (weight in vacuo) of benzoic acid in grams, m_s; the corrected resistance thermometer change, ΔR_c; the term f in the factor 1 + f used to convert the standard energy of combustion of the benzoic acid to actual bomb conditions; the correction for ignition energy and nitric acid formation, q; the correction to the energy equivalent of the calorimeter to bring it to that of the standard calorimeter system Δe_i; and the calculated energy equivalent of the standard calorimeter, E_s. Seven experiments led to an energy equivalent of 138454.1 j ohm^{-1} with a standard deviation of the mean of 10.4 j ohm^{-1}.

The standard calorimeter for the experiments with aluminum carbide differed from that in the calibration experiments only in the omission of water from the bomb in the aluminum carbide experiments.

2.3 Examination of the Products of the Combustion

The products of combustion of the aluminum carbide were examined to determine the quantities of carbon dioxide and nitrogen dioxide formed in the reaction, and to characterize the solid combustion products. Qualitative tests on the gaseous products for NO [31] and CO [32] were negative. The carbon dioxide formed in each experiment was measured by absorption in Ascarite [33]. The nitrogen dioxide formed was determined by absorption on specially purified manganese dioxide [34].

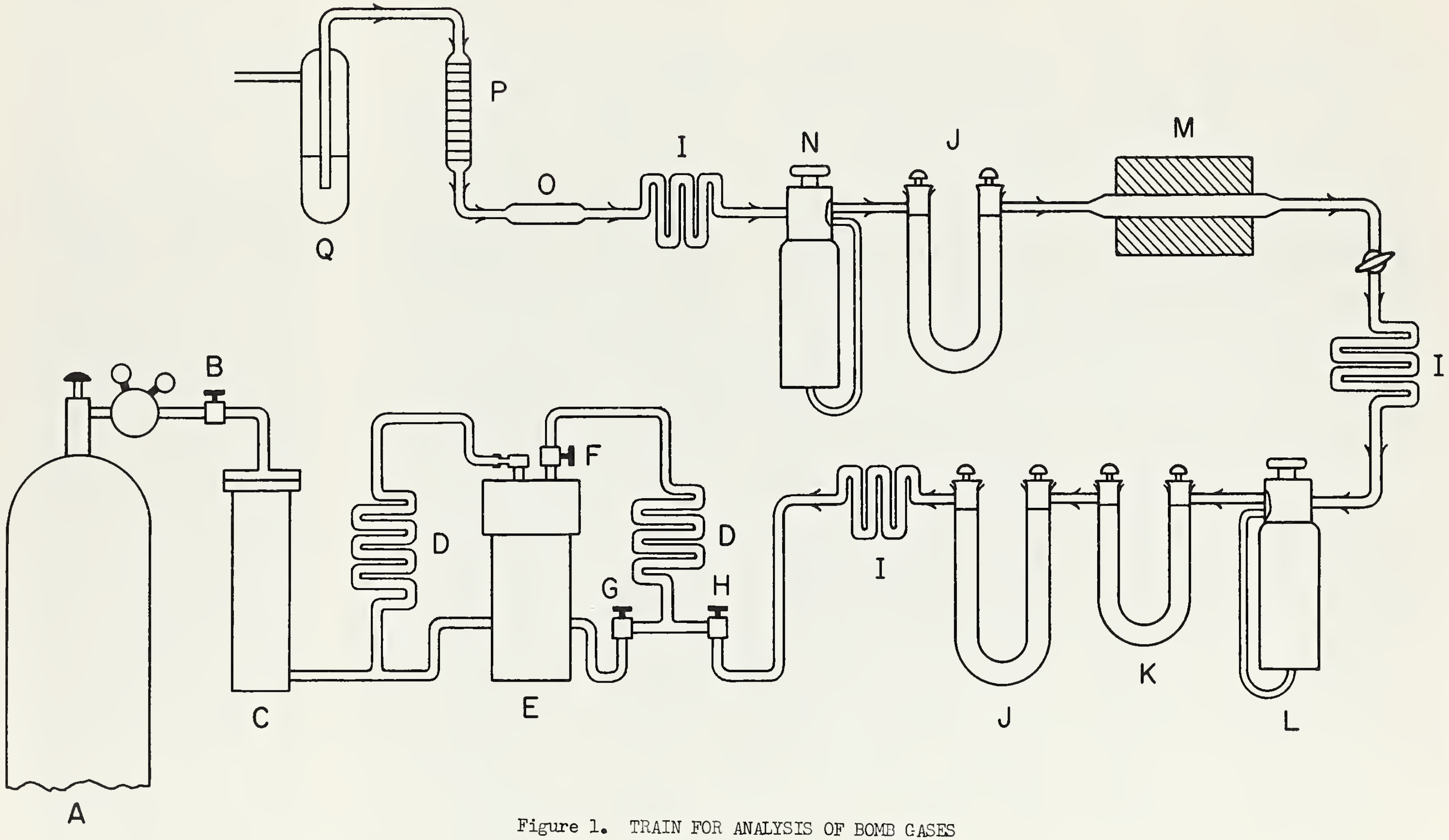


Figure 1. TRAIN FOR ANALYSIS OF BOMB GASES

(A) Cylinder of high purity nitrogen, (B) Micro-regulating valve, (C) Absorption tube containing Ascarite and magnesium perchlorate, (D) Coiled copper tube, (E) Combustion bomb, (F) Bomb outlet valve, (G) Bypass Valve, (H) Valve, (I) Glass tubing coil, (J) Drying tube, (K) Nitrogen dioxide absorption tube, (L) and (N) Carbon dioxide absorbers, (M) Furnace, (O) Guard tube containing magnesium perchlorate and Ascarite, (P) Flowmeter, (Q) Bubbler.

A semi-schematic diagram of the analytical train is given in Figure 1. Both the apparatus and analytical procedures are similar in many respects to those used by Prosen and Rossini [35]. A is a cylinder of high purity nitrogen under pressure. The nitrogen passes through a monel tube, C, containing successive layers of Ascarite and magnesium perchlorate. The flow rate of the nitrogen is adjusted with the micro-regulating valve, B. The coiled copper tubes, D, lead to the inlet and outlet valves on the combustion bomb, E. The valves, F and H are used to control the flow rate of gases from the combustion bomb. When the inlet and outlet valves to the bomb are closed, and valves G and H are open, the train may be flushed with nitrogen, bypassing the combustion bomb. This is often found useful when checking for leaks immediately prior to an analysis. The tube, J, contains magnesium perchlorate for removal of moisture and K, containing manganese dioxide backed by magnesium perchlorate, absorbs nitrogen dioxide. Carbon dioxide formed in the combustion reaction is absorbed in L, which contains Ascarite backed by magnesium perchlorate. Any carbon monoxide formed in the combustion is converted to carbon dioxide in the furnace, M, and is then dried over magnesium perchlorate in J, and absorbed in the tube N, which also contains Ascarite backed by magnesium perchlorate. The furnace, M, is a tube wound with nichrome and containing a vycor tube filled with copper oxide which is kept at 500°C. O is a guard tube containing successive layers of magnesium perchlorate and Ascarite to prevent back diffusion of carbon dioxide and moisture from the air. P is a float-type flowmeter and Q is a bubbler.

During the period immediately preceding the combustion experiment, the absorption tubes, K, L and N are flushed, filled with nitrogen and weighed. The tubes are replaced in the train for the analysis. Immediately after the experiment, the valve, F, is attached to the outlet valve on the bomb. After inserting the bomb, the train is flushed with nitrogen by way of the bypass around the bomb for about ten minutes, and then valve, G, is closed. H is opened and the gases are released from the bomb at a rate of about 200 ml/minute. When the pressure in the bomb reaches one atmosphere, the inlet valve is opened and nitrogen is passed through the bomb at the foregoing rate for one hour. The absorption tubes are removed from train, cleaned and reweighed. The true mass of the absorbed carbon dioxide was calculated using the method outlined by Rossini [36].

The reproducibility of the weighings of the absorption tubes was 0.0001-0.0005 g. In blank experiments in which the same quantity of nitrogen was passed through as in an analysis, no weight changes could be detected outside of these limitations. The accuracy of these analytical procedures was checked from time-to-time by determining the quantity of carbon dioxide produced from the combustion of a sample of benzoic acid. These checks indicated that the analyses were accurate to ±0.01 percent for absorption of 3.8 grams of carbon dioxide. In the aluminum carbide experiments, the mass of carbon dioxide collected was about 0.77 gram. The amount of nitrogen dioxide collected varied from 1.5-4.0 mg.

2.4 Identification of Solid Product

The solid product from the combustions was characterized by X-ray diffraction, on the basis of patterns maintained at the National Bureau of Standards and those published by Newsome, et al. [37]. In each experiment a large fraction of the product aluminum oxide was deposited in extremely finely divided form on the wall of the bomb. The remaining alumina, in the form of a fused mass, was on the reaction disc. The alumina on the disc was alpha alumina only, and that on the bomb wall was a different crystalline form, similar to the delta alumina. Because all of the alpha aluminum oxide remained on the reaction disc, it was possible to separate the two alumina phases and determine the quantity of each obtained in an experiment.

The X-ray data for the transition alumina obtained in the present study are given in Table 3, along with the data obtained by Rooksby [38] and Stumpf [37] for delta alumina. The pattern given by Stumpf was obtained from delta alumina prepared by calcination of pure alpha alumina monohydrate (böhmite). He has pointed out that delta alumina prepared by this method exhibits slightly diffuse diffraction lines indicative of small crystal size or crystal imperfection [39]. Rooksby investigated several ways of preparing delta alumina and obtained the pattern given here from alumina prepared by calcination of ammonium aluminum sulphate with ammonium molybdate at 950°C. He found that a more crystalline delta alumina resulted from this method than from the calcination of böhmite. It will be seen that there are differences between the Rooksby and Stumpf patterns. Even with the variations in the diffraction patterns observed, it is generally acknowledged that delta alumina is a definite crystalline form. However, until the situation is further clarified, a choice can not be made as to which is the better pattern.

The X-ray pattern for the transition alumina found in this study is more nearly similar to the Rooksby pattern than to that reported by Stumpf. However, it has some features in common with the Stumpf pattern which are lacking in Rooksby's. Each pattern has some distinctive lines.

Table 3

X-Ray Data for Finely Divided Aluminum Oxide Formed in the Combustion Bomb

			Delta-Al_2O_3			
Present work			Rooksby [38]		Stumpf [37]	
θ	d	I	d	I	d	I
degrees	A°		A°		A°	
			7.97	8		
			6.58	10		
17.42	5.08	11	5.07	20	5.02	30
					4.55	30
21.82	4.06	12	4.05	20	4.07	20
23.60	3.76	4				
25.02	3.55	6	3.56	7		
25.09	3.412	7	3.40	10		
27.06	3.292	12	3.29	15		
27.64	3.224	5	3.21	10		
29.26	3.049	7	3.03	10		
30.49	2.929	3				
31.21	2.863	6			2.87	40
31.55	2.833	8				
32.04	2.791	31	2.783	30		
32.74	2.732	18	2.737	30	2.73	80
34.45	2.601	47	2.593	70	2.58	30
35.11	2.553	8				
36.54	2.457	62	2.457	70	2.43	60
37.65	2.387	19				
38.96	2.309	36	2.311	40		
39.44	2.282	36	2.277	30	2.28	40
39.70	2.268	33				
41.69	2.164	13	2.156	25		
44.72	2.024	3				
					1.91	20
45.70	1.983	69	1.989	70	1.99	80
46.35	1.957	37	1.950	65	1.95	30
50.66	1.800	4	1.793	7	1.80	20
53.84	1.701	3	1.701	4		
56.99	1.614	12	1.616	10		
57.41	1.603	11	1.602	15		
59.94	1.541	11	1.543	10	1.54	40
60.86	1.520	9				
61.52	1.506	20	1.507	20	1.51	30
					1.49	40
63.57	1.462	5	1.462	8		
					1.45	30
64.78	1.437	3				
65.87	1.418	4				
66.60	1.402	60	1.407	60	1.40	60
67.13	1.393	100	1.392	100	1.39	100
					1.29	20
					1.26	10
76.23	1.247	4	1.250	4		
77.16	1.235	6	1.238	9		
81.24	1.183	17	1.180	4		
84.92	1.141	10			1.14	20
85.20	1.137	8	1.134	10		

Foster, et al. [25] observed a delta-like alumina in a study of the equilibrium diagram for the $A\ell_4C_3$- $A\ell_2O_3$ system. Newsome, et al. [37] report that delta alumina is definitely stabilized by nitrogen and it can be prepared by fusion together of alumina and aluminum nitride. These earlier studies suggest that the formation of the delta alumina in this study probably is promoted by the nitrogen and carbon in the aluminum carbide sample.

3.0 Results

3.1 Heat Measurements

In Table 4 are listed m_s, the mass of sample; $m(CO_2)$, the mass of CO_2; ΔR_c the corrected resistance thermometer change; Δe_2, the correction for the deviation of this calorimeter from the standard calorimeter; and $-\Delta U_B$, the observed energy of reaction at 28°C.

Table 4

Heat Measurements on Aluminum Carbide Samples

Experiment No.	m_s	$m(CO_2)$	ΔR_c	Δe_2	$-\Delta U_B$ 28°C
	g	g	ohm	j ohm^{-1}	j
10	.852498	.771016	.178892	-27.5	24763.4
11	.851387	.770745	.178673	-27.5	24733.1
12	.851040	.764905	.178031	-27.5	24644.2
13	.849675	.765961	.178751	-29.5	24743.5
16	.851301	.766513	.178648	-28.8	24729.4
18	.848726	.765632	.177593	-29.8	24583.2
19	.854470	.771409	.179115	-29.4	24793.9
20	.850351	.767780	.179008	-29.1	24779.2

To ΔU_B were applied corrections listed in Table 5. These include corrections for the combustion of impurities on the basis of analysis 4 (Table 1b),

Table 5

Corrections to Combustion Data on Aluminum Carbide

Experiment No.	$q_{A\ell N}$	$q_{A\ell}$	q_{Fe}	q_C	q_1	q_2	q_3	Σ corr.
	j	j	j	j	j	j	j	j
10	-137.3	-264.4	-3.8	-279.6	-22.0	5.3	-4.5	-706.3
11	-136.7	-264.4	-3.8	-279.5	-22.0	5.3	-4.5	-705.6
12	-136.6	-262.3	-3.7	-277.5	-22.0	5.2	-4.4	-701.3
13	-137.5	-262.7	-3.7	-277.9	-22.0	5.0	-4.5	-703.3
16	-136.7	-262.9	-3.7	-278.0	-22.0	5.1	-4.5	-702.7
18	-137.1	-262.6	-3.7	-277.7	-22.0	5.2	-4.5	-702.4
19	-136.0	-264.6	-3.8	-279.8	-22.0	5.0	-4.5	-705.7
20	-135.5	-263.3	-3.7	-278.5	-22.0	5.0	-4.5	-702.5

$A\ell N$ (1.30%), $A\ell$ (1.0%), C (1.0%), and Fe (0.06%); q_1, the ignition energy, q_2, the correction to standard state, and q_3, the correction to 25°C.

In making the correction for the combustion of $A\ell N$ it was assumed that the $A\ell N$ burned according to the reactions (8) and (9).

$$A\ell N(s) + 7/4\ O_2(g) \rightarrow \frac{1}{2}\ A\ell_2O_3(s) + NO_2(g) \qquad (8)$$

$$A\ell N(s) + 3/4\ O_2(g) \rightarrow \frac{1}{2}\ A\ell_2O_3(s) + \frac{1}{2}\ N_2(g) \qquad (9)$$

Since the NO_2 formed was measured, it was possible to obtain the amount of $A\ell N$ burned in reaction (9) by difference. In both cases, the energies of reaction were calculated using the heats of formation of $A\ell N$ [20], $A\ell_2O_3$ [3], and NO_2 [40].

Corrections for the energies of combustion of the remaining impurities were made assuming the following reactions using heat data from the literature.

$$A\ell(s) + \frac{3}{4}\ O_2(g) \rightarrow \frac{1}{2}\ A\ell_2O_3(s) \qquad (10)$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad [40] \qquad (11)$$

$$Fe(s) + \frac{3}{4}\ O_2(g) \rightarrow \frac{1}{2}Fe_2O_3(s) \quad [40] \qquad (12)$$

The corrections for the deviation of the gases from the ideal gas law were made according to the procedure outlined by Prosen [41].

The corrected energies of combustion, which are the energies of combustion of aluminum carbide in the original sample, are given in column 2 of Table 6. The ratio of CO_2 observed to that calculated from analysis 4, is shown in column 3. The observed fraction of delta phase in the alumina formed is given in column 4. The mass of aluminum carbide burned, m_s', was calculated from the observed mass of CO_2, corrected for the mass of CO_2 originating from the combustion of the free carbon in the original sample. m_s' is considered to be the best measure of the amount of reaction that occurred, because the aluminum carbide was apparently not entirely homogeneous. The lack of homogeneity is suggested by the scatter in the values for CO_2 (obs/calc). Values greater than 1.0 can only be accounted for if the percent carbon in the sample burned was greater than that calculated from analysis 4, which showed the highest carbon content of all the analyses. The range of values of the ratio CO_2 (obs/calc) is about half the percentage range of values for carbon found in the several analyses of the aluminum carbide sample. The standard energy of combustion of aluminum carbide in j g^{-1} based on m_s', but not corrected for variations observed in $A\ell_2O_3$ formed, is shown as ΔU^o_{298} ($A\ell_4C_3$) in column 6.

Table 6

Heat of Combustion of $A\ell_4C_3$

Expt. No.	$q\ A\ell_4C_3$	CO_2 (obs/calc)	$A\ell_2O_3$ $\frac{\delta}{\alpha+\delta}$	m_s'	$\Delta U^{\circ}_{298}(A\ell_4C_3)$ (obs)	$\Delta U^{\circ}_{298}(A\ell_4C_3)$ (to α-$A\ell_2O_3$)
	j			g	j g^{-1}	j g^{-1}
10	24057.1	1.0018	.768	.806580	29826.1	30215.6
11	24027.5	1.0027	.641	.806293	29800.0	30127.4
12	23942.4	.9956	.456	.800176	29922.0	30155.2
13	24040.2	.9985	.475	.801280	30002.2	30245.1
16	24026.7	.9973	.471	.801857	29963.8	30204.6
18	23880.8	.9992	.517	.800936	29816.1	30080.5
19	24088.2	1.0000	.517	.806976	29850.0	30114.4
20	24076.7	1.0001	.472	.803183	29976.6	30217.9

Mean	29894.6	30170.2
Standard Deviation of the Mean	±28.5	±20.8
	1028.59 ±1.0 kcal $mole^{-1}$	1038.07 ±.7 kcal $mole^{-1}$

As shown in column 4, Table 6, the delta aluminum oxide constituted a large fraction of the alumina formed in the combustion of the aluminum carbide. In order to improve the accuracy of the calculated energy of combustion of aluminum carbide, we have applied a correction for the formation of this alumina to the energies of combustion given in column 6.

Presumably, this correction would be proportional to the difference between the energies of formation of the alpha and delta aluminas. Unfortunately, there exist no experimental data from which we could make a reliable estimate of the energy difference between these two aluminas. However, from our knowledge of the energy of combustion of the carbide and the fraction of delta alumina formed in the present experiments, it is possible to obtain an estimate of the difference between the energies of formation of the two aluminas from the following relationship:

$$\Delta U_{obs} = \Delta U_{\alpha,only} + \text{Fraction } \delta\ [\Delta Uf(\delta\text{-}A\ell_2O_3) - \Delta Uf\ (\alpha\text{-}A\ell_2O_3)]$$

Here, ΔU_{obs} is the observed energy of combustion per gram of aluminum carbide, $\Delta U_{\alpha,only}$ is the energy of combustion of the carbide, if it burns to alpha alumina only, and $\Delta Uf(\delta\text{-}A\ell_2O_3)$ and $\Delta Uf(\alpha\text{-}A\ell_2O_3)$ are the energies of formation of alpha and delta alumina respectively, equivalent to one gram of $A\ell_4C_3$. It will be noted that this equation is linear with slope $[\Delta Uf(\delta\text{-}A\ell_2O_3) - \Delta Uf(\alpha\text{-}A\ell_2O_3)]$ and intercept, $\Delta U_{\alpha,only}$.

Consequently, the energies of combustion of aluminum carbide and the respective delta fractions were fitted to this equation by the method of least squares. The resulting equation is

$$\Delta U_{obs} = -30170.2 + 511.5 \text{ Fraction } \delta \text{ j g}^{-1}$$

The slope gives the energy difference (511.5 j) between the delta and alpha aluminas for 1.4165 g, which is equivalent to one gram of aluminum carbide. For one mole of alumina (101.96 g) this energy difference which is equal to the enthalpy difference [$\Delta Hf(\delta\text{-}A\ell_2O_3) - \Delta Hf(\alpha\text{-}A\ell_2O_3)$] becomes 36815 j or 8.8 kcal.

The energies of combustion of aluminum carbide corrected to the formation of alpha alumina only are listed in column 7, Table 6. The mean value for the energy of combustion of aluminum carbide is $\Delta E_{298} = -1038.1 \pm 0.7$ kcal mole^{-1}. Correction to constant pressure process leads to $\Delta H_{298} = 1039.9 \pm 0.7$ kcal mole^{-1} for reaction (1).

3.2 Heat of Formation of Aluminum Carbide

Combining the heat of combustion for aluminum carbide with ΔHf°_{298} [CO_2] = -94.05 ± 0.01 kcal mole^{-1} [40] and $\Delta Hf^{\circ}_{298}[\alpha\text{-}A\ell_2O_3]$ = -400.4 ± 0.3 kcal mole^{-1} [3] we obtain $\Delta Hf^{\circ}_{298}[A\ell_4C_3] = -43.0 \pm 0.8$ kcal mole^{-1}.

The overall standard deviation [0.8 kcal mole^{-1}] of the heat of formation of aluminum carbide is the root mean square of the uncertainty, 0.3 kcal mole^{-1}, assigned to the heat of formation of aluminum oxide; 0.01 kcal mole^{-1} for the uncertainty in the heat of formation of carbon dioxide; and 0.7 kcal mole^{-1} found for the standard deviation of the mean of the heat of combustion of the aluminum carbide. It should be pointed out also that not included in the standard deviation of $\Delta Hf^{\circ}_{298}[A\ell_4C_3]$ is the uncertainty in the correction [8.8 kcal mole^{-1}] applied for the difference between the heats of formation of delta and alpha aluminum oxide. In Figure 2 is given a plot of the energy of combustion of the carbide as a function of the fraction of delta alumina formed. It shows that the accuracy of the estimated energy difference would be improved if measurements of the heat of combustion of aluminum carbide were available in the ranges, 0-45 and 77-100 percent delta alumina. Under the circumstances of the present measurements, it was not possible to control the amount of this alumina phase formed.

The authors are grateful to Mr. Howard Swanson for his assistance in obtaining the X-ray diffraction pattern, and for his many helpful discussions on the characterization of the aluminas.

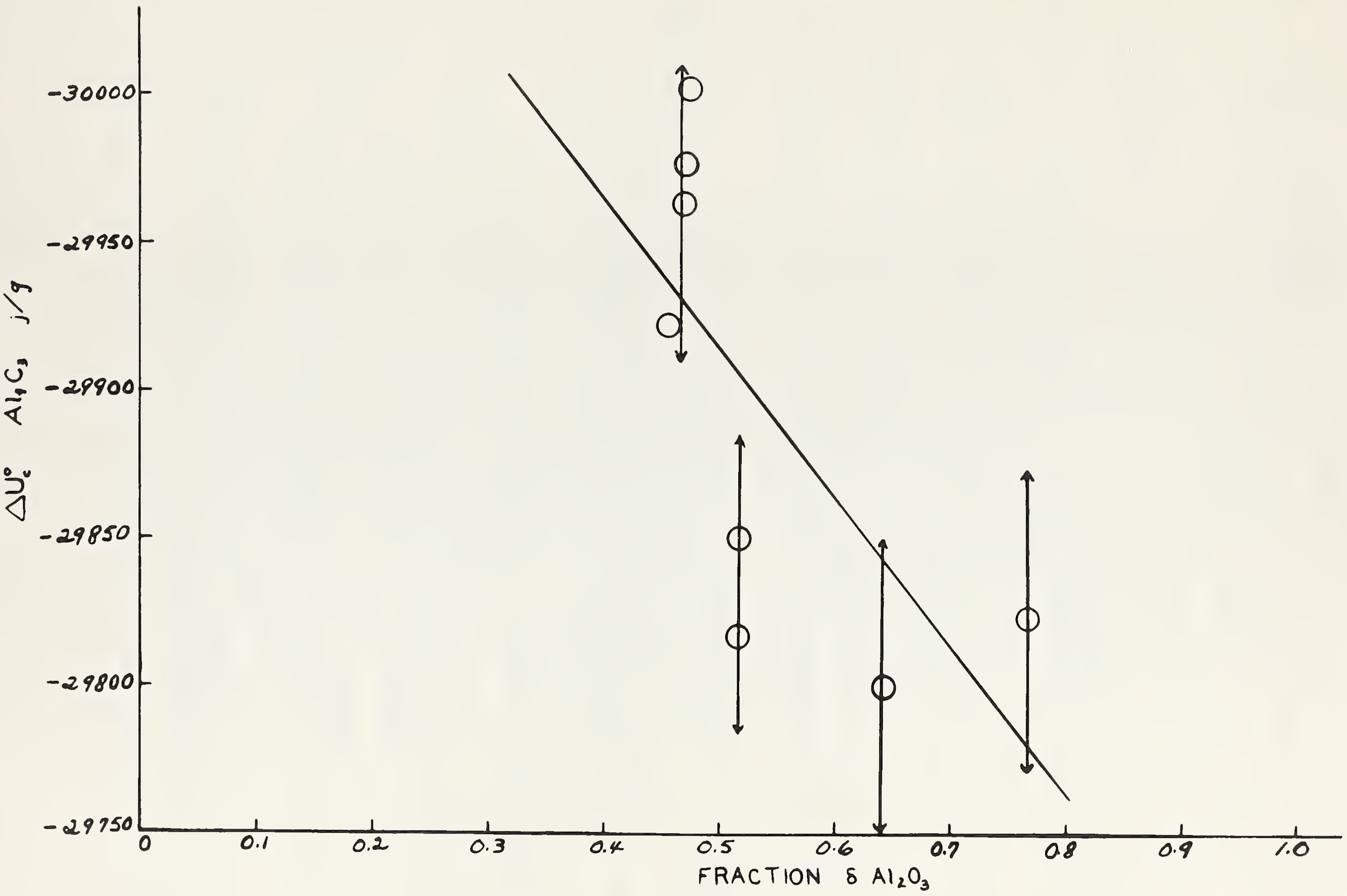


Figure 2. HEAT OF COMBUSTION OF $A\ell_4C_3$ AS A FUNCTION OF FRACTION δ-$A\ell_2O_3$

4. References

[1] A. Meichsner and W. A. Roth, Z. Elektrochem. 40, 19-26 (1934).

[2] W. A. Roth, Z. Elektrochem. 48, 267 (1942).

[3] A. D. Mah, J. Phys. Chem. 61, 1572-3 (1957).

[4] M. Berthelot, Compt. rend. 132, 281-291 (1901); ann. chim. phys. [7] 22, 464-479 (1901).

[5] L. Wöhler and K. Hofer, Z. anorg. allgem. Chem. 213, 249-254 (1933).

[6] N. Kameyama and F. Yoshida, Denki Kagaku 12, 171-175 (1944).

[7] W. G. Saba and G. T. Furukawa, NBS Report 7587, 1 July 1962. Chapter B-2, pp. 34-43, 135, 136.

[8] A. C. Victor, W. R. Thurber and T. B. Douglas, NBS Report 7437, 1 January 1962, Chapter A3, pp. 13-18.

[9] G. T. Furukawa, T. B. Douglas, W. G. Saba, and A. C. Victor, this Report, Chapter 2.

[10] C. S. Campbell, Met. Soc. Conf. 7, 412-16 (1962).

[11] (a) W. H. Evans, J. Hilsenrath, and H. W. Woolley, NBS Report 6928, 1 July 1960. Appendix A, Table A-13; (b) W. H. Evans, Loc. cit. Appendix B, Table B-39; (c) G. T. Furukawa, M. L. Reilly, J. H. Piccirelli, T. B. Douglas, A. C. Victor and A. R. Blandoin, Loc. cit. Appendix B, Table B-1.

[12] O. Ruff, Z. Electrochem. 24, 157-162 (1918).

[13] W. A. Chupka, J. Berkowitz, C. F. Giese, and M. G. Inghram, J. Phys. Chem. 62, 611-4 (1958).

[14] D. J. Meschi and A. W. Searcy, J. Phys. Chem. 63, 1175-8 (1959).

[15] C. H. Prescott and W. B. Hincke, J. Am. Chem. Soc. 50, 3228-3237 (1928).

[16] M. V. Stackelberg, E. Schnoorenberg, R. Paulus, and K. F. Spiess, Z. physik. chem. A175, 127-139 (1935).

[17] M. V. Stackelberg, and K. F. Spiess, Z. physik. chem. A175, 140-153 (1935).

[18] S. Satoh, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 34, 50-59 (1938).

[19] J. Efimenko, R. F. Hampson, R. F. Walker, and T. B. Douglas, NBS Report 6645, 1 January 1960, Chapter A5, pp. 32-52.

[20] G. T. Armstrong and L. A. Krieger, NBS Report 6928, 1 July 1960, Chapter 4, pp. 35-38.

[21] K. Grjotheim, O. Herstad, K. Stahl-Johannessen, Royal Norwegian Council for Scientific and Industrial Research, Trondheim, Norway, Unpublished work. Private communication from O. Herstad to G. T. Furukawa, 29 October 1963.

[22] C. H. Prescott, Jr., and W. B. Hincke, J. Am. Chem. Soc. 49, 2753-59 (1927).

[23] R. Brunner, Z. Elektrochem. 38, 55-68 (1932).

[24] W. D. Treadwell and A. Gyger, Helv. Chim. Acta 16, 1214-25 (1933).

[25] L. M. Foster, G. Long, and M. S. Hunter, J. Am. Ceram. Soc. 39, 1-11 (1956).

[26] J. H. Cox and L. M. Pidgeon, Can. J. Chem. 41, 671-83 (1963).

[27] K. Motzfeldt, Tek. Ukeblad. 109, 1137-42 (1962).

[28] W. B. Frank, Aluminum Company of America, unpublished communication, November 1963.

[29] R. S. Jessup, "Precise Measurement of Heat of Combustion with a Bomb Calorimeter", National Bureau of Standards Monograph 7, 26 February 1960.

[30] (a) International Union of Pure and Applied Chemistry Information Bulletin Number 14B, Butterworth Scientific Publications, London, 1961; (b) Chem. Eng. News 39, No. 47, 43 (1961).

[31] A. A. Noyes and E. H. Swift, Qualitative Chemical Analysis of Inorganic Substances (The MacMillan Company, N. Y., 1942) p. 368.

[32] M. Shepherd, Anal. Chem. 19, 77 (1947).

[33] R. Goulden, Comprehensive Analytical Chemistry, ed. by C. L. Wilson and D. W. Wilson, (El sevier Publishing Company, N. Y., 1960) p. 412.

[34] R. Belcher and G. Ingram, Analytica chimica acta, 4, 401 (1950).

[35] E. J. Prosen and F. D. Rossini, J. Research NBS <u>27</u>, 289 (1941)

[36] F. D. Rossini, Chapter 4 in "Experimental Thermochemistry", ed. by F. D. Rossini, (Interscience Publishers, Inc., New York, 1956).

[37] J. W. Newsome, H. W. Heiser, H. S. Russell and H. C. Stumpf, Aluminum Company of America, Alcoa Research Laboratories. Technical Paper No. 10 (Revised 1960), pp. 13, 35.

[38] H. P. Rooksby, J. Applied Chem. <u>8</u>, 44 (1958).

[39] H. C. Stumpf, Aluminum Company of America, unpublished communication, March 1963.

[40] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Lavine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500 (U. S. Government Printing Office Washington, D. C., 1952).

[41] E. J. Prosen, Chapter 6 in "Experimental Thermochemistry", ed. by F. D. Rossini (Interscience Publishers Inc., New York, 1956).

Chapter 2

HEAT CAPACITY AND ENTHALPY MEASUREMENTS ON ALUMINUM CARBIDE ($A\ell_4C_3$) FROM 15° TO 1173°K. THERMODYNAMIC PROPERTIES FROM 0° to 2000°K*

by George T. Furukawa, Thomas B. Douglas,
William G. Saba, and Andrew C. Victor

ABSTRACT

Measurements of the heat capacity and relative enthalpy were made on aluminum carbide ($A\ell_4C_3$) from 15° to 1173°K. The thermodynamic properties were calculated up to 2000°K from the data by judicious extrapolation above 1173°K. In conjunction with the heat-of-formation data on $A\ell_4C_3$ obtained by King and Armstrong, third-law calculations have been made of the vapor pressure of several high-temperature equilibria involving $A\ell_4C_3$ and comparisons made with published observations. Results of the comparison show fairly close agreement in the heats of reaction but wide variations in the Gibbs free energy of reaction.

1. Introduction

The results of heat-capacity and enthalpy measurements on aluminum carbide, $A\ell_4C_3$, in the range 15° to 1173°K presented in this paper have been obtained in connection with a research program at the National Bureau of Standards to provide accurate thermodynamic and related data on the "light" elements and their compounds. No heat-capacity measurements on $A\ell_4C_3$ have been previously published, except for the relative enthalpy measurements in the range 273° to 693°K by Satoh [1][1] on a sample that contained only 74.74 percent $A\ell_4C_3$, the impurities being 23.43 and 1.83 percent $A\ell_2O_3$ and SiO_2, respectively. The work reported by Satoh is based on only three measurements in the above temperature range.

---

* This work was sponsored by the Advanced Research Projects Agency, Department of Defense, under ARPA Order No. 20.

[1] Numbers in brackets refer to literature references at the end of this paper.

Aluminum carbide, $A\ell_4C_3$, is a yellow rhombohedral crystal of space group D_{3d}^5 with a = 8.53Å and α = 22°28' [2]. Each carbon atom is surrounded by aluminum atoms and the shortest C-C distance is 3.16Å [2], indicating that the carbon atoms are not bonded to one another. There are two structurally different carbon atoms, and the C-$A\ell$ distance ranges from 1.90 to 2.22Å. One of the carbon structures has six aluminum atoms at 2.17Å, and the other has one aluminum atom at 1.90Å, three at 1.94Å, and one at 2.22Å. On hydrolysis, $A\ell_4C_3$ yields methane. Other aluminum carbides that have been reported are $A\ell_2(C_2)_3$ [3] and $A\ell_3C$ [4]. The carbide $A\ell_2(C_2)_3$, made by reacting acetylene with aluminum at 450 to 500°C, yields acetylene on hydrolysis [3]. The carbide $A\ell_3C$, observed in the $A\ell$-$A\ell_2O_3$-$A\ell_4C_3$ phase investigations reported by Baur and Brunner [4], should yield CH_4 on hydrolysis.

2. Sample

The measurements of the low-temperature heat capacity and the high-temperature relative enthalpy were made on the same aluminum carbide sample kindly supplied by the Aluminum Company of America, ALCOA Research Laboratories, through the courtesy of George Long. The material had been prepared by heating a stoichiometric mixture of aluminum powder and lampblack in an atmosphere of argon to 1800°C. Qualitative spectrochemical analyses were made on representative specimens of the sample by the Spectrochemistry Section of the National Bureau of Standards. The results are summarized in Table 1.

Chemical analyses were performed by Rolf A. Paulson of the Applied Analytical Research Section of the National Bureau of Standards. These results are given in Table 2. Specimens 1 and 2 were sampled from the original $A\ell_4C_3$ preparation as received. Specimen 3 was sampled from that portion of the $A\ell_4C_3$ preparation on which the low-temperature heat-capacity measurements had been completed. The percentage $A\ell_4C_3$ was determined by dissolving a sample in hot sulfuric acid. The evolved gases, taken to be CH_4 and H_2, were burned and the combustion products collected. The amount of CO_2 collected was converted to $A\ell_4C_3$ and the excess H_2O over that attributable to CH_4 was reckoned to have been formed from H_2 released from the acid by free aluminum and iron. The insoluble residue from the hot sulfuric acid treatment was taken to be free carbon. Aliquot portions of the sulfuric acid solution were analyzed for total aluminum as $A\ell_2O_3$ by precipitating $A\ell(OH)_3$ with ammonium hydroxide and by igniting to $A\ell_2O_3$. The excess of aluminum over that attributable to $A\ell_4C_3$, free aluminum metal, and $A\ell N$ was assumed to be $A\ell_2O_3$ in the original sample. The iron, determined in specimen 3 only, was analyzed colorimetrically using the thiocyanate-complex method on an aliquot portion of the sulfuric acid solution. The percentage $A\ell N$ was determined by the Kjeldahl method on separate samples of the $A\ell_4C_3$ preparation.

The results of the chemical analysis agree with the usual composition found (of about 95 percent $A\ell_4C_3$) in samples prepared by the same method [5]. The small discrepancies in the analyses can be attributed to either uncertainties in the analytical methods or small inhomogeneities in the sample. The approximate summation of the analyses to 100 percent is an indication of the reliability of the analytical methods used. E. E. Hughes of the Applied Analytical Research Section, National Bureau of Standards, analyzed the gases generated by the action of an acid on the $A\ell_4C_3$ sample and found no acetylene or methylacetylene, indicating that $A\ell_2(C_2)_3$ was not present in the $A\ell_4C_3$ preparation. No effort was made to determine whether $A\ell_3C$ was present.

M. v. Stackelberg et al. [6,7] reported the conditions for formation and the crystal structure of the compound $A\ell_5C_3N$ ($A\ell_4C_3 \cdot A\ell N$). The results of the heat-capacity measurements presented in this paper were processed assuming that the nitrogen found in the chemical analysis came from $A\ell N$ mixture with $A\ell_4C_3$.

For the analysis of high-temperature relative-enthalpy measurements the average of the chemical analyses obtained in specimens 1 and 2 was normalized to yield 100 percent total analysis. The iron content, the chemical analysis for which was not made in specimens 1 and 2, was considered too small to contribute significantly to the results of the experimental data. In the processing of the heat-capacity data obtained at low temperatures, the chemical analysis obtained on specimen 3 was used, after normalizing to give a total analysis of 100 percent.

The corrections for the impurities were made assuming that the relative enthalpies were additive. The contributions from $A\ell$, $A\ell_2O_3$, and $A\ell N$ impurities were adjusted in accordance with the tabular values of thermodynamic functions obtained through the analysis of the literature data in connection with the light element research program [8]. The values for C were based mostly on the measurements of De Sorbo and Tyler [9]. The corrections for Fe were obtained primarily from the heat-capacity data reported by Simon and Swain [10] and by Kelley [11].

3. Low-Temperature Calorimetry

3.1 Apparatus and Method

The low-temperature heat-capacity measurements were made from about 18° to 380°K in an adiabatic calorimeter similar in design to that described previously [12]. The calorimeter vessel, which was filled with sample as described in Section 3.2 and sealed by means of a specially designed gold-gasket closure [13], was suspended within the adiabatic shield system by means of a Nylon string instead of the filling tube shown in the above reference. The adiabatic shield was controlled automatically by means of a combination of electronic and electromechanical equipment. Details of the design of the calorimeter used, its operation, and the automatic adiabatic control system will be described in a later publication.

The platinum resistance thermometer used in the measurements was calibrated in accordance with the International Practical Temperature Scale of 1948 [14]. The temperatures in degrees Kelvin (°K) were obtained by adding 273.15 deg to the temperatures in degrees Celsius (°C). Below 90°K, the thermometer was calibrated on the NBS-1955 provisional scale which is numerically 0.01 deg lower than the former NBS-1939 provisional scale [15]. The resistance measurements were made by means of a Mueller bridge and a high sensitivity galvanometer to the nearest 0.00001 ohm. The temperatures were calculated from the resistance by inverse interpolation in a table of resistance given as a function of the temperature at closely spaced regular intervals.

The electrical power introduced into the calorimeter heater (100 ohms of constantan wire) was measured by means of a Wenner potentiometer in conjunction with a volt box, standard resistor, and saturated standard cells. A constant-current power supply stable to 10 ppm or better was used to facilitate the power measurements. The duration of each heating interval was measured by means of a high precision interval timer operated on 60-cycle frequency standard provided at the National Bureau of Standards. The 60-cycle frequency standard is based on a 100 kc/s quartz oscillator which is stable to 0.5 ppm over a period of three months. The estimated uncertainty in the readings of the interval timer was not greater than ±0.01 sec for any heating period, none of which was less than 2 min in these experiments.

3.2 Results

A sample of 153.8063 g mass was poured into the calorimeter vessel in a controlled-atmosphere box filled with argon gas (dew-point of -50°C). At the same time, samples of the $A\ell_4C_3$ were sealed in test tubes under dry argon gas for chemical analysis. The calorimeter vessel plus the sample was evacuated and purged with dry helium gas several times. Finally, helium gas at a pressure of 5.8 cm Hg was sealed in the container with the sample. After completion of the measurements the calorimeter vessel was opened in the controlled-atmosphere box and additional samples taken for chemical analysis. As mentioned earlier, the analysis of the low-temperature heat data was based on the chemical analysis of the sample on which the measurements had been made (chemical analysis of specimen 3).

On the calorimeter vessel plus the sample ("gross"), 108 heat-capacity determinations were made and on the empty vessel ("tare"), 87 determinations were made. The experimental data of each series of measurements were fitted to empirical equations over selected, overlapping temperature intervals by the method of least squares using a digital computer. Details of the computer routines used will be described in a later publication. Briefly, the overlapping equations were joined at temperatures of the most favorable combinations of values of heat capacity and its first and second derivatives. The values of heat capacity obtained at regularly spaced integral temperatures by this process were smoothed by a 9-point cubic smoothing code [16] on the computer. The deviations of the observations of each series of measurements from the final smoothed values are shown in Figures 1 and 2.

The net values of heat capacity obtained by differencing the smoothed gross and tare values at the corresponding temperatures, were corrected for the impurities and the helium exchange gas and again smoothed on the computer wherever necessary. These values were then converted to molal units using atomic weights based on carbon-12 [17]. A Debye heat-capacity function, fitted to the smoothed values at the lower temperatures, was used to obtain the values from 0° to 18°K.

A consideration was given at this point regarding the utility of a table of thermodynamic functions. Unfortunately, most scientists that use tables of thermodynamic functions are accustomed to the calorie as an energy unit. The values of heat capacity were converted, with reluctance and regret, to the unit cal/deg mole using the relation 1 define calorie = 4.1840 joules. These values of heat capacity from 0° to 390°K were later combined with the high-temperature heat data (see Section 5).

Heat-capacity determinations usually require two series of measurements, one on the sample plus the calorimeter vessel and the other on the empty vessel. By conducting the two series of measurements under as identical conditions as possible, certain errors that occur equally in both measurements may be cancelled in the final processing of the data. The data from both series of measurements are most useful in certain applications, such as in the numerical evaluation of the precision and accuracy of the original observations, in the correlation of the temperature scale, etc. These data are, however, not directly useful where the heat capacity of the substance is needed for the comparison of the precision and accuracy of measurements with other laboratories. The method used in processing the experimental data as outlined above yields the final smoothed values of heat capacity. The relation of these values with the original observations is linked through a somewhat tortuous path.

To meet the above requirements for evaluating the precision of the observation and for comparing the results with other laboratories a "compromised" list of experimental data is given in Table 3. The values of "observed molal heat capacity" given in the units of j/deg mole in Table 3 were obtained by subtracting the smoothed tare heat capacity from the gross heat capacity at the observed temperatures (mid temperatures of the enthalpy increments). The tare heat capacities at the corresponding temperatures were obtained by interpolation in the table of smoothed tare heat capacities mentioned earlier. Corrections have been made for the impurities and for the helium gas. These observed molal heat capacities are plotted in Figure 3.

4. High-Temperature Relative Enthalpy Measurements

4.1 Method and Apparatus

The relative enthalpy measurements were made from 273° to 1173°K (0° to 900°C) by the "drop" method using a Bunsen ice calorimeter. Details of the method have been described previously [18]. Briefly, the method involved suspending the samples sealed in a container (for the present measurements the container consisted mostly of the alloy Ni(80%)-Cr(20%)) in a furnace. When a constant, known temperature is attained, the container and its contents are dropped, with nearly free fall, into a Bunsen ice calorimeter in which is determined the heat evolved by the container plus sample in cooling to 273.15°K. In order to account for the enthalpy of the container and the heat lost during the drop, a similar experiment is made with the empty container at the same furnace temperature. The difference between the two values of heat evolved in the ice calorimeter is a measure of the enthalpy change of the sample between 273.15°K and the temperature in the furnace.

In the furnace used the sample is surrounded by a silver pipe 10 in. long and of 1/2 in. wall thickness, in order to minimize the temperature gradients around the sample and thus improve the accuracy of measuring its temperatures. Customarily, the temperature of this furnace (and hence that of the sample) is measured by a calibrated platinum resistance thermometer (precision, ±0.002 deg) from 0 to 600°C, and by a calibrated Pt--Pt-10% Rh thermocouple (precision, ±0.01 deg.) at all temperatures. The routine simultaneous measurement by both instruments at and below 600°C ensures that the thermocouple readings are consistent with the thermometer readings, which are more accurate. Unfortunately, shortly before the measurements on $A\ell_4C_3$ were begun, the thermometer suffered an accident and it was consequently necessary to use the thermocouple alone at all the temperatures.

Just before the measurements of the relative enthalpy of $A\ell_4C_3$, similar measurements were carried out on a sample of Calorimetry-Conference standard sample of α-$A\ell_2O_3$ in a silver container (six at 400°, two at 600°, and two at 700°C), in order to check the overall accuracy. Compared with the smoothed values published earlier by the Bureau [31], the mean enthalpies of the $A\ell_2O_3$ found at these three temperatures were respectively +0.02 ±0.06, -0.01 ±0.01, and -0.02 ±0.01 percent higher.

4.2 Results

The results of the enthalpy measurements are summarized in Table 4. Each value in the second column represents the net relative enthalpy of the sample obtained from a single measurement on the sample plus container after subtracting the mean of several individual measurements made earlier on the same container when empty. The values given have been corrected for the contribution of the impurities to the heats measured. By correcting for the heat of fusion of the free aluminum present, a small hump in the uncorrected enthalpies near the melting point of this element, 932°K, was largely eliminated. Using the method of least squares and giving equal weight to the mean enthalpy of the sample at each furnace temperature, the constants of the following equation were obtained:

$$H_T - H_{273.15} = 19{,}771.1 + 47.5557T + 1.927 \times 10^{-4}\, T^2 - 13.4524 \times 10^3 \log_{10} T \,. \quad \text{cal/mole} \qquad (1)$$

The equation has more significant figures than the precision of the observations. The number of figures has been retained to permit comparison with the final values of thermodynamic functions given in Table 6. The values calculated from equation (1) are given in column 4 of Table 4 for comparison with the observed values.

5. Correlation of the Low and High Temperature Heat Data with the Vapor-Pressure Data

The low-temperature heat-capacity data overlap the high-temperature relative-enthalpy data in the range 273.15° to 380°K. Numerical integration of the smoothed values of the low-temperature heat-capacity yielded 2933 cal/mole for the enthalpy change between 273.15° and 373.15°K. The high-temperature relative enthalpy measurements (see Table 4) give an average value of 2939 cal/mole and the enthalpy equation (eq. 1) gives 2947 cal/mole for this temperature interval. The smoothed values of heat capacity from the low-temperature measurements were merged with the values of heat capacity calculated from the relative enthalpy equation (eq. 1) in a manner such that the resultant enthalpy change from 273.15° to 373.15°K would be about the average of the mean values determined by the two methods. After a process of adjusting and smoothing, the final values of heat capacity that were obtained yielded 2936 cal/mole for the enthalpy change of this temperature interval. In Fig. 4, the final selected values of heat capacity are compared with those from the low-temperature measurements and from the enthalpy equation (eq. 1) in the interval 270° to 390°K. Table 4 shows also for comparison the values of $H_T-H_{273.15}$ obtained from the thermodynamic functions in Table 6 based on the final selected values of heat capacity.

A table of thermodynamic functions up to 2000°K was desired but the upper temperature limit of the high-temperature relative enthalpy measurements was about 1200°K. An attempt was made, therefore, to extrapolate an appropriate equation above 1200°K to 2000°K on the basis of entropy calculated from high-temperature vapor-pressure data involving $A\ell_4C_3$.

The most recent vapor-pressure data considered best for the purpose are those of Meschi and Searcy [19] in the region from 1500° to 1800°K, obtained by means of the Knudsen effusion method and by the torsion-effusion method. The average second-law value of ΔH^o at 1600°K reported for the reaction

$$Al_4C_3(c) \rightarrow 4Al(g) + 3C(c) \qquad (2)$$

from the dissociation-pressure measurements was 356 ±12 kcal/mole. (Henceforth, any thermodynamic property at T°K will be symbolized, for example by ΔH^o (T°K).) Using the vapor-pressure equation ($\log_{10} P = -1.95 \times 10^4/T + 6.79$) given by Meschi and Searcy [19], ΔG^o (1800°K) was calculated to be 132 kcal/mole. Combining the values of ΔH^o and ΔG^o, ΔS^o (1800°K) becomes -124 cal/deg mole. (Henceforth, the abbreviation e.u. will be used synonymously with cal/deg mole.) The value of S^o (1800°K) of $Al_4C_3(c)$ [8] then becomes 96 ±7 e.u. (The uncertainty of ±7 e.u. is based on the uncertainty ±12 kcal/mole assigned by Meschi and Searcy [19] on ΔH^o (1600°K).)

Prescott and Hincke [20] investigated the high-temperature equilibrium reaction between aluminum carbide and nitrogen

$$4AlN(c) + 3C(c) = Al_4C_3(c) + 2N_2(g) , \qquad (3)$$

in the region 1774° to 1909°K. The value of ΔH^o reported was 253.63 kcal/mole. From the vapor-pressure equation ($\log_{10} P = -27697/T + 9.891$) given, ΔG^o (1800°K) was calculated to be 90.6 kcal/mole. The value of S^o (1800°K) of $Al_4C_3(c)$ [8] was calculated to be 94 e.u. However, v. Stackelberg et al. [6,7] reported the formation and crystal structure of the intermediate compound Al_5C_3N, similar in appearance and properties to Al_4C_3, and pointed out that the equilibrium reaction investigated by Prescott and Hincke [20] involved instead —

$$4Al_5C_3N(c) + 3C(c) \rightarrow 5Al_4C_3(c) + 2N_2(g) \qquad (4)$$

In an earlier investigation, Prescott and Hincke [21] reported $\Delta H^o = 507.76$ kcal/mole for the equilibrium reaction in the region 1967° to 2293°K between aluminum oxide and carbon —

$$2Al_2O_3(c) + 9C(c) = Al_4C_3(c) + 6CO(g) \qquad (5)$$

By extrapolating the vapor-pressure equation ($\log_{10} P = -18,480/T + 8.21$) given, ΔG^o (1800°K) was calculated to be 102 kcal/mole. This gives 64 e.u. for S^o (1800°K) of $Al_4C_3(c)$ [8,22], which is considerably lower than the value calculated from the data of the Al_4C_3-N_2 system [20].

This difference probably arises from the complex and uncertain nature of the reactants and products involved in the $A\ell_2O_3$-C system. The formation of two aluminum oxycarbides has been reported [23] in phase studies of the $A\ell_2O_3$-$A\ell_4C_3$ system. The value for S° (2000°K), in the range of the measurements of Prescott and Hincke [21], was calculated to be 71 e.u., which is also considerably lower (see Tables 5 and 6) than the values calculated previously for lower temperatures.

Brunner [24] also investigated the equilibria of the $A\ell_2O_3$-C system in the region 1853° to 2253°K. The value of S° (1800°K), calculated by extrapolation over a short temperature interval of the reported data ($\log_{10} P = -16{,}900/T + 7.56$) is 46 e.u. A treatment of the approximate vapor pressures reported by Ruff [25] on the Aℓ-C system yielded S° (1800°K) to be 111 e.u.

The values of S° (1800°K) obtained are summarized in Table 5; they vary from 46 to 111 e.u. The disagreement may be readily rationalized when the difficulties of vapor-pressure measurements at high temperatures are considered. The substances in equilibrium may be considerably different from those expected. The possible impurity phases present are expected to undergo chemical reaction with the sample and contribute considerably to the observed vapor pressures. The slope of ℓnP versus $1/T$, from which the heat of dissociation ΔH° is calculated, may, therefore, be dependent significantly upon the impurities. A small displacement of the temperature does not, however, affect the slope very much at high temperatures. On the other hand, the value of ΔG° is dependent upon the absolute pressure and temperature. If $\delta\Delta H^\circ = 0$, the following relations exist: $\delta\Delta S^\circ = nR\,\delta\ell nP$ and $\delta\Delta G^\circ = -nRT\,\delta\ell nP$, where n is the number of moles of the gas involved in the equilibrium and R is the molal gas constant. For the $A\ell_2O_3$-C system at 1800°K, an error in the pressure by a factor of 2 corresponds to a $\delta\Delta G^\circ$ of 14.9 kcal/mole since six moles of CO are involved. This in turn corresponds to $\delta\Delta S^\circ$ of 8.3 e.u. Since the dissociation reaction $A\ell_4C_3(c) \rightarrow 4A\ell(g) + 3C(c)$ involves only four moles of $A\ell(g)$ the error from this source is not amplified on the molal basis as much. For this reaction, the 5 e.u. variation in ΔS° (1800°K) shown in Table 5 corresponds to about 90 percent variation in the vapor pressure, assuming ΔH° is correct. In the $A\ell_4C_3$-N_2 system, with only two moles of $N_2(g)$ involved, the amplification of the error in the vapor-pressure measurements should be even less.

The high-temperature relative enthalpy data could not be reasonably extrapolated above 1200°K up to the entropies calculated from the vapor-pressure data, for even the lowest reasonable value of 94 e.u. for the entropy of $A\ell_4C_3(c)$ at 1800°K (based on Prescott and Hincke [20]) would require the heat capacity to be unreasonably high at 1800°K (approximately 65 cal/deg mole). The extrapolation of equation (1) based on the high-temperature relative enthalpy data seemed the most reasonable course to follow. The equation is of the form generally used for high-temperature heat capacities and is well behaved in terms of heat capacity and its derivatives up to 2000°K.

The various thermodynamic functions were calculated from the heat capacity, using the usual thermodynamic relations [13], by numerical methods on the IBM 7094 computer. The value of S° (1800°K) obtained is 91.0 e.u., which is well within the uncertainty of the vapor-pressure data. Kelley [26] estimated S° (298.15°K) to be 26.3 e.u., using primarily the vapor-equilibrium data reported by Brunner [24]. The value obtained from the heat-capacity measurements is 21.3 e.u.

King and Armstrong [27] recently obtained 43.0 ±0.7 kcal/mole for the heat of formation at 298.15°K from combustion measurements on $A\ell_4C_3$. (The figure after the ± is the standard deviation of the mean. See the above reference (Chapter 1 of this report) for details regarding the estimated uncertainty.) The vapor-pressure relations $\log_{10} P$ versus $1/T$ were calculated between 1000° and 2000°K for the reactions designated by equations (2), (3), and (5), by combining the above heat of formation with the thermodynamic functions and thermochemical data of appropriate substances [8,22]. These calculations are summarized in Tables 7, 8, and 9 and in Figure 5. The results of the high-temperature equilibrium measurements on the above reactions reported by the various investigators previously mentioned [19, 20, 21, 24] and others are also given in Figure 5 for comparison.

For the $A\ell_4C_3$ dissociation equilibrium, the single vapor-pressure measurement of Chupka et al. [28] is shown to be over an order of magnitude (18 e.u.) lower. Campbell [29] reported ΔG° (1193°K) = 35.8 kcal mole for the reaction:

$$A\ell_4C_3(c) \longrightarrow 4A\ell(\ell) + 3C(c) \ , \qquad (6)$$

calculated from the activity coefficient obtained from the measurements of the vapor pressure of aluminum monofluoride over the $A\ell_4C_3$-$A\ell$-C system and over pure aluminum at 1193°K (920°C). The value plotted in Figure 5 was obtained after converting to the basis of aluminum vapor [8]. The deviation, $\delta\log_{10} P$, is about -0.38, which corresponds to $\delta\Delta S°$ (1200°K) of -7 e.u. The value of S° (1200°K) for $A\ell_4C_3(c)$ obtained from the heat-capacity and enthalpy measurements with extrapolation of only 25 deg is 73.1 e.u.; an error in this essentially measured value by -7 e.u. is quite unreasonable.

The vapor-pressure equation obtained by Meschi and Searcy [19] is shown to have a slope (-1.95×10^4 deg) fairly close to that calculated from the thermal data. (The average slope between 1000° and 2000°K is -1.892×10^4 deg.) The $\log_{10} P$ is, however, lower by about 0.7 at 1800°K, corresponding to $\delta\Delta S°$ of -12.8 e.u. An error in the extrapolation of the entropy by this amount at 1800°K seems very unlikely. The smaller variation (5 e.u.) in S° (1800°K) shown in Table 5 arise from the contribution of the variation in the ΔH° (1800°K) (Meschi and Searcy [19] obtained 356 kcal/mole and the value calculated from the thermal data is 343.3 kcal mole.).

Prescott and Hincke [20] followed the equilibrium reaction of $A\ell_4C_3$(c) and N_2(g) between 1774° and 1909°K manometrically by means of a McLeod gauge. M. v. Stackelberg et al. [6,7] reported an intermediate compound, $A\ell_5C_3N$, in the nitridation of $A\ell_4C_3$ to $A\ell N$. The calculation of the $A\ell_4C_3$-N_2 equilibrium (Table 8 and Figure 5) was performed on the assumption that the intermediate compound $A\ell_5C_3N$ was not formed. Figure 5 shows that the $\log_{10}$ P versus 1/T slope of the vapor-pressure equation (-27697 deg) given by Prescott and Hincke [20] is fairly close to that calculated from thermal data. (The average slope between 1000° and 1800°K is -28308 deg.) The $\log_{10}$ P at, for example, 1800°K is about 0.57 higher, which corresponds to $\delta\Delta S^\circ$ of 5.2 e.u. The smaller $\delta\Delta S^\circ = 3$ e.u. shown in Table 5 arises from the contribution of the variation in ΔH° (1800°K). Hincke and Prescott [20] obtained ΔH° (1800°K) = 253.63 kcal/mole; the thermal data yielded 257.1 kcal/mole.

Figure 5 shows that the vapor-pressure data on the $A\ell_2O_3$-C system obtained by Prescott and Hincke (1967° to 2293°K) [21] and Brunner (1853° to 2253°K) [24] converge at about 2250°K and differ considerably from that calculated from the thermal data. These variations are probably from non-equilibrium conditions in the experiments and from the oxycarbides formed in the $A\ell_2O_3$-C system.

The results of these comparisons show that the heats of reaction (eqs. (2) and (3)) can be obtained from the vapor-pressure data alone to within a few percent. The values of Gibbs free energy of reaction obtained from vapor-pressure data and from thermal data have been, however, found to differ considerably (over 10 percent). These large deviations may be attributed to the activity coefficients of the substances involved being other than unity or to possible surface impoverishment of components of the reactions. The low vapor pressures observed for the $A\ell_4C_3$ decomposition reaction can be explained on the basis of the above causes. However, the high values observed for the $A\ell_4C_3$-N_2 reaction can not be explained on the same basis. In addition, if the compound $A\ell_5C_3N$ [6] was formed and $\Delta G^\circ < 0$ for its formation from $A\ell_4C_3$ and $A\ell N$, then the vapor pressures observed (eq. 4) should be lower than those calculated from the thermal data for eq. (3). The high observed values are probably due to non-equilibrium conditions that still existed. Prescott and Hincke [20] added N_2 to $A\ell_4C_3$ and determined the pressure of N_2 as a function of the time.

The high values reported by various investigators for the $A\ell_2O_3$-C system may be explained, depending upon the equilibrium reaction, on the basis of formation of aluminum oxycarbides. According to the phase diagram investigations reported by Foster, Long and Hunter [23], $A\ell_2O_3$ and $A\ell_4C_3$ can not co-exist at equilibrium. Therefore, the equilibrium investigated by Prescott and Hincke [21] could be

$$A\ell_4O_4C(c) + 3C(c) = 2A\ell_2OC(c) + 2CO(g) \qquad (7)$$

or

$$2A\ell_2O_3(c) + 3C(c) = A\ell_4O_4C(c) + 2CO(g) \qquad (8)$$

instead of eq. (5). At the upper temperatures (above 2100°K) liquid phases may have been present. If $\Delta G^\circ < 0$ for the formation of the oxycarbides from Al_2O_3 and Al_4C_3, then the equilibria represented by eq. (8) should yield a higher vapor pressure. Another possible equilibrium observed by Prescott and Hincke [21], according to the phase diagram of Foster et al. [23], is

$$2Al_2OC(c) + 3C(c) = Al_4C_3(c) + 2CO(g) , \qquad (9)$$

but for this reaction the observed vapor pressures should be lower than those calculated for eq. (5). Prescott and Hincke [21] used an "excess" of Al_2O_3; the reactions given by eqs. (7), (8), and (9) are possible depending upon the "excess". Brunner [24], on the other hand, used stoichiometric amounts of Al_2O_3 and C corresponding to eq. (5) and his results are also high.

The equilibrium reactions:

$$Al_2O_3(c) + 3C(c) = Al_2OC(c) + 2CO(g) , \qquad (10)$$

$$2Al_2O_3(c) + 3C(c) = Al_4O_4C(c) + 2CO(g) , \qquad (8)$$

and

$$Al_4O_4C(c) + 6C(c) = Al_4C_3(c) + 4CO(g) , \qquad (11)$$

were recently investigated by Cox and Pidgeon [30] using a differential thermal analysis method on each of three samples having Al_2O_3 to C ratios of 2:3, 2:6, and 2:9. These vapor-pressure results are also higher than those calculated for eq. (5). According to the phase diagram of Foster et al. [23], only the reaction given by eq. (8) is possible. The curves corresponding to eqs. (8) and (11) are close to the results reported by Brunner [24] and Prescott and Hincke [21], respectively.

Although there should be expected some uncertainty in the extrapolation of the relative enthalpy measurements, the uncertainty is considered to be smaller than the variations between the observed and calculated vapor pressures. The observations may not have been made under truly equilibrium conditions because of unknown kinetic effects. No thermal data are available on the aluminum oxycarbides. Further work is needed to resolve the differences.

6. Acknowledgements

The authors are indebted to Willis R. Thurber for all the measurements on the sample with the "drop" calorimeter, and to Rolf A. Paulson of the Applied Analytical Research Section of the National Bureau of Standards for the chemical analyses on the samples. The processing of the heat measurements would not have been possible without the chemical analysis. The gift of the Al_4C_3 sample by the Aluminum Company of America, ALCOA Research Laboratories, through the courtesy of George Long, is gratefully acknowledged.

7. References

[1] S. Satoh, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 34, 50 (1938).

[2] M. v. Stackelberg and E. Schnorrenberg, Zeit. physik. Chem. B27, 37 (1934).

[3] J. F. Durand, Bull. Soc. Chim. 35, 1141 (1924).

[4] E. Baur and R. Brunner, Zeit. Elektrochem. 40, 154 (1934).

[5] George Long, private communication.

[6] M. v. Stackelberg, E. Schorrenberg, R. Paulus, and K. F. Spiess, Zeit. physik. Chem. A175, 127 (1935).

[7] M. v. Stackelberg and K. F. Spiess, Zeit. physik. Chem. A175, 140 (1935).

[8] "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds", National Bureau of Standards Report No. 6928, July 1, 1960.

[9] W. DeSorbo and W. W. Tyler, J. Chem. Phys. 21, 1660 (1953).

[10] F. Simon and R. C. Swain, Zeit. physikal. Chem. 28B, 189 (1935).

[11] K. K. Kelley, J. Chem. Phys. 11, 16 (1943).

[12] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, J. Research NBS 35, 39 (1945).

[13] G. T. Furukawa, M. L. Reilly, and J. H. Piccirelli, publication pending.

[14] H. F. Stimson, J. Research NBS 65A, 139 (1961).

[15] H. J. Hoge and F. G. Brickwedde, J. Research NBS 22, 35 (1939).

[16] E. T. Whittaker and G. Robinson, "The Calculus of Observations. A Treatise on Numerical Mathematics", Fourth Edition, Blackie and Sons, London 1944, pp. 285-316.

[17] "IUPAC Revises Atomic Weight Values", Chem. Eng. News 39, 42 (1961).

[18] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Research NBS 57, 67 (1956).

[19] D. J. Meschi and A. W. Searcy, J. Phys. Chem. 63, 1175 (1959).

[20] C. H. Prescott, Jr. and W. B. Hincke, J. Am. Chem. Soc. 50, 3228 (1928).

[21] C. H. Prescott, Jr. and W. B. Hincke, J. Am. Chem. Soc. 49, 2753 (1927).

[22] J. Hilsenrath, C. W. Beckett, W. S. Benedict, L. Fano, H. J. Hoge, J. F. Masi, R. L. Nuttall, Y. S. Touloukian, and H. W. Woolley, "Tables of Thermal Properties of Gases", National Bureau of Standards Circular 564, November 1, 1955.

[23] L. M. Foster, G. Long, and M. S. Hunter, J. Am. Ceram. Soc. 39, 1 (1956).

[24] R. Brunner, Zeit. Elektrochem. 38, 55 (1932).

[25] O. Ruff, Zeit. Elektrochem. 24, 157 (1918).

[26] K. K. Kelley, Contributions to the Data on Theoretical Metallurgy. VIII. The Thermodynamic Properties of Metal Carbides and Nitrides, U. S. Bureau of Mines Bulletin No. 407, 1937.

[27] R. C. King and G. T. Armstrong, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds", National Bureau of Standards Report No. 8186, January 1964, Chapter 1.

[28] W. A. Chupka, J. Berkowitz, C. F. Giese and M. G. Inghram, J. Phys. Chem. 62, 611 (1958).

[29] C. S. Campbell, Met. Soc. Conf. 7, 412 (1961).

[30] J. H. Cox and L. M. Pidgeon, Can. J. Chem. 41, 671 (1963).

[31] D. C. Ginnings, J. Phys. Chem. 67, 1917 (1963).

Table 1

Spectrochemical Analysis of the Sample of Aluminum Carbide ($A\ell_4C_3$)

Element	%	Element	%	Element	%
Ag	- (?)	Hf	-	Sb	-
Aℓ	> 10	Hg	-	Sc	-
As	-	In	-	Si	0.01-0.1
Au	-	Ir	-	Sn	-
B	-	La	-	Sr	-
Ba	-	Mg	0.001 -0.01	Ta	-
Be	-	Mn	0.0001-0.001	Te	-
Bi	-	Mo	-	Th	-
Ca	0.0001-0.001	Nb	-	Ti	0.001-0.01
Cd	-	Ni	0.001 -0.01	Tℓ	-
Ce	-	Os	-	U	-
Co	-	P	-	V	0.01-0.1
Cr	0.001-0.01(?)	Pb	-	W	-
Cu	0.001-0.01	Pd	-	Y	-
Fe	0.1-1.0	Pt	-	Zn	-
Ga	-	Rh	-	Zr	0.001-0.01
Ge	-	Ru	-		

- : Not detected.

Table 2

Chemical Analysis of the Sample of Aluminum Carbide ($A\ell_4C_3$)

Component	Percentage by Weight Specimen 1	 Specimen 2	 Specimen 3
$A\ell_4C_3$	94.9	94.8	94.8
Free $A\ell$	1.2	1.3	1.0
Free C	0.9	0.7	1.0
$A\ell N$	1.4	1.3	1.3
$A\ell_2O_3$	2.0	2.0	2.2
Free Fe			0.06
Total	100.4	100.1	100.36

TABLE 3. OBSERVED HEAT CAPACITY OF ALUMINUM CARBIDE

MOLECULAR WEIGHT = 143.9594, $^{0}K = ^{0}C + 273.15^{0}$

T ^{0}K	C_p J/DEG/MOLE
RUN 1	
80.9304	19.039
87.5349	22.750
95.5198	27.145
102.6529	31.166
109.1860	34.903
115.2630	38.389
120.9611	41.644
126.3603	44.702
RUN 2	
83.3668	20.442
83.7841	20.682
92.0007	25.212
99.2987	29.260
105.9164	33.041
112.1039	36.581
118.3925	40.182
125.2915	44.100
132.5943	48.216
140.0859	52.360
148.2666	56.796
156.8223	61.313
165.0743	65.555
173.0867	69.543
181.1510	73.440
189.9219	77.545
199.0012	81.640
RUN 3	
208.2596	85.650
194.8391	79.768
204.7784	84.152
214.3612	88.195
223.6167	91.931
232.5986	95.409
241.3449	98.662
250.2226	101.831
259.2433	104.929
RUN 4	
19.4395	0.154
21.2826	0.214
23.1934	0.298
26.1223	0.468
28.9497	0.690
31.8285	0.978
34.7029	1.356
37.9361	1.897
RUN 5	
18.3556	0.125
20.5917	0.194
22.9086	0.286
25.3911	0.425
28.2211	0.628
31.0744	0.900
34.2214	1.292
38.0580	1.925
42.2987	2.823
RUN 6	
32.2736	1.037
35.9656	1.554
39.9007	2.283
44.3825	3.329
48.7699	4.578
53.7296	6.250
60.1927	8.834
67.1891	12.007
RUN 7	
47.9512	4.334
53.8036	6.274
60.2681	8.859
67.1238	11.979
74.4382	15.603
82.5811	20.002
RUN 8	
53.6690	6.221
59.9095	8.700
67.0407	11.949
73.8189	15.264
80.9261	19.085
88.8040	23.473
96.7037	27.812
104.9602	32.491
113.3395	37.293
RUN 9	
202.6976	83.252
212.7334	87.532
222.8071	91.600
233.1927	95.614
244.9902	99.979
257.7564	104.411
270.1210	108.507
282.1421	112.178
RUN 10	
228.2582	93.736
238.8640	97.746
249.4063	101.545
260.0404	105.168
282.9258	112.385
RUN 11	
287.5948	113.747
299.1951	117.040
310.6701	120.112
322.1925	122.999
RUN 12	
280.8853	111.785
291.7646	114.978
303.4013	118.188
314.9180	121.232
326.3407	124.053
337.6879	126.647
348.8494	129.087
RUN 13	
332.8417	125.529
344.3231	128.107
355.7442	130.520
367.1535	132.793
RUN 14	
332.3944	125.383
338.2360	126.747
349.3925	129.181
354.7007	130.379
365.6101	132.607
376.3752	134.648

Table 4

High-Temperature Enthalpy Measurements on Aluminum Carbide (Al_4C_3)[a]

Furnace temperature °K	Relative enthalpy of Al_4C_3, $H_T-H_{273.15}$			
	Individual measurement[b] cal/mole	Mean observed cal/mole	From eq. (1) cal/mole	Final (table 6) cal/mole
373.2	2913 2940 2963	2939[c]	2947.1	2935.6
473.2	6281 6324 6310	6305	6332.0	6322.1
573.2	9992 9989 10020 9989 9988 9987	9994	9987.6	9978.1
673.2	13892 13875 13862	13876	13828	13818
773.2	17787 17800	17794	17802	17792
873.2	21895 21873	21884	21879	21869
973.2	25974 25985	25980	26036	26026
1073.2	30299[d] 30277	30288	30260	30250
1173.2	34578[d] 34506[d]	34542	34538	34528

[a] Mol. wt. = 143.9594.

[b] Sample mass = 6.650g except for (c).

[c] The value found from the measurements with the adiabatic calorimeter is 2933.0 cal/mole.

[d] Sample mass = 6.647g.

Table 5

Comparison of the Entropy of Aluminum Carbide ($A\ell_4C_3$) at 1800°K Calculated from Vapor-Pressure Data

Source	System or Reaction	Range °K	S°,e.u. 1800°K
Meschi and Searcy [19]	$A\ell_4C_3(c) \rightarrow 4A\ell(g) + 3C(c)$	1500-1800	96 ±7
Prescott and Hincke [20]	$4A\ell N(c) + 3C(c) = A\ell_4C_3(c) + 2N_2(g)$	1774-1909	94
Prescott and Hincke [21]	$2A\ell_2O_3(c) + 9C(c) = A\ell_4C_3(c) + 6CO(g)$	1967-2293	64
Brunner [24]	" "	1853-2253	46
Ruff [25]	$A\ell_4C_3(c) = 4A\ell(g) + 3C(c)$	1700-2500	111
This work (Calorimetric)	Extrapolation		91.0

TABLE 6

THERMODYNAMIC FUNCTIONS FOR ALUMINUM CARBIDE (AL_4C_3)
SOLID PHASE

GRAM MOLECULAR WT.=143.9594 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG MOLE	S^0_T CAL/DEG MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.000	0.000	0.001	0.001	0.000
10.00	0.000	0.001	0.002	0.012	0.005	0.004
15.00	0.001	0.004	0.006	0.062	0.017	0.021
20.00	0.003	0.010	0.013	0.195	0.041	0.065
25.00	0.006	0.021	0.027	0.520	0.095	0.162
30.00	0.012	0.040	0.052	1.207	0.188	0.355
35.00	0.020	0.071	0.091	2.486	0.334	0.707
40.00	0.032	0.117	0.149	4.667	0.549	1.299
45.00	0.050	0.180	0.230	8.094	0.833	2.236
50.00	0.073	0.262	0.335	13.106	1.183	3.636
55.00	0.102	0.364	0.467	20.042	1.603	5.628
60.00	0.139	0.487	0.626	29.236	2.083	8.350
65.00	0.184	0.630	0.814	40.956	2.612	11.939
70.00	0.236	0.792	1.028	55.444	3.191	16.532
75.00	0.297	0.972	1.269	72.910	3.801	22.265
80.00	0.366	1.169	1.534	93.495	4.437	29.264
85.00	0.443	1.380	1.823	117.31	5.089	37.648
90.00	0.528	1.605	2.133	144.41	5.753	47.529
95.00	0.621	1.841	2.462	174.85	6.424	59.007
100.00	0.722	2.087	2.808	208.66	7.099	72.175
105.00	0.830	2.341	3.171	245.84	7.776	87.117
110.00	0.945	2.604	3.549	286.42	8.456	103.91
115.00	1.066	2.873	3.939	330.41	9.138	122.62
120.00	1.194	3.148	4.343	377.80	9.819	143.32
125.00	1.329	3.429	4.757	428.60	10.499	166.07
130.00	1.469	3.714	5.182	482.79	11.175	190.92
135.00	1.614	4.002	5.617	540.34	11.843	217.91
140.00	1.765	4.294	6.059	601.21	12.503	247.10
145.00	1.921	4.589	6.509	665.35	13.154	278.51
150.00	2.081	4.885	6.966	732.73	13.795	312.20
155.00	2.246	5.183	7.429	803.29	14.427	348.19
160.00	2.416	5.481	7.897	876.98	15.048	386.50
165.00	2.589	5.780	8.369	953.75	15.658	427.16
170.00	2.766	6.080	8.846	1033.5	16.258	470.20
175.00	2.946	6.379	9.325	1116.3	16.846	515.62
180.00	3.130	6.678	9.808	1202.0	17.424	563.46
185.00	3.317	6.976	10.293	1290.5	17.991	613.71
190.00	3.507	7.273	10.780	1381.9	18.546	666.39
195.00	3.700	7.569	11.269	1476.0	19.090	721.51
200.00	3.895	7.864	11.759	1572.8	19.622	779.08
205.00	4.093	8.157	12.250	1672.2	20.141	839.11
210.00	4.293	8.448	12.742	1774.2	20.649	901.59
215.00	4.495	8.738	13.233	1878.6	21.144	966.52
220.00	4.700	9.025	13.725	1985.6	21.628	1033.9
225.00	4.906	9.311	14.216	2094.9	22.101	1103.8
230.00	5.113	9.594	14.707	2206.6	22.564	1176.1
235.00	5.323	9.875	15.197	2320.5	23.016	1250.8
240.00	5.534	10.153	15.687	2436.7	23.459	1328.1
245.00	5.746	10.429	16.175	2555.1	23.893	1407.7
250.00	5.959	10.703	16.662	2675.6	24.317	1489.8
255.00	6.174	10.974	17.147	2798.3	24.732	1574.3
260.00	6.389	11.242	17.632	2922.9	25.136	1661.3
265.00	6.606	11.508	18.114	3049.6	25.530	1750.6
270.00	6.824	11.771	18.595	3178.2	25.914	1842.4
273.15	6.961	11.936	18.897	3260.2	26.151	1901.5
275.00	7.042	12.032	19.074	3308.7	26.288	1936.6
280.00	7.261	12.290	19.551	3441.1	26.651	2033.1
285.00	7.481	12.545	20.026	3575.2	27.005	2132.1
290.00	7.701	12.797	20.498	3711.1	27.351	2233.4
295.00	7.922	13.047	20.969	3848.7	27.695	2337.1
298.15	8.062	13.202	21.264	3936.3	27.909	2403.6
300.00	8.144	13.294	21.437	3988.1	28.035	2443.1

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

THIS TABLE SUPERSEDES TABLE B-59 OF NBS REPORT 7437 AND TABLE B-37 OF NBS REPORT 6928.

THIS TABLE IS THE SAME AS TABLE B-59 REVISED OF NBS REPORT 7587.

TABLE 6(CONT.)

THERMODYNAMIC FUNCTIONS FOR ALUMINUM CARBIDE (AL_4C_3)
SOLID PHASE

GRAM MOLECULAR WT.=143.9594 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG MOLE	S^0_T CAL/DEG MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
300.00	8.144	13.294	21.437	3988.1	28.035	2443.1
310.00	8.587	13.780	22.367	4271.7	28.694	2662.1
320.00	9.032	14.256	23.288	4561.8	29.314	2890.4
330.00	9.478	14.721	24.199	4857.9	29.894	3127.8
340.00	9.925	15.175	25.100	5159.6	30.439	3374.3
350.00	10.371	15.619	25.990	5466.5	30.952	3629.8
360.00	10.817	16.051	26.868	5778.5	31.435	3894.1
370.00	11.262	16.473	27.736	6095.2	31.893	4167.1
373.15	11.403	16.604	28.007	6195.8	32.032	4254.9
380.00	11.707	16.885	28.592	6416.3	32.324	4448.8
390.00	12.151	17.286	29.437	6741.6	32.726	4738.9
400.00	12.594	17.677	30.270	7070.7	33.104	5037.5
425.00	13.694	18.610	32.304	7909.4	33.973	5819.8
450.00	14.782	19.486	34.268	8768.6	34.746	6652.1
475.00	15.858	20.307	36.166	9646.0	35.439	7532.7
500.00	16.920	21.080	38.000	10540.	36.064	8459.9
550.00	18.996	22.493	41.489	12371.	37.145	10448.
600.00	21.009	23.753	44.761	14252.	38.050	12605.
650.00	22.955	24.883	47.838	16174.	38.818	14921.
700.00	24.837	25.902	50.739	18132.	39.479	17386.
750.00	26.656	26.827	53.483	20120.	40.055	19992.
800.00	28.415	27.670	56.085	22136.	40.561	22732.
850.00	30.116	28.442	58.558	24175.	41.010	25599.
900.00	31.762	29.151	60.913	26236.	41.411	28586.
950.00	33.356	29.806	63.162	28316.	41.772	31688.
1000.00	34.900	30.413	65.313	30413.	42.099	34900.
1050.00	36.398	30.976	67.374	32525.	42.396	38218.
1100.00	37.851	31.502	69.353	34652.	42.669	41636.
1150.00	39.263	31.993	71.255	36792.	42.919	45152.
1200.00	40.634	32.453	73.087	38944.	43.150	48761.
1250.00	41.968	32.885	74.853	41106.	43.364	52460.
1300.00	43.265	33.292	76.557	43280.	43.563	56245.
1350.00	44.529	33.676	78.205	45463.	43.748	60114.
1400.00	45.760	34.039	79.799	47654.	43.922	64065.
1450.00	46.961	34.382	81.343	49855.	44.085	68093.
1500.00	48.132	34.708	82.841	52063.	44.239	72198.
1550.00	49.275	35.018	84.294	54278.	44.384	76377.
1600.00	50.392	35.313	85.705	56501.	44.521	80627.
1650.00	51.483	35.594	87.077	58730.	44.651	84947.
1700.00	52.549	35.862	88.412	60966.	44.774	89334.
1750.00	53.593	36.119	89.711	63208.	44.892	93787.
1800.00	54.614	36.364	90.978	65455.	45.004	98305.
1850.00	55.613	36.599	92.212	67708.	45.111	102884.
1900.00	56.592	36.824	93.416	69966.	45.213	107525.
1950.00	57.552	37.041	94.592	72229.	45.311	112226.
2000.00	58.492	37.249	95.741	74497.	45.406	116984.

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

THIS TABLE SUPERSEDES TABLE B-59 OF NBS REPORT 7437 AND TABLE B-37 OF NBS REPORT 6928.

THIS TABLE IS THE SAME AS TABLE B-59 REVISED OF NBS REPORT 7587.

Table 7

Thermodynamics of the Dissociation of Aluminum Carbide ($A\ell_4C_3$)

Reaction: $A\ell_4C_3(c) \rightarrow 4A\ell(g) + 3C(c)$

T °K	ΔS° cal/deg mole	ΔH° kcal/mole	ΔG° kcal/mole	$-\log_{10} P$
298.15	140.07	353.0	312.2	57.23
1000	133.78	349.1	215.3	11.76
1100	133.13	348.4	201.9	10.03
1200	132.53	347.7	188.6	8.590
1300	131.97	347.0	175.4	7.374
1400	131.44	346.3	162.3	6.333
1500	130.93	347.5	149.1	5.433
1600	130.46	344.8	136.1	4.646
1700	130.01	344.1	123.1	3.955
1800	129.57	343.3	110.1	3.341
1900	129.17	342.5	97.1	2.793
2000	128.76	341.7	84.2	2.301

Table 8

Thermodynamics of the Reaction:

$4A\ell N(c) + 3C(c) \rightarrow 2N_2(g) + A\ell_4C_3(c)$

T °K	$\Delta S°$ cal/deg mole	$\Delta H°$ kcal/mole	$\Delta G°$ kcal/mole	$-\log_{10} P$
298.15	89.41	261.0	234.3	85.90
1000	89.78	260.4	170.6	18.64
1100	89.38	259.9	161.6	16.06
1200	89.00	259.5	152.7	13.91
1300	88.65	259.1	143.8	12.09
1400	88.34	258.7	135.0	10.54
1500	88.06	258.3	126.2	9.19
1600	87.81	257.9	117.4	8.02
1700	87.58	257.5	108.6	6.98
1800	87.38	257.1	99.9	6.06

Table 9

Thermodynamics of the Reaction:

$2Al_2O_3(c) + 9C(c) \longrightarrow Al_4C_3(c) + 6CO(g)$

T °K	ΔS° cal/deg mole	ΔH° kcal/mole	ΔG° kcal/mole	$-\log_{10} P$
298.15	267.8	599.3	519.4	63.46
1000	262.6	594.2	331.6	12.08
1100	261.0	592.5	305.4	10.11
1200	259.5	590.8	279.4	8.48
1300	258.1	589.0	253.5	7.10
1400	256.8	587.2	227.7	5.92
1500	255.5	585.4	202.1	4.91
1600	254.3	583.6	176.7	4.02
1700	253.2	581.6	151.2	3.24
1800	252.1	579.8	126.0	2.55
1900	251.1	577.9	100.9	1.93
2000	250.1	576.1	75.8	1.38

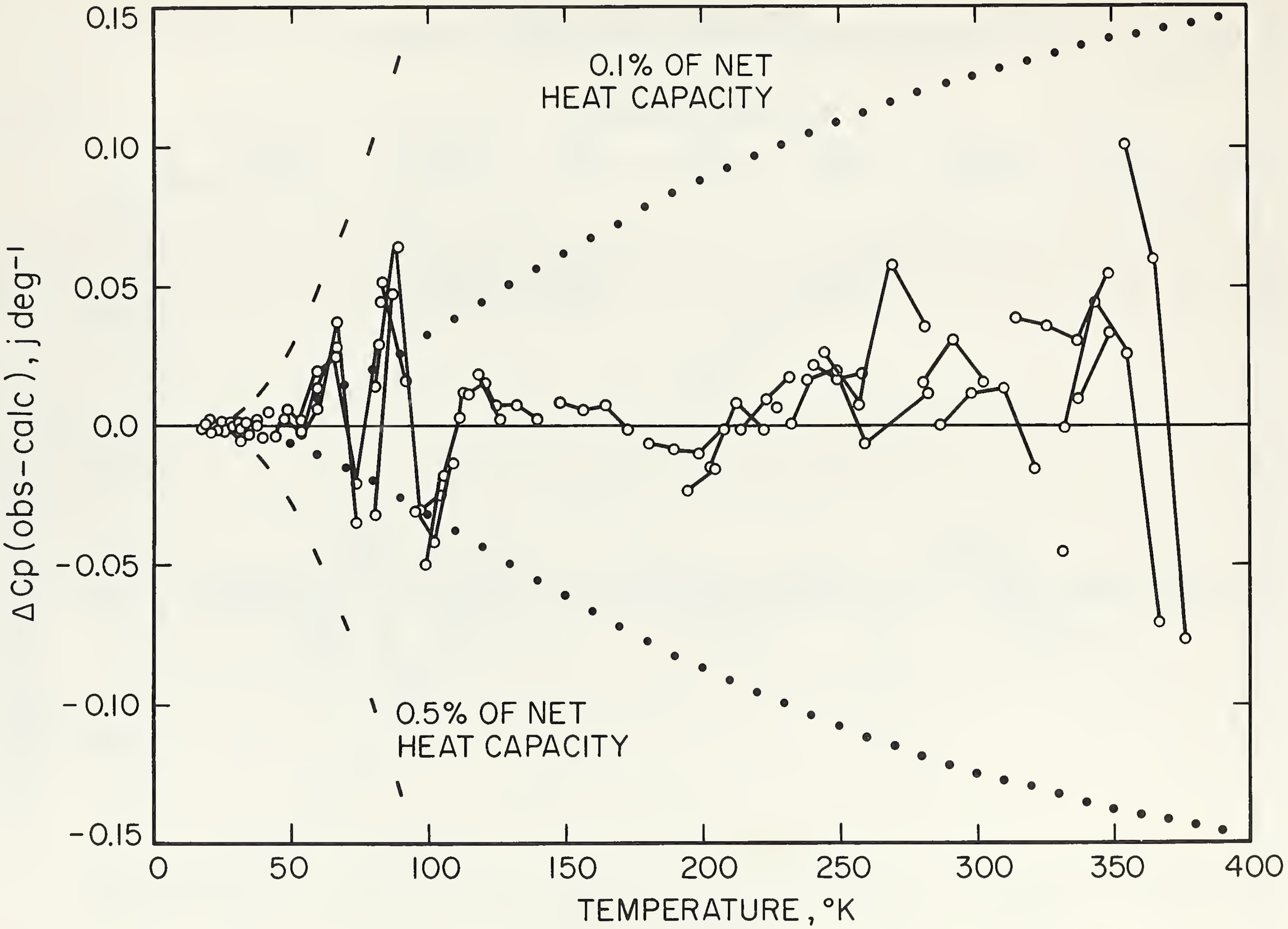


Fig. 1. Deviations of the Heat-Capacity Measurements on Sample Plus Calorimeter Vessel

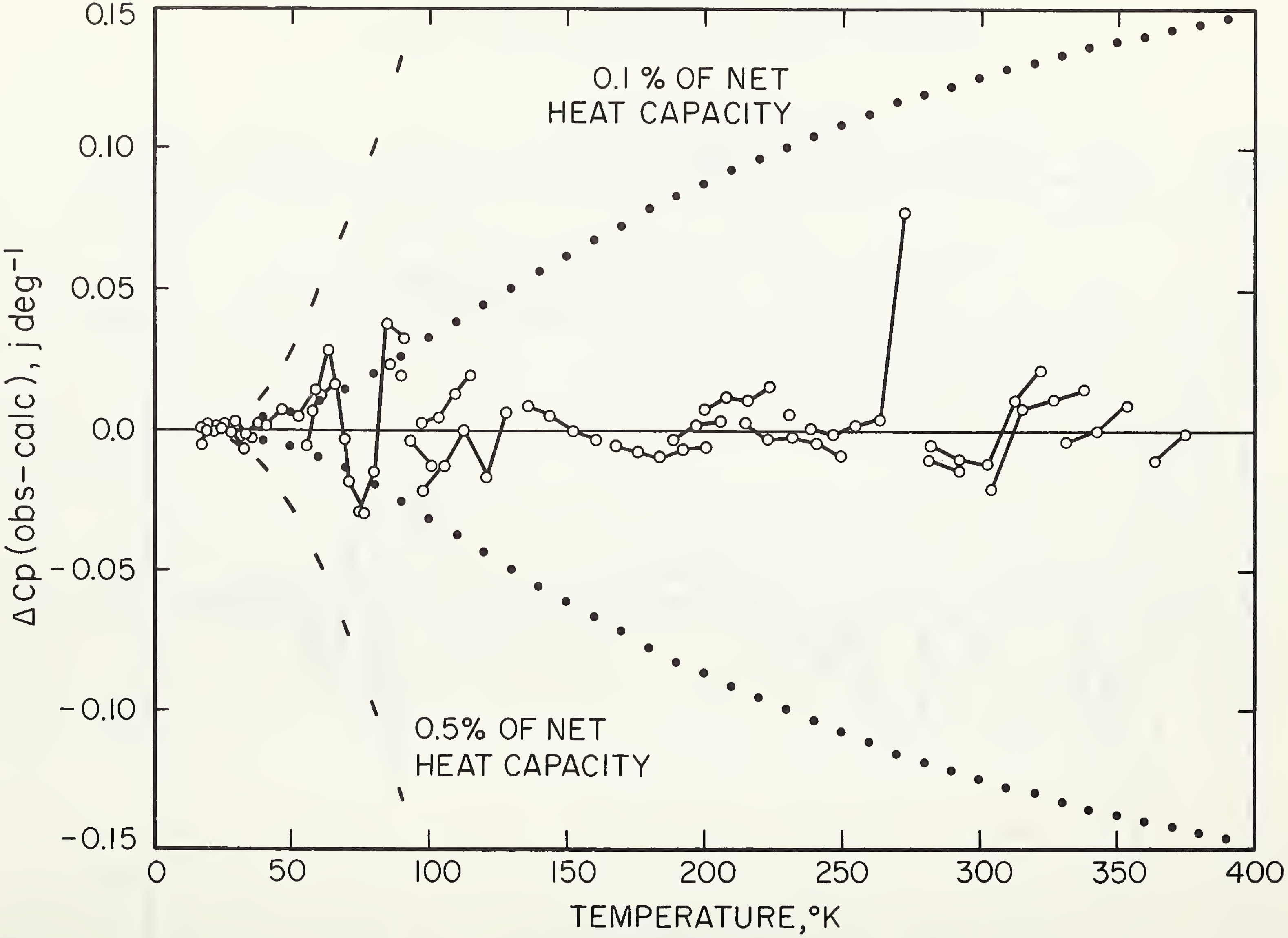


Fig. 2. Deviations of the Heat-Capacity Measurements on the Empty Vessel

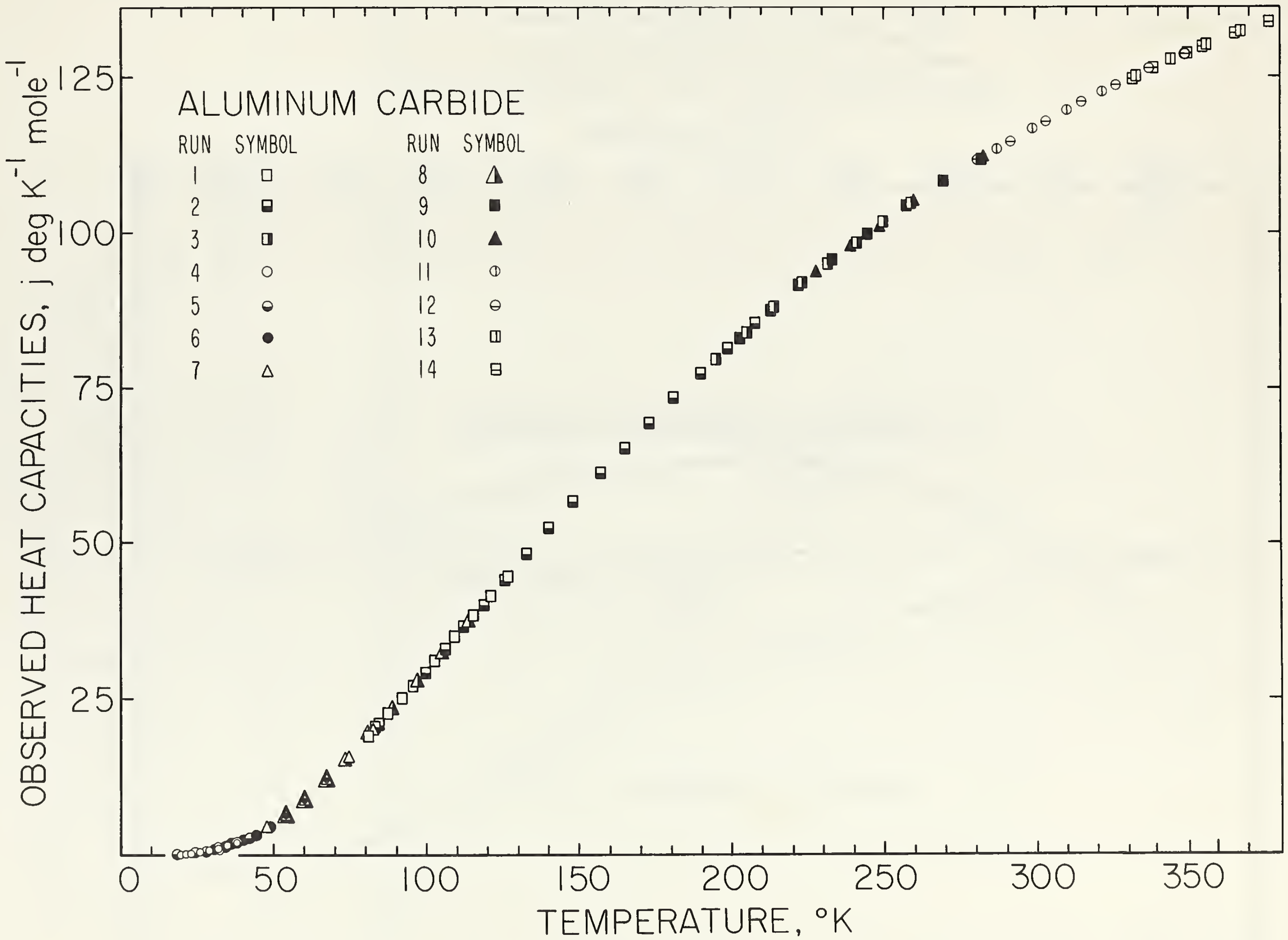


Fig. 3. Observed Values of the Molal Heat Capacity of Aluminum Carbide

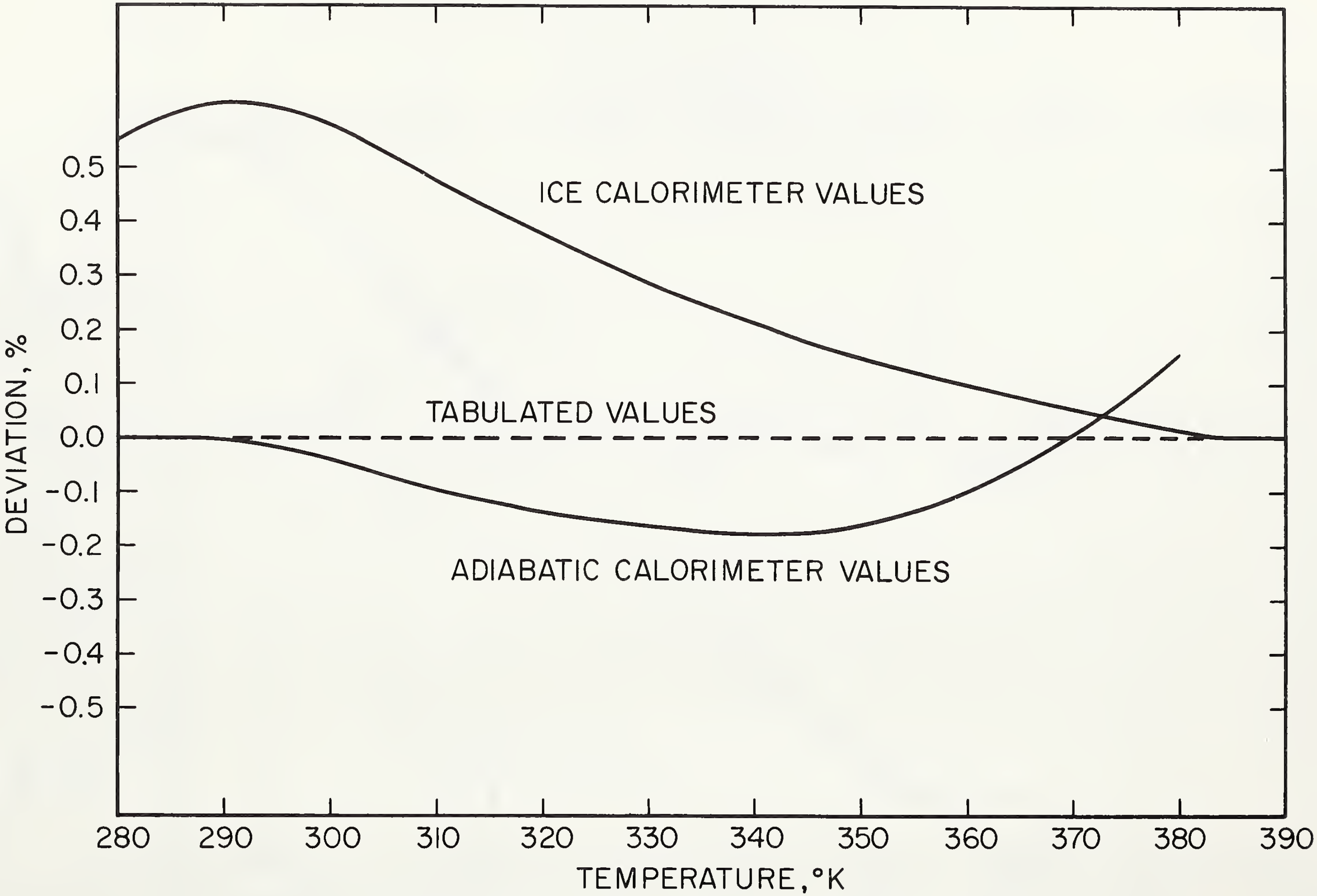


Fig. 4. Comparison of the Final Selected Values of Heat Capacity (Table 6) with those of the Low-Temperature Measurements and those Derived from the Enthalpy Equation (eq. (1))

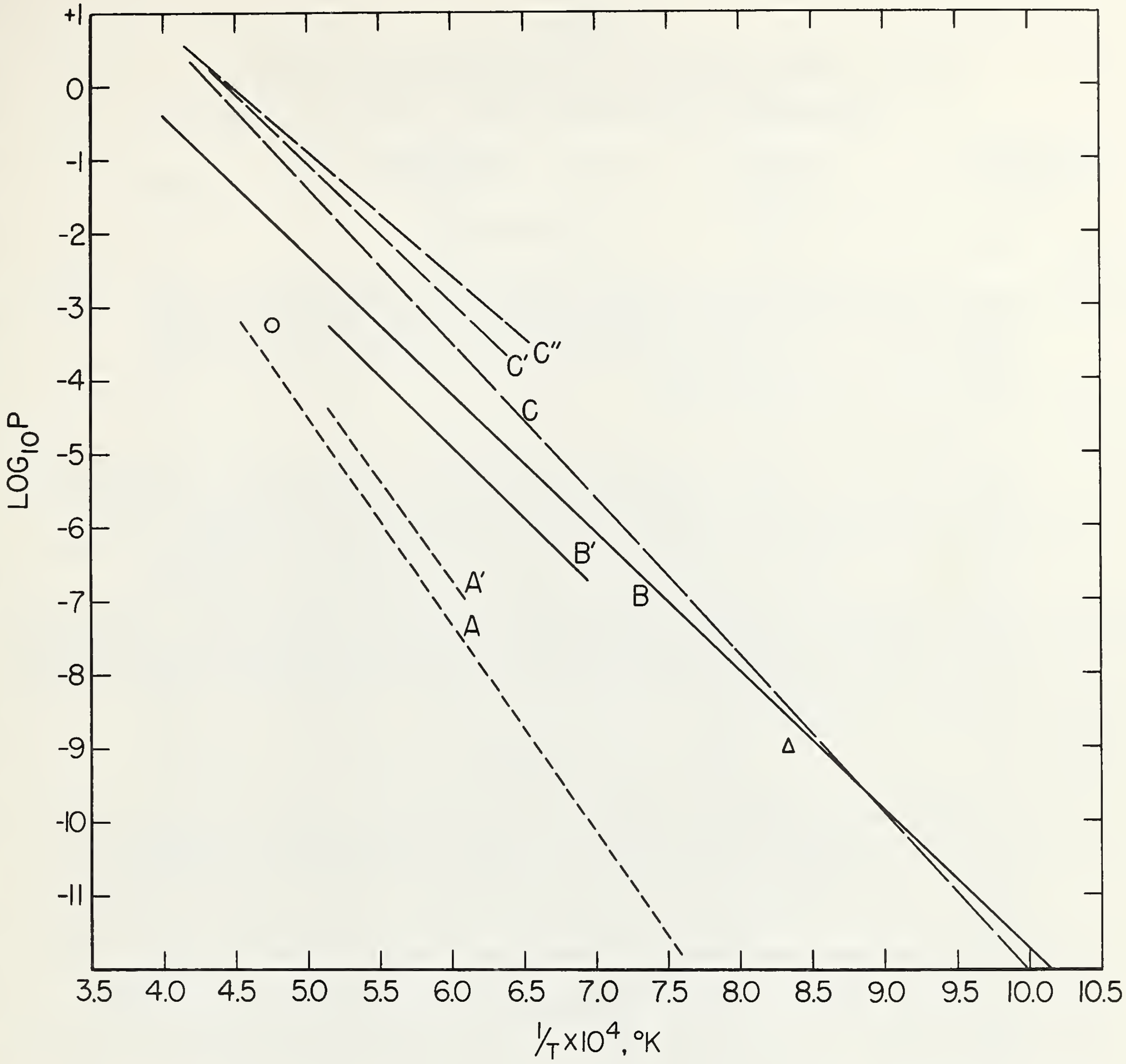


Fig. 5. Comparison of Vapor Pressures ($\log_{10}$ P vs. 1/T) Calculated from Heat of Formation and Thermodynamic Data with Published Values Obtained in High-Temperature Equilibrium Measurements.

(a) --- $4A\ell N(c) + 3C(c) \rightarrow A\ell_4C_3(c) + 2N_2(g)$: A = calculation from thermal data, A' = Prescott and Hincke [20].

(b) — $A\ell_4C_3(c) \rightarrow 4A\ell(g) + 3C(c)$: B = calculation from thermal data, B' = Meschi and Searcy [19], ⊙ = Chupka *et al*. [28], ▲ = Campbell [29].

(c) — - — $2A\ell_2O_3(c) + 9C(c) = A\ell_4C_3(c) + 6CO(g)$: C = calculation from thermal data, C' = Prescott and Hincke [21], C'' = Brunner [24].

Chapter 3

BERYLLIUM ALUMINATE (CHRYSOBERYL), $BeO \cdot Al_2O_3$ MEASUREMENTS OF THE HEAT CAPACITY FROM 16° to 380 °K

by George T. Furukawa and William G. Saba

1. Introduction

The heat capacity of beryllium aluminate (chrysoberyl), $BeO \cdot Al_2O_3$, was measured in the range 16° to 380 °K. (Henceforth, the name chrysoberyl will be used synonymously with beryllium aluminate, $BeO \cdot Al_2O_3$.) The thermodynamic properties were calculated from the results of the measurements.

Chrysoberyl occurs in nature in various shades of green, brown, and yellow, or red by transmitted light, with orthorhombic, dipyramidal crystal structure (a_o 5.47, b_o 9.39, c_o 4.42; all ±1 percent.) [1]. The gem variety that is red by transmitted light (Cr impurity has been reported) is known as alexandrite and the variety that exhibits chatoyancy, as cat's eye. Iron is the usual impurity, substituting for Be and Al in the ferrous and ferric forms, respectively. The ferric form in amounts up to six percent by weight Fe_2O_3 has been reported [1]. Titanium has also been reported as impurity, presumably due to mechanical inclusion of rutile.

2. Sample

The known naturally occurring chrysoberyl samples were considered too impure for the investigation. A sample was specially prepared on request by the Semi-Elements, Inc. by arc fusion of a stoichiometric mixture of high-purity BeO and Al_2O_3 powder. The procedure involved the formation of a melted mass within a relatively large charge of the mixture so that the powdered mixture would serve as the "container" for the melted sample to avoid chemical contamination. The fused sample was slowly cooled to room temperature and any material that was not fused adhering to the outer surface was removed mechanically. The fused material was crushed and sieved to collect particles between 10 and 50 mesh sizes (between 0.3 and 2 mm).

The material as received contained many particles that appeared gray, presumably from traces of graphite from the electrodes used in the arc fusion process. Qualitative spectrochemical examination of the sample by the Spectrochemistry Section of the National Bureau of Standards showed the limits of percentage impurities given in Table 1.

Table 1

Spectrochemical Analysis of the Beryllium Aluminate ($BeO \cdot Al_2O_3$) Sample[a]

Element	Percentage Limit	Element	Percentage Limit
Si	< 0.01	Ca	0.001 - 0.01
Cu	0.01 - 0.1	V	0.0001- 0.001
Ni	0.01 - 0.1	Sn	< 0.001
Fe	0.001- 0.01	Pb	< 0.001
Mg	0.001- 0.01	Ag	< 0.0001

[a] Analysis by Martha Darr, Spectrochemistry Section of the National Bureau of Standards.

Alvin Van Valkenburg of the Constitution and Microstructure Section of the National Bureau of Standards examined the $BeO \cdot Al_2O_3$ sample by the petrographic (microscopic) method. He found the particle size to be about 200 microns. Since the material was subjected to a grinding process for the microscopic examination, the original $BeO \cdot Al_2O_3$ crystals were, therefore, considered larger than 200 microns. The index of refraction was in agreement with that previously reported for the substance. The crystals were clear but showed some growth defects, presumably from rapid crystallization. A small volume of what appeared to be voids was observed. No impurity phases of BeO or Al_2O_3 crystal were found.

H. Steffen Peiser of the Crystal Chemistry Section of the National Bureau of Standards also examined the $BeO \cdot Al_2O_3$ sample by X-ray diffraction techniques. The diffraction pattern showed several strong lines characteristic of the $BeO \cdot Al_2O_3$ crystal. No lines characteristic of separate crystalline phases of BeO, Al_2O_3, or $BeO \cdot 3Al_2O_3$ were found. A small amount of impurity phase was observed that could not be identified nor its amount estimated from the X-ray results.

Thomas J. Murphy of the National Bureau of Standards Applied Analytical Research Section chemically analyzed two samples for Al and Be. One sample was hand picked to be clear and free from gray coloration; the other was a sample that represented the bulk lot and contained many particles with the gray coloration. The samples were first dissolved in concentrated hydrochloric acid in a sealed ampoule by heating for 24 hours at 250° to 300 °C within a pressurized bomb. A known mixture of BeO and

Al_2O_3 was treated in the same manner as a control on the analysis. The aluminum was precipitated as the 8-hydroxyquinolate, $Al(C_9H_6ON)_3$, after buffering with acetate to the pH of 4.2 - 4.5. The precipitate was ignited to Al_2O_3 and weighed. The beryllium was precipitated as $Be(OH)_2$ at the pH of 8-9 with ammonium hydroxide, ignited to BeO, and weighed. The results of the chemical analyses summarized in Table 2 show the sample to be highly pure.

Table 2

Chemical Analysis of the Beryllium Aluminate ($BeO \cdot Al_2O_3$) Samples[a]

Sample	Percentage by Weight		Molar Ratio
	Al_2O_3	BeO	Al_2O_3/BeO
Hand Picked	80.25	19.73	0.998
Random	80.33	19.72	1.000
Theoretical	80.30	19.70	1.000

[a] Analysis by Thomas J. Murphy, Applied Analytical Research Section of the National Bureau of Standards.

The amount of graphite impurity was considered insignificant, and the sample was taken to be 100 percent pure in the processing of the heat-capacity data.

3. Apparatus and Method

The heat-capacity measurements were made in an adiabatic calorimeter similar in principle and design to that described previously [2]. The sample vessel was suspended within the adiabatic shield system by means of a Nylon cord instead of the filling tube shown in the above reference. The adiabatic shields were controlled automatically by means of electronic and electro-mechanical equipment. The details of the calorimeter design and the automatic control equipment will be described in a subsequent publication.

The electrical power input to the calorimeter heater was measured by means of a Wenner potentiometer with reference to saturated standard cells and standard resistors calibrated at the National Bureau of Standards. A volt box was employed for the measurement of the voltage drop across the calorimeter heater. Adjustments were made in the calculation of the power for the current in the volt box and for the resistance of the potential leads to the calorimeter heater.

The time interval of heating was determined by means of a precision timer operated on a 60 c/s frequency, furnished at the National Bureau of Standards, that is based on a 100 kc/s quartz oscillator maintained stable within 0.5 ppm in three months. The oscillator frequency is compared and adjusted periodically with the WWV frequency broadcasts.

Temperatures were determined by means of a platinum-resistance thermometer and a high precision Mueller bridge. The thermometer was calibrated by the Temperature Physics Section of the National Bureau of Standards. The calibration above 90 °K was in accordance with the 1948 International Practical Temperature Scale [3], and between 10° and 90 °K in accordance with the National Bureau of Standards 1955 provisional scale [4]. (The provisional scale as it is presently maintained at the National Bureau of Standards, and referred to as degrees K (NBS-1955), is numerically 0.01 deg lower than the former NBS-1939 scale [4].)

The 1961 atomic weights based on carbon-12 were used to convert the mass of sample investigated to molal basis [5]. Wherever the energy unit calorie is used, the conversion from the cgs unit of energy joule was made using the relation: 1 defined calorie = 4.1840 joules.

4. Heat-Capacity Measurements and Results

The chrysoberyl sample, being considered quite stable, was poured directly into the calorimeter vessel; that is, the sample was handled in the usual laboratory atmosphere. The vessel with its contents was pumped to a high vacuum and purged with dry helium gas several times and finally sealed with a few cm-Hg pressure of helium gas. The mass of sample investigated was 210.4113 g.

The heat-capacity measurements were made on the calorimeter vessel plus the sample from about 16° to 380 °K. This was followed by another series of measurements in the same temperature range on the empty vessel. The analyses and calculations on these measurements were performed on the IBM 7094 computer. Since some of the details of these calculation procedures are given in Chapter 2 of this report dealing with the heat-capacity measurements on Al_4C_3, only a brief description will be given here.

From the measurements, smooth values of heat capacity at regular temperature intervals were obtained for the calorimeter vessel plus the sample and for the empty vessel. The heat capacity of the sample was obtained by differencing the smoothed values from the two series of measurements at the corresponding regular temperatures. A correction was made wherever significant for the heat capacity of helium gas. The values of heat capacity of the sample so obtained were smoothed further wherever necessary and finally converted to molal basis. The precision of the heat-capacity measurements on chrysoberyl is shown in Figures 1

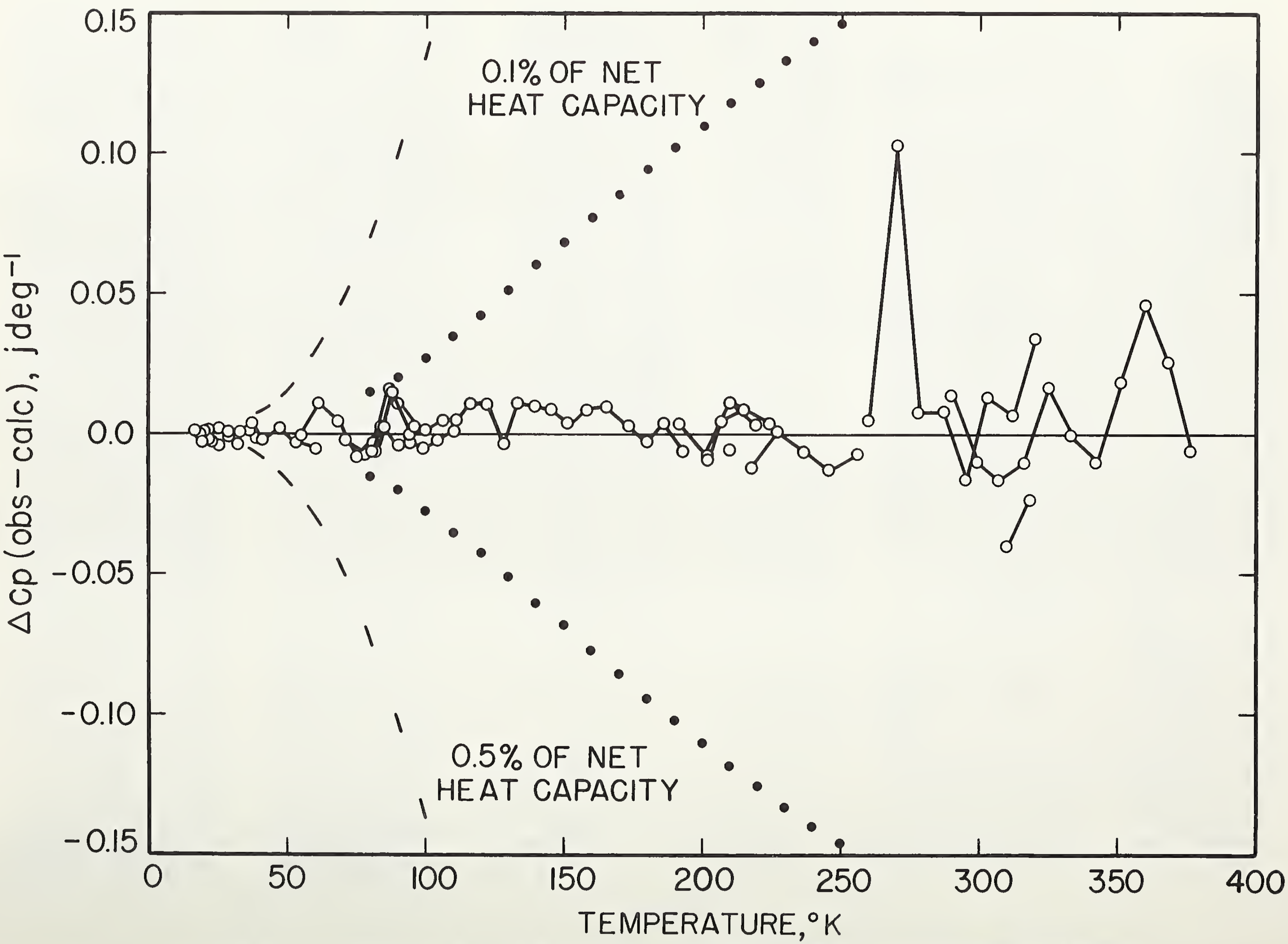


Fig. 1. Deviations of the Heat-Capacity Measurements on Calorimeter Vessel Plus Beryllium Aluminate ($BeO \cdot Al_2O_3$)

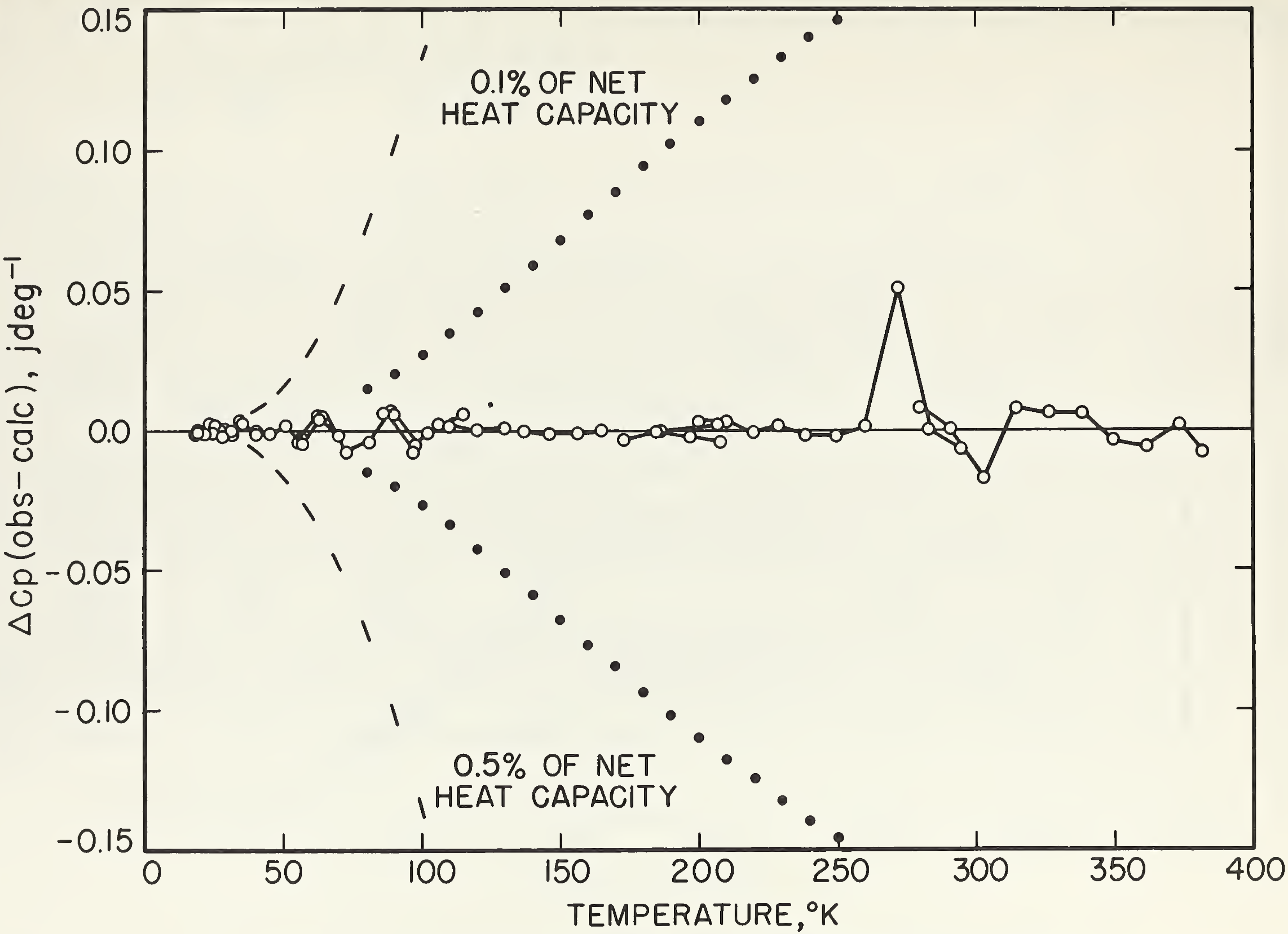


Fig. 2. Deviations of the Heat-Capacity Measurements on the Empty Calorimeter Vessel Used with Beryllium Aluminate ($BeO \cdot Al_2O_3$)

TABLE 3. OBSERVED HEAT CAPACITY OF BERYLLIUM ALUMINATE (BE $O.AL_2O_3$)

MOLECULAR WEIGHT = 126.9728, $^0K = ^0C + 273.15^0$

T	C_P
^0K	J/DEG/MOLE
RUN 1	
80.5473	9.004
85.1541	10.601
89.5817	12.213
94.1573	13.972
99.0805	15.979
104.3141	18.235
109.8372	20.731
RUN 2	
81.6181	9.368
87.7681	11.557
93.6407	13.773
99.6463	16.223
105.4574	18.746
110.7585	21.160
116.0659	23.675
121.6485	26.400
127.4847	29.315
133.3266	32.309
139.1501	35.326
145.0459	38.408
151.3929	41.737
158.0993	45.261
165.1286	48.935
172.4762	52.734
179.4524	56.295
186.1141	59.649
193.0372	63.060
RUN 3	
54.5979	2.637
61.0699	3.832
68.1901	5.443
75.1174	7.308
81.4060	9.297
87.3603	11.408
RUN 4	
70.8972	6.134
77.5194	8.033
83.6752	10.081
89.7941	12.305
95.9958	14.715
RUN 5	
28.7003	0.323
33.3094	0.515
37.3141	0.742
41.4620	1.043
46.6291	1.550
52.9692	2.382
59.5633	3.521
RUN 6	
19.2684	0.092
20.8630	0.120
22.8544	0.158
25.2148	0.216
RUN 7	
16.4504	0.045
18.3613	0.079
20.2893	0.112
22.4282	0.152
25.2495	0.213
28.2888	0.306
31.7145	0.438
35.3961	0.626
39.3311	0.877
RUN 8	
201.7985	67.283
207.5974	70.018
215.3999	73.600
224.0728	77.459
RUN 9	
209.6930	70.985
218.4723	74.970
227.3537	78.883
236.6705	82.834
246.3094	86.771
255.8343	90.521
259.9653	92.108
269.0604	95.546
277.9055	98.641
286.5293	101.591
294.8939	104.322
303.1446	106.945
311.5147	109.488
320.0179	111.998
RUN 10	
309.7608	108.934
317.7316	111.301
RUN 11	
290.0458	102.762
298.7850	105.567
307.3395	108.215
315.9789	110.797
324.7663	113.340
333.5567	115.764
342.3312	118.096
350.9917	120.335
359.5197	122.458
367.8734	124.451
376.1640	126.394
RUN 12	
191.3362	62.230
201.1287	66.960
210.4197	71.327
219.2943	75.347

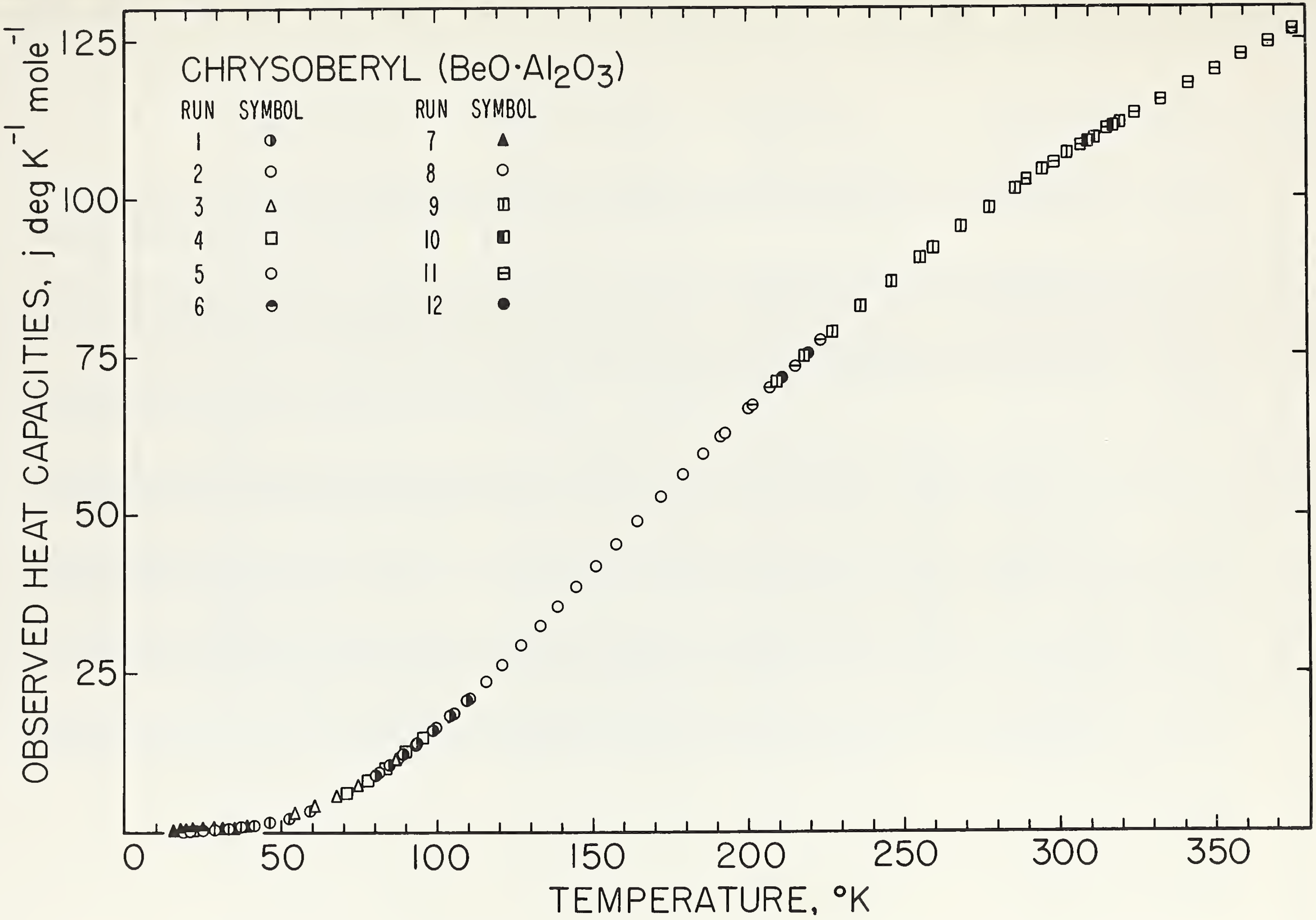


Fig. 3. Observed Values of the Molal Heat Capacity of Beryllium Aluminate ($BeO \cdot Al_2O_3$). (The numerical values are given in Table 3)

TABLE 4

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM ALUMINATE ($BE\ O \cdot AL_2O_3$)
SOLID PHASE

GRAM MOLECULAR WT.=126.9728 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G^0_T-H^C_0)/T$	$(H^0_T-H^C_0)/T$	S^0_T	$(H^0_T-H^C_0)$	C^0_P	$-(G^0_T-H^C_0)$
DEG K	$\frac{CAL}{DEG-MOLE}$	$\frac{CAL}{DEG-MOLE}$	$\frac{CAL}{DEG-MOLE}$	$\frac{CAL}{MOLE}$	$\frac{CAL}{DEG-MOLE}$	$\frac{CAL}{MOLE}$
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.000	0.000	0.000	0.000	0.000
10.00	0.000	0.001	0.001	0.008	0.003	0.003
15.00	0.001	0.003	0.004	0.040	0.011	0.013
20.00	0.002	0.006	0.009	0.128	0.026	0.042
25.00	0.004	0.012	0.017	0.311	0.050	0.104
30.00	0.007	0.022	0.029	0.649	0.088	0.215
35.00	0.011	0.035	0.046	1.219	0.143	0.401
40.00	0.017	0.053	0.070	2.119	0.221	0.689
45.00	0.025	0.077	0.102	3.474	0.327	1.116
50.00	0.034	0.109	0.143	5.441	0.466	1.724
55.00	0.047	0.149	0.196	8.198	0.644	2.567
60.00	0.062	0.199	0.261	11.942	0.860	3.703
65.00	0.080	0.259	0.339	16.863	1.115	5.197
70.00	0.102	0.331	0.432	23.151	1.407	7.121
75.00	0.127	0.413	0.541	30.994	1.737	9.547
80.00	0.157	0.507	0.664	40.588	2.108	12.552
85.00	0.191	0.613	0.804	52.143	2.519	16.216
90.00	0.229	0.731	0.960	65.822	2.956	20.622
95.00	0.272	0.861	1.133	81.748	3.419	25.848
100.00	0.320	1.001	1.320	100.06	3.911	31.973
105.00	0.372	1.151	1.524	120.90	4.430	39.077
110.00	0.429	1.313	1.742	144.40	4.972	47.235
115.00	0.492	1.484	1.975	170.65	5.533	56.523
120.00	0.558	1.665	2.223	199.76	6.112	67.014
125.00	0.630	1.854	2.485	231.80	6.706	78.777
130.00	0.707	2.053	2.759	266.84	7.311	91.882
135.00	0.788	2.259	3.047	304.93	7.925	106.39
140.00	0.874	2.472	3.346	346.10	8.546	122.37
145.00	0.965	2.692	3.657	390.39	9.171	139.87
150.00	1.060	2.919	3.978	437.81	9.799	158.96
155.00	1.159	3.151	4.310	488.38	10.427	179.67
160.00	1.263	3.388	4.651	542.08	11.053	202.07
165.00	1.371	3.630	5.001	598.91	11.678	226.20
170.00	1.483	3.876	5.358	658.85	12.298	252.09
175.00	1.599	4.125	5.724	721.87	12.912	279.80
180.00	1.719	4.378	6.096	787.96	13.521	309.34
185.00	1.842	4.633	6.475	857.07	14.123	340.77
190.00	1.969	4.890	6.859	929.17	14.716	374.10
195.00	2.099	5.150	7.249	1004.2	15.301	409.37
200.00	2.233	5.411	7.644	1082.2	15.877	446.60
205.00	2.370	5.673	8.043	1163.0	16.444	485.82
210.00	2.510	5.936	8.446	1246.6	17.000	527.04
215.00	2.652	6.200	8.852	1333.0	17.547	570.28
220.00	2.798	6.464	9.262	1422.0	18.084	615.56
225.00	2.946	6.728	9.674	1513.8	18.610	662.90
230.00	3.097	6.992	10.089	1608.1	19.127	712.31
235.00	3.250	7.255	10.506	1705.0	19.633	763.80
240.00	3.406	7.519	10.924	1804.4	20.130	817.37
245.00	3.563	7.781	11.344	1906.3	20.617	873.04
250.00	3.723	8.042	11.766	2010.6	21.094	930.81
255.00	3.885	8.303	12.188	2117.2	21.561	990.70
260.00	4.049	8.562	12.611	2226.2	22.018	1052.7
265.00	4.214	8.820	13.035	2337.4	22.466	1116.8
270.00	4.382	9.077	13.459	2450.8	22.904	1183.0
273.15	4.488	9.238	13.726	2523.4	23.174	1225.9
275.00	4.551	9.332	13.883	2566.4	23.331	1251.4
280.00	4.721	9.586	14.307	2684.1	23.749	1321.9
285.00	4.893	9.838	14.731	2803.9	24.157	1394.5
290.00	5.066	10.089	15.155	2925.7	24.556	1469.2
295.00	5.241	10.337	15.578	3049.4	24.945	1546.0
298.15	5.351	10.493	15.844	3128.4	25.185	1595.5
300.00	5.417	10.584	16.000	3175.1	25.325	1625.0
305.00	5.593	10.828	16.422	3302.7	25.697	1706.0
310.00	5.772	11.071	16.843	3432.1	26.060	1789.2
315.00	5.951	11.312	17.263	3563.3	26.415	1874.4
320.00	6.131	11.551	17.681	3696.2	26.763	1961.8
325.00	6.312	11.787	18.099	3830.9	27.104	2051.3
330.00	6.493	12.022	18.515	3967.2	27.437	2142.8
335.00	6.676	12.254	18.930	4105.2	27.762	2236.4
340.00	6.859	12.485	19.344	4244.8	28.081	2332.1
345.00	7.043	12.713	19.756	4386.0	28.392	2429.8
350.00	7.228	12.939	20.167	4528.8	28.697	2529.6
355.00	7.413	13.163	20.576	4673.0	28.995	2631.5
360.00	7.598	13.385	20.984	4818.7	29.287	2735.4
365.00	7.784	13.605	21.390	4965.8	29.575	2841.3
370.00	7.971	13.823	21.794	5114.4	29.860	2949.3
373.15	8.089	13.959	22.048	5208.8	30.039	3018.3

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

and 2 in which the deviations of the observed values from the smoothed values are plotted for each series of measurements.

Figure 3 shows the plot of the "observed molal heat capacity." Table 3 gives the numerical values. These values were obtained by differencing the heat capacity of the empty vessel and that of the vessel plus sample at the observed temperatures (mid-temperature of the heating interval) of the latter series of measurements. The heat capacity of the empty vessel at the corresponding temperatures was obtained by interpolation in the table of smooth values at regular temperature intervals described earlier. The values were corrected for the heat capacity of the helium gas and for curvature wherever significant and converted to molal basis.

5. Thermodynamic Functions

The smoothed values of heat capacity were used to derive the various thermodynamic functions. The values of heat capacity below 16 °K, the lower limit of the measurements, were obtained by extrapolation using a Debye heat-capacity function fitted to the observed values. The thermodynamic relations involving the heat capacity were evaluated by numerical integration on the IBM 7094 computer. These results based on the low-temperature measurements are given in Table 4.

The thermodynamic properties obtained at the low temperatures were combined with those obtained at the high temperature (Chapter 4). Some adjustments were made for joining the two measurements smoothly. The combined table is given in Appendix B (B-83 Revised). In the interval 273.15° to 373.15 °K where the adjustments in the low-temperature data were made, the enthalpy increment of the final table of thermodynamic functions is 2683.6 cal/mole. The value based only on the low-temperature data is 2685.4 cal/mole, showing that the adjustment to the low-temperature data was small.

A comparison of the heat capacity of chrysoberyl with that of an equimolar mixture of BeO and Al_2O_3 is shown in Figure 4. The values for BeO were selected from the preliminary measurements obtained at National Bureau of Standards and those for Al_2O_3 were previously published [6]. The results below 40 or 50 °K shown in Figure 3 are uncertain because of large errors in the heat capacity at the lower temperatures. The comparison shows that the heat capacity of chrysoberyl is higher than that of an equimolar mixture of BeO and Al_2O_3. A minimum deviation occurs at about room temperature. Within ±80° of the room temperature the deviation from addivity is about 1 percent.

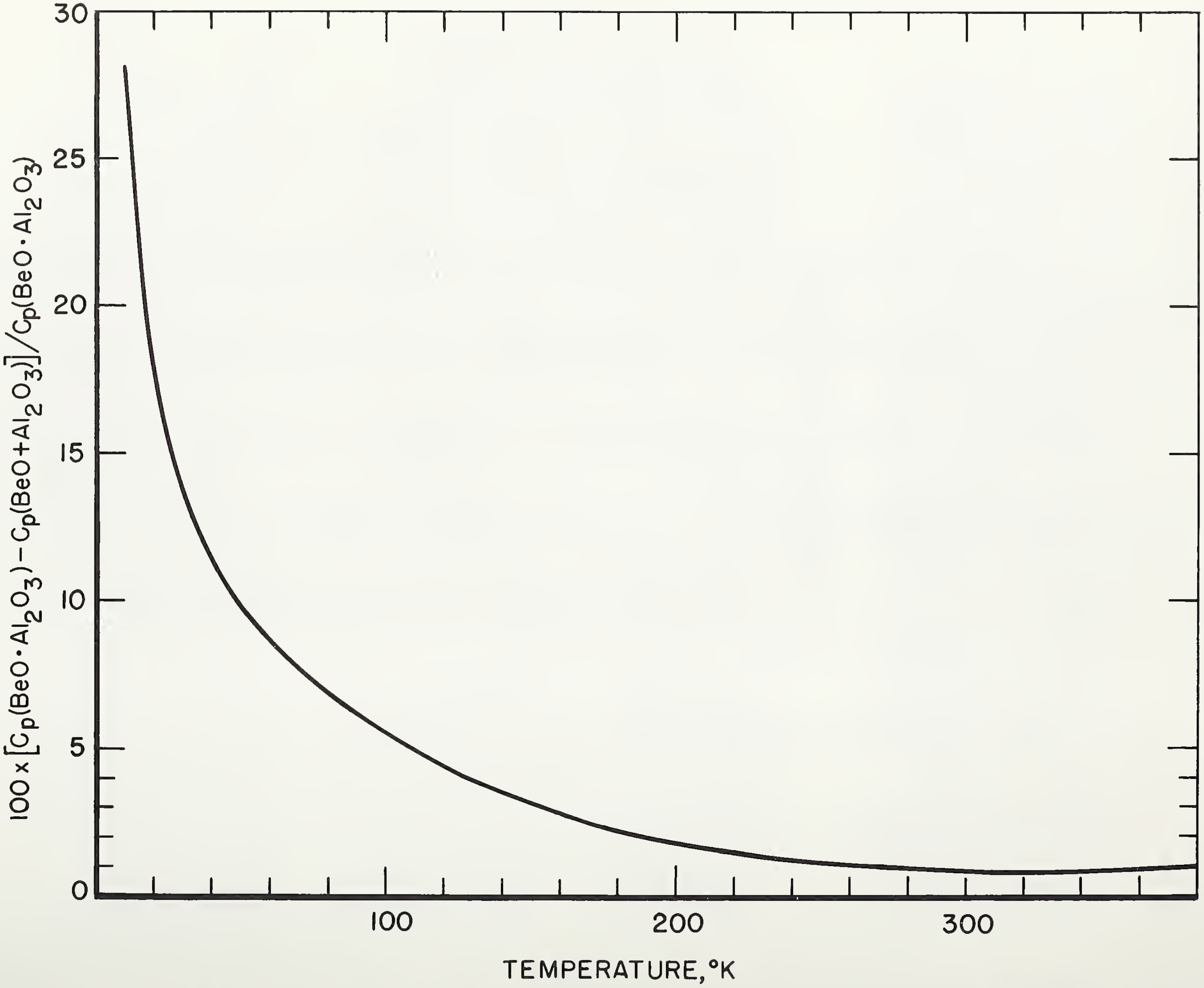


Fig. 4. Comparison of the Heat Capacity of Beryllium Aluminate ($BeO \cdot Al_2O_3$) with that of Equimolar Mixture of BeO and Al_2O_3

6. References

[1] C. Palache, H. Berman, and C. Frondel; "The System of Mineralogy," Vol. 1, J. Wiley and Sons, New York, 1944.

[2] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedabl; J. Research NBS 35, 39 (1945).

[3] H. F. Stimson, J. Research NBS 65A, 139 (1961).

[4] H. J. Hoge and F. G. Brickwedde, J. Research NBS 22, 351 (1939).

[5] "IUPAC Revises Atomic Weight Values," Chem. Eng. News 39, 42 (1961).

[6] G. T. Furukawa, T. B. Douglas, R. E. McCaskey and D. C. Ginnings, J. Research NBS 57, 67 (1956).

Chapter 4

$BeO \cdot Al_2O_3$: MEASUREMENTS AT THE NATIONAL BUREAU OF STANDARDS OF ITS RELATIVE ENTHALPY FROM 273 TO 1173°K

by

Thomas B. Douglas and William H. Payne

The relative enthalpy of a sample of $BeO \cdot Al_2O_3$ (here called "sample 1") was measured from 273 to 1173°K in 1962, and the results, together with a provisional table of thermodynamic functions based on them, were presented in an earlier report [1]. Since then, a new, purer sample of the compound (here called "sample 2") has become available, and low-temperature heat-capacity measurements on it are described in the present report (Chapter 3). In 1963 a complete series of high-temperature enthalpy measurements (from 273 to 1173°K) also were made on sample 2. Recently, small corrections have been applied to the earlier [1] high-temperature data on sample 1, and the results for both samples are therefore presented together below.

The details of preparation, examination, and analysis of the two samples may be found in the earlier report [1] and Chapter 3 of the present report, but may be summarized below for comparison.

Sample 1. Prepared by heating a 1:1-mole-ratio mixture of powdered BeO and Al_2O_3 (each purer than 99.9%) at 1775 and, after further grinding and pressing, at 1800°C (which is below the melting point). X-ray examination detected as separate phases no BeO, but possibly a little α-Al_2O_3 and small indeterminate amounts of unidentified impurities not so found in sample 2; the most important x-ray impurity line (CuK_α) was at 21.9° (2θ) 4.25Å[2]. Chemical analysis [3] indicated (stoichiometrically) 80.88 ±0.03 weight % of Al_2O_3 and 19.05 ±0.05 weight % of BeO. (The theoretical percentages for $BeO \cdot Al_2O_3$ are 80.30 and 19.70 respectively.)

Sample 2. Prepared by arc-melting a 1:1-mole-ratio mixture of pure BeO and Al_2O_3. X-ray examination detected as separate phases no BeO nor Al_2O_3 and only one impurity phase (in about one-third the amount) as so found in sample 1 [2]. Chemical analysis [3] indicated (stoichiometrically) 80.25 weight % of Al_2O_3 and 19.73 weight % of BeO for a "hand-picked" specimen, and corresponding values of 80.33 and 19.72 for a "random" specimen. Qualitative spectrochemical analysis [4] indicated between 0.01 and 0.1% each of Cu and Ni, but less (probably) than 0.01% each of Si and the seven other metallic elements looked for.

Thus, while the phase and chemical composition of sample 1 are believed to be known with rather high accuracy, sample 2 was definitely purer and, within the precision of the analyses, may be assumed to be pure $BeO \cdot Al_2O_3$.

The high-temperature enthalpy measurements were made by the "drop" method using a Bunsen ice calorimeter. In brief the method, which has been described in detail in previous publications [5], is as follows. The sample, enclosed in a suitable container, is suspended inside a thick-wall silver pipe in a furnace until it comes to a constant, known temperature. It is then dropped, with nearly free fall, into the ice calorimeter, which measures the heat then evolved by the sample plus container in cooling to 0°C. In order to account for the enthalpy of the container itself and the small but appreciable heat lost during the drop, similar measurements are made with the empty container at the same furnace temperature. In the present case the furnace temperature was measured by two independently calibrated Pt--Pt-10% Rh thermocouples, each serving as a check on the other, and the sample was sealed, in an atmosphere of air, in a flame-welded container of pure silver.

In Table 1 are given the corrected but unsmoothed observed heat values, their weighted means, and the values calculated from an empirical equation derived to represent the smoothed values.

Columns 2 and 3 give the heat values obtained in individual measurements on the two respective samples (of different mass) in their containers. Column 2 has been corrected for the excess Al_2O_3 in the sample, as well as by small amounts to refer the results to the temperatures in column 1; column 3 required no such corrections. It was considered unnecessary to make corresponding heat measurements on the actual empty containers that were used with the samples, since the container material (silver) is free of transitions over the entire temperature range and is easily annealed to a reproducible state. The empty-container values in column 4 are smoothed values calculated from an empirical equation derived earlier from precise results on two different containers of the same masses as those used with the present samples.

Columns 5, 6, and 8 give the net enthalpy values for the sample, each value in column 5 or 6 being derived from the corresponding value in column 2 or 3 after subtracting the value in column 4 and converting the difference to the basis of one "mole" of $BeO \cdot Al_2O_3$.

As shown by column 7, the mean values for sample 2 are almost consistently higher than those for sample 1 by several tenths of a percent, and above 300°C columns 5 and 6 do not overlap. The cause for this systematic discrepancy between the two samples is not known. Despite the generally better precision for sample 1 (column 5 compared with column 6), it was decided to give half as much weight to the mean

Table 1

Enthalpy Measurements on $BeO \cdot Al_2O_3$

1	2	3	4	5	6	7	8	9	10
Furnace Temperature t°C[a]	Measured heat (cal)[b]			$H_t-H_{0°C}$, net for sample (cal/mole)[b,c]					
	Sample 1[d] and container	Sample 2[e] and container	Empty container[f]	Sample 1	Sample 2	Sample 2 minus sample 1 (%)	Weighted mean obs.[g]	Calculated from eq. (1)	Weighted mean obs. -calcd (%)
100.0	188.32 186.85 187.41	244.06 241.24 239.99	74.27	2656 2622 2635	2719 2674 2654	+1.7	2667	2683	-0.6
200.0	402.30 401.99	513.77 517.16 518.72	150.34	5867 5860	5820 5874 5899	0.0	5864	5899	-0.6
300.0	631.47 630.42	816.75 814.63 814.88	227.85	9399 9375	9430 9396 9400	+0.2	9402	9410	-0.1
400.0	869.35 869.47	1127.88 1128.47	306.81	13100 13103	13148 13158	+0.4	13136	13121	+0.1
500.0	1115.32 1116.50	1453.23 1452.79	387.39	16951 16979	17068 17061	+0.6	17031	16985	+0.3
600.0	1368.43 1369.63	1784.33 1790.15 1786.53 1785.58	469.83	20926 20954	21050 21143 21085 21070	+0.7	21038	20977	+0.3
700.0	1629.33 1628.59	2125.53 2125.60	554.42	25032 25014	25159 25160	+0.5	25114	25081	+0.1
800.0	1893.45 1893.45 1893.27 1894.93 1893.76	2472.93 2475.09	641.42	29156 29156 29152 29191 29163	29329 29364	+0.6	29286	29290	-0.0
900.0	2165.42 2164.90 2164.79	2831.93 2830.61	731.15	33400 33388 33385	33641 33620	+0.7	33551	33596	-0.1

[a] International Temperature Scale of 1948, as modified in 1954.

[b] 1cal = 4.1840 joules.

[c] Molecular weight = 126.973

[d] The values in this column are on the basis of a corrected sample mass of $BeO \cdot Al_2O_3$ of 5.4525 gm, and were obtained after correcting for temperature "errors" averaging 0.4 deg, and after subtracting the relative enthalpy of 0.1820 gm of Al_2O_3 impurity [5].

[e] Mass of sample 2 = 7.9290 gm.

[f] From a 4-constant empirical equation which deviates from the mean values observed for two containers (with masses of parts identical with those actually used for samples 1 and 2) by amounts varying from 0.01 to 1.1 cal.

[g] Calculated by giving half as much weight to the mean for sample 1 as to the mean for sample 2.

for this sample as to that for sample 2 (at a given temperature), because of the much lower amount of impurity in sample 2. The weighted means so obtained are given in column 8.

The following simple equation was derived to represent the relative high-temperature enthalpy of $BeO \cdot Al_2O_3$ (in cal/mole at T°K):

$$H_T - H_{273.15} = 34.9703T + 0.0039875T^2 + 1092300/T - 13848.6 \qquad (1)$$

The coefficients of the equation were derived by the least-squares method, and are based on the values of column 8 of Table 1 (weighted equally) except that several of the values obtained in the range 273° - 390°K by precise adiabatic calorimetry (see Chapter 3) also were included in order to make the equation approximate closely a smooth heat-capacity -- temperature function that would represent adequately both the low- and high-temperature calorimetry on $BeO \cdot Al_2O_3$. The values calculated from equation (1) for the temperatures in column 1 are given in column 9, and clearly represent the values observed by the drop calorimetry (columns 5 and 6) within their precision.

Further small adjustments were made in the heat capacities given by equation (1) between 273 and approximately 400°K (but not by more than 0.6% at and above 298°K). The final table of thermodynamic functions for crystalline $BeO \cdot Al_2O_3$ is given in Appendix B (Table B-83 Revised). This table is based on both the low-temperature calorimetry described in Chapter 3 and the high-temperature calorimetry described in the present chapter, with extrapolation from 1200° to 2150°K (the approximate melting point) by use of the heat capacities given by equation (1) in this temperature interval. This new table (B-83 Revised) supersedes the preliminary table of thermodynamic functions from 298 to 2143°K given earlier [1].

A practical purpose in measuring the enthalpy or heat capacity of such a substance as $BeO \cdot Al_2O_3$ is to improve on the rough estimate of the property as being the sum of the values of the same property (at the same temperature) for the same amounts of BeO and Al_2O_3, for which precise measurements have previously been made at NBS by drop calorimetry from 273 to 1173°K [7,5]. The enthalpy of $BeO \cdot Al_2O_3$ relative to that at 0°C may be compared with the additive values first. The values in Appendix B (Table B-83 Revised) are higher than additive by 0.6% at 100° and 200°C but from 300° to 900°C the agreement averages 0.1% and remains within 0.2%.(Comparing the unsmoothed mean observed values in Table 1, sample 1 is lower by about 1% at 100°C and by an average of 0.3% from 200° to 900°C, whereas sample 2 is higher by 0.6% at 100°C and by an average of 0.2% from 200° to 900°C.)

In Chapter 3 the heat capacity of $BeO \cdot Al_2O_3$ is compared with the additive values at low temperatures and found to be higher, the deviation decreasing with temperature to the neighborhood of 1% at room temperature. Using smoothed values, a similar comparison is made in Table 2 at and above room temperature. The heat capacity is, of course, more sensitive than the relative enthalpy to errors in the calorimetric data, so that the deviations shown for temperatures above 400°K must be considered within the combined experimental uncertainties.

Table 2

Deviations of the Smoothed High-Temperature Heat Capacity of $BeO \cdot Al_2O_3$ from Additivity Based on that of a Mixture of the Two Component Oxides at the Same Temperature

Temperature (°K)	Heat Capacity C_p°, cal/mole		ΔC_p° (Compound minus mixture) (%)
	1 $BeO \cdot Al_2O_3$ [a]	1 BeO [b] + Al_2O_3 [c]	
300	25.32	25.15	+0.7
400	31.34	31.07	+0.9
500	34.59	34.65	-0.2
600	36.72	37.00	-0.8
700	38.32	38.64	-0.8
800	39.64	39.86	-0.6
900	40.80	40.80	0.0
1000	41.85	41.54	+0.7
1100	42.84	42.15	+1.6
1200	43.78	42.66	+2.6

[a] From Table B-83 Revised (Appendix B).

[b] At 300°K, from reference [6]; above 300°K, smoothed values from reference [7].

[c] At 300°K, from reference [5]; above 300°K, the smoothed values from reference [8].

References

1. NBS Report 7587, National Bureau of Standards, Washington, D. C., 1 July 1962, pp. 44-54,172.

2. The X-Ray examinations were reported by H. S. Peiser, of NBS.

3. The chemical analyses were performed by T. J. Murphy, of NBS.

4. The spectrochemical analyses were performed by M. Darr, of NBS.

5. G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Research Natl. Bur. Standards 57, 67-82 (1956).

6. G. T. Furukawa and M. L. Reilly, private communication.

7. A. C. Victor and T. B. Douglas, J. Research Natl. Bur. Standards 67A, 325-329 (1963).

8. D. C. Ginnings, J. Phys. Chem. 67, 1917-1918 (1963).

Chapter 5

SOLID $Li_3A\ell F_6$: THERMODYNAMIC FUNCTIONS FROM 298 to 1000°K BASED ON RECENT MEASUREMENTS OF ITS RELATIVE ENTHALPY AT THE NATIONAL BUREAU OF STANDARDS

by Thomas B. Douglas and John E. Neufer

So far as is known, the system LiF-$A\ell F_3$ contains one solid compound, $Li_3A\ell F_6$, which melts congruently at approximately 790°C (1063°K) [1]. (This is analogous to the corresponding well-known sodium compound, which occurs naturally as the mineral cryolite.) The condensed-phase heat capacity and relative enthalpy of LiF and $A\ell F_3$ have already been measured accurately in both the low- and high-temperature ranges. Those of $Li_3A\ell F_6$ are currently being measured at the National Bureau of Standards; the measurements from 273 to 973°K have now been completed, and are reported here.

The sample was prepared and furnished by the Oak Ridge National Laboratory, of Oak Ridge, Tennessee, through the courtesy of R. E. Thoma and G. M. Hebert. Anhydrous $A\ell F_3$ was first heated with NH_4HF_2 to replace any oxygen by fluorine, and the product was then fused with LiF in a graphite crucible. Some lumps of the sample had a slight black coloration which is presumed to be due to carbon from the graphite crucible used, but in the NBS analyses described below no appreciable amount of carbon was found. The sample was examined at ORNL by X-ray diffractometer and petrographic microscope and found to be a single-phase material within the sensitivity of these methods (estimated to be 1% by volume for the petrographic technique). Further analysis showed 0.04% of water and 0.06% of other oxygen.

A specimen of the dried sample was later analyzed chemically at the National Bureau of Standards by R. A. Paulson and J. Maienthal, with the results shown in Table 1. Except for the small amount of sodium, these analyses clearly agree with the theoretical or stoichiometric values within the analytical precision, and consequently no corrections for composition have been applied to the thermal results.

Table 1

Chemical Analysis of a Dried Sample Nominally $Li_3A\ell F_6$

Chemical Element	Percentage by Weight			
	Found		Theoretical	Difference
	Individual Analysis	Mean		
Li	12.87 12.94 12.95	12.92	12.87	+0.05
Na	0.12 0.07	0.10	0	+0.10
Aℓ	16.68 16.79	16.74	16.68	+0.06
F	70.29 70.56	70.43	70.45	-0.02
Sum	--	100.2	100	+0.2

The "drop" method, employing a Bunsen ice calorimeter and a silver-core furnace, was used to measure the enthalpy of the sample relative to the ice-point temperature. A brief description of the method is given in Chapter 4, and a more detailed account appeared in an earlier publication [2]. Since a suitable resistance thermometer was not available, the temperature of the sample in the furnace was measured in each case by <u>two</u> Pt--Pt-10% Rh thermocouples which had been independently calibrated a year earlier at the Bureau.

Special mention may be made of the choice of sample container, since this often presents a problem in high-temperature work. High-temperature enthalpy measurements on $Li_3A\ell F_6$ had been attempted earlier in this laboratory by W. H. Payne. At that time no sample of the compound was available, so one was synthesized by prolonged heating of a mixture of pure $A\ell F_3$ and LiF above the melting point of the latter, after sealing specimens of this sample in first a silver container and later in one of Pt-10% Rh, both containers being intended for use in the enthalpy measurements. Although it is believed that no appreciable <u>chemical</u> reaction between the sample and either of these container materials is thermodynamically possible, after many hours at the high temperature the molten sample repeatedly began leaking through the walls of both types of container, so that no useful data could be obtained. This is believed to be a mechanical failure, and parallels similar leakage of $Na_3A\ell F_6(\ell)$ through Pt-Rh near 1400°K reported by O'Brien and Kelley [3].

For the measurements reported here, Pt-10% Rh was adopted as a container material, and after weighing in the sample, the container was welded gas-tight by a flame. During the welding the system lost 7.8 mg in weight (about 0.1% of the mass of the sample), presumably owing to expulsion of a little air, evaporation of a trace of the noble metal, and also possibly the hydrolysis of a trace of the sample. After the thermal measurements, the sample used will be chemically analyzed in order to furnish a more reliable basis for final corrections. For the measurements in the liquid range the present sample and container will be encased in an outer base-metal container as a precaution against leakage, which, however, may be avoided because with the present sample there is no need for prolonged heating to ensure homogeneity and complete fusion.

The observed heats and derived net relative enthalpies for the sample are recorded in Table 2, together with a comparison with the values calculated from the empirical equations derived to represent the smoothed results and stated below. For each furnace temperature the individual measurements are listed in chronological order (though the furnace temperatures themselves were in somewhat random order). Of course, no particular individual measurement on the empty container should be associated with a particular one for the container with sample.

Table 2

Enthalpy Measurements on $Li_3A\ell F_6$(solid)

Furnace temperature t °C[a]	Measured Heat[b]		$H_t - H_{0°C}$, $Li_3A\ell F_6$ [b,c]			
	Container with sample[d] cal	Empty container cal	Mean observed cal/mole	Calculated from eq.(1) or (2) cal/mole	Obs. minus calc. cal/mole	Obs. minus calc. %
50.0	124.30 125.16 125.29	(21.023)[f]	2427.4	2419.7	+7.7	+0.3
100.0	256.24 258.12	44.72 44.70 41.99 42.28 41.41 41.80 42.36	5010.6	5018.2	-7.6	-0.2
200.0	542.28 540.32	86.84 86.15 87.14	10621	10619	+2	+0.0
300.0	842.89 843.88	129.57 130.79 130.82 132.19 131.46 132.09	16631	16631	0	0.0
400.0	1160.3 (1179.1)[e]	178.29 177.08 177.04 176.88	22967	22967	0	0.0
450.0	1321.8	(185.07)[f]	26167[g]	26239	-72[g]	-0.3[g]
487.0	1477.9	(219.47)[f]	29403[g]	29464	-61[g]	-0.2[g]
500.0	1525.6 1523.9	226.47 228.21 227.18 225.58 226.03 (222.70)[e] 226.50 226.04 226.68 225.34 225.51	30336	30336	0	0.0

Table 2 (continued)

Enthalpy Measurements on $Li_3A\ell F_6$(solid)

Furnace temperature t °C[a]	Measured Heat[b]		$H_t - H_{0°C}$, $Li_3A\ell F_6$ [b,c]			
	Container with sample[d] cal	Empty container cal	Mean observed cal/mole	Calculated from eq.(1) or (2) cal/mole	Obs. minus calc. cal/mole	Obs. minus calc. %
600.0	(1871.4)[e] 1865.2 1868.1 1866.3	273.70 272.47 273.52	37226	37226	0	0.0
700.0	2226.6 2224.5	322.33 324.74 322.48 322.31	44453	44452	+1	0.0
800.0	--	372.39 372.61 371.80 371.68	--		--	--

[a] International Temperature Scale of 1948, as modified in 1954.

[b] 1 cal = 4.1840 joules; calibration factor of ice calorimeter used = 270.47 j/gm Hg.

[c] Molecular weight of $Li_3A\ell F_6$ = 161.789.

[d] Sample mass ($Li_3A\ell F_6$) = 6.9246 gm.

[e] These results were discarded on statistical grounds, and were not used in deriving the smoothed values (eqs (1) and (2)).

[f] These results were not measured, but were calculated from a least-squares-derived empirical cubic function of temperature which accurately represented the measured empty-container enthalpies at the other temperatures.

[g] These observed values were not used in deriving the smoothed values (eqs (1) and (2)), as they were believed to be considerably less accurate than the mean results farther from the transition temperature.

$Na_3A\ell F_6$ has been found to undergo a crystalline transformation at 845°K (572°C) [3]. It became evident in the present investigation that $Li_3A\ell F_6$ also shows one, and the measurements at 450 and 478°C were made in order to narrow the temperature range in which the transformation temperature lies. (A cooling-curve method is more straightforward, and will probably be used later to pinpoint this temperature more closely.) Though the unrepeated measurements at 450 and 478°C seem to be of inferior accuracy (in part because the transformation may not have been allowed sufficient time to be completed at 478°), it appears that the transition temperature lies between these two limits, and 470°C (=743.15°K) was provisionally assumed. It may be noted that such an uncertainty in the transformation temperature of several degrees creates little uncertainty in the thermodynamic properties of either crystalline form.

Using a least-squaring code and equal weighting, separate empirical equations for the two crystalline forms (labeled "α" and "β") were derived from the mean net enthalpies in the fourth column of Table 2 (omitting the values for 450 and 487°C) to represent the smoothed values. These equations (in cal/mole and at T°K) are:

$$273°\text{-}743.15°\text{K:}\ H^o_T(\alpha)-H^o_{273.15}(\alpha) = 64.1398T + 0.0070246\ T^2 - 13653.13 \log_{10} T + 15{,}220.6 \qquad (1)$$

$$743.15°\text{-}1000°\text{K:}\ H^o_T(\beta)-H^o_{273.15}(\alpha) = 32.2649T + 0.0193630\ T^2 + 9015.61 \log_{10} T - 32223.5 \qquad (2)$$

Equations (1) and (2) give 765.8 cal/mole as the heat of transformation at the assumed transformation temperature, 743.15°K (sensitivity to temperature: less than 0.1% per deg). (In contrast, the corresponding value reported for $Na_3A\ell F_6$ is 2160 cal/mole [3].)

Thermodynamic functions for $Li_3A\ell F_6$ from 298.15° to 1000°K were calculated from eqs (1) and (2), and are given in Appendix B of this report (Table B-106). It will be noted that the entropy and free energy are expressed in terms of $S^o_{298.15}$, which is presently unknown and must be determined or estimated. Later heat-capacity measurements at lower and higher temperatures (planned at NBS) will not only evaluate this constant, the heat of fusion, and properties of the liquid, but also will enable a minor revision of Table B-106.

In the absence of experimental data on a mixed salt such as $Li_3A\ell F_6$, the assumption of additivity is a crude but often useful one -- i.e., the assumption that in the same physical state the properties are the sum of those for the binary components of the mixed salt at the same temperature. The heat capacity of one mole of $Li_3A\ell F_6$ is compared with that of a mixture of three moles of LiF and one mole of $A\ell F_3$ in Table 3. The heat capacity of $Li_3A\ell F_6$ is greater by amounts varying from approximately 1% at 300° to approximately 12% at 1000°K. The heat capacity of the compound $BeO \cdot A\ell_2O_3$ is much more nearly additive at comparable temperatures (Chapter 4). It may be that the existence of a complex ion such as $A\ell F_6^{---}$ is mainly responsible for the considerable departure of $Li_3A\ell F_6$ from additivity, though several major factors may be involved.

Table 3

Deviation from Additivity of the Heat Capacity of Solid $Li_3A\ell F_6$

Temperature (°K)	Heat Capacity (cal/deg K) $1Li_3A\ell F_6$ [a]	Heat Capacity (cal/deg K) $3LiF + A\ell F_3$ [b]	Difference (% of that for mixture)
300	48.59	47.98	+1.3
400	54.94	53.67	2.4
500	59.30	57.32	3.5
600	62.69	60.22	4.1
700	65.50	62.78	4.3
800	68.14	63.02	8.1
900	71.47	64.66	10.5
1000	74.91	66.65	12.4

[a] From Table B-106, this report.

[b] From reference [4].

REFERENCES

[1] E. M. Levin and H. F. McMurdie, Phase Diagrams for Ceramists, Part I, The American Ceramic Society, Solumbus, Ohio, 1956, p. 658; reproduced by permission in NBS Report 7093, National Bureau of Standards, Washington, D. C., 1 January 1961, p. 220.

[2] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Research Natl. Bur. Standards 57, 67-82 (1956).

[3] C. J. O'Brien and K. K. Kelley, J. Amer. Chem. Soc. 79, 5616-5618 (1957).

[4] NBS Report 6928, National Bureau of Standards, Washington, D. C., 1 July 1960, Tables B-25 and B-5 respectively.

Li_2BeF_4: RECENT MEASUREMENTS AT THE NATIONAL BUREAU OF STANDARDS OF ITS HIGH-TEMPERATURE ENTHALPY; RESULTING THERMODYNAMIC FUNCTIONS

by Thomas B. Douglas and William H. Payne

Introduction

The temperature-composition phase diagram of the condensed phases of the LiF-BeF_2 system has been investigated in a number of laboratories; the results are in substantial agreement, and a composite diagram based on them has been published [1]. Based on some of this work, two versions of the phase diagram were published in compilations [2] and reproduced (by permission) in an earlier NBS report [3]. While no congruent-melting compound between the two components exists, two compounds ($LiBeF_3$ and Li_2BeF_4) have been established, and of these, Li_2BeF_4 is nearly congruent-melting and hence the better known.

As part of its program of establishing the thermodynamic properties of such light-element compounds, the National Bureau of Standards expects within the next year to have measured the heat of formation and the low- and high-temperature relative enthalpy and heat capacity of solid and liquid Li_2BeF_4. These enthalpy measurements from 273° to 873°K have been completed and are reported here.

Preparation of the Sample and Choice of Its Container

The sample was prepared and furnished by the Oak Ridge National Laboratory, of Oak Ridge, Tenn., through the courtesy of R. E. Thoma. After combining LiF and BeF_2, NH_4HF_2 was distilled from the material in order to replace any oxygen by fluorine, and according to subsequent petrographic and X-ray examinations the white crystalline sample consisted of a single phase within the detection limits of these methods.

After receipt of the sample at NBS, a specimen was encased in a container of pure silver and then heated in an efficient dry box at about 400°C for an hour or so in order to remove any volatile impurities that may have been produced by the accidental entrance of moisture in handling. The silver container was then sealed gas-tight by flame-welding; it was then encased in a nichrome container sealed mechanically by a gold gasket, preparatory to the thermal measurements described below, as a further precaution against escape of the toxic sample by volatilization or leakage.

Composition of the Sample

The same specimen on which these thermal measurements were made was later analyzed chemically and spectrochemically at the Bureau. The results of the chemical analyses, which were performed by J. Maienthal and R. A. Paulson, are given in Table 1.

Table 1

Chemical Analysis of the Sample

Chemical Element	Percentage by Weight			
	Found		Theoretical	Difference
	Individual Analysis	Mean		
Li	13.87[a] 13.85[a]	13.85[b]	14.03	-0.18
Be	9.36 9.33	9.34_5	9.11	$+0.23_5$
F	76.42 75.90 75.56 75.91	75.95	76.86	-0.91
Ca	<0.01	0.00_5	0	$+0.00_5$
Mg	0.01	0.01	0	+0.01
Cr	<0.01	0.00_5	0	$+0.00_5$
Sr	0.02	0.02	0	+0.02
Sum	- - -	99.18	100	- 0.82

A qualitative spectrochemical analysis was performed by E. K. Hubbard, and indicated (in addition to the elements listed in Table 1): 0.001-0.01% each of Ag, Al, Cu, Fe, K, Mn, Na, Si, Ti, and Zr; and 0.0001-0.001% each of Ba, Ni, and Pb; whereas As, Au, B, Bi, Cd, Ce, Co, Cs, Ga, Ge, Hf, In, Ir, La, Mo, Nb, Os, P, Pd, Pt, Rb, Rh, Ru, Sb, Sc, Sn, Ta, Te, Th, Tl, U, V, W, Y, and Zn were looked for but not detected.

In interpreting these analyses (only Table 1 was used), it was assumed that the metals were present in their highest oxidation states, and the deficiency of fluorine over the total equivalents of metal was assumed to be accounted for by oxygen, which was not analyzed for. Using the mean analyses shown in Table 1, this procedure accounted for 99.8% by weight of the sample. However, the percentage of fluorine is obviously the least precisely determined, so the percentage of this element was assumed to be 76.34, on which basis the percentages add to exactly 100%. The elemental composition of the sample then becomes the same as that of Table 2, which was used as the basis of correcting the thermal results to pure Li_2BeF_4 in the manner detailed below.

Calorimetric Method

The "drop" method, employing a Bunsen ice calorimeter and a silver-core furnace, was used. A brief description of the method is given in Chapter 4, and a more detailed account may be found in an earlier

Table 2

Assumed Chemical Composition of the Sample
(derived from Table 1--see text)

Substance	Assumed No. of Moles (relative)	Substance	Assumed No. of Moles (relative)
Li_2BeF_4	1	SrF_2	0.0002
BeO	0.0269	CaF_2	0.0001
BeF_2	0.0121	CrF_3	0.0001
MgF_2	0.0004		

publication [4]. At each furnace temperature separate measurements were made on the empty container and the container with the sample, using in both cases the same nichrome outer container, but different though entirely comparable silver inner containers having identical masses of parts. Since a suitable resistance thermometer was not available, the temperature of the sample (or container) in the furnace was measured in each run by <u>two</u> Pt--Pt-10% Rh thermocouples which had been independently calibrated at the Bureau a few months earlier.

Data Obtained

The observed heats and derived net enthalpies for the sample are recorded in Table 3--together with the corrections for impurities and for premelting (discussed below), the corrected unsmoothed mean results, and the smoothed results represented by the empirical equations given later. For each furnace temperature the individual measurements in column 3 or 4 are listed in chronological order (though the furnace temperatures themselves were selected in somewhat random order). Of course, no particular individual measurement on the empty container should be associated with a particular one for the container with sample.

Given also in Table 3 (column 2) are the times the sample was in the furnace. These times were deliberately varied considerably in order to detect any trend in the results arising from lack of thermal or phase equilibrium, which is sometimes a serious problem when the sample, such as the present one, undergoes premelting or fusion. However, there is little if any correlation between columns 2 and 3 which might be attributed to such lack of equilibrium.

Corrections for Impurities; Smoothed Results

To the mean net relative enthalpy of the sample for each furnace temperature was applied a correction for the impurities (substances other than Li_2BeF_4) listed in Table 2 on the basis of replacing them by the same mass of Li_2BeF_4. The correction for BeO was computed from the smoothed results of Victor and Douglas [5]. That for BeF_2 (including

Table 3

Enthalpy Measurements on Li_2BeF_4

Furnace temperature °C [a]	Time sample in furnace min.	Measured heat [b]		$H(t) - H(0°C)$, Li_2BeF_4 [b,c]					
		Container with sample [d] cal	Empty container [i] cal	Corrections for Impurities [e] cal/mole	Corrections for Premelting [f] cal/mole	Mean observed (corrected) cal/mole	Calculated from eq. (1) or (2) cal/mole	Observed minus calculated cal/mole	Observed minus calculated %
50.0	56 60	145.64 145.93	90.46 90.85	+5	0	1634	1616	+18	+1.1
100.0	54 59	298.41 298.21	186.58 187.13 185.94 186.13 186.13 186.82 186.93 187.09	+8	0	3310	3322	-12	-0.4
200.0	44 33	619.71 620.16	382.68 383.29 385.00 383.37 383.26	+16	0	7002	7001	+1	+0.0
300.0	46 30 62	959.71 959.62 959.39	586.75 586.95	+24	0	11038	11037	+1	+0.0
400.0	44 46	1329.54 1330.68	798.66 798.37	-32	-297	15424	15431	-7	-0.0
425.0	35 48	1430.93 1431.28	849.61 849.35	-26	-545	16588	16585	+3	+0.0
450.0	58 38	1552.74 1552.76	906.23 905.51	-12	-1380	17764	17761	+3	+0.0

Table 3 (continued)

Furnace temper- ature °C [a]	Time sample in furnace min.	Measured heat [b]		$H(t) - H(0°C)$, Li_2BeF_4 [b,c]					
		Container with sample [d] cal	Empty container [i] cal	Corrections for		Mean observed (corrected) cal/mole	Calculated from eq. (1) or (2) cal/mole	Observed minus calculated	
				Impurities [e] cal/mole	Premelting [f] cal/mole			cal/mole	%
470.0	42 86[g]	1935.38 1935.14	946.77 947.22	+111	0	29285	29312	-27	-0.1
500.0	41 78[h]	2058.49 2059.66	1014.22 1013.50 1013.70	+118	0	31004	30977	+27	+0.1
550.0	47 76 48	2260.61 2260.43 2261.51	1125.13 1122.70 1125.28 1123.61 1124.49	+127	0	33714	33752	-38	-0.1
600.0	62 39	2469.64 2469.52	1236.55 1237.19	+138	0	36564	36527	+37	+0.1

[a] International Temperature Scale of 1948, as modified in 1954.

[b] 1 cal. = 4.1840 joules

[c] Molecular weight of Li_2BeF_4 = 98.884

[d] Sample mass = 3.3463 gm.

[e] For all temperatures above 300°C this column includes a correction of - 70 cal (per mole of Li_2PeF_4) for the assumed heat of fusion of the impurities (see text).

[f] See text.

[g] Temperature of sample with container first raised momentarily to 500°C to hasten completion of fusion.

[h] Temperature of sample with container held at 525°-550°C for first 10 min. of heating period to insure completion of fusion.

[i] Before computing the mean net enthalpy of the sample, the mean empty-container heats at four temperatures were increased by the following amounts — -1.52 cal. (400°), +0.94 cal. (425°), -1.37 cal. (450°), and +0.99 cal. (470°) — to accord with a smooth plot of $\Delta H/t$ vs. t.

the small amounts of other fluorides as BeF_2) was computed from the unpublished heat capacities recently determined at the U. S. Bureau of Mines, Tuscaloosa Metallurgical Research Center, University, Alabama [6]. In addition, in the absence of knowledge as to what fraction of the impurities existed in an amorphous condition and as to what fraction of them was present in liquid solution at any given temperature, a correction was arbitrarily applied above 300°C for half the heat of fusion of the impurities calculated for the same number of gram-atoms of Li_2BeF_4. The algebraic sum of these corrections is listed for each temperature in column 5 of Table 3.

According to the phase diagram of the LiF-BeF_2 system [1], crystalline Li_2BeF_4 decomposes into crystalline LiF and a liquid solution at a peritectic temperature which is listed in one reference [1] as 454°C. The liquidus curve below the peritectic temperature was extrapolated on the phase diagram [1] to a temperature of approximately 472° (=745°K) for the composition Li_2BeF_4, and consequently the (metastable) melting point of pure Li_2BeF_4 was assumed to be exactly 745°K, even though a sample of this composition actually becomes completely liquid only at a "freezing point" a few degrees higher than this. The thermal results were therefore corrected to a basis of the above melting point, and the actual instability over the few degrees between the peritectic temperature and the "freezing point" was ignored. This thermodynamically sound procedure not only avoids the complication of treating a small discontinuity for which the thermal data are inadequate to account rigorously, but forms a simple basis (see below) for deducing corrections for premelting in the impure sample.

Both the chemical analysis of the sample and its relative enthalpies as thus far corrected indicate a considerable premelting error at 450°C, as well as probably some such effect at one or more lower temperatures. If the impurity were all BeF_2, the LiF-BeF_2 phase diagram indicates premelting at only 400°, 425°, and 450°C. This was assumed to be the case for the present sample, and the mean observed relative enthalpies below 400°C were used to derive a tentative empirical equation for the solid (in cal/mole at T°K) which was later assumed to hold up to the melting point:

$$Li_2BeF_4(c),\ 273°\text{-}745°K:\ H^\circ_T(c)-H^\circ_{273.15°K} = 21.676T + 0.01786T^2 - 7253 \quad (1)$$

This equation (with its two independent constants determined by least squares from four observed values) agrees with the data to the amounts shown in the last two columns of Table 3. The fit at 50° and 100°C is somewhat poorer than desirable; but a less simple fit, corresponding to the expected sign of curvature of the heat-capacity--temperature curve of a solid (negative if not zero), has no experimental basis from the observed values at 50° and 100°C.

An empirical equation to represent the relative enthalpy of the liquid was then derived. The Li_2BeF_4 was assumed to be entirely liquid at and above 470°C, and from these four mean values was derived (in cal/mole at T°K):

$$Li_2BeF_4\ (\ell),\ 745°\text{-}873°K:\ H^\circ_T(\ell) - H^\circ_{273.15}(c) = 55.500T - 11933 \qquad (2)$$

As can be noted from Table 3, the observed values above 450°C are not sufficiently precise to indicate the small temperature coefficient of the heat capacity, and it was for this reason that a liquid heat capacity invariant with temperature over this range was assumed.

Equations (1) and (2) give for the heat of fusion of Li_2BeF_4 at the assumed melting point, 745°K, 10606 cal/mole. (This corresponds to an entropy of fusion of 2.03 entropy units per gram-atom.)

If the impurities are insoluble in the main substance when solid but form ideal solutions with the liquid (the "solvent"), the enthalpy correction for premelting at temperature T is

$$\Delta H = -nL_f/\left\{\exp\left[L_f\,(T_m-T)/RT_m\,T\right] -1\right\}, \qquad (3)$$

where for the main substance T_m is its absolute melting point and L_f is its heat of fusion per mole at T, and where n is the number of moles of impurity in solution in one mole of the main substance, R being the molar gas constant. The proper application of equation (3) to a salt (such as in the present case) is not straightfoward because of lack of knowledge as to what (if any) constant molecular weights of solvent and solutes correspond to ideal-solution behavior.

It was found, however, that with the assumption of a molecular weight for Li_2BeF_4 equal to its formula weight and a constant empirical value $n = 0.0314$, equation (3) gives not only the "best" but also a highly consistent set of corrections for premelting of the present sample. The corrections so calculated (for 400°, 425°, and 450°C) are listed in Table 3 in column 6, and lead to the small final deviations from equation (1) shown in the last two columns. (Corrections of roughly the same respective magnitudes can be calculated by ignoring equation (3) and using instead the Li_2BeF_4 (c) liquidus curve of the LiF-BeF_2 phase diagram.) The corrections for premelting are probably at least roughly correct, but the excellent agreement shown is probably to some extent fortuitous, owing to the several assumptions involved.

The thermodynamic functions for Li_2BeF_4 given in Appendix B (Table B-107) were calculated from equations (1) and (2), with extrapolation to 1500°K. The entropy and free energy are expressed in terms of $S^\circ_{298.15}$, which is presently unknown and hence must be supplied from experiment or estimated in order to give absolute values of these functions. Forthcoming measurements of the low-temperature heat capacity planned at the Bureau will provide not only a value of this constant, but will enable a refinement of the thermodynamic functions in the neighborhood of room temperature.

References

[1] "Phase Diagrams of Nuclear Reactor Materials", R. E. Thoma, Editor, Report ORNL-2548 (TID-4500(15th ed.)), Oak Ridge National Laboratory, Oak Ridge, Tenn., Nov. 20, 1959, p. 33.

[2] "Phase Diagrams for Ceramists": Part I (E. M. Levin, H. F. McMurdie, and F. P. Hall), 1956, Fig. 655; Part II (E. M. Levin and H. F. McMurdie), 1959, Fig. 1316. American Ceramic Society, Columbus, Ohio.

[3] "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds", NBS Report 7093, National Bureau of Standards, Washington, D.C., 1 January 1961, p. 218.

[4] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, "Thermal Properties of Aluminum Oxide from 0 to 1,200°K", J. Research National Bureau of Standards 57, 67-82 (1956).

[5] A. C. Victor and T. B. Douglas, "Thermodynamic Properties of Magnesium Oxide and Beryllium Oxide from 298 to 1,200°K", J. Research Natl. Bureau of Standards 67A, 325-329 (1963).

[6] Private communication from C. Rampacek to G. T. Furukawa 3 June 1963.

Chapter 7

A COMPUTER PROGRAM FOR THE ESTIMATION OF THERMODYNAMIC PROPERTIES OF MOLECULAR HYDROGEN (REAL GAS)

by

Harold W. Woolley

A FORTRAN computer program has been prepared by the writer for the thermodynamic properties of hydrogen with real gas effects, based on P-V-T data for natural hydrogen for the region 273K to 600K and up to 500 amagats according to the approximate correlation given in Research Paper 1932 by Woolley, Scott and Brickwedde, J. Research NBS 41, 379-475 (1948), combined with recent spectroscopic data for H_2^1. The program has been prepared as a preliminary interim product in connection with a more extensive project of calculation and theoretical estimation of hydrogen properties for less accessible conditions, sponsored by AEDC, Tullahoma, Tenn.

The program prepared iterates to two arbitrarily chosen initial and incremented variables. The first variable can be chosen as any of the following: T, $H-H^\circ_0$, $E-E^\circ_0$, P or S. The second variable can be any different variable among: Density, P or S. For each point calculated, the printout gives the corresponding values of a number of thermodynamic properties of interest, including those listed for chosen variables and also free energies, specific heats and thermodynamic derivatives.

Since the program can be used at chosen variables outside the range of the measurements, it is necessary to emphasize the approximate nature of the original fit and the uncertainty of extended extrapolation. A revision of the correlation to take account of the precise P-V-T measurements of Michels, de Graaff, Wassenaar, Levelt and Louwerse (Physica 25, 25-42 (1959)) appears desirable before the representation can be regarded as sufficiently satisfactory to warrant the publication of extended derived tables. For the region of those measurements, tables of derived thermodynamic properties versus temperature and density have been published by Michels, de Graaff and Wolkers (Physica 25, 1097-1124 (1959)). (Or see de Graaff's thesis, Amsterdam, 1960.)

Chapter 8

APPARATUS DEVELOPMENTS FOR PURIFICATIONS AND ANALYSES (THERMAL) TO 1000°C

by Augustus R. Glasgow, Jr.

This is an informal report on apparatus developments in a laboratory being equipped for purifications and analyses (thermal) to 1000°C. At present the entire program is directed towards the preparation of high-purity crystals of BeF_2 of a single polymorphic form. Apparatus developed for this research is given in this report.

High - Temperature Valve

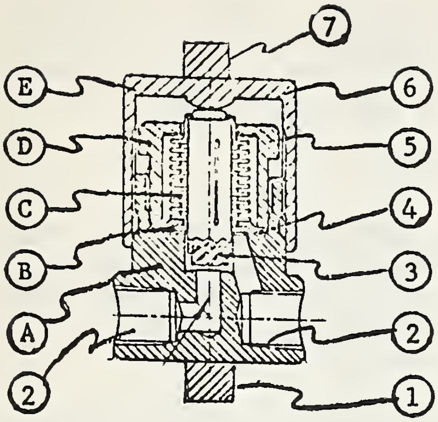
A high-temperature valve operable to 1000°F (540°C) in an oxidizing atmosphere has been developed for use with inorganic fluorides. This valve is part of the apparatus that is being used in the exploratory experiments for the preparation of pure polymorphs of BeF_2 by the slow crystallization under a high vacuum of degassed BeF_2 liquid.

Valves constructed with a body and bellows of Monel are available commercially.1/ They are excellent for use with fluorides because of the chemical resistance of Monel to hydrogen fluoride and to fluorine. As furnished commercially1/, these valves have a maximum operating temperature of only 250°F (121°C). However when constructed as shown in figure 1, the operating temperature for an oxidizing atmosphere can be extended to 1000°F (540°C). An even higher temperature 1100°F (593°C) can be employed if the valve is in a reducing atmosphere. The alterations (1 to 7 in figure 1) in the commercial valve were: (1) Monel square rod, welded to body A; (2) Monel ultra-high vacuum coupling, see figure 2, welded to valve; (3) original stem-point disc of Kel-F replaced with disc of softened nickel2/; (4) Kel-F gasket seal replaced with softened nickel2/; (5) brass retaining nut replaced by Monel; (6) brass cap replaced by Monel; and (7) square of Monel machined on cap, to turn valve at higher-temperature.

In tests with a helium leak detector, this valve maintained a high vacuum under the following conditions: at room temperature and at higher temperature (500 to 550°C) for both the open and the closed valve positions.

1/ Similar to Hoke catalog number M482M or M483M.

2/ High-purity nickel, 99.85 percent, was heat treated in a vacuum furnace for 2 hours at 1800°F by W. A. Willard and W. D. Jenkins of the Metallurgy Division at NBS. After heat treatment, the nickel had a value of 10 to 15 on the Rockwell B and 57 to 60 on the Brinell Hardness scales. The purity of the nickel used is described in the following reference; W. D. Jenkins, T. G. Digges, and C. R. Johnson, Creep of high-purity nickel, J. Research NBS 53, 329 (1954) RP 2551.



A - Monel body

B - Nickel gasket seal

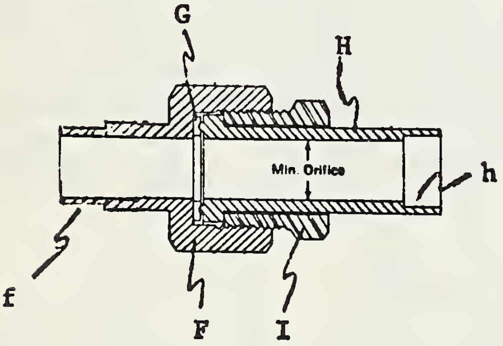
C - Monel bellows, Monel stem, and nickel stem point disc assembly

D - Monel retaining nut

E - Monel cap

1 - 7 ; Alterations in commercial valve see text.

FIGURE 1 HIGH-TEMPERATURE VALVE



F - Monel body

f - Welded to high-temperature valve at position 2 in figure 1

G - Nickel gasket seal

H - Monel gland

h - Socket weld connection to experimental vessel and to vacuum line

I - Monel nut

FIGURE 2 ULTRA-HIGH VACUUM COUPLING

In the above tests, the ultra-high vacuum coupling[3], shown in figure 2, provided a union type of connection. This coupling was found to hold a high vacuum at elevated temperatures (500-550°C) when the body, gland, and nut were all made of Monel and the gasket seal was nickel.

Trap For Fluorides

Figure 3 is the trap used in collecting the products evolved from solid fluorides when they are degassed by fusion in a high vacuum at higher temperatures. Fabrication was from nickel metal and Monel alloy because these materials offer good chemical resistance to hydrogen fluoride and fluorine even at higher temperatures.

The openings to the trap terminated in ultra-high vacuum couplings of Monel which were attached to the coupling on the high-temperature valve. The trap with the attached valves was then used in the following analytical operations: evacuation while heating to 540°C; collection of the by-products under vacuum conditions; isolation of the trapped material from the remainder of the system; and the direct transfer of the trap contents with heating under high-vacuum conditions into an apparatus for analyses, such as a solids mass spectrometer.

Two of these traps were part of a Monel system that was used for the evacuation of the sample. One trap was used to collect by-products that were solids at room temperature and the other, after refrigeration with liquid nitrogen, was used to collect liquids and gases. This method of trapping in the closed-system operation of the purifications processes at higher temperatures served a two-fold purpose, namely: one, a safer method for handling the highly toxic materials; and two, a more complete analysis, since not only the product but the by-products can be analyzed.

Rupture - Disc Ampoule

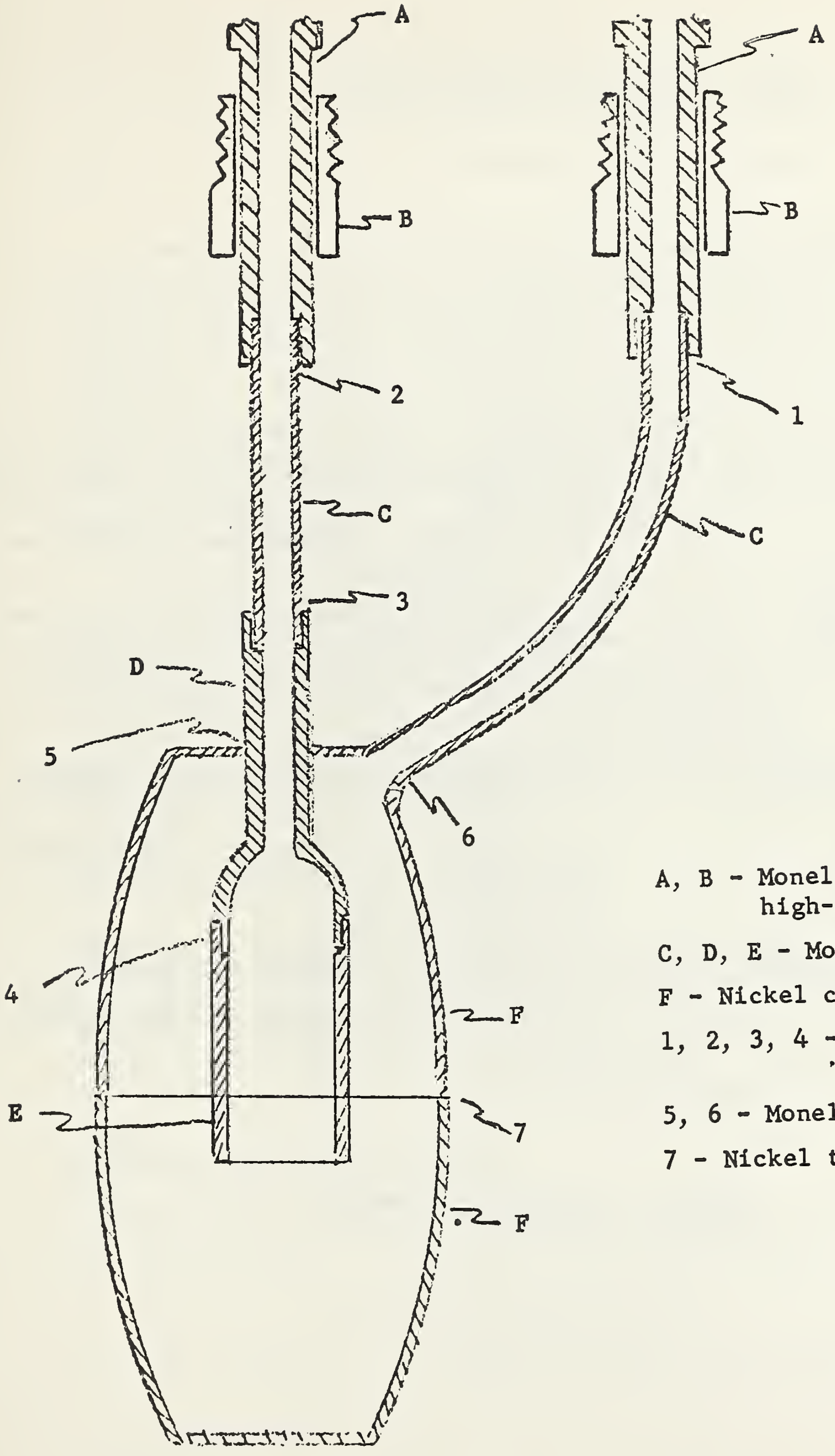
In the new "hydrofluorothermal" process[4] under development for the preparation of BeF_2 crystals, a rupture-disc ampoule was designed for the anhydrous addition of hydrogen fluoride to the cavity of a closed bomb. At room temperature the disc, with a rupture limit near 10 atmospheres, confined the acid in the ampoule under anhydrous conditions. At higher temperatures, where the internal pressures of HF in the ampoule is 10 and 30 atmospheres at 100 and 150°C, respectively, the disc is ruptured and the acid is released to the cavity. The ampoule is shown in figure 4.

A rupture disc of 0.001 inch platinum was selected because discs of this thickness were found to rupture near 10 atmospheres in experiments in which nitrogen gas pressures from a cylinder were applied. Parts B and C were fabricated from platinum-iridium alloy to provide greater rigidity in their reuse by replacing disc D and tube A.

---

[3] Similar to Cajon Catalog number 4 VC.

[4] This process with BeF_2 is similar to the hydrothermal process with SiO_2; HF replaces H_2O and NH_4F is substituted for NaOH as the flux material.



A, B - Monel gland and nut of high-vacuum coupling

C, D, E - Monel

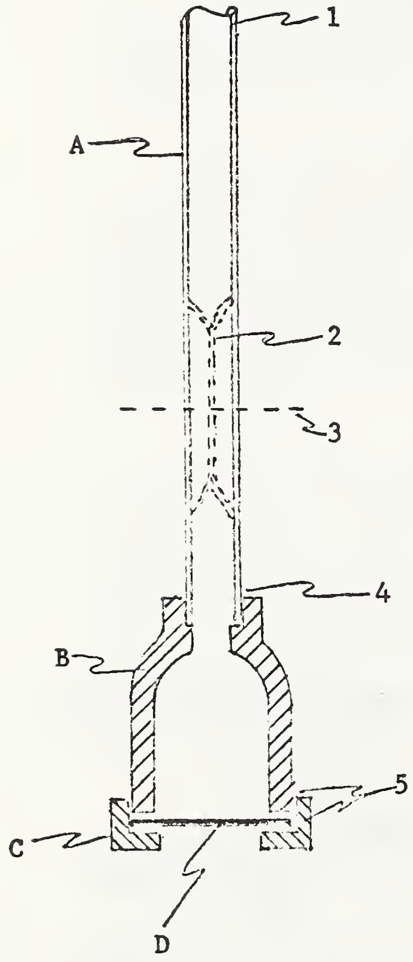
F - Nickel crucibles

1, 2, 3, 4 - Monel to Monel welds

5, 6 - Monel to nickel weld

7 - Nickel to nickel weld

FIGURE 3 NICKEL-MONEL TRAP FOR FLUORIDES



A - Platinum tube, 1/8 inch 00,.010 inch wall

B - Platinum - iridium body, 90% Pt and 10% Ir alloy

C - Platinum - iridium ring, 90% Pt and 10% Ir alloy

D - Platinum disc, foil .001 inch thick

1 - Connected to manifold for hydrogen fluoride

2 - Tube closed by pliers with parallel jaws

3 - Tube cut here

4 - Tube gold soldered to part B

5 - Disc gold soldered to parts B and C

FIGURE 4 RUPTURE-DISC AMPOULE

Chapter 9

THERMODYNAMIC PROPERTIES OF SOME SELECTED COMPOUNDS OF ALKALI METALS

by G. T. Furukawa and M. L. Reilly

Analyses of the low-temperature heat-capacity data on the borohydrides, fluorides, and chlorides of sodium and potassium and on potassium bromide have been made. The tetrahedral borohydride ion (BH_4^-) behaves very similarly to the halides in many ways. Both $NaBH_4$ and KBH_4 have the face-centered cubic crystalline structure at room temperature similar to the halides of the two alkali metals. Lithium borohydride exists, however, in the orthorhombic form. The low-temperature heat-capacity data on $LiBH_4$ were also included in the analysis. (No high-temperature relative enthalpy data were available on $LiBH_4$.)

The smoothed low-temperature values of heat capacity of the sodium and potassium salts were joined with the heat capacities derived from high-temperature relative enthalpy equations. In the following section, the source of low-temperature data for each of the substances is given and briefly discussed along with the enthalpy equations used at the higher temperatures. The method of analysis is similar to that described in previous NBS Reports on Light-Element Compounds. The tables of thermodynamic properties are given in Appendix B.

Lithium Borohydride, $LiBH_4$, 21.78188

Hallett and Johnston [1] determined the heat capacity of lithium borohydride from 16° to 303 °K. This material, which exists in the orthorhombic form, does not exhibit the solid-solid transition that sodium and potassium borohydrides show. The latter substances crystallize in the face-centered cubic form. Thermodynamic properties were calculated from 0° to 300 °K from the data.

Sodium Fluoride, NaF, 41.9882

The heat-capacity data reported by King [2] (54° to 296 °K) were analyzed along with the Debye-Einstein heat-capacity function:

$$C = D\left({}^{340}/_{T}\right) + E\left({}^{391}/_{T}\right)$$

given also by King for extrapolation below 54 °K. The low-temperature values were joined with the enthalpy equations:

$$H_T - H_{298.15} = 10.40T + 1.94 \times 10^{-3}\ T^2 - 0.33 \times 10^5/T - 3{,}384$$
$$(298° \text{ to } 1{,}285\ °K)$$

and

$$H_T - H_{298.15} = 16.40T + 170$$
$$(1285° \text{ to } 1{,}900\ °K),$$

given by Kelley [3]. The heat of fusion 8,030 cal/mole given by Kelley was used.

Sodium Chloride, NaCl, 58.4428

The low temperature measurements of Clusius, Goldmann, and Perlick [4] (11° to 268 °K) were combined with the high temperature enthalpy equations:

$$H_T - H_{298.15} = 1098T + 1.95 \times 10^{-3}\ T^2 - 3{,}447$$
$$(298° \text{to } 1073\ °K)$$

and

$$H_T - H_{298.15} = 16.00\ T + 260$$
$$(1073° \text{ to } 1700\ °K)$$

given by Kelley [3] to obtain the thermodynamic functions from 0° to 1700 °K. The heat of fusion 6,850 cal/mole given by Kelley was used.

Sodium Borohydride, $NaBH_4$, 37.83268

Johnston and Hallett [5] measured the heat capacity of $NaBH_4$ from 16° to 301 °K. A solid-solid transition observed at 189.9 °K is interpreted to be an order-disordered type. Douglas and Harman [6] measured the relative enthalpy from 0° to 400 °C and obtained the enthalpy equation:

$$H_t - H_{0°C} = 2.4384t + 8.083 \times 10^{-4}\ t^2$$
$$-133.0 \log_{10} [t + 273.15)/273.15]$$
$$(t = °C,\ 0° \text{ to } 400\ °C)$$

to represent their data. No slow transition extending over a broad temperature range similar to KBH_4 was found. Thermodynamic properties from 0° to 700 °K were calculated from the data.

Potassium Fluoride, KF, 58.1004

Westrum and Pitzer [7] reported heat-capacity measurements from 16° to

316 °K and relative enthalpy measurements from 298° to 530 °K. These values were joined with the enthalpy equations:

$$H_T - H_{298.15} = 11.88T + 1.11 \times 10^{-3}\ T^2 + 0.72 \times 10^5/T - 3{,}882$$
$$(298° \text{ to } 1130\ °K)$$

and

$$H_T - H_{298.15} = 16.00T - 310$$
$$(1{,}130° \text{ to } 1{,}800\ °K)$$

given by Kelley [3]. The heat of fusion 6,750 cal/mole given by Kelley was used.

Potassium Chloride, KCl, 74.5550

A number of investigators have reported heat-capacity measurements at low temperatures on potassium chloride. The following data were selected to obtain smoothed values of heat capacity up to 300 °K:

Southard and Nelson [8] (17° to 287 °K)
Feodosiev [9] (-191° to 25 °C)
Clusius, Goldmann, and Perlick [4] (11° to 268 °K)
Sayre and Beaver [10] (69° to 80 °K)
Strelkov, Itskevich, Kostryukov and Mirskaya [11] (12° to 298 °K)
Berg and Morrison [12] (3° to 270 °K).

The low-temperature values were joined with the high temperature enthalpy equations:

$$H_T - H_{298.15} = 9.89T + 2.60 \times 10^{-3}\ T^2 - 0.77 \times 10^5/T - 2{,}922$$
$$(298° \text{ to } 1043\ °K)$$

and

$$H_T - H_{298.15} = 16.00T - 440$$
$$(1043° \text{ to } 1500\ °K)$$

given by Kelley [3] to obtain the thermodynamic properties up to 1500 °K. The heat of fusion 6,100 cal/mole given by Kelley was used.

Potassium Bromide, KBr, 119.0110

The measurements of Clusius, Goldmann, and Perlick [4] (10° to 270 °K) were joined with the enthalpy equation:

$$H_T - H_{298.15} = 10.65T + 2.26 \times 10^{-3}\ T^2 - 0.49 \times 10^{-5}/T - 3{,}212$$
$$(298° \text{ to } 1000\ °K)$$

given by Kelley [3] to obtain the thermodynamic properties up to 1000 °K.

Potassium Borohydride, KBH_4, 53.94488

Low-temperature heat-capacity measurements on KBH_4 have been made by Furukawa, Reilly, and Henning [13] (16° to 376 °K), Shigi [14] (60° to 240 °K), and Stull, et al [15] (15° to 300 °K). Shigi reported his results only graphically. The results of Furukawa, *et al*, and Stull, *et al* are in fair agreement. Douglas and Harman [6] reported relative enthalpy measurements from 0° to 400 °C.

$$H_t - H_{0°C} = 4.0898t - 2.9030 \times 10^{-3} t^2 + 2.641 \times 10^{-6} t^3$$
$$-1{,}482.7 \log_{10} [t + 273.15)/273.15]$$
$$(t = °C, 0° \text{ to } 400 °C).$$

A relatively sharp solid-solid transition at 77 °K and a broad transition that extends from about 250° to 450 °K were observed. These transitions are probably order-disorder type. The results of Furukawa, *et al* [13] and Douglas and Harman [6] were joined to obtain a table of thermodynamic properties from 0° to 700 °K.

References

[1] N. C. Hallett and H. L. Johnston, J. Am. Chem. Soc. 75, 1496 (1953).

[2] E. G. King, J. Am. Chem. Soc. 79, 2056 (1957).

[3] K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds," U. S. Bureau of Mines Bulletin No. 584, 1960.

[4] K. Clusius, J. Goldmann and A. Perlick, Zeit. Naturforsch 4A, 424 (1949).

[5] H. L. Johnston and N. C. Hallett, J. Am. Chem. Soc. 75, 1467 (1953).

[6] T. B. Douglas and A. W. Harman, J. Research NBS 60, 117 (1958).

(7) E. F. Westrum, Jr. and K. S. Pitzer, J. Am. Chem. Soc. 71, 1940 (1949).

[8] J. C. Southard and R. A. Nelson, J. Am. Chem. Soc. 55, 4865 (1933).

[9] N. Feodosiev, Zhur. Fiz. Khim. 12, 291 (1938).

[10] E. V. Sayre and J. J. Beaver, J. Chem. Phys. 18, 584 (1950).

[11] P. G. Strelkov, E. S. Itskevich, V. N. Kostryukov, and G. G. Mirskaya, Zhur. Fiz. Khim 28, 645 (1954).

[12] W. T. Berg and J. A. Morrison, Pro. Roy. Soc. (London) A242, 467 (1957).

[13] G. T. Furukawa, M. L. Reilly, and J. M. Henning, NBS Report 4613, August 27, 1956. A formal publication of the results is in process.

[14] T. Shigi, Busseiron Kenkyu, 92, 43 (1956).

[15] D. R. Stull, unpublished measurements Dow Thermal Laboratory, Midland, Michigan.

Chapter 10

HIGH-TEMPERATURE THERMODYNAMIC FUNCTIONS FOR ZIRCONIUM AND UNSATURATED ZIRCONIUM HYDRIDES

by Thomas B. Douglas

Zirconium metal will dissolve hydrogen gas in continuously varying amounts approaching the composition ZrH_2, forming solid metallic-like hydrides possessing a wide range of decomposition pressures which depend strongly on the temperature and composition. After critical consideration of the published thermodynamic data, particularly as to their thermodynamic interconsistency, the author recently published under another research program an article in which are derived an interconsistent set of thermodynamic properties (integral and differential enthalpies, heat capacities, entropies, and Gibbs free energies) for the system over the composition range from Zr to $ZrH_{1.25}$ and over the temperature range 298 to 1200°K [1]. The resulting tables of these properties for zirconium and six compositions of zirconium hydride (together with a table for normal H_2 gas adapted from that in an earlier publication [3]) are reproduced in Appendix B of this report. Details are presented and discussed in the complete article [1].

The article mentioned constitutes a more comprehensive correlation than that published by the author in an earlier article [17]. Since tables for Zr and zirconium hydrides in an earlier report [19] were based on the earlier correlation, they should be considered superseded by the new tables in the present report (except for Zr metal below 298°K).

The temperature-composition phase diagram of the part of the Zr-H system treated is shown in Figure 1. The three crystalline phases involved are labeled α, β, and δ. The tables give the thermodynamic properties along the dotted vertical lines, and in a two-phase field correspond to an equilibrium mixture of the component solid phases having the indicated overall composition. There is considerable uncertainty as to the exact phase-field boundaries in some cases (notably the $\beta/(\alpha+\beta)$ boundary). In addition, in practice two or more solid phases often equilibrate slowly or incompletely. For these reasons, the thermodynamic properties actually encountered in two-phase fields are in many cases subject to considerable uncertainty. This is particularly true of the heat capacity: in a two-phase field the equilibrium value of this property is determined not only by the sum of those of the component phases but to a greater extent, if the pertinent phase-field boundaries are far from vertical, by the energy changes associated with changes in the amounts of the two phases with temperature.

FIGURE 1

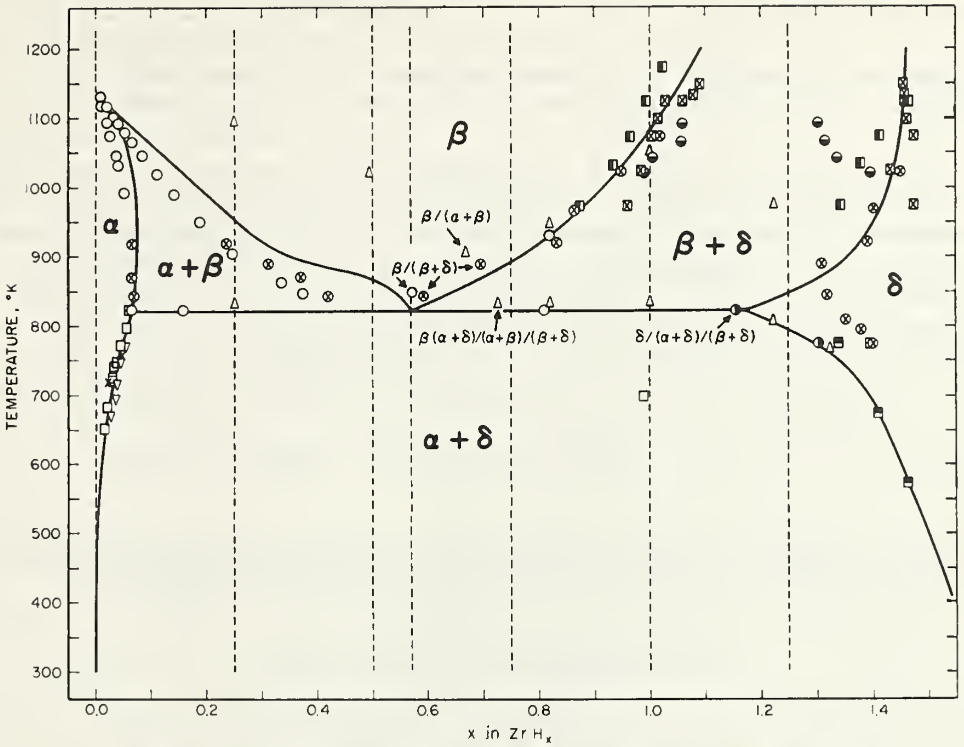


Figure 1. *Phase diagram (partial) of the zirconium-hydrogen system.*

(Observed points on phase boundaries are shown as follows. *From equilibrium hydrogen pressures:* ◒ Hall, Martin, and Rees [2]; ☐ Gulbransen and Andrew [4]; ☒ Edwards, Levesque, and Cubicciotti [5]; ○ Ells and McQuillan [6]; X Mallett and Albrecht [7]; ⊗ LaGrange, Dykstra, Dixon, and Merten [8] *From hydrogen diffusion:* ▽ Schwartz and Mallett [9]. *From X-ray diffraction:* △Vaughan and Bridge [10]. *From thermal expansion:* ◧ Beck [12]; ⊟ Espagno, Azou, and Bastien [14]. *From enthalpy:* ◐ Douglas [17]. The interconsistent thermodynamic functions formulated in this paper correspond to the solid-curve boundaries, and are tabulated along the dotted lines.)

The unit of energy is the defined thermochemical calorie (= 4.1840 joules). The properties are tabulated for one "mole" of ZrH$_x$ (i.e., for an amount containing one gram atom of Zr and x gram atoms of H). The components and standard states to which the differential (partial molal) properties apply are one gram atom of alpha-zirconium at all temperatures (to avoid discontinuities at the transformation temperature of the metal, 1136°K) and one mole of H$_2$ gas in the usual standard state of the ideal gas at 1 atm pressure. The subscripts 1 and 2 refer to the components Zr and H$_2$, respectively. The tabulation includes, in addition to evenly spaced temperatures, the temperatures at which the particular composition crosses phase-field boundaries and also the assumed transformation temperature of zirconium metal (1136°K) and eutectoid temperature (820°K). The β eutectoid composition is taken to correspond to ZrH$_{0.57}$, so that the properties are tabulated also for this "odd" composition, not only because of its special interest but also because the properties were conveniently derived separately for β phases richer and poorer than this composition.

The experimental data given greatest weight in the correlation may be mentioned briefly. The absolute entropy values tabulated were derived from those of Zr, which are based on a correlation by G. T. Furukawa and M. L. Reilly [11] of the low-temperature heat-capacity data on the metal. (The most extensive of these data are those of Todd (53 to 297°K) [13], Skinner and Johnston (14 to 298°K) [18], and Burk et al. (20 to 200°K) [15].) Douglas and Victor [16] measured the relative enthalpy of six compositions between 273 and 1173°K, though these data were given no weight in two-phase fields except where independent evidence of composition equilibrium in the measurements was found. Of the numerous decomposition-pressure measurements, those of Edwards et al. [5], Ells and McQuillan [6], and La Grange et al. [8] were used quantitatively in the correlation.

The heat, entropy, and Gibbs-free-energy changes for the reaction

$$\mathrm{Zr}\ (\alpha) + \frac{1}{2}x\,\mathrm{H_2}(\mathrm{g},\ 1\ \mathrm{atm}) \rightarrow \mathrm{ZrH_x}$$

may be found from the tables for any temperature and hydride composition (x) listed, by using the following respective equations:

$$\Delta H = (\overline{H}_1 - H_1{}^{o}) + \frac{1}{2}x\,(\overline{H}_2 - H_2{}^{o})$$

$$\Delta S = (\overline{S}_1 - S_1{}^{o}) + \frac{1}{2}x\,(\overline{S}_2 - S_2{}^{o})$$

$$\Delta G = (\overline{G}_1 - G_1{}^{o}) + \frac{1}{2}x\,(\overline{G}_2 - G_2{}^{o})$$

REFERENCES

[1] T. B. Douglas, High-temperature thermodynamic functions for zirconium and unsaturated zirconium hydrides, J. Research NBS 67A, 403-426 (1963).

[2] M. N. A. Hall, S. L. H. Martin, and A. L. G. Rees, Solubility of hydrogen in zirconium and zirconium-oxygen solid solutions, Trans. Faraday Soc. 41, 306-316 (1945).

[3] J. Hilsenrath, C. W. Beckett, W. S. Benedict, L. Fano, H. J. Hoge, J. F. Masi, R. L. Nuttall, Y. S. Touloukian, and H. W. Woolley, Tables of thermal properties of gases, NBS Circ. 564, pp.290-292 (U. S. Government Printing Office, Washington, D. C., Nov. 1, 1955).

[4] E. A. Gulbransen and K. F. Andrew, Solubility and decomposition pressures of hydrogen in alpha-zirconium, J. Metals 7, 136-144 (1955).

[5] R. K. Edwards, P. Levesque, and D. Cubicciotti, Solid solution equilibria in the zirconium-hydrogen system, J. Amer. Chem. Soc. 77, 1307-1311 (1955).

[6] C. E. Ells and A. D. McQuillan, A study of the hydrogen-pressure relationships in the zirconium-hydrogen system, J. Inst. Metals 85, 89-96 (1956).

[7] M. W. Mallett and W. M. Albrecht, Low-pressure solubility and diffusion of hydrogen in zirconium, J. Electrochem. Soc. 104, 142-146 (1957).

[8] L. D. LaGrange, L. J. Dykstra, J. M. Dixon, and U. Merten, A study of the zirconium-hydrogen and zirconium-hydrogen-uranium systems between 600 and 800°, J. Phys. Chem. 63, 2035-2041 (1959).

[9] C. M. Schwartz and M. W. Mallett, Observations on the behavior of hydrogen in zirconium, Trans. Amer. Soc. Metals 46, 640-651 (1954).

[10] D. A. Vaughan and J. R. Bridge, High-temperature X-ray diffraction investigation of the Zr-H system, J. Metals 8, 528-531 (1956).

[11] G. T. Furukawa and M. L. Reilly, National Bureau of Standards, Washington, D. C., private communication.

[12] R. L. Beck, Thermophysical properties of zirconium hydride, Trans. Amer. Soc. Metals 54, 556-564 (1962).

[13] S. S. Todd, Heat Capacities at low temperatures and entropies of zirconium, zirconium nitride, and zirconium tetrachloride, J. Am. Chem. Soc. 72, 2914-2915 (1950).

[14] L. Espagno, P. Azou, and P. Bastien, Dilatometric study of the zirconium-hydrogen system between ambient and 500°, Compt. rend. 248, 2003-2005 (1959).

[15] D. L. Burk, I. Estermann, and S. A. Friedberg, The low temperature specific heats of titanium, zirconium, and hafnium, Z. physik. Chem. (Neue Folge, Frankfurt) 16, 183-193 (1958).

[16] T. B. Douglas and A. C. Victor, Heat content of zirconium and of five compositions of zirconium hydride from 0 to 900°C, J. Research NBS 61, 13-23 (1958) RP2878.

[17] T. B. Douglas, The zirconium-hydrogen system: some thermodynamic properties from a heat content study, J. Amer. Chem. Soc. 80, 5040-5046 (1958).

[18] G. B. Skinner and H. L. Johnston, Low temperature heat capacities of inorganic solids. VIII. Heat capacity of zirconium from 14 to 300°K, J. Am. Chem. Soc. 73, 4549-4550 (1951).

[19] Preliminary report on the thermodynamic properties of selected light-element and some related compounds, NBS Report 7093, National Bureau of Standards, Washington, D.C., 1 January 1961, pp. 180-185, 205, 242-247.

Chapter 11

RECENT PUBLICATIONS ON OXIDES AND HYDROXIDES OF THE LIGHT METALS

by Thomas W. Mears

X-ray diffraction studies have been carried out on irradiated polycrystalline beryllium oxide [1]. Samples were cold-pressed, sintered, and irradiated at 110°C with a dosage of 1.5×10^{21} nvt (fast). The data shows selective reflection broadening and displacement. The observations are reproduced by a model of the damaged BeO lattice in which interstitial clusters expand the random spacings between close-packed BeO layers normal to the hexad axis. They are not reproduced by a model containing only vacancy clusters.

The dense, orthorhombic β-form of beryllium hydroxide was prepared directly from the orthogonal α-form and from the amorphous form by the hydrothermal method at 140°, 200°, and 220°C and at pressures of 3.57, 15.35 and 22.62 atm., respectively [2]. At the two higher temperatures, essentially all the beryllium hydroxide goes to the β-form within one day. Sodium hydroxide and silica seem to have a catalytic effect.

A similar set of experiments has also been carried out using aluminum hydroxide [3] and following the hydration with NMR spectroscopy. Alumina trihydrate (bayerite) was prepared by reacting, at room temperature, a 1N aluminum chloride solution with a slight excess of ammonium hydroxide. Samples of the trihydrate were dehydrated under vacuum at 100°, 150°, 200°, 250°, 300°, 400°, and 500°C. Nuclear magnetic resonance studies show that below 200°C only absorbed water is released, but between 200° and 250° the starting material begins to decompose to hydrous alumina. The intermediate hydrate, boehmite, was not noted above 250°C. Upon rehydration at room temperature under saturated water vapor for 15 hours, material that was dehydrated below 200° shows some regained bound water. However, above 250° no alumina hydrates (aluminum hydroxide) was formed.

A paper on the solubility of zirconium in magnesium was noted [4], but this paper is unavailable in the NBS library.

REFERENCES

[1] H. L. Yokel and B. Borie, Acta Cryst. 16, 589 (1963).

[2] A. Guillemaut and A. Lecocq, Compt. rend. 257, 1260 (1963).

[3] T. Saito, Bull. Chem. Soc. Japan 34, 757 (1961).

[4] E. F. Emley and P. Duncomb, J. Inst. Metals 90, 336 (1962).

CHAPTER 12

HIGH TEMPERATURE STUDIES ON Al_2O_3

by J. J. Diamond and A. L. Dragoo

I. Automatic Pyrometer

In order to improve the precision of temperature measurements, a recording automatic optical pyrometer was developed for us by Leeds and Northrup. While awaiting calibration, it was tested and updating modifications were completed by Leeds and Northrup.

The brightness of a hemispherical liquid Al_2O_3 drop was measured perpendicular as well as parallel to the plane of the liquid-solid interface. Essentially the same brightness was obtained in each case. This indicated that the brightness observed was due to the emittance of the liquid $Al\ O_3$ and not to the result of the observation of the interface through a transparent liquid.

Continuation of the temperature measurements back from the interface along the Al_2O_3 rod indicated a decrease in temperature of 400°C over a distance of 3 mm from the interface. It is estimated on the basis of this data and the data in NBS Report No. 7587, for the rate of vaporization of Al_2O_3 <u>in vacuo</u>, that about 0.4% of the total weight loss of the sample occurs over this length of rod (3 mm) during the vaporization of liquid drop of Al_2O_3 <u>in vacuo</u>.

II. Rate of Vaporization in Ar and H_2O

The qualitative results for the vaporization of liquid Al_2O_3 in the presence of 1 atm. of Ar, He, O_2, H_2, N_2 and H_2O were described in NBS Report No. 7587. Quantitative vaporization studies in Ar and H_2O have been initiated at pressures of about 1 atm.

The vaporization process can be described as steady state diffusion from a hemispherical source through a gas. The rate of flow, q, outward from the surface of the liquid alumina is given by

$$q = -2\pi a^2 D(\partial c/\partial r)_{r=a} = 2\pi D(c_b - c_a)[ab/(a-b)] \qquad (1)$$

where r = a is the radius of the hemisphere, r = b is the radius of a surrounding gas "film", D is the diffusion coefficient, and c_a and c_b are the concentrations of the vaporized species at a and b respectively. This equation can be obtained from Barrer's [1] solution for the steady state diffusion of a gas through a hollow spherical shell.

Since the vaporized molecules are dispersed by convection of the ambient gas before reaching the reaction flask, b becomes the radius at which $c_b = 0$.

Fonda [2] has shown, for the case of the vaporization of a tungsten filament in the presence of argon, that the diffusion coefficient is essentially that for self-diffusion of the tungsten species. Consequently, the diffusion coefficient can be defined according to Glasstone [3]

$$D = 1/3\ \bar{c}\ L \qquad (2)$$

where $\bar{c}$ is the mean velocity and L is the mean free path. Glasstone [4] also expresses the mean velocity as

$$\bar{c} = (8RT/\pi M)^{1/2} \qquad (3)$$

where R is the gas constant, T is the absolute temperature of the vapor species and M is its molecular weight. Since [5]

$$L = V/\sqrt{2}\ \pi N\sigma^2 \qquad (4)$$

where V is the volume, N is the number of molecules of gas present and σ is the collision diameter,

$$L = \alpha/P \qquad (5)$$

where P is the total pressure and α is a proportionality constant. Thus equation (2) becomes, for a particular vaporized species "i",

$$D_i = 1/3\ (8RT/\pi M_i)^{1/2}(\alpha_i/P). \qquad (6)$$

Consequently the rate of flow of species "i" at r = a is

$$q_i = 2\pi/3(8RT/\pi M_i)^{1/2}(\alpha_i/P)[ab/(b-a)]c_i \qquad (7)$$

Assuming that the vaporized species behave as an ideal gas, then

$$c_i = n_i/V = p_i/RT$$

and equation (6) becomes

$$\begin{aligned} q_i &= 2\pi a^2(8/9\pi RTM_i)^{1/2}(\alpha_i/P)[b/a(b-a)]p_i \qquad (8)\\ &= 2\pi a^2(K_i/P)p_i \end{aligned}$$

where $K_i = \alpha_i[b/a(b-a)](8/9\pi RTM_i)^{1/2}$.

The rate of weight loss, W, from the drop of liquid alumina is the total rate of flow, q, per unit area, i.e.,

$$W = q/2\pi a^2 = \Sigma q_i/2\pi a^2 = (1/P)[K_1 p_1 + K_2 p_2 + \ldots]. \qquad (9)$$

Drowart, et al. [6] have shown that the major vapor species in equilibrium with liquid Al_2O_3 under neutral conditions are Al, AlO, and O. Thus equation (9) can be written for vaporization in Ar as

$$W(\text{in Ar}) = (1/P_{Ar})[K_{Al}p_{Al} + K_{AlO}\,p_{AlO} + K_O\,p_O]$$

where p_{Al}, p_{AlO} and p_O are the partial pressures of the gases in equilibrium with the liquid Al_2O_3.

Since the collision diameter [7] for water vapor (4.65×10^{-8} cm) is greater that for argon (3.67×10^{-8} cm), the proportionality constant, α, for the mean free path should be less for water vapor than for argon on the basis of equations (4) and (5). If b is only a function of the pressure of the ambient gas, then the coefficients K_i for vaporization in water vapor should be less than the K_i for vaporization in Ar. Consequently, if water vapor behaves as an inert gas, the rate of weight loss in water vapor should be less than in Ar.

The results obtained in Ar and H_2O are as follows:

Sample	Gas	Pressure atm.	Time sec.	Rate of weight loss $\mu g\ cm^{-2} sec^{-1}$
2	H_2O	0.987	690	1.07
2	Ar	1.000	1200	0.294
3	H_2O	0.998	540	1.82
2	Ar	0.994	1260	0.361
3	H_2O	0.993	660	1.34
2	Ar	0.993	1080	0.233
1	Ar	0.993	1080	0.368
1	Ar	0.998	1140	0.329
3	H_2O	1.001	480	1.07

The average rates of vaporization for about 1 atm. of ambient gas are:

Ambient Gas	Average Rate of Weight loss $\mu g\ cm^{-2} sec^{-1}$
Ar	0.31 ± 0.04
H_2O	1.3 ± 0.3

Although the rate of weight loss in water vapor is only four times that in Ar, the increase is significant. Furthermore, this increase does not agree with expected results. This contradiction indicates that either b depends on the nature of the ambient gas, or the partial pressures of species in addition to Al, AlO and O are a major contribution in the water vapor case. The second alternative seems the more reasonable of the two. The appearance of other vapor species may result from the reaction of water molecules with the liquid Al_2O_3 to form a more volatile liquid aluminum hydroxide. The possibility of absorption concurs with our previous observations of bubbling when liquid Al_2O_3 freezes in the presence of water vapor.

References

[1] R. M. Barrer, Diffusion In and Through Solids (Cambridge University Press, Cambridge, 1951), pp.5,6.

[2] G. R. Fonda. Phys. Rev. 31, 260 (1928).

[3] S. Glasstone. Textbook of Physical Chemistry, 2nd ed. (D. Van Nostrand Co., Inc., New York, 1946), p. 281.

[4] ibid., p. 286.

[5] ibid., p. 275.

[6] J. Drowart, G. De Maria, R. P. Burns and M. G. Inghram. J. Chem. Phys. 32, 1366 (1960).

[7] S. Dushman and J. M. Lafferty. Scientific Foundations of Vacuum Technique, 2nd ed., (John Wiley and Sons, Inc., New York, 1962), p. 32.

Chapter 13

MASS SPECTROMETRIC STUDY OF THE BeO-BeF_2 SYSTEM AT HIGH TEMPERATURES

by J. Efimenko

The reaction of BeF_2(g) with BeO(s) was investigated mass spectrometrically to provide thermodynamic data not available previously.

Experimental

The mass spectrometer with high temperature Knudsen cell source is of the type used by W. A. Chupka and M. G. Inghram(1). The characteristic features of this instrument are a) differential pumping on the analyzer, ionization and Knudsen cell sections, b) mechanical shutter between Knudsen cell and ionization sections, c) simultaneous ion collection by 50% transmission grid, electron multiplier or a Faraday box, d) neutral and ionized beam having the same path direction along the analyzer tube.

The reaction was performed by passing BeF_2 vapor through a baffled, granulated layer of BeO contained inside a Knudsen effusion cell. This arrangement permitted control of reaction temperature and provided near equilibrium reaction sampling. The low-melting BeF_2 was contained in a tantalum tube attached to the bottom of the molybdenum effusion cell. This effusion cell was heated by electron bombardment while the heat conducted along the tantalum tube volatilized the beryllium fluoride. The temperature gradient established along the tube insured that no BeF_2 would condense elsewhere in the reaction cell. A deep hole, located radially in the molybdenum cell bottom, served to detect the reaction temperature with an optical pyrometer. The temperature of the BeF_2 source was monitored with a Pt-Pt Rh (10%) thermocouple spot-welded to the tantalum tube opposite the BeF_2 level.

The BeO used was a low density solid prepared at NBS. This material was crushed in an alumina mortar to provide an ungraded, granulated material. The BeF_2 was obtained from the Brush Beryllium Company and was partly dehydrated by heating to 400°C for 12 hours.

The first set of data was taken under the conditions that produced a high partial pressure or concentration of BeF_2. In order to check whether equilibrium or near equilibrium conditions in the reaction zone were attained, a change was made to allow the BeO to be heated to a much higher temperature. This required only the lengthening of the tantalum tube containing the BeF_2. At each mass position of interest, the mechanical shutter interposed in the effusion beam path gave the background intensity. All mass scanning was done by varying the magnetic field only. The electron bombardment power supply was regulated and controlled within ±2°C by means of a Hall-effect sensor. The ion currents from the detector, on passing through 10^{10} ohm resistors, were displayed as voltages with a two-pen recorder.

Results

The data from the first set of experimental conditions, the computed equilibrium constants and heat of reaction at 0°K are shown in Table I. The data and results for the higher temperature conditions are presented in Table II. The experimental heat of reaction did not require absolute measurements and could be obtained simply from the intensity ratio of product and reactants. Plots of log A versus 1/T are shown in Figures 1 and 2, corresponding to the low and high temperature data. The quantity A is the ratio of mass 72 intensity to the intensity of mass 47. The slopes of these straight lines were obtained by the method of least squares. Included is the standard deviation error. From the available heats of formation of BeO(s), $BeF_2(g)$ and the experimental heat of reaction, Table VI, the heat of formation of mass 72 was computed: $\Delta H^\circ_{298,f} = -283.5$ Kcal/mol , $\Delta H^\circ_{0,f} = -283.3$ Kcal/mol.

The ionization cross sections for the molecular species were obtained by additivity of atomic cross sections and the ion intensity ratios, A, were converted to equilibrium constants which were used to compute the free energies of reaction. With the aid of free energy functions for BeO(s), $BeF_2(g)$ and mass 72 $(Be_2OF_2)(g)$, the heat of reaction at absolute zero was computed for each experimental point. In Table V are shown the heats of reaction computed from revised free energy functions for $BeF_2(g)$, as described in the following section.

Discussion

The reaction occurring between beryllium oxide and beryllium fluoride at high temperatures is chiefly the following:

$$BeO(s) + BeF_2(g) \rightleftarrows Be_2OF_2(g)$$

A number of observations support the assignment to mass position 72, the species Be_2OF_2. Before the study of this reaction was initiated, BeF_2 was studied mass spectrometrically alone. It produced predominantly BeF_2^+ (47) and BeF^+ (28). The heating of BeO alone confirmed the known species Be^+ (9), O^+ (16), $(BeO)_3^+$ (75) and $(BeO)_2^+$ (50). When the two reactants, BeO and BeF_2 were heated together, the intensity of mass position 72 changed as the temperature was varied and responded positively to the presence of the shutter in the effusion beam path. The relative appearance potential curve for $(Be_2OF_2)^+$ differs from those of BeF_2^+ and $(BeO)_3^+$. It was not possible to check the presence of mass 73 and 74 which would contain O^{17} and O^{18} due to the large background created by the high temperatures.

In a complex system, identification solely by means of mass to charge ratio is not sufficient. Silica present in abundance could produce Si_2O^+ (72) at high temperatures; alumina in the presence of hydrogen compounds as water could form $(Al_2OH_2)^+$ (72) at the proper high temperature. It was observed that, at the first heating of the reactants, a number of transient masses appeared whose intensities diminished or died out completely after an outgassing period at higher temperatures. Only the species at mass position 72 would positively increase with temperature throughout a number of check runs.

Under molecular flow conditions, the major portion of the $BeF_2(g)$ volatilized passed on through the BeO layer. Its intensity was a measure of its concentration in the BeO reaction chamber. At the higher temperatures, the intensities of $(BeO)_3^+$ were measureable. Moderate intensities of the molybdenum oxides were observed at the upper temperatures. In a complex system, a number of simultaneous reactions may occur and it appears that the reduction of BeO by molybdenum metal at the higher temperatures was one of the minor reactions. Analysis by x-ray diffraction was carried out on the BeO solid before and after reaction to check whether any new solid phase had been created. The x-ray results showed only the BeO phase with a slight contamination of molybdenum oxide.

Since 70 ev ionizing electrons were used, some fragmentation of BeF_2^+ and $Be_2OF_2^+$ must have taken place. Omission of fragmentation correction is not a large error for heat of reaction by the slope procedure, however, it may be a significant error in the equilibrium constant.

The reliability of experimental measurements is exhibited by the heat of reaction at absolute zero. The ΔH_0^o values in Table I and II were obtained from the free energy functions for $BeF_2(g)$, Table A-51, BeO(s), Table 2-8 and $Be_2OF_2(g)$, Table A-86. There is only a slight temperature trend in these ΔH_0^o values, probably due to the uncertainty in free energy functions for $BeF_2(g)$.

The experimentally determined heats of reaction were corrected to 0°K by the use of the Einstein functions (3), as shown in Table III. First the heats of reaction were corrected on the basis of bending frequencies of 825 cm^{-1} (as used for Table A-51). The enthalpy function was obtained from combination of the entropy and free energy functions of Reference 3. Comparison of these ΔH_0^o values, experimental and those based on Table A-51, suggest that there may be an error in the free energy functions of $BeF_2(g)$. A lower estimate of the bending frequency for $BeF_2(g)$ was selected on the basis of the evidence presented by Hildenbrand (4) and the conclusion given in Ch. 14 of this report in order to create thermodynamic consistency of the existing data for BeF_2. The experimental heats of reaction were again corrected to 0°K, as shown in Table III.

To show the trend with temperature, corrected free energy functions for $BeF_2(g)$ were computed on the basis of bending frequencies of 240 cm^{-1}, shown in Table IV. Using the free energies obtained from the smooth lines of Figures 1 and 2 and the corrections of Table IV, the new ΔH_0° values in Table V were obtained. Examination of the ΔH_0° values indicate closer agreement with the experimentally determined values.

References

1. W. A. Chupka and M. G. Inghram, J. Phys. Chem., 59, 100 (1955).
2. J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc., 78, 546 (1956).
3. NBS Monograph 49, "Tables of Einstein Functions," 1962.
4. D. L. Hildenbrand, Research Labs., Philco Corp., Newport Beach, Calif. "Entropies of Some Gaseous Metal Dihalides" (Jan. 1964, preprint)

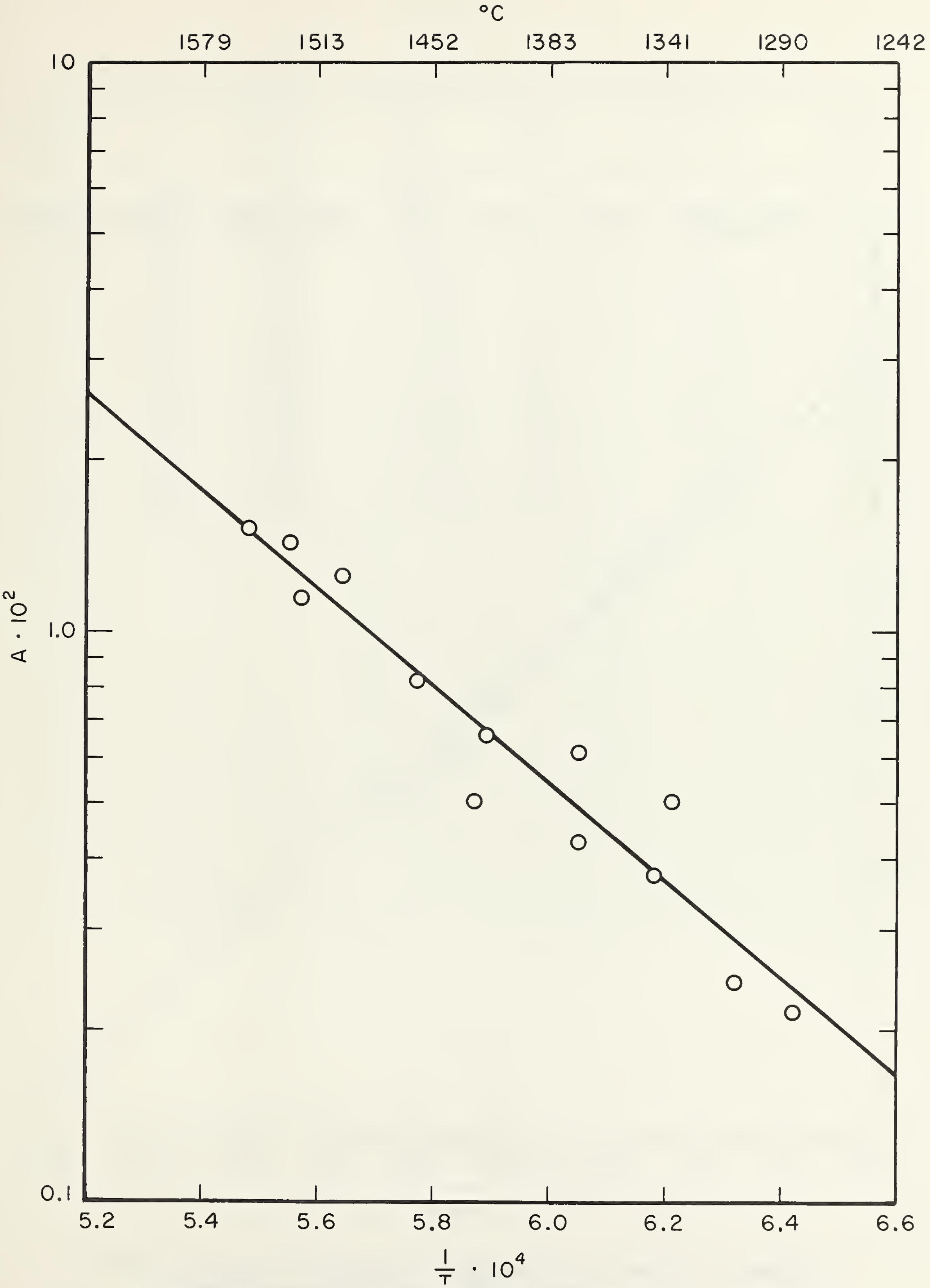


FIGURE 1. Formation of Be_2OF_2(g) between 1570°K and 1890°K
$\Delta H°\langle 1730°K\rangle = 39.25 \pm 3.5$ Kcal/mol.

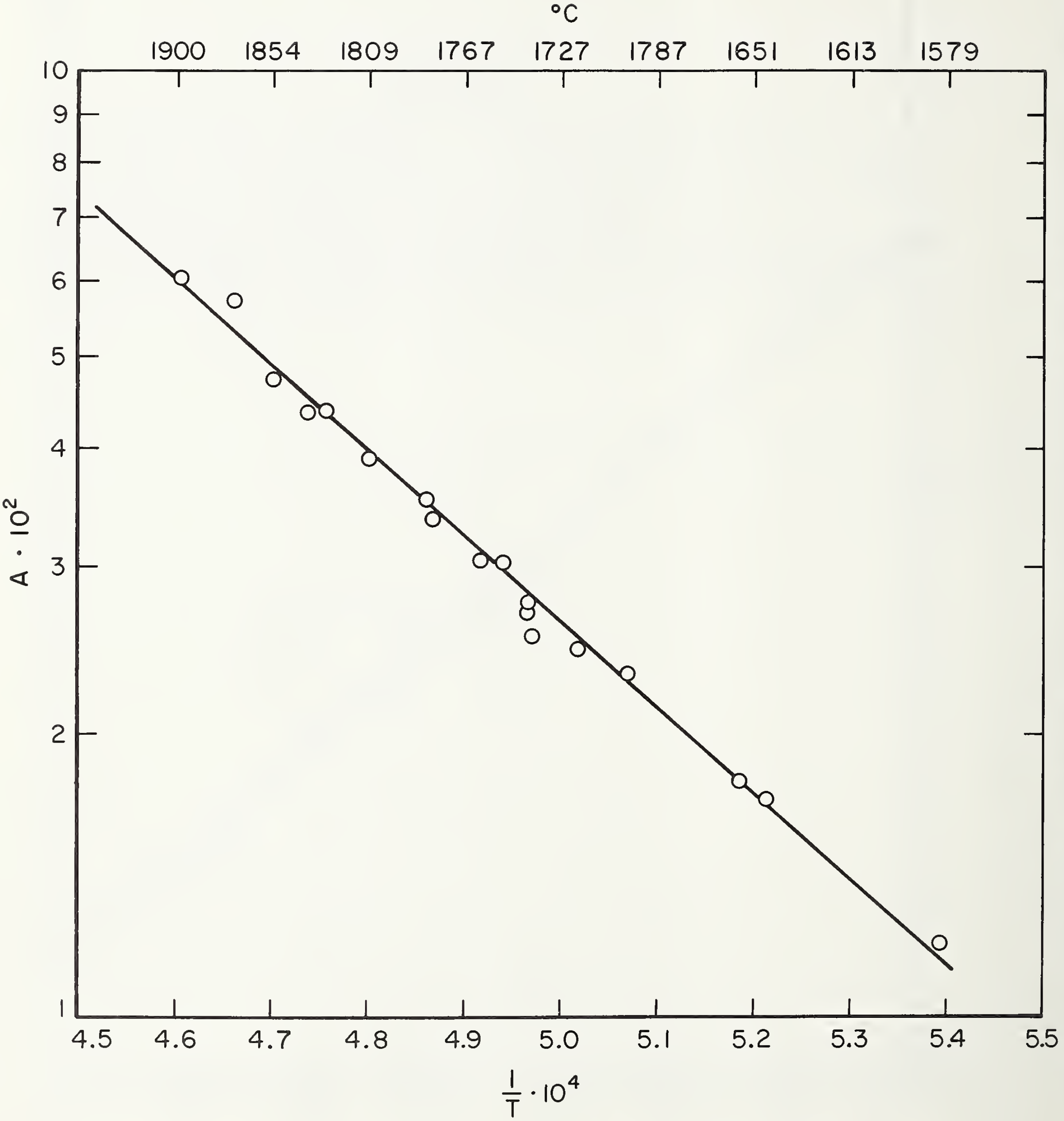


FIGURE 2. Formation of Be$_2$OF$_2$(g) between 1870°K and 2200°K
$\Delta H^\circ\langle 2035^\circ K\rangle = 40.68 \pm 0.86$ Kcal/mol.

TABLE I

Mass Spectrometric Temperature - Intensity Data

Index No.	t°C	$T^{\circ}K_{Corr.}$	I^{+}_{72} Volt	I^{+}_{47} Volt	$K^{*}x10^{3}$	ΔH°_{0}
4	1285	1570	0.013	7.3	0.908	46.3
5	1307	1592.5	0.011	6.6	0.852	47.3
1	1337	1623	0.025	6.7	1.90	45.6
13	1343	1629	0.017	5.7	1.52	46.5
6	1383	1670	0.040	8.4	2.43	46.0
3	1425	1713	0.081	15.0	3.06	46.5
12	1431	1719	0.081	20.4	2.04	47.9
7	1465	1753	0.126	19.2	3.35	47.2
2	1500	1789	0.530	50.8	5.32	46.6
11	1522	1811	0.470	52.0	4.61	47.7
8	1530	1819	0.470	42.0	5.72	47.1
10	1548	1838	0.700	61.0	5.86	47.4
9	1600	1891	1.200	80.0	7.66	47.9

TABLE II

Mass Spectrometric Temperature - Intensity Data

Index No.	t°C	T°K$_{Corr.}$	I^{+}_{72} Volt	I^{+}_{47} Volt	K*x10^{2}	ΔH°_{0}
28	1738	2032	0.050	1.98	1.29	49.3
21	1740	2034	0.024	0.87	1.40	49.2
22	1740	2034	0.020	0.74	1.35	49.4
23	1783	2077	0.029	0.86	1.72	49.1
24	1820	2110	0.075	1.41	2.71	48.0
27	1825	2119	0.138	3.40	2.07	49.5
25	1855	2150	0.108	2.37	2.32	49.6
26	1875	2169	0.228	4.00	2.91	49.0
43	1582	1872	0.009	0.75	0.61	48.2
42	1640	1937	0.019	1.08	0.90	48.4
31	1655	1947	0.017	0.99	0.91	48.6
32	1700	1992	0.032	1.38	1.18	48.7
41	1713	2013	0.040	1.62	1.26	48.9
33	1750	2045	0.051	1.68	1.55	48.8
40	1760	2054	0.087	2.85	1.55	49.0
34	1785	2079	0.093	2.64	1.80	49.0
39	1810	2105	0.110	2.82	2.00	49.8
35	1829	2125	0.153	3.50	2.23	49.2
38	1838	2134	0.153	3.40	2.30	49.2
36	1857	2153	0.273	4.30	3.24	48.2
37	1898	2195	0.295	4.90	3.07	49.3

The chronological sequence of experimental measurements is recorded by the index numbers. Equilibrium constants, K* are computed from the data; the ΔH°_{0} values, heat of reaction at absolute zero, were computed from free energy functions. In Table 2, data with index nos. 21-28 and index nos. 31-43 were taken at a day interval. The data of Table 2 were taken 6 months after the data of Table 1.

TABLE III

Correction of Experimental Heat of Reaction to Absolute Zero

νcm^{-1}	ΔH°_{1700}, Kcal/mol	ΔH°_0, Kcal/mol	ΔH°_{2000} Kcal/mol	ΔH°_0 Kcal/mol
825	39.3	39.2_9	40.68	41.3_0
240		40.7_1		42.7_6

TABLE IV

Corrections for Free Energy Functions of BeF_2

T°K	$\Delta - \frac{(F^\circ_T - H^\circ_0)}{T}$
1100	+3.56
1200	3.64
1300	3.72
1400	3.80
1500	3.89
1600	3.93
1700	3.98
1800	4.02
1900	4.07
2000	4.12
2100	+4.16

These corrections were obtained by taking the differences of free energy functions corresponding to 2 vibrational modes at 240cm^{-1} and the free energy functions based on the vibrational frequencies at 825cm^{-1}.

TABLE V

Heat of Reaction, ΔH^o_o, Using Corrected Free Energy Functions for BeF_2 (g)

T°K	ΔH^o_o
1550	38.5
1600	38.0
1700	37.9
1800	37.6
1900	37.4
2000	37.5
2100	37.2
2200	37.0

The free energy values were taken from the lines given in Figures 1 and 2.

TABLE VI

Auxiliary Date for Computations

	Value		Source
Window Transmissivity,	$5.00 \pm 0.63 \times 10^{-6}$		Author
Relative Ionization Cross-sections,			ref. (2)
Be ,	6.31		
O ,	3.29		
F ,	1.85		
Standard Heat of Formation			
	ΔH^o_o Kcal/mol	ΔH^o_{298} Kcal/mol	
BeO(s)	-142.28	-143.1 ± 4	NBS Report 6928, July 1960, Table C-2
BeF_2 (g)	-182.45	-182.9 ± 5	
Enthalphy of Reaction			
ΔH°_{298}	42.22 Kcal/mol		computed
ΔH^o_o	41.38 Kcal/mol		computed
ΔH°<2035>	40.68 ± 0.80 Kcal/mol		this work
Enthalphy and Free Energy Functions			
BeO	NBS Report 6484 July, 1959		Table 2-8
BeF_2	NBS Report 6928 July, 1960		Table A-51
Be_2OF_2	NBS Report 8186 Jan., 1954		Table A-68

Chapter 14

BERYLLIUM FLUORIDE, BeF_2: COMPARISON OF HEAT-CAPACITY AND RELATIVE-ENTHALPY DATA WITH VAPOR-PRESSURE DATA

by G. T. Furukawa and M. L. Reilly

Through the courtesy of C. Rampacek, Research Director, U. S. Bureau of Mines, Tuscaloosa Metallurgy Research Center, an unpublished set of low-temperature heat-capacity and relative-enthalpy data obtained at the above laboratory on BeF_2 from 8° to 1200°K was made available to us. Information supplied us with the heat data showed that the chemical analysis given by the supplier of the original sample was 19.2 percent Be and 79.8 percent F. The chemical analysis of the material after treating with HF was 19.9 percent Be and 78.8 percent F. The theoretical composition is 19.17 percent Be and 80.83 percent F. Petrographic analysis showed the treated sample to be largely crystalline with a minor amount of glassy BeF_2. The two principal impurities of the sample investigated were considered to be BeO and H_2O. Because of the lack of further quantitative information on the impurity content, analyses of the heat data received were made on the assumption that the BeF_2 sample was 100 percent pure.

Although C. Rampacek supplied a table of thermodynamic functions up to 300°K based on the low-temperature measurements, the original observed low-temperature data were analyzed again in order to join them smoothly with the high-temperature relative-enthalpy data, which had not been analyzed. The observed low-temperature heat-capacity and the high-temperature relative-enthalpy data supplied by C. Rampacek are plotted in Figures 1 and 2, respectively.

The low-temperature data, as shown in Figure 1, are very precise and exhibit the usual sigmoidal shape of a simple solid. The filled-in circles are mean heat capacities evaluated from the high-temperature relative enthalpy data at the lower temperatures.

The high-temperature relative-enthalpy data, as shown in Figure 2, exhibit "humps" at about 505°, 825°, 1040° and 1100°K. Heating curves of both cristobalite and quartz forms of BeF_2 exhibit large endothermic effects around 545° to 550°C and small endothermic effects in the 740° to 780°C range [1,2]. A small endothermic effect was observed in the quartz form at 220°C [2].

Because of the nature of relative - enthalpy measurements by the "drop method", the observations shown for BeF_2 are considered not under equilibrium conditions. At the ice-point temperature higher-energy states are expected to be frozen in. Only approximate calculations can be made with the data.

The hump at 505°K was taken to be the transformation from the high- to the low-temperature quartz form of BeF_2. The hump at 825°K was taken to be the crystallization from the liquid of the quartz form, although both quartz and cristobalite forms or both forms may crystallize [1,2]. The humps in the 1040° to 1100°K range are taken to be crystallization of the cristobalite form of BeF_2. Although a system that attains equilibrium rapidly would undergo the various transitions, in the case of BeF_2 the transitions are considered on the bases of the heat data to occur only when the material is "annealed" at temperatures in the vicinity of the transition. It is expected that only partial transition occurred in each case.

The analysis of the relative-enthalpy data involved the following procedure. As shown in Figure 2, if the humps are disregarded, the enthalpy curve is almost continuous. Therefore the heat capacity was considered continuous from 273° to 1200°K and joined smoothly with the low-temperature data. At the various temperatures where the humps occurred, the difference between the highest relative-enthalpy value and the "continous enthalpy curve" was taken to be the "heat of transition" and added to the thermal functions calculated from the values of the "continuous heat capacity". The "transitions" in the range 1040 to 1100°K were not added so that the values of thermal functions above this range can be considered relative to the quartz form of BeF_2.

The thermodynamic functions calculated on the bases of the above analysis are given in Table B-58 (Revised) of Appendix B. The thermodynamic functions given in the earlier Table B-58 (NBS Report 7437) are based on approximations and are to be henceforth disregarded.

The difference in heat capacity between BeF_2 (g) [3] and BeF_2 (ℓ) (Table B-58 of the present report) in the region of 1000°K is -6.0 cal/deg mole. Using this ΔC_p and the vapor-pressure data of Greenbaum <u>et al.</u> [4] with the relations

$$\Delta G^\circ = \Delta H_o^\circ - \Delta C_p \, T \, \ell n \, T + IT,$$

$$\Delta H^\circ = \Delta H_o^\circ + \Delta C_p \, T,$$

and

$$\Delta S^\circ = \Delta C_p + \Delta C_p \, \ell n \, T - I,$$

for the reaction: $BeF_2(\ell) \rightarrow BeF_2(g)$

ΔH° (1000°K) = 52.3 Kcal/mole and ΔS° (1000°K) = 37.6 cal/deg mole (e.u.).

The latter values are close to those reported by Greenbaum <u>et al.</u> [4].

The S° of BeF_2 (g) at 1000°K is 66.28 e.u.. [3] Substracting ΔS° of vaporization, S° of BeF_2 (ℓ) at saturation pressure becomes 28.7 e.u.. This is approximately, 5 e.u. lower than the value given in Table B-58. The value in Table B-58 is expected to be low since the "transitions" are probably incomplete.

These discrepancies indicate that further work on BeF_2 is needed.

References

1. D. F. Kirkina, A. V. Novoselova, and Yu. P. Simanov, Doklady Akad. Nauk SSSR 107, 837 (1956).

2. A. V. Novoselova, O. N. Breusov, D. F. Kirkina, and Yu. P. Simanov, Zhur. Neorg. Khim. 1, 2670 (1956).

3. Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds, NBS Report 6928, July 1, 1960, Table A-51.

4. M. A. Greenbaum, J. N. Foster, M. L. Arin, and M. Farber, J. Phys. Chem. 67, 36 (1963).

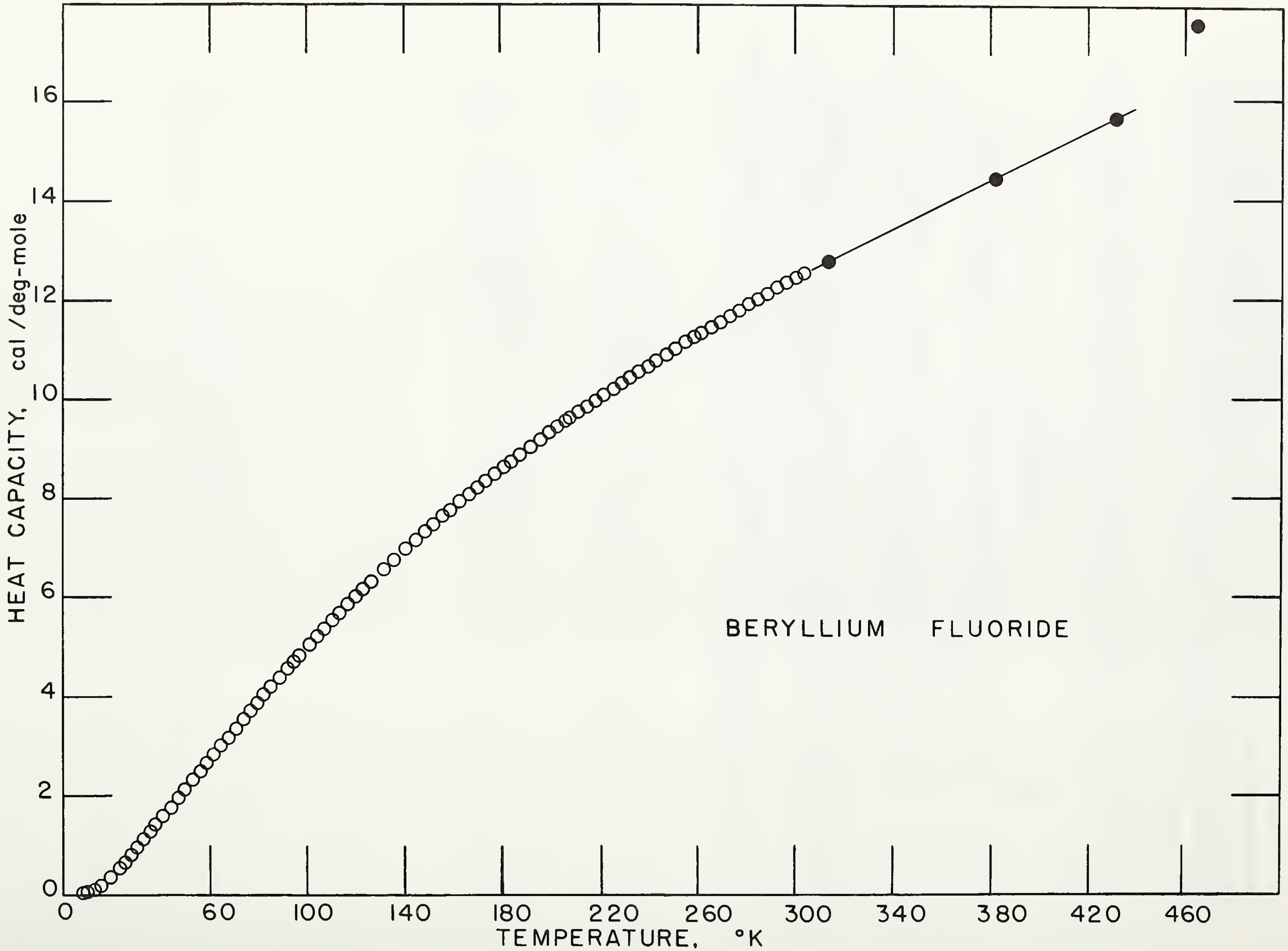


FIGURE 1. Observed Molal Heat Capacity of Beryllium Fluoride, BeF_2
(U.S. Bureau of Mines, Tuscaloosa Metallurgy Research Center)

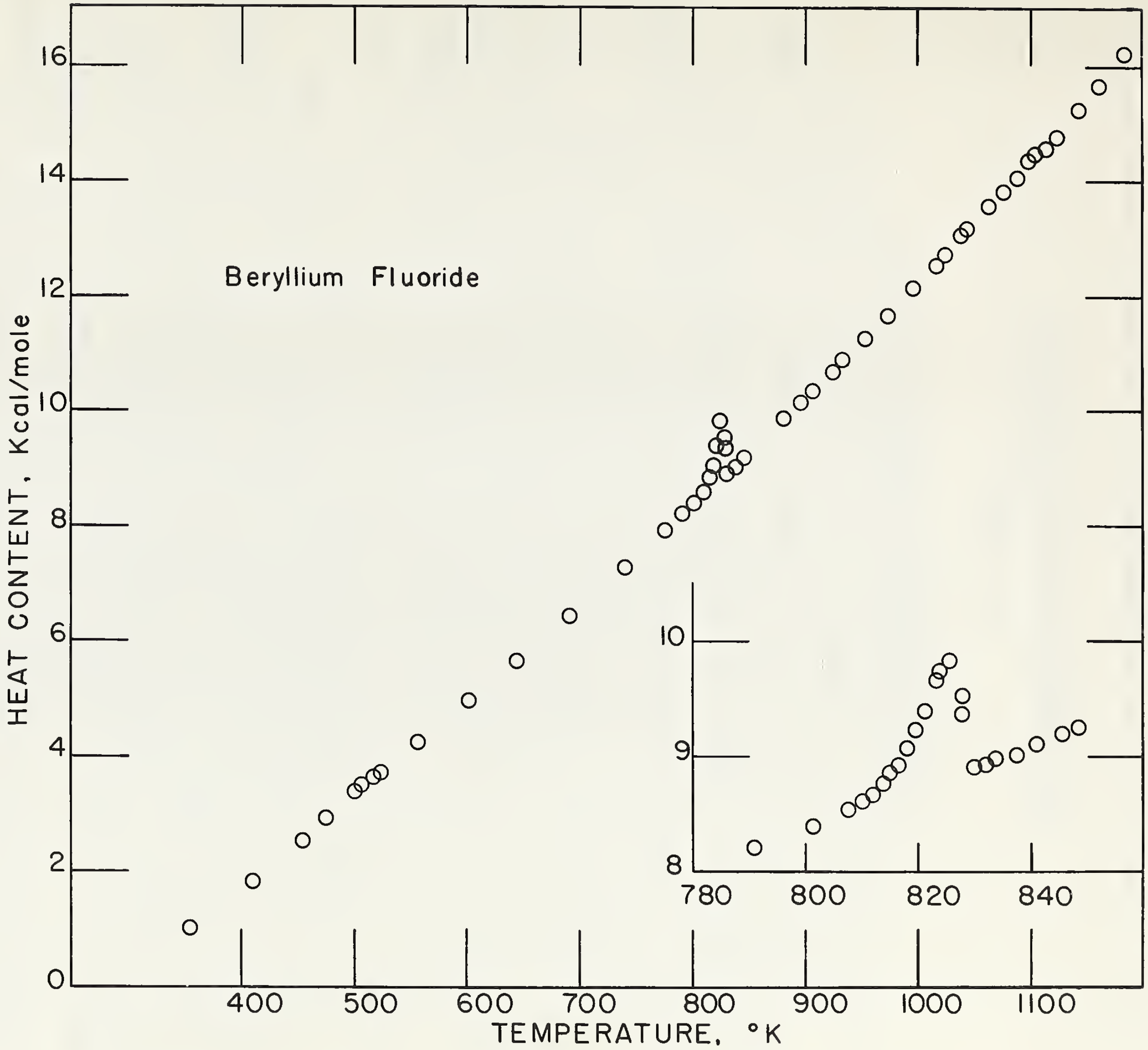


FIGURE 2. Relative Enthalpy (H_T-$H_{273.15}$) of Beryllium Fluoride, BeF_2
(U.S. Bureau of Mines, Tuscaloosa Metallurgy Research Center)

Chapter 15

HIGH-TEMPERATURE MATRIX SPECTROSCOPY

D. E. Mann

1. Oxides of Lithium: Li_2O, LiO, and Li_2O_2

The results of an investigation of the vapor above heated lithium oxide (Li_2O) have recently been published (D. White, K. S. Seshadri, and D. F. Dever; D. E. Mann; M. J. Linevsky: J. Chem. Phys. 39, 2463-2473 (1963)), and summarized by the authors as follows. The vapor was investigated mass spectrometrically and by infrared matrix-isolation spectroscopy. The vapor composition and Knudsen effusion rates were measured as functions of temperatures, and the matrix spectra of the principal lithium oxide species -- Li_2O, LiO, Li_2O_2-- were identified and analyzed for different isotopic abundances. The predominant vapor species $Li^7{}_2O$ is probably linear with $\underline{r}$ (Li-O) = 1.59 Å, and has fundamentals ν_1,ν_2,ν_3 at ⌈760⌉, ⌈140⌉, and 987 cm^{-1}, respectively. The diatomic molecule Li^7O has ν = 745 cm^{-1} and an estimated bond length $\underline{r}$ = 1.62 Å. The previously undetected molecule $Li^7{}_2O_2$ was shown to resemble the alkali halide dimers in having a planar rhombic (V_h) structure for which the O-Li-O angle and Li-O bond length were estimated to be 116° and 1.90 Å, respectively. Its B_{2u} and B_{3u} frequencies were found at 324 and 522 cm^{-1}, respectively, in a krypton matrix. The remaining unobserved modes were estimated in cm^{-1} as follows: $\nu_1(A_g)$ = 400, $\nu_2(A_g^1)$ = 250, $\nu_3(B_{1g})$ = 300, and $\nu_4(B_{1u})$ = 270. The investigation also provided high-temperature heats of reaction involving these molecules. Using the best pertinent tables of thermodynamic functions available to them, the authors calculated the following standard heats of formation ($\Delta H_0^0(f)$) for the three gases Li_2O, LiO, and Li_2O_2: -43.7 ± 2.5, + 16.0 ± 5, and +27.5 ± 6 kcal/mole, respectively.

2. Al_2O: Aluminum Suboxide

A recent and as yet unpublished spectroscopic investigation (Linevsky, White and Mann) has provided evidence that Al_2O has a bent, symmetric structure. Preliminary, tentative results give the following approximate values for the fundamental frequencies: ν_1: 715 cm^{-1}, ν_2: 240 cm^{-1}; ν_3: 1000 cm^{-1}. The apex angle is estimated to be in the neighborhood of 135°. Rough estimates, based on the application of the Laurie-Hershbach relation give 1.68 Å for the Al-O bond length in Al_2O. There is no reason to suppose that the electronic ground state is other than a singlet.

3. Estimates of the Structure and Spectra of Be_2OF_2

The existence of an isoelectronic beryllum analogue of B_2O_3, viz., Be_2OF_2, is not surprising. In the absence of any structural or spectroscopic data it is probably most reasonable to assume that Be_2OF_2 is geometrically and vibrationally similar to B_2O_3, at least for the purpose of making approximate thermodynamic calculations.

The following guesses may serve until relevant experimental data or more sophisticated estimates become available.

1. Configuration: "V" shape, similar to B_2O_3.
2. Symmetry: C_{2v}
3. Apex angle, $\measuredangle$ Be-O-Be ≈ 150°
4. Be-O distance: 1.40 Å

5. Be-F distance: 1.36 Å

6. O-Be-F grouping: linear

7. Electronic multiplicity of ground state: 1

8. Symmetry number: $\sigma = 2$

9. Vibrational Spectrum (with degeneracies)

1	1200 cm^{-1}	(1)
2	600	(1)
3	400	(1)
4	100	(1)
5	300	(1)
6	1500	(1)
7	900	(1)
8	300	(1)
9	300	(1)

In Chapter 13 of this report are described new mass-spectrometric observations, at the National Bureau of Standards, on a gas species identified as Be_2OF_2. Included are not only calculated Second-law heats of formation of this molecule, but also Third-law values made possible by the above estimated molecular constants.

4. Thermodynamic Functions

Tables of ideal-gas thermodynamic functions based on the foregoing observed and estimated molecular constants were recently calculated by digital computer at the National Bureau of Standards by William H. Evans, and are given in Appendix A of this report (oxides of lithium, Table A-87 ff;

Al_2O, "Table A-57 Revised"; Be_2OF_2, Table A-86). In calculating the tables for the lithium oxides, small adjustments in the molecular constants were first made to place them on a basis of natural lithium (atomic weight = 6.94). The present table for Al_2O supersedes those given in earlier reports of this series (NBS Report 6484, 1 July 1959, Table 1-53; NBS Report 6928, 1 July 1960, Table A-57).

Chapter 16

NEW LITERATURE RELATING TO HEATS OF FORMATION OF FLUORINE COMPOUNDS OF SELECTED ELEMENTS

by M. C. Bracken and G. T. Armstrong

The following material comprises references to additions made since the previous such summary [Chapter 5, NBS Report 7796, 1 January 1963] to the files of articles in the Combustion Calorimetry Group of the Heat Division relating to the heats of formation of fluorine and its compounds with selected elements. The selected elements are Aℓ, B, Be, Br, C, Cℓ, F, H, Hg, I, Li, Mg, N, Na, O, Pb, Ti, W, and Zr. The search was carried out in a systematic way by scanning the Chemical Abstracts Physical Chemistry Sections, and Sections 16, 17, 20, 28, through the 1963 issues, Chemical Titles through 1963, and the current issues of several journals in which relevant material is frequently published. Relevant material has also come to us through other channels. Nevertheless, omissions undoubtedly have occurred because subject and formula indices to the abstracts were not available, and, of course, because of the lag between appearance of an article in a journal not examined and the appearance of its abstract in Chemical Abstracts. Because the collection is intended to form a working file, reviews by others have been used. For the same reason some material of borderline value is included, such as theoretical studies, empirical correlations, and stability studies, which are inadequate in themselves, but may be helpful in comparing other, more precise, studies. No attempt has been made at a critical evaluation or selection of values.

The articles have been examined except for a few in foreign journals that are not readily available. In these cases reliance has been placed upon the abstract for the contents of the article.

New information is listed in Table 1, the substance table. In Table 1 substances are arranged in the alphabetical order of the element symbols, as has been done in previous reviews, but no attempt is made here to differentiate information relating to different phases of the same substance. The brief description in the table of the information given in an article is not necessarily a complete itemization of data to be found in it. Where information for several compounds separately is described in an article, each is separately discussed in the table. Where the information on several substances is not independent, as where two or more substances appear in a reaction for which the heat was measured, one substance is selected for discussion and the others are merely given a cross reference.

Numbers in brackets refer to references at the end of this chapter. The references to the sources of information are listed in alphabetical order by last name of the leading author.

Of more than routine interest to persons involved in evaluating thermodynamic properties of many substances is the availability of three large compilations, references [41,42], [50], and [85].

Reference [85] is the volume in the most recent edition of Landolt-Börnstein that is devoted to thermal properties of materials. Reference [50] is a reprint of Bureau of Mines Bulletins 383, 384, 393, and 406 authored by K. K. Kelley under the general title "Contributions to the Data on Theoretical Metallurgy", which have long been out of print.

References [41,42] are a two volume compendium edited by Gurvich and others, and published in 1962 under the title "Thermodynamic Properties of Individual Substances. Handbook." The volumes total over 2000 pages of discussion and tables and cover much the same series of elements as is covered in the present work. In Table 2 is given a list of compounds covered in References [41,42] which would be included in the scope of the present chapter. For the substances listed in Table 2, [41,42] give a discussion of the available literature and selected values of molecular constants, thermodynamic functions, dissociation energies (where applicable) and heats of formation. For some gases P-V-T data, critical constants, and virial coefficients are given as shown by the footnotes to Table 2.

In another review [69] not amenable to reference by substance, McCullough reviewed experimental calorimetric methods and their accuracies suitable for measurements on organo-metallic and organic fluorine compounds.

Principal abbreviations used in Table 1:

calc.	calculated
correl.	correlated
equil.	equilibrium
est.	estimated
meas.	measured
rev.	reviewed
subl.	sublimation
tab.	tabulated
thermo.	thermodynamic

Table 1

Recent Contributions to the Thermochemistry of Selected Fluorine Containing Substances

$A\ell F$	[9] meas. ion intensities and calc. ΔH for the reactions: $Ca(g) + A\ell F(g) = A\ell(g) + CaF(g)$; $Ba(g) + A\ell F(g) + BaF(g)$; and $Sr(g) + A\ell F(g) = A\ell(g) + SrF(g)$. [66] calc. ΔHf by applying new data on $A\ell F_3$. [67] tab. thermo. functions. [91] gave a bibliography on the vapor pressure. [109] rev. thermo. properties. See FMg.
$A\ell FO$	[25] determined the equilibrium constant and calc. the free energy change for the reaction: $A\ell F_3(g) + A\ell_2O_3(c) = 3A\ell OF(g)$ by effusion measurements. They calc. ΔHf for $A\ell OF$. [67] discussed and tab. thermo. functions.
$A\ell F_3$	[6,21] meas. heat of combustion of powdered Aℓ in F_2. [66] meas. equil. of the reaction: $\frac{3}{2}A\ell F_3 + H_2O = \frac{1}{3}A\ell_2O_3 + 2HF$ between 849 and 1312°K, and calc. ΔH of the reaction and ΔHf of $A\ell F_3$. [67] discussed and tab. thermo. properties. [68] meas. ΔH of subl. [88] rev. ΔHf. [91] gives a bibliography on the vapor pressure. [97, 109] rev. thermo. properties. [110] est. ΔHf and ΔFf. See AℓFO.
$A\ell F_4Li$	[97] rev. thermo. properties.
$A\ell F_4Na$	[66] meas. equil. in the reaction: $\frac{2}{3}NaA\ell F_4 + H_2O = \frac{1}{3}A\ell_2O_3 + 2HF + \frac{2}{3}NaF$, between 1033 and 1340°K, and calc. ΔHf and S of $NaA\ell F_4$.
$A\ell F_6H_8N_2$	[86] est. ΔHf.
$A\ell F_6Li_3$	[97] rev. thermo. properties.
$A\ell F_6Na_3$	[66] meas. equil. in the reaction: $\frac{2}{3}Na_3A\ell F_6 + H_2O = \frac{1}{3}A\ell_2O_3 + 2HF + 2NaF$, between 1101 and 1315°K, and calc. ΔH for the reaction and ΔHf of $Na_3A\ell F_6$. [97] rev. thermo. functions.
BBrF	[94] rev. thermo. properties.
$BC\ell F$	[67] discussed and tab. thermo. functions.
BF	[67] tab. thermo. functions.

BFO	[24] meas. equil. in the reaction: $B_2O_3(\ell) + BF_3(g) = 3BFO(g)$, and calc. ΔH for the reaction and ΔHf and S of BFO(g) [44] calc. ΔHf of BFO from the temperature dependence of equil. in the reaction: $B_3F_3O_3(g) = 3BFO(g)$. [67] discussed and tab. thermo. functions. [89] est ΔHf.
BF_2	[64] calc. ΔHf of BF_2 from previously meas. appearance potentials using the reactions: $e + BF_3(g) = BF_2^+(g) + F + 2e$, and $e + BF_3(g) = BF_2^+(g) + F^- + e$. [67] discussed and tab. thermo. functions. [91] gave a bibliography on the vapor pressure. [94] rev. thermo. properties.
BF_2^+	See BF_2.
BF_2HO	[94] rev. thermo. properties.
BF_3	[6,40] meas. heat of combustion of powdered B in F_2. [67] tab. thermo. functions. [77] meas. equil. constant of the reaction: $B^{10}F_3(g) + B^{11}F_3(\ell) = B^{11}F_3(g) + B^{10}F_3(\ell)$. [88] rev. ΔHf. [91] gave a bibliography on the vapor pressure. [107] gave enthalpy and fugacity in tables and graphs. [109] rev. thermo. properties. See BFO, BF_2, $B_3F_3O_2$, F_3N.
B_2F_4	[91] gave a bibliography on the vapor pressure.
$B_3FH_2O_3$	[83] mass spectrometrically meas. equil. in the reactions: $2B_2O_3F_2H(g) = B_3O_3FH_2(g) + B_3O_3F_3(g)$; and $2B_2O_3FH_2(g) = B_2O_3H_3(g) + B_3O_3F_2H\ (g)$. They calc. ΔH and ΔS for the reactions and ΔHf of $B_3FH_2O_3$. [87] est. ΔHf. [95,97] rev. thermo. properties.
$B_3F_2HO_3$	[83] mass spectrometrically meas. equil. in the reaction: $H_2(g) + B_3O_3F_3(g) = HF(g) + B_3O_3F_2H(g)$. They calc. ΔH and ΔS for the reaction and ΔHf of $B_3F_2HO_3$. [87] est. ΔHf. [95,97] rev. thermo. properties. See $B_3FH_2O_3$.
$B_3F_3O_3$	[24,27,44,89] meas. equil. constants for the reaction: $B_2O_3(\ell) + BF_3(g) = (BOF)_3(g)$, and calc. ΔH for the reaction and ΔHf of $(BFO)_3$. [67] discussed and tab. thermo. functions. [87,89] est. ΔHf. [97] rev. thermo. properties. See BFO, $B_3F_2HO_3$, $B_3FH_2O_3$.

$BeBr_2$	[59] tab. S°_{298}, $(H^\circ-H^\circ_0)/T$, $-(G-H^\circ_0)/T$ and heat capacity of the gas from 298 to 2500°K.
$BeC\ell F$	[67] discussed and tab. thermo. functions.
BeF	[9,10] est. D (BeF). [34] mention an unpublished value for ΔHf by Greenbaum, et al. [35] meas. equil. pressures in the reaction: $BeF_2(g) + Be(s,\ell) = 2BeF(g)$, over the range 1425-1675°K, and calc. ΔF, ΔS, and ΔH for the reaction, and ΔH and S of BeF(g). [67] discussed and tab. thermo. functions. [95] rev. thermo. properties.
BeF^+	[103] calc. entropy of gas.
BeF_2	[33] meas. equil. in the reaction: $BeO(s) + 2HF(g) = BeF_2(g) + H_2O(g)$, in the range 943-1243°K, and calc. ΔF, ΔH, and ΔS for the reaction and ΔHf and S of $BeF_2(g)$. [34] meas. melting point and vapor pressure of BeF_2 over the range 883-1223°K, and calc. ΔH and ΔS of vaporization. [38,39] meas. heat of the reaction: $PbF_2 + Be = BeF_2 + Pb$, and calc. ΔHf of BeF_2. [40] meas. heat of combustion of Be in F_2 (preliminary tests). [59] tab. S°_{298}, $(H^\circ-H^\circ_0)/T$, $-(G-H^\circ_0)/T$ and heat capacity of the gas from 298 to 2500°K. [67] discussed and tab. thermo. functions. [88] rev. ΔHf. [91] gave a bibliography on the vapor pressure. [96,109] rev. thermo. properties. [110] est. ΔHf. See NaF, BeF.
BeF_3Li	[94] rev. thermo. properties.
$BrCF_3$	See CF_3H.
BrF_5	[88] rev. ΔHf.
Br_3CF	[105] calc. force constants to use in thermo functions.
$CC\ell FO$	[67] discussed and tab. thermo. functions.
$CC\ell F_2$	[49] calc. bond energy $CF_2C\ell-C\ell$ and ΔHf of $CC\ell F_2$. See CF_2.
$CC\ell F_2H$	[45] made electron impact study and obtained information about ΔHf.
$CC\ell F_3$	[57] meas. heat of the reaction: $CC\ell F_3 + 4Na = NaC\ell + 3NAF + C$, and calc. ΔHf of $CC\ell F_3$. [58] carried out additional measurements and recalc. ΔHf. See CF_3.

$CC\ell_2F$	[49] calc. bond energy $CFC\ell_2$-$C\ell$ and ΔHf of $CC\ell_2F$.
$CC\ell_2FH$	[45] made electron impact study and obtained information about ΔHf.
$CC\ell_2F_2$	[47] est. Cp as an example. [57] meas. heat of the reaction: $CC\ell_2F_2 + 4Na = 2NaC\ell + 2NaF + C$, and calc. ΔHf of $CC\ell_2F_2$. [58] made additional measurements and recalc. ΔHf. See $CC\ell F_2$.
$CC\ell_3F$	[105] calc. force constants for thermo. functions. See $CC\ell_2F$.
CDF_3	[105] calc. force constants for thermo functions.
CF	[47] lists a bond energy value for (C-F). [67] tab. thermo. functions. [100] calc. D(CF-F) and D(C-F) from predissociation spectra of CF and CF_2. [112] listed heat of formation, reference enthalpy, reference entropy, and heat capacity equations. See CF_2.
CFH_3	[112] listed heat of formation, reference enthalpy, reference entropy, and heat capacity equations. See FH.
CF_2	[13] est. ΔHf on the basis of experimental data. [45] calc. ΔHf from mass spectrometer measurements on CF_3H, $CC\ell F_2H$, $CC\ell_2FH$, and $CC\ell_3H$. [49] calc. bond energies CF_2-F and CF_2-$C\ell$. [65] rev. earlier data on appearance potentials of $C_6H_5F^+$ and $C_6H_4F_2^+$ from $C_6H_5CF_3$ and calc. ΔHf of CF_2. [67] discussed and tab. thermo. functions. [100] calc. D(CF-F) from the predissociation spectrum of CF_2, and calc. ΔHf of CF_2. [112] listed heat of formation, reference entropy, reference enthalpy, and heat capacity equations.
CF_2H_2	[112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity. See FH.
CF_2O	[67] discussed and tab. thermo. functions. [112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity. See FH.

CF_3	[49] calc. bond energies in CF_3-$C\ell$ and CF_2-F. [67] discussed and tab. thermo. functions. [112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity. See CF_2.
CF_3H	[18] meas. activation energies and equil. for the bromination reaction of CF_3H, and calc. D(CF_3-H), and ΔH and ΔS for the reaction: $CF_3H + Br_2 = HBr + CF_3Br$. [45] reported an electron impact study giving information about ΔHf. [105] calc. force constants for thermo. functions. [112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity. See FH.
CF_4	[11] correl. heat of subl. [67] discussed and tab. thermo. functions. [73] calc. thermo. functions from 100 to 1400°K. [88] rev. ΔHf. [109] rev. thermo. properties. [112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity. See FH.
C_2FH_3	[7] calc. S_{298}, Cp_{298}, Cp_{1000}.
$C_2F_2H_2$	[7] calc. S_{298}, Cp_{298}, Cp_{1000}. [55] meas. energy of the reaction: $C_2H_2F_2(g) + 2O_2(g) = 2CO_2 + 2HF(30H_2O)$, and calc. ΔHf of $C_2F_2H_2$.
C_2F_2	[112] listed heat of formation, reference enthalpy, reference entropy, and heat capacity equations.
$C_2F_2O_4$	[5] meas. vapor pressure.
C_2F_3H	[7] calc. S_{298}, Cp_{298}, Cp_{1000}. [55] meas. energy of the reaction: $C_2HF_3(g) + \frac{3}{2} O_2(g) + H_2O(\ell) = 2CO_2(g) + 3HF(30H_2O)$, and calc. ΔHf of C_2HF_3.
C_2F_4	[7] calc. S_{298}, Cp_{298}, Cp_{1000}. [56] meas. ΔH for the reaction: $C_2F_4(g) + 4Na = 2C(s) + 4NaF(s)$, and calc. ΔHf of C_2F_4. [96] rev. thermo. properties.
$C\ell F$	[67] tab. thermo. functions. [112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity.

$C\ell FMg$	[67] discussed and tab. thermo. functions.
$C\ell FO_3$	[17] correl. and discussed high temperature entropy.
$C\ell F_2N$	[60] meas. vapor pressure. [79] rev. thermo. and other properties.
$C\ell F_3$	[67] discussed and tab. thermo. functions. [70] meas. vapor pressures and equilibria of $C\ell F_3$-HF solutions. [78] meas. heat of reaction of $C\ell F_3$ with H_2O. [84] meas. vapor pressures of $C\ell F_3$-HF solutions.
$C\ell F_3O_2$	[93] est. ΔHf.
F	[63] meas. appearance potential of the benzoyl ion in the reaction: $C_6H_5COF + e = C_6H_5CO^+ + F + 2e$. [67] tab. thermo. functions. [112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity. See BF_2, CF, CF_2.
F^-	[19,20] correl. entropy and heat capacity of aqueous ion. [90] calc. entropy of aqueous ion. [108] calc. ΔHf of aqueous ion by correlating existing data. [110] est. ΔHf and ΔFf of gaseous ion. See BF_2.
FH	[2,3] correl. heat of vaporization and association of vapor. [6] meas. heat of combustion of HLi, HNa, HK, H_2Ca, H_2Sr, and H_2Ba in F_2. [8] discussed solubility and heat of solution in NaF and in NaF-ZrF_4. [26] rev. ΔHf based on the reactions: $SiO_2(s) + F_2 = SiF_4(g) + O_2$, and $SiF_4(g) + 2H_2O(g) = SiO_2(s) + 4HF(g)$. [28] calc. equil. of HF with H_2, H_2O, CO, CO_2, COF_2, CH_4, CH_3F, CH_2F_2, CHF_3, CF_4 from 400 to 1500°K. [31] meas. heat of reaction: $C_6H_{12}N_2F_4(soln) + 8O_2(g) + 196H_2O(\ell) = 6CO_2(g) + N_2(g) + 4HF \cdot 50H_2O(\ell)$. [32] meas. heat of reaction: $C_5F_{11}N(\ell) + 2.25O_2(g) + 21H_2O(\ell) = 2HF \cdot 10H_2O(\ell) + 2.25\ CF_4(g) + 2.75\ CO_2(g) + 0.5\ N_2(g)$. [36,37,38,39] meas. heat of solution of $A\ell_2O_3$, B_2O_3 and $A\ell_4B_2O_9$ in aqueous HF. [47] lists a bond energy value, and uses the heat of formation to calculate the heat of reaction: $4HF(g) + SiO_2(s) = SiF_4(g) + 2H_2O(g)$. [51] correl. enthalpies and entropies for the reactions: $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) = HF(g)$, and $Ca(OH)_2(s) + 2HF(g) = CaF_2(s) + 2H_2O(g)$, and the analogous reactions involving $HC\ell$, from 298 to 1000°K.

FH (Cont.)	[52] correl. ΔS for the reaction: $BaCO_3(s) + 2HF(g) = BaF_2(s) + H_2O(g) + CO_2(g)$, and the corresponding reaction forming CaF_2, from 298 to 1000°K. [52] correl. ΔS for the reaction: $MgO(s) + 2HF(g) = MgF_2(s) + H_2O(g)$, and the analogous reaction involving $HC\ell$ and $MgC\ell_2$. [53] correl. heat of reaction of HF and MgO with that of HF and CaO, and the heats of reaction of HF with $CaTiO_3$, $CaSiO_3$, $MgTiO_3$, and $MgSiO_3$. [62] recalc. earlier data to derive association constants, ΔH, and ΔS for the reactions: $HF + (HF)_{q-1} = (HF)_q$ for q = 2,6; 2,3,6; 2,4,6; 2,5,6; 2,6,7,8,9----. [67] discussed and tab. thermo. functions. [73] recalc. vapor phase imperfections and review ΔHf. [88] rev. ΔHf. [106] gave an enthalpy diagram and tabulate enthalpy as a function of temperature and percent HF in the $HF-H_2O$ system. [109] rev. thermo. properties. [112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity. See $A\ell F_3$, $A\ell F_4Na$, $A\ell F_6Na_3$, BeF_2, $C_2F_2H_2$, C_2F_3H, FH_4N.
(FH)n	[2] calc. association of HF gas. See FH.
FH_4N	[14] studied the system $NH_4F-HF-H_2O$. [111] est. ΔHf and ΔFf.
FHg	[109] rev. thermo. properties.
FI	[112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity.
FLi	[6] meas. heat of combustion of powdered Li in F_2. [8] discussed thermodynamics of the system LiF-NaF, $LiF-NaC\ell$. [54] correl. ΔS of vaporization with reduced temperature. [67] discussed and tab. thermo. functions. [71] calc. ground state energy of LiF(g) exactly. [90] meas. heat of solution. [91] gave a bibliography on the vapor pressure. [103] calc. entropy of the gas. [109] rev. thermo. properties. [110,111] est. ΔHf and ΔFf. See F_4Zr.
FMg	[9] est. D(MgF). [10,22] meas. ion intensities and calc. D°_{298} for MgF, and ΔH°_{298} for the reactions: $Mg(g) + A\ell F(g) = A\ell(g) + MgF(g)$; $Mg(g) + MgF_2(s) = 2MgF(g)$; $Mg(g) + MgF_2(g) = 2MgF(g)$. [23] calc. ΔHf of the crystal [67] tab. thermo. functions.

FMg^+	[103] calc. entropy of gas.
FN	[67] discussed and tab. thermo. functions. [79] rev. thermo. and other properties.
FNO	[112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity.
FNO_2	[94] rev. thermo. properties. [104] calc. C_p^o, S^o, $(H^o-E_0^o)/T$, $-(F-E_0^o)/T$ from 100 to 1000°K.
FNO_3	[95] rev. thermo. properties.
FN_3	[79] rev. thermo. and other properties.
FNa	[6] meas. heat of combustion of powdered Na in F_2. [8] discussed thermodynamics of the systems $NaF-BeF_2$ and $NaF-MgF_2$. [12] discussed thermodynamics of the system $NaF-NaC\ell$. [15] studied thermodynamics of the system $NaF-ZrF_4$. [16] discussed thermodynamics of the system $NaF-MgF_2$. [54] correl. ΔS of vaporization with reduced temperature. [67] discussed and tab. thermo. functions. [91] gave a bibliography of the vapor pressure. [103] calc. entropy of the gas. [109] rev. thermo. properties. [110, 111] est. ΔHf and ΔFf. See $A\ell F_4Na$, $A\ell F_6Na_3$, $CC\ell F_3$, $CC\ell_2F_2$, C_2F_4, FH, F_4Zr.
FO	[47] lists bond energy value.
FOTi	[97] rev. thermo. properties.
F_2	[43] gave a bibliography of thermophysical properties of F_2 with 51 references. [47] lists bond energy value. [67] tab. thermo. functions. [109] rev. thermo. properties. [112] listed heat of formation, reference enthalpy, reference entropy, and equations for heat capacity.
F_2HN	[60] meas. melting point and density of the liquid. [79] rev. thermo. and other properties.
F_2H_2	See FH.
F_2H_5N $(NH_4F \cdot HF)$	See FH_4N.
F_2Hg	[109] rev. thermo. properties. [110] est. ΔHf and ΔFf.

F_2Hg_2	[110] est. ΔHf.
F_2Li_2	[67] tab. thermo. functions.
F_2Mg	[6] meas. heat of combustion of powdered Mg in F_2. [59] tab. S°_{298}, $(H^\circ-H^\circ_0)/T$, $-(G^\circ-H^\circ_0)/T$ and heat capacity of the gas from 298 to 2500°K. [67] discussed and tab. thermo. functions. [91] gave a bibliography on the vapor pressure. [109] rev. thermo. properties. [110] est. ΔHf and ΔFf. See FH, FMg, FNa.
F_2N	[67] discussed and tab. thermo. functions. [79] rev. thermo. and other properties. [82] meas. equil. in the reaction: $N_2F_4 = 2NF_2$, and calc. ΔH for the reaction. [94] rev. thermo. properties. See F_2N_2O.
F_2N_2	[4] meas. heat of reaction with NH_3 and calc. ΔHf. [67] discussed and tab. thermo. functions. [79] rev. thermo. and other properties. [81] meas. heat of the reaction: $N_2F_2(g) + 3KI(aq) = 2KF(aq) + N_2 + KI_3$ (pH = 3.3), and calc. ΔHf of N_2F_2.
F_2N_2O	[48] studied the equil.: $2NO + N_2F_4 = 2NF_2NO = 2NO + 2NF_2$, and determined equil. constants at 25°C, and as a function of temperature, from which they calc. ΔH and ΔS for the reaction and ΔHf of NF_2NO.
F_2Na_2	[67] discussed and tab. thermo. functions.
F_2O	[75] provided auxiliary functions used in a previous table of thermo. functions. [92] rev. properties. [101] meas. vapor pressure, liquid density, viscosity, critical temperature, heat capacity of the liquid, thermal dissociation rate, and calc. critical volume, critical pressure, heat of vaporization and heat of formation.
F_2OTi	[97] rev. thermo. properties.
F_2O_2	[92] rev. properties. [93] lists ΔH for several reactions.
F_2O_3	[92] rev. properties.
F_2O_4	[92] rev. properties.

F_2Pb	[6] meas. heat of combustion of powdered Pb in F_2. [46] made a differential thermal analysis from 25 to 800°C. [91] gave a bibliography on the vapor pressure. [109] rev. thermo. properties. [110] est. ΔHf and ΔFf. See BeF_2.
F_2Ti	[109] rev. thermo. properties. [110] est. ΔHf and ΔFf.
F_2Zr	[109] rev. thermo. properties. [110] est. ΔHf and ΔFf.
F_3Li_3	[67] tab. thermo. functions.
F_3N	[61] meas. ΔE for the reaction: $B(c) + NF_3(g) = BF_3(g) + \frac{1}{2}N_2(g)$, and calc. ΔHf of NF_3. [67] tab. thermo. functions. [79] rev. thermo. and other properties. [88] rev. ΔHf. [99] tab. C_p^o, $(H^o-E_0^o)/T$, and S^o from 273.16 to 2500°K.
F_3Ti	[109] rev. thermo. properties. [101] est. ΔHf and ΔFf.
F_3Zr	[109] rev. thermo. properties. [110] est. ΔHf and ΔFf.
F_4H_7N ($NH_4F \cdot 3HF$)	See FH_4N.
F_4N_2	[79] rev. thermo. and other properties. See F_2N, F_2N_2O.
F_4OW	[91] gave a bibliography on the vapor pressure.
F_4Pb	[109] rev. thermo. properties.
F_4Ti	[88] rev. ΔHf. [91] gave a bibliography on the vapor pressure. [110] est. ΔHf and ΔFf.
F_4Zr	[1] meas. vapor pressure 681-913°K, calc. ΔH subl. [8] discusses thermodynamics of the systems ZrF_4-LiF and ZrF_4-NaF. [29] meas. vapor pressure 713-873°K, calc. ΔH subl. [88] rev. ΔHf. [91] gave a bibliography on the vapor pressure. [109] rev. thermo. properties. [110] est. ΔHf and ΔFf. See FH.

F_5I	[74,76] calc. thermo. functions from 10° to 1300°K. [88] rev. ΔHf.
F_6H_6	See FH.
F_6W	[88] rev. ΔHf. [91] gave a bibliography on the vapor pressure. [98] tab. heat capacity, heat content, free energy, entropy from 100 to 1500°K. See F_7NOW.
F_7I	[95] rev. thermo. properties.
F_7NOW	[30] roughly determined equil. of formation.

Table 2

Some Substances for which Thermodynamic and Thermochemical Data are Given in [41,42]

F
F^-
F_2 (b,c,d)
FO
F_2O(c)
$C\ell F$
BrF
IF
HF (b,c)
DF
TF
NF
NF_2
NF_3 (b,c)
FNO
FCO
F_2CO
$FHCO$
$FC\ell CO$
CF_4 (b,c,d)
CH_3F (b,c,d)

CHF_3 (b,c)
$CF_3C\ell$ (b,c)
CF_3Br (c)
CF_3I (c)
$CFC\ell_3$ (b,c,d)
$CFBr_3$ (c)
CH_2F_2 (c)
$CF_2C\ell_2$ (b,c,d)
CF_2Br_2 (c)
CF_2I_2 (c)
$CH_2FC\ell$ (c)
CH_2FBr (c)
CH_2FI
$CHF_2C\ell$ (b)
CHF_2Br (c)
CHF_2I (c)
$CHFC\ell_2$ (b,d)
$CHFC\ell Br$
$CHFBr_2$ (c)
$CF_2C\ell Br$ (c)
$CF_2C\ell I$

CF_2BrI
$CFC\ell_2Br$ (c)
$CFC\ell Br_2$ (c)
C_2F_4 (b,c)
$C_2H_2F_2$ (b,c)
C_2H_3F (b)
C_2HF_3
$C_2F_3C\ell$ (b,c)
$C_2FC\ell_3$
$C_2H_2FC\ell$
$C_2HF_2C\ell$ (b,c)
$C_2HFC\ell_2$
$C_2F_2C\ell_2$
C_2HF
C_2F_2
CF
CF_2
CF_3
C_2F
CHF
CH_2F

CHF_2
FCN
BF
BF_2
BF_3 (b,c)
FBO
$A\ell F$
$A\ell F_2$
$A\ell F_3$ (c)
BeF
BeF_2 (c)
MgF
MgF_2 (c)
LiF (c)
Li_2F_2 (a)
NaF (c)
PbF
PbF_2 (c)
HgF

---

[a] Thermodynamic functions are not tabulated.
[b] P-V-T data are discussed.
[c] Critical constants are given.
[d] Virial coefficients are tabulated 293.15-6000°K.

REFERENCES

[1] Akishin, P. A., Belousov, V. I., and Sidorov, L. N., Zh. Neorg. Khim. 8, 1520 (1963).

[2] Armitage, J. W., and Gray, P., J. Chem. Soc. (London) 1963, No. 3, 1807-13.

[3] Armitage, J. W., Gray, P., and Wright, P. G., J. Chem. Soc. (London) 1963, No. 3, 1796-1806.

[4] Armstrong, G. T. and Marantz, S., J. Chem. Phys. 38, 169-72 (1963).

[5] Arvia, A. J., Aymonina, P. J., and Schumacher, H. J., Anales Asoc. Quim. Arg. 50, 135-43 (1962).

[6] Aubert, M., and Sivolobov, N., Publ. Sci. Tech. Min. Air (France), Notes Tech. No. 125, 38 pp. (1963).

[7] Beckwith, W. F., and Fahien, R. W., Chem. Eng. Progr., Symp. Ser. 59 (44), 75-87 (1963).

[8] Blander, M., U. S. At. Energy Comm. ORNL-3293, 97 pp. (1962).

[9] Blue, G. D., Univ. Microfilms (Ann Arbor, Mich.), Order No. 63-3915, 149 pp.; Dissertation Abstr. 23, 4123-4 (1963).

[10] Blue, G. D., Green, J. W., Ehlert, T. C., and Margrave, J. L., Nature 199, 804-5 (1963).

[11] Bondi, A., J. Chem. Eng. Data 8, 371-81 (1963).

[12] Bradley, R. S., Am. J. Sci. 260, 374-82 (1962).

[13] Brewer, L., Margrave, J. L., Porter, R. F., and Wieland, K., J. Phys. Chem. 65, 1913 (1961).

[14] Buettner, J. P., and Jache, A. W., Inorg. Chem. 2, 19-22 (1963).

[15] Cantor, S., and Carlton, T. S., J. Phys. Chem. 66, 2711-13 (1962).

[16] Cantor, S., and Ward, W.T., J. Phys. Chem. 67, 1868-70 (1963).

[17] Chipman, J., Pure Appl. Chem. 5, 669-82 (1962).

[18] Corbett, P., Tarr, A., and Whittle, E., Bull. Soc. Chim. Belg. 71, 778-9(1962).

[19] Criss, C. M., and Cobble, J. W., Private Communication, 1963.

[20] Criss, C. M., and Cobble, J. W., Private Communication, 1963.

[21] Domalski, E. S., NBS Report 7587, July 1, 1962.

[22] Ehlert, T. C., Private Communication, September 16, 1963.

[23] Emons, H. H. and Roewer, G., Z. Phys. Chem. (Leipzig) 222, 65-77 (1963).

[24] Farber, M. and Blauer, J., Trans. Faraday Soc. 58, 2090-94 (1962).

[25] Farber, M., and Petersen, H. L., Trans. Faraday Soc. 58, 836-40 (1963).

[26] Feder, H. M., Hubbard, W. N., Wise, S. S., and Margrave, J. L., J. Phys. Chem. 67, 1963.

[27] Fischer, H. D., Kiehl, J., and Cane, A., U. S. Dept. Com., Office Tech. Serv., AD 274,243, 22 pp. (1961).

[28] Gal'kin, N. P., Shubin, V. A., and Krylov, A. S., Khim. Prom. 1962 (10) 750-3.

[29] Galkin, N. P., Tumanov, Yu. N., Tarasov, V. I., and Shishkov, Yu. D., Zh. Neorgan. Khim. 8 (9), 2021-23 (1963).

[30] Geichman, J. R., Smith, E. A., and Ogle, P. R., Inorg. Chem. 2(5), 1012-15 (1963).

[31] Good, W. D., Douslin, D. R., and McCullough, J. P., J. Phys. Chem. 67, 1312-14 (1963).

[32] Good, W. D., Todd, S. S., Messerly, J. F., Lacina, J. L., Dawson, J. P., Scott, D. W., and McCullough, J. P., J. Phys. Chem. 67, 1306-11 (1963).

[33] Greenbaum, M. A., Arin, M. L., and Farber, M., J. Phys. Chem. 67, 1191-4 (1963).

[34] Greenbaum, M. A., Foster, J. N., Arin, M. L., and Farber, M., J. Phys. Chem. 67, 36-40 (1963).

[35] Greenbaum, M. A., Yates, R. E., Arin, M. L., Arshadi, M., Weiher, J., and Farber, M., J. Phys. Chem. 67, 703-706 (1963).

[36] Gross, P., Fulmer Research Institute Rept. R 163/10/17, December, 1962.

[37] Gross, P., Fulmer Research Institute Rept. R 163/12/24, June, 1963.

[38] Gross, P., Fulmer Research Institute Rept. R 163/13/23, September, 1963.

[39] Gross, P., Fulmer Research Institute Rept. R163/14/20, December, 1963.

[40] Gross, P., Hayman, C., Levi, D. L., and Stuart, M. C., U. S. Dept. Com., Office Tech. Serv., PB Rept 153,445, 32 pp. (1960).

[41] Gurvich, L. V., Khachkuruzov, G. A., and Medvedev, V. A., et al.: Termodinamicheskie svoistva individual'nykh veshchestv. Spravochnik. Tom. 1. Vychislenie termodinamicheskikh svoistv.

[42] Gurvich, L. V., Khachkuruzov, G. A., and Medvedev, V. A., et. al.: Termodinamicheskie svoistva individual'nykh veshchestv. Spravochnik. Tom. 2. Tablitsy termodinamicheskikh svoistv.

[43] Hall, L. A., and McCarty, R. D., NBS Report 7676, April 1, 1963.

[44] Hildenbrand, D. L., Theard, L. P., and Saul, A. M., J. Chem. Phys. 39, 1973-8 (1963).

[45] Hobrock, D. L., and Kiser, R. W., 146th National ACS Meeting, Denver, Colo., Jan. 21, 1964.

[46] Hogan, V. D., and Freeman, E. S., 146th National ACS Meeting, Denver, Colo., Jan. 23, 1964.

[47] Huyskens, P., and Zeegers-Huyskens, Th., Industrie Chimique Belge, 28, 251-70 (1963).

[48] Johnson, F. A., and Colburn, C. B., Inorg. Chem. 2, 24-6 (1963).

[49] Kaufman, E. D., and Reed, J. F., J. Phys. Chem. 67, 896-902 (1963).

[50] Kelley, K. K., U. S. Bur. of Mines Bull. 601, 452 pp. (1962).

[51] Kireev, V. A., Zh. Fiz. Khim. 36, 2547-50 (1962)

[52] Kireev, V. A., Zh. Obshch. Khim. 33 (3), 724-8 (1963).

[53] Kireev, V. A., Zh. Obshch. Khim. 33 (5), 1391-6 (1963).

[54] Kirshenbaum, A. D., Cahill, J. A., McGonigal, P. J., and Grosse, A. V., J. Inorg. Nucl. Chem. 24, 1287-96 (1962).

[55] Kolesov, V. P., Martynov, A. M., Shtekher, S. M., and Skuratov, S. M., Zh. Fiz. Khim. 36, 2078-81 (1962).

[56] Kolesov, V. P., Zenkov, I. D., and Skuratov, S. M., Zh. Fiz. Khim. 36, 89-92 (1962).

[57] Kolesov, V. P., Zenkov, I. D., and Skuratov, S. M., Zh. Fiz. Khim. 36, 2082-4(1962); See also Russ. J. Phys. Chem. 36, 1120-2 (1962).

[58] Kolesov, V. P., Zenkov, I. D., and Skuratov, S. M., Zh. Fiz. Khim. 37, 720 (1963); See also Russ. J. Phys. Chem. 37, 378-9 (1963).

[59] Krasnov, K. S., and Svettsov, V. I., Izv. Vysshikh Uchebn. Zavedenii. Khim. i Khim. Tekhnol. 6, 167-70 (1963).

[60] Lawton, E. A., and Weber, J. Q., J. Am. Chem. Soc. 85, 3595-7 (1963).

[61] Ludwig, J. R., and Cooper, W. J., J. Chem. Eng. Data 8, 76-7 (1963).

[62] Maclean, J. N., Rossotti, J. C., and Rossotti, H. S., J. Inorg. Nucl. Chem. 24, 1549-54 (1962).

[63] Majer, J. R. and Patrick, C. R., Trans. Faraday Soc. 58, 1274-8 (1963).

[64] Margrave, J. L., J. Phys. Chem. 66, 1209-10 (1962).

[65] Margrave, J., Nature 197, 376 (1963).

[66] Mashovets, V. P., and Yudin, B. F., Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met. 5, 95-105 (1962).

[67] McBride, B. J., Heimel, S., Ehlers, J. G., and Gordon, S., "Thermodynamic Properties to 6000° K for 210 Substances Involving the First 18 Elements", Report No. NASA SP-3001, 1963 (Office of Technical Services, U. S. Department of Commerce, Washington, D. C., 20230).

[68] McCory, L. D., Paule, R. C., and Margrave, J. L., J. Phys. Chem. 67, 1086 (1963).

[69] McCullough, J. P., Symposium on Heats of Formation of Propellant Ingredients, JANAF Thermochemical Panel Meeting July 18-19, 1961.

[70] McGill, R. M., Wendolkowski, W. S., and Barber, E. J., J. Phys. Chem. 61, 1101-1105(1957).

[71] McLean, A. D., J. Chem. Phys. 39, 2653-65 (1963).

[72] Medvedev, V. A., Zh. Fiz. Khim. 37 (6), 1403-6 (1963).

[73] Nagarajan, G., Australian J. Chem. 15, 566-8 (1962).

[74] Nagarajan, G., Bull. Soc. Chim. Belg. 72, 5-15 (1962).

[75] Nagarajan, G., Bull. Soc. Chim. Belges 72, 16-24 (1963).

[76] Nagarajan, G., Z. Naturforsch. 17a, 871-4 (1962).

[77] Nakane, R., Watanabe, T., and Kurihara, O., Bull. Chem. Soc. Japan 35, 1747-8 (1962).

[78] Oliver, G. D., and Grisard, J. W., U. S. At. Energy Comm. AECD-4065, Oct., 24, 1950.

[79] Pankratov, A. V., Uspekhi Khim. 32, 336-52 (1963).

[80] Pankratov, A. V., and Khananova, E. Ya., Russ. J. Inorg. Chem. 7, 897-8 (1962).

[81] Pankratov, A. V., Zercheninov, A. N., Talakin, O. G., Sokolov, O. M., and Knyazeva, N. A., Zh. Fiz. Khim. 37, 1399-1401 (1963).

[82] Piette, L. H., Johnson, F. A., Booman, K. A., and Colburn, C. B., J. Chem. Phys. 35 (4), 1481-2 (1961).

[83] Porter, R. F., and Sholette, W. P., J. Chem. Phys. 37, 198-9 (1962).

[84] Rogers, M. T., Speirs, J. L., and Panish, M. B., J. Phys. Chem. 61, 366(1957).

[85] Schafer, K., and Lax, E., Editors. Landolt-Bornstein, Zahlenwerte und Functionen aus Physik, Chemie, Astronomie, Geophysik und Techik. Sechste Auflage II Band, Eigenschaften

der Materie in ihren aggregatzustanden, 4 Teil, Kalorische Zustandgrossen. (Springer-Verlag, Berlin, Gottingen, Heidelberg, 1961).

[86] Shidlovskii, A. A., Teoriya Vzrvchatykh Veshchestv. Sb. Statei 1963, 543-6.

[87] Sholette, W. P., and Porter, R. F., J. Phys. Chem. 67, 177-82 (1963).

[88] Skinner, H. A., Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July 20, 1963.

[89] Smith, D. D., and Lawrence, R. W., U. S. Dept. Com., Office Tech. Serv., AD 264,655, 90 pp. (1961).

[90] Stephenson, C. C., Hopkins, H. P., Jr., and Wulff, C. A., 146th National ACS Meeting, Denver, Colo., Jan. 21, 1964.

[91] Stevenson, F. D. and Hill, S. D., U. S. Bur. Mines, Inform. Circ. No. 8147, 35 pp. (1963).

[92] Streng, A. G., Chem. Revs. 63, 607-24 (1963).

[93] Streng, A. G., J. Am. Chem. Soc. 85, 1380-5 (1963).

[94] Stull, D. R., Chao, J., Dergazarian, T. E., Hadden, S. T., Prophet, H., Rizos, J. A., and Swanson, A. C., Quarterly Supplement No. 8, December 31, 1962, JANAF Interim Thermochemical Tables, (The Dow Chemical Company, Midland, Michigan, December 30, 1960).

[95] Stull, D. R., Chao, J., Dergazarian, T. E., Prophet, H., Rizos, J. A., and Swanson, A. C., Quarterly Supplement No. 9, March 31, 1963, JANAF Interim Thermochemical Tables, (The Dow Chemical Company, Midland, Michigan, December 30, 1960.)

[96] Stull, D. R., Chao, J., Dergazarian, T. E., Prophet, H., Rizos, J. A., Swanson, A. C., and Wollert, S. K., Quarterly Supplement No. 10, June 30, 1963, JANAF Interim Thermochemical Tables, (The Dow Chemical Company, Midland, Michigan, December 30, 1960.)

[97] Stull, D. R., Chao, J., Dergazarian, T. E., Prophet, H., Rizos, J. A., Swanson, A. C., and Wollert, S. K., Quarterly Supplement No. 11, September 30, 1963, JANAF Thermochemical Tables, (The Dow Chemical Company, Midland, Michigan, December 30, 1960.)

[98] Sundaram, S., Z. Physik. Chem. (Frankfurt) 34, 225-32 (1962).

[99] Sundaram, S., Z. Physik. Chem. (Frankfurt) 36, 376-77 (1963).

[100] Thrush, B. A., and Zwolenik, J. J., Trans. Faraday Soc. 59, 582-7 (1963).

[101] Toole, R. C., Univ. Minn. Summary Rept., Oct. 1, 1949-May 1, 1951, ATI-109 454.

[102] Tsoiman, G. I., Inzh. Fiz. Zh., Akad. Nauk Belorussk. SSR 6 (7), 121-3 (1963).

[103] Vasil'ev, V. P., and Vasil'eva, V. N., Zh. Fiz. Khim. 37, 1089-94 (1963).

[104] Venkateswarlu, K., and Rajalakshmi, K. J., Acta Phys. Polon. 22, 417-21 (1963).

[105] Venkateswarlu, K., and Thanalakshmi, R., Acta Phys. Polon. 22, 425-7 (1962).

[106] Vieweg, R., Chem. Tech. (Berlin) 16, No. 1, 12-14 (1963).

[107] Viswanath, D. S., Univ. Microfilms (Ann Arbor, Mich.), Order No. 62-6659, 248 pp.; Dissertation Abstr. 23, 3279 (1963).

[108] Vorob'ev, A. F., Privalova, N. M., and Skuratov, S. M., Vestn. Mosk. Univ., Ser. II, Khim. 18 (4), 39-45 (1963).

[109] Wicks, E. E., and Block, F. E., U. S. Bur. Mines. Bull. 605, 1963.

[110] Wilcox, D. E., University of California, UCRL-10397, August 1, 1962.

[111] Wilcox, D. E., and Bromley, L. A., Ind. Eng. Chem. 55, 32-39 (1963).

[112] Williams, M. M., U. S. Dept. Com., Office Tech. Serv., AD 255,963, 31 pp. (1961).

APPENDIX A

IDEAL-GAS THERMODYNAMIC FUNCTIONS

(For the sources of the data, see Chapter 15.)

Table A-57 REVISED. Thermodynamic Functions for $A\ell_2O$(gas)

AL20 T K	-(F-H0)/T	(H-H0)/T	S	CP	(H-H0)	-(F-H298)/T
273.15	52.274	9.169	61.442	10.662	2504.4	62.429
298.15	53.082	9.304	62.387	10.906	2774.1	62.387
50.00	38.064	7.960	46.024	8.044	398.0	93.546
75.00	41.304	8.040	49.344	8.379	603.0	78.292
100.00	43.635	8.172	51.807	8.756	817.2	71.375
125.00	45.474	8.322	53.797	9.078	1040.3	67.667
150.00	47.005	8.472	55.477	9.361	1270.8	65.499
175.00	48.322	8.618	56.940	9.629	1508.2	64.174
200.00	49.482	8.761	58.243	9.896	1752.3	63.352
225.00	50.522	8.902	59.424	10.162	2003.0	62.851
250.00	51.467	9.041	60.509	10.425	2260.3	62.564
275.00	52.335	9.179	61.514	10.680	2524.2	62.423
300.00	53.140	9.314	62.454	10.923	2794.3	62.387
325.00	53.891	9.447	63.338	11.152	3070.2	62.426
350.00	54.596	9.576	64.172	11.364	3351.7	62.522
375.00	55.261	9.702	64.963	11.559	3638.3	62.658
400.00	55.891	9.824	65.715	11.739	3929.5	62.826
425.00	56.490	9.941	66.431	11.903	4225.1	63.017
450.00	57.061	10.055	67.116	12.052	4524.6	63.226
475.00	57.608	10.163	67.771	12.188	4827.6	63.448
500.00	58.132	10.268	68.399	12.311	5133.8	63.680
550.00	59.120	10.464	69.583	12.525	5754.9	64.163
600.00	60.038	10.643	70.681	12.703	6385.8	64.661
650.00	60.896	10.807	71.704	12.851	7024.7	65.164
700.00	61.703	10.958	72.661	12.975	7670.5	65.666
750.00	62.464	11.096	73.560	13.079	8321.9	66.162
800.00	63.184	11.223	74.407	13.168	8978.1	66.652
850.00	63.868	11.339	75.207	13.244	9638.5	67.131
900.00	64.519	11.447	75.966	13.309	10302.3	67.601
950.00	65.141	11.547	76.687	13.365	10969.2	68.061
1000.00	65.735	11.639	77.374	13.414	11638.7	68.509
1050.00	66.305	11.724	78.030	13.457	12310.5	68.947
1100.00	66.853	11.804	78.657	13.495	12984.4	69.374
1150.00	67.379	11.878	79.257	13.528	13659.9	69.791
1200.00	67.886	11.948	79.834	13.557	14337.1	70.198
1250.00	68.375	12.012	80.388	13.584	15015.6	70.594
1300.00	68.847	12.073	80.921	13.607	15695.4	70.981
1350.00	69.304	12.131	81.435	13.628	16376.3	71.359
1400.00	69.746	12.184	81.931	13.647	17058.2	71.728
1450.00	70.175	12.235	82.410	13.664	17740.9	72.088
1500.00	70.590	12.283	82.873	13.680	18424.5	72.440
1550.00	70.994	12.328	83.322	13.694	19108.9	72.784
1600.00	71.386	12.371	83.757	13.707	19793.9	73.120
1650.00	71.767	12.412	84.179	13.719	20479.6	73.448
1700.00	72.138	12.450	84.589	13.729	21165.8	73.770
1750.00	72.500	12.487	84.987	13.739	21852.5	74.085
1800.00	72.852	12.522	85.374	13.748	22539.7	74.393
1850.00	73.196	12.555	85.751	13.757	23227.3	74.695
1900.00	73.531	12.587	86.118	13.765	23915.3	74.991
1950.00	73.858	12.617	86.475	13.772	24603.7	75.281
2000.00	74.178	12.646	86.824	13.778	25292.5	75.565
2050.00	74.491	12.674	87.165	13.785	25981.6	75.844

Table A-57 REVISED. Thermodynamic Functions for $A\ell_2O$(gas) - Continued

2100.00	74.796	12.700	87.497	13.791	26671.0	76.117
2150.00	75.095	12.726	87.821	13.796	27360.6	76.386
2200.00	75.388	12.750	88.139	13.801	28050.6	76.649
2250.00	75.675	12.774	88.449	13.806	28740.7	76.908
2300.00	75.956	12.796	88.752	13.810	29431.1	77.162
2350.00	76.232	12.818	89.049	13.814	30121.7	77.412
2400.00	76.502	12.839	89.340	13.818	30812.5	77.657
2450.00	76.767	12.859	89.625	13.822	31503.5	77.899
2500.00	77.027	12.878	89.904	13.825	32194.7	78.136
2600.00	77.532	12.914	90.447	13.832	33577.6	78.599
2700.00	78.020	12.949	90.969	13.837	34961.0	79.048
2800.00	78.492	12.980	91.472	13.842	36345.0	79.483
2900.00	78.948	13.010	91.958	13.847	37729.5	79.904
3000.00	79.389	13.038	92.428	13.851	39114.4	80.314
3100.00	79.817	13.064	92.882	13.855	40499.6	80.712
3200.00	80.233	13.089	93.322	13.858	41885.3	81.099
3300.00	80.636	13.113	93.748	13.861	43271.3	81.476
3400.00	81.027	13.135	94.162	13.864	44657.5	81.843
3500.00	81.408	13.155	94.564	13.867	46044.0	82.201
3600.00	81.779	13.175	94.955	13.869	47430.8	82.550
3700.00	82.141	13.194	95.335	13.871	48817.8	82.890
3800.00	82.493	13.212	95.705	13.873	50205.0	83.223
3900.00	82.836	13.229	96.065	13.875	51592.5	83.547
4000.00	83.171	13.245	96.416	13.877	52980.0	83.865
4100.00	83.499	13.260	96.759	13.878	54367.8	84.175
4200.00	83.818	13.275	97.093	13.880	55755.7	84.479
4300.00	84.131	13.289	97.420	13.881	57143.8	84.776
4400.00	84.436	13.303	97.739	13.883	58532.0	85.067
4500.00	84.736	13.316	98.051	13.884	59920.3	85.352
4600.00	85.028	13.328	98.356	13.885	61308.7	85.631
4700.00	85.315	13.340	98.655	13.886	62697.2	85.905
4800.00	85.596	13.351	98.947	13.887	64085.9	86.174
4900.00	85.871	13.362	99.234	13.888	65474.6	86.438
5000.00	86.142	13.373	99.514	13.889	66863.5	86.696
5100.00	86.406	13.383	99.789	13.890	68252.4	86.950
5200.00	86.666	13.393	100.059	13.890	69641.4	87.200
5300.00	86.922	13.402	100.324	13.891	71030.5	87.445
5400.00	87.172	13.411	100.583	13.892	72419.6	87.686
5500.00	87.418	13.420	100.838	13.892	73808.8	87.923
5600.00	87.660	13.428	101.088	13.893	75198.1	88.156
5700.00	87.898	13.436	101.334	13.894	76587.4	88.385
5800.00	88.132	13.444	101.576	13.894	77976.8	88.610
5900.00	88.362	13.452	101.814	13.895	79366.3	88.832
6000.00	88.588	13.459	102.047	13.895	80755.8	89.050

This table has been computed for the harmonic oscillator-rigid rotator approximation using the following values for molecular weight; I_A, I_B, and I_C (in units of 10^{-39} gm cm^2); and σ respectively:

69.9604, 0.8469, 21.586, 22.433, 2.

The electronic multiplicity was assumed to be unity. The frequencies and their degeneracies were taken as:

715. (1), 240. (1), 1000. (1).

The table is in units of calories, moles, and °K, and for the ideal gas at a standard state of 1 atm pressure. The subscript "298" indicates the temperature 298.15°K.

Table A-86. Thermodynamic Functions for Be_2OF_2(gas)

BE2OF2

T K	-(F-H0)/T	(H-H0)/T	S	CP	(H-H0)	-(F-H298)/T
273.15	56.984	12.870	69.854	17.647	3515.5	71.495
298.15	58.129	13.294	71.424	18.200	3963.7	71.424
50.00	40.089	8.298	48.387	9.070	414.9	119.363
75.00	43.531	8.720	52.252	10.110	654.0	96.381
100.00	46.107	9.225	55.332	11.386	922.5	85.744
125.00	48.225	9.786	58.011	12.662	1223.3	79.935
150.00	50.060	10.363	60.424	13.807	1554.5	76.485
175.00	51.701	10.928	62.628	14.800	1912.3	74.350
200.00	53.195	11.467	64.662	15.661	2293.4	73.014
225.00	54.576	11.976	66.551	16.415	2694.5	72.192
250.00	55.862	12.454	68.316	17.085	3113.4	71.717
275.00	57.071	12.903	69.973	17.689	3548.2	71.484
300.00	58.212	13.325	71.536	18.239	3997.4	71.424
325.00	59.294	13.722	73.016	18.743	4459.8	71.490
350.00	60.325	14.098	74.423	19.207	4934.2	71.650
375.00	61.310	14.453	75.763	19.636	5419.9	71.880
400.00	62.253	14.789	77.043	20.032	5915.8	72.163
425.00	63.160	15.109	78.268	20.399	6421.2	72.486
450.00	64.032	15.412	79.444	20.739	6935.5	72.840
475.00	64.873	15.701	80.574	21.053	7458.0	73.218
500.00	65.685	15.976	81.661	21.344	7988.0	73.613
550.00	67.232	16.488	83.720	21.863	9068.5	74.439
600.00	68.687	16.955	85.642	22.307	10173.0	75.293
650.00	70.062	17.382	87.443	22.690	11298.2	76.160
700.00	71.364	17.773	89.137	23.019	12441.1	77.027
750.00	72.603	18.132	90.735	23.303	13599.3	77.888
800.00	73.784	18.463	92.247	23.550	14770.8	78.738
850.00	74.912	18.769	93.682	23.764	15953.8	79.576
900.00	75.993	19.052	95.045	23.952	17146.8	80.397
950.00	77.031	19.314	96.345	24.116	18348.6	81.203
1000.00	78.028	19.558	97.586	24.261	19558.1	81.991
1050.00	78.987	19.785	98.772	24.389	20774.4	82.762
1100.00	79.913	19.997	99.910	24.503	21996.8	83.516
1150.00	80.806	20.195	101.001	24.604	23224.5	84.253
1200.00	81.669	20.381	102.050	24.695	24457.0	84.973
1250.00	82.505	20.555	103.060	24.776	25693.8	85.676
1300.00	83.314	20.719	104.033	24.849	26934.4	86.363
1350.00	84.099	20.873	104.972	24.915	28178.6	87.035
1400.00	84.861	21.018	105.879	24.974	29425.8	87.692
1450.00	85.601	21.156	106.757	25.029	30675.9	88.335
1500.00	86.320	21.286	107.606	25.078	31928.6	88.963
1550.00	87.020	21.409	108.429	25.123	33183.6	89.578
1600.00	87.702	21.526	109.227	25.164	34440.8	90.179
1650.00	88.366	21.636	110.002	25.202	35700.0	90.768
1700.00	89.014	21.742	110.755	25.237	36961.0	91.345
1750.00	89.645	21.842	111.487	25.269	38223.6	91.910
1800.00	90.262	21.938	112.200	25.298	39487.8	92.464
1850.00	90.864	22.029	112.893	25.325	40753.4	93.007
1900.00	91.453	22.116	113.569	25.351	42020.3	93.539
1950.00	92.028	22.199	114.228	25.374	43288.4	94.061
2000.00	92.591	22.279	114.870	25.396	44557.7	94.573
2050.00	93.143	22.355	115.498	25.416	45828.0	95.076

Table A-86. Thermodynamic Functions for Be_2OF_2(gas) - Continued

2100.00	93.682	22.428	116.110	25.435	47099.3	95.570
2150.00	94.211	22.498	116.709	25.453	48371.5	96.054
2200.00	94.729	22.566	117.294	25.470	49644.6	96.530
2250.00	95.237	22.630	117.867	25.485	50918.5	96.998
2300.00	95.735	22.693	118.427	25.500	52193.1	97.458
2350.00	96.223	22.753	118.976	25.513	53468.4	97.910
2400.00	96.703	22.810	119.513	25.526	54744.4	98.354
2450.00	97.174	22.866	120.040	25.538	56021.0	98.792
2500.00	97.636	22.919	120.556	25.550	57298.2	99.222
2600.00	98.537	23.021	121.558	25.570	59854.2	100.062
2700.00	99.408	23.116	122.523	25.589	62412.2	100.876
2800.00	100.250	23.204	123.454	25.606	64972.0	101.666
2900.00	101.066	23.287	124.353	25.621	67533.4	102.433
3000.00	101.857	23.365	125.222	25.635	70096.2	103.178
3100.00	102.624	23.439	126.063	25.647	72660.3	103.903
3200.00	103.369	23.508	126.877	25.658	75225.6	104.608
3300.00	104.094	23.573	127.667	25.669	77791.9	105.295
3400.00	104.798	23.635	128.433	25.678	80359.3	105.964
3500.00	105.484	23.694	129.178	25.687	82927.5	106.617
3600.00	106.153	23.749	129.902	25.695	85496.6	107.254
3700.00	106.804	23.802	130.606	25.702	88066.4	107.875
3800.00	107.439	23.852	131.291	25.709	90637.0	108.482
3900.00	108.060	23.900	131.959	25.715	93208.2	109.076
4000.00	108.665	23.945	132.610	25.721	95780.0	109.656
4100.00	109.257	23.988	133.245	25.726	98352.3	110.224
4200.00	109.836	24.030	133.865	25.731	100925.2	110.779
4300.00	110.402	24.069	134.471	25.736	103498.5	111.323
4400.00	110.955	24.107	135.063	25.740	106072.3	111.856
4500.00	111.497	24.144	135.641	25.744	108646.5	112.378
4600.00	112.029	24.179	136.207	25.748	111221.1	112.890
4700.00	112.549	24.212	136.761	25.752	113796.1	113.392
4800.00	113.059	24.244	137.303	25.755	116371.4	113.885
4900.00	113.559	24.275	137.834	25.758	118947.1	114.368
5000.00	114.050	24.305	138.354	25.761	121523.0	114.843
5100.00	114.531	24.333	138.865	25.764	124099.3	115.309
5200.00	115.004	24.361	139.365	25.766	126675.8	115.766
5300.00	115.469	24.387	139.856	25.769	129252.5	116.216
5400.00	115.925	24.413	140.337	25.771	131829.5	116.659
5500.00	116.373	24.438	140.810	25.773	134406.8	117.093
5600.00	116.813	24.461	141.275	25.776	136984.2	117.521
5700.00	117.246	24.485	141.731	25.778	139561.9	117.942
5800.00	117.673	24.507	142.179	25.779	142139.7	118.356
5900.00	118.092	24.528	142.620	25.781	144717.8	118.763
6000.00	118.504	24.549	143.053	25.783	147296.0	119.165

This table has been computed for the harmonic oscillator-rigid rotator approximation using the following values for the molecular weight; I_A, I_B, and I_C (in units of 10^{-39} gm cm^2); and σ respectively:

72.0206, 0.9981, 50.3145, 51.3126, 2.

The electronic multiplicity was assumed to be unity. The frequencies and their degeneracies were taken as:

1200. (1), 600. (1), 400. (1), 100. (1), 300. (3), 1500. (1), 900. (1).

The table is in units of calories, moles, and °K, and for the ideal gas at a standard state of 1 atm pressure. The subscript "298" indicates the temperature 298.15°K.

LI2O

T K	-(F-H0)/T	(H-H0)/T	S	CP	(H-H0)	-(F-H298)/T
273.15	43.832	9.834	53.667	11.642	2686.3	54.743
298.15	44.701	9.996	54.697	11.876	2980.3	54.697
50.00	29.486	7.230	36.716	8.127	361.5	89.091
75.00	32.509	7.719	40.228	9.189	579.0	72.245
100.00	34.793	8.172	42.965	9.811	817.2	64.596
125.00	36.658	8.540	45.198	10.187	1067.5	60.500
150.00	38.242	8.838	47.080	10.459	1325.7	58.110
175.00	39.624	9.087	48.710	10.698	1590.2	56.654
200.00	40.851	9.303	50.154	10.934	1860.5	55.753
225.00	41.958	9.497	51.456	11.175	2136.9	55.204
250.00	42.969	9.677	52.646	11.419	2419.3	54.890
275.00	43.899	9.847	53.745	11.660	2707.8	54.736
300.00	44.763	10.007	54.770	11.893	3002.2	54.697
325.00	45.570	10.161	55.731	12.116	3302.4	54.740
350.00	46.328	10.308	56.637	12.324	3607.9	54.843
375.00	47.044	10.449	57.494	12.518	3918.5	54.992
400.00	47.723	10.584	58.307	12.697	4233.7	55.174
425.00	48.369	10.713	59.082	12.861	4553.2	55.381
450.00	48.984	10.837	59.821	13.011	4876.6	55.607
475.00	49.574	10.955	60.529	13.148	5203.6	55.848
500.00	50.138	11.068	61.206	13.272	5533.9	56.099
550.00	51.203	11.278	62.482	13.489	6203.1	56.622
600.00	52.193	11.470	63.663	13.670	6882.2	57.160
650.00	53.118	11.646	64.764	13.820	7569.6	57.703
700.00	53.987	11.806	65.793	13.947	8263.9	58.245
750.00	54.807	11.952	66.759	14.053	8963.9	58.780
800.00	55.582	12.086	67.669	14.144	9668.9	59.308
850.00	56.319	12.210	68.528	14.221	10378.1	59.825
900.00	57.020	12.323	69.343	14.288	11090.9	60.331
950.00	57.689	12.428	70.117	14.345	11806.7	60.826
1000.00	58.329	12.525	70.854	14.395	12525.3	61.309
1050.00	58.942	12.615	71.558	14.439	13246.2	61.781
1100.00	59.531	12.699	72.230	14.478	13969.1	62.241
1150.00	60.097	12.777	72.875	14.512	14693.9	62.689
1200.00	60.643	12.850	73.493	14.542	15420.2	63.126
1250.00	61.169	12.918	74.087	14.569	16148.0	63.553
1300.00	61.677	12.982	74.659	14.593	16877.1	63.969
1350.00	62.168	13.042	75.210	14.615	17607.3	64.375
1400.00	62.643	13.099	75.742	14.634	18338.5	64.772
1450.00	63.104	13.152	76.256	14.652	19070.6	65.159
1500.00	63.550	13.202	76.753	14.667	19803.6	65.537
1550.00	63.984	13.250	77.234	14.682	20537.4	65.907
1600.00	64.406	13.295	77.700	14.695	21271.8	66.268
1650.00	64.815	13.337	78.153	14.707	22006.9	66.622
1700.00	65.214	13.378	78.592	14.718	22742.5	66.967
1750.00	65.602	13.416	79.019	14.728	23478.7	67.305
1800.00	65.981	13.453	79.434	14.738	24215.3	67.637
1850.00	66.350	13.488	79.838	14.746	24952.5	67.961
1900.00	66.710	13.521	80.231	14.754	25690.0	68.279
1950.00	67.062	13.553	80.615	14.762	26427.9	68.590
2000.00	67.405	13.583	80.988	14.769	27166.2	68.895
2050.00	67.741	13.612	81.353	14.775	27904.8	69.195

2100.00	68.069	13.640	81.709	14.781	28643.7	69.489
2150.00	68.391	13.666	82.057	14.787	29382.8	69.777
2200.00	68.705	13.692	82.397	14.792	30122.3	70.060
2250.00	69.013	13.716	82.730	14.797	30862.0	70.338
2300.00	69.315	13.740	83.055	14.801	31602.0	70.611
2350.00	69.611	13.763	83.373	14.805	32342.1	70.879
2400.00	69.901	13.784	83.685	14.809	33082.5	71.142
2450.00	70.185	13.805	83.990	14.813	33823.1	71.401
2500.00	70.464	13.826	84.290	14.817	34563.8	71.656
2600.00	71.007	13.864	84.871	14.823	36045.8	72.153
2700.00	71.531	13.899	85.430	14.829	37528.4	72.635
2800.00	72.037	13.933	85.970	14.834	39011.6	73.101
2900.00	72.527	13.964	86.490	14.839	40495.2	73.554
3000.00	73.000	13.993	86.994	14.843	41979.3	73.994
3100.00	73.460	14.021	87.480	14.847	43463.8	74.421
3200.00	73.905	14.046	87.952	14.850	44948.7	74.837
3300.00	74.338	14.071	88.409	14.853	46433.9	75.241
3400.00	74.758	14.094	88.852	14.856	47919.4	75.635
3500.00	75.167	14.116	89.283	14.859	49405.1	76.019
3600.00	75.565	14.136	89.702	14.861	50891.2	76.393
3700.00	75.953	14.156	90.109	14.864	52377.4	76.758
3800.00	76.330	14.175	90.505	14.866	53863.9	77.115
3900.00	76.699	14.192	90.891	14.868	55350.6	77.463
4000.00	77.058	14.209	91.268	14.869	56837.4	77.804
4100.00	77.410	14.225	91.635	14.871	58324.5	78.136
4200.00	77.753	14.241	91.993	14.873	59811.7	78.462
4300.00	78.088	14.256	92.343	14.874	61299.0	78.781
4400.00	78.416	14.270	92.685	14.875	62786.5	79.093
4500.00	78.736	14.283	93.020	14.877	64274.1	79.399
4600.00	79.051	14.296	93.347	14.878	65761.8	79.698
4700.00	79.358	14.308	93.667	14.879	67249.6	79.992
4800.00	79.660	14.320	93.980	14.880	68737.6	80.280
4900.00	79.955	14.332	94.287	14.881	70225.6	80.563
5000.00	80.245	14.343	94.587	14.882	71713.8	80.841
5100.00	80.529	14.353	94.882	14.883	73202.0	81.113
5200.00	80.808	14.364	95.171	14.883	74690.3	81.381
5300.00	81.081	14.373	95.455	14.884	76178.7	81.644
5400.00	81.350	14.383	95.733	14.885	77667.1	81.902
5500.00	81.614	14.392	96.006	14.886	79155.6	82.156
5600.00	81.873	14.401	96.274	14.886	80644.2	82.406
5700.00	82.128	14.409	96.538	14.887	82132.9	82.651
5800.00	82.379	14.418	96.797	14.887	83621.6	82.893
5900.00	82.626	14.425	97.051	14.888	85110.4	83.131
6000.00	82.868	14.433	97.301	14.888	86599.2	83.365

This table has been computed for the harmonic oscillator-rigid rotator approximation using the following values for molecular weight, moment of inertia (in units of 10^{-39} gm cm^2), and σ respectively:

29.8774, 5.8256, 2.

The electronic multiplicity was assumed to be unity. The frequencies and their degeneracies were taken as:

764. (1), 141. (2), 993. (1).

The table is in units of calories, moles, and °K, and for the ideal gas at a standard state of 1 atm pressure. The subscript "298" indicates the temperature 298.15°K.

Table A-88. Thermodynamic Functions for Li_2O_2(gas)

LI2O2

T K	-(F-H0)/T	(H-H0)/T	S	CP	(H-H0)	-(F-H298)/T
273.15	51.552	12.298	63.849	16.998	3359.1	65.423
298.15	52.647	12.708	65.355	17.383	3789.0	65.355
50.00	35.666	7.967	43.633	8.119	398.4	111.446
75.00	38.924	8.151	47.074	9.051	611.3	89.444
100.00	41.319	8.553	49.872	10.505	855.3	79.209
125.00	43.284	9.094	52.378	11.997	1136.8	73.596
150.00	44.994	9.691	54.685	13.311	1453.6	70.254
175.00	46.533	10.288	56.822	14.401	1800.4	68.185
200.00	47.945	10.859	58.804	15.283	2171.9	66.890
225.00	49.255	11.392	60.647	15.993	2563.2	66.095
250.00	50.481	11.882	62.363	16.566	2970.4	65.637
275.00	51.635	12.329	63.964	17.030	3390.6	65.413
300.00	52.725	12.737	65.463	17.408	3821.2	65.355
325.00	53.760	13.109	66.869	17.720	4260.4	65.418
350.00	54.744	13.448	68.192	17.978	4706.7	65.569
375.00	55.682	13.757	69.440	18.195	5159.0	65.786
400.00	56.579	14.040	70.620	18.378	5616.2	66.052
425.00	57.438	14.300	71.739	18.533	6077.6	66.354
450.00	58.263	14.539	72.802	18.666	6542.7	66.683
475.00	59.055	14.759	73.814	18.780	7010.8	67.032
500.00	59.817	14.963	74.780	18.880	7481.5	67.395
550.00	61.261	15.327	76.588	19.042	8429.8	68.150
600.00	62.608	15.642	78.250	19.168	9385.1	68.923
650.00	63.871	15.917	79.788	19.268	10346.2	69.700
700.00	65.060	16.159	81.219	19.348	11311.6	70.473
750.00	66.182	16.374	82.557	19.414	12280.8	71.234
800.00	67.245	16.566	83.811	19.468	13252.8	71.982
850.00	68.255	16.738	84.993	19.513	14227.4	72.712
900.00	69.216	16.893	86.109	19.551	15204.0	73.426
950.00	70.133	17.034	87.167	19.583	16182.4	74.122
1000.00	71.010	17.162	88.172	19.611	17162.2	74.799
1050.00	71.850	17.279	89.130	19.634	18143.4	75.459
1100.00	72.657	17.387	90.044	19.655	19125.6	76.101
1150.00	73.432	17.486	90.918	19.673	20108.8	76.727
1200.00	74.178	17.577	91.756	19.689	21092.9	77.336
1250.00	74.897	17.662	92.560	19.704	22077.7	77.929
1300.00	75.592	17.741	93.333	19.716	23063.2	78.506
1350.00	76.263	17.814	94.077	19.727	24049.3	79.069
1400.00	76.912	17.883	94.795	19.737	25036.0	79.618
1450.00	77.540	17.947	95.487	19.746	26023.1	80.153
1500.00	78.150	18.007	96.157	19.755	27010.6	80.676
1550.00	78.741	18.064	96.805	19.762	27998.5	81.186
1600.00	79.316	18.117	97.432	19.769	28986.8	81.684
1650.00	79.874	18.167	98.041	19.775	29975.3	82.170
1700.00	80.417	18.214	98.631	19.780	30964.2	82.646
1750.00	80.945	18.259	99.205	19.785	31953.4	83.111
1800.00	81.460	18.302	99.762	19.790	32942.8	83.565
1850.00	81.962	18.342	100.304	19.794	33932.4	84.011
1900.00	82.452	18.380	100.832	19.798	34922.2	84.446
1950.00	82.930	18.417	101.347	19.802	35912.2	84.873
2000.00	83.397	18.451	101.848	19.806	36902.4	85.291
2050.00	83.853	18.484	102.337	19.809	37892.8	85.701

Table A-88. Thermodynamic Functions for Li_2O_2(gas) - Continued

2100.00	84.299	18.516	102.814	19.812	38883.3	86.103
2150.00	84.735	18.546	103.281	19.814	39873.9	86.497
2200.00	85.161	18.575	103.736	19.817	40864.7	86.884
2250.00	85.579	18.602	104.182	19.819	41855.6	87.263
2300.00	85.988	18.629	104.617	19.822	42846.6	87.636
2350.00	86.389	18.654	105.043	19.824	43837.8	88.001
2400.00	86.782	18.679	105.461	19.826	44829.0	88.361
2450.00	87.167	18.702	105.870	19.828	45820.4	88.714
2500.00	87.546	18.725	106.270	19.829	46811.8	89.061
2600.00	88.281	18.767	107.048	19.832	48794.9	89.738
2700.00	88.990	18.807	107.797	19.835	50778.3	90.393
2800.00	89.674	18.844	108.518	19.838	52761.9	91.028
2900.00	90.336	18.878	109.214	19.840	54745.8	91.643
3000.00	90.977	18.910	109.887	19.842	56730.0	92.240
3100.00	91.597	18.940	110.537	19.844	58714.3	92.820
3200.00	92.199	18.968	111.168	19.846	60698.8	93.383
3300.00	92.783	18.995	111.778	19.847	62683.4	93.931
3400.00	93.351	19.020	112.371	19.849	64668.2	94.465
3500.00	93.902	19.044	112.946	19.850	66653.2	94.985
3600.00	94.439	19.066	113.505	19.851	68638.2	95.492
3700.00	94.962	19.087	114.049	19.852	70623.4	95.986
3800.00	95.471	19.108	114.579	19.853	72608.7	96.468
3900.00	95.968	19.127	115.094	19.854	74594.1	96.939
4000.00	96.452	19.145	115.597	19.855	76579.5	97.399
4100.00	96.925	19.162	116.087	19.856	78565.1	97.849
4200.00	97.387	19.179	116.566	19.857	80550.7	98.289
4300.00	97.839	19.195	117.033	19.857	82536.4	98.720
4400.00	98.280	19.210	117.490	19.858	84522.2	99.141
4500.00	98.712	19.224	117.936	19.859	86508.0	99.554
4600.00	99.135	19.238	118.372	19.859	88493.9	99.958
4700.00	99.548	19.251	118.799	19.860	90479.8	100.355
4800.00	99.954	19.264	119.218	19.860	92465.8	100.743
4900.00	100.351	19.276	119.627	19.861	94451.9	101.124
5000.00	100.741	19.288	120.028	19.861	96438.0	101.499
5100.00	101.123	19.299	120.422	19.861	98424.1	101.866
5200.00	101.498	19.310	120.807	19.862	100410.3	102.226
5300.00	101.866	19.320	121.186	19.862	102396.5	102.580
5400.00	102.227	19.330	121.557	19.863	104382.7	102.928
5500.00	102.582	19.340	121.921	19.863	106369.0	103.271
5600.00	102.930	19.349	122.279	19.863	108355.3	103.607
5700.00	103.273	19.358	122.631	19.864	110341.6	103.937
5800.00	103.609	19.367	122.976	19.864	112328.0	104.263
5900.00	103.941	19.375	123.316	19.864	114314.4	104.583
6000.00	104.266	19.383	123.650	19.864	116300.8	104.898

This table has been computed for the harmonic oscillator-rigid rotator approximation using the following values for molecular weight; I_A, I_B, I_C (in units of 10^{-39} gm cm^2); and σ respectively:

45.8768, 2.3367, 13.7929, 16.1296, 4.

The electronic multiplicity was assumed to be unity. The frequencies and their degeneracies were taken as:

270. (1), 400. (1), 330. (1), 250. (1), 530. (1) 300. (1).

The table is in units of calories, moles, and °K, and for the ideal gas at a standard state of 1 atm pressure. The subscript "298" indicates the temperature 298.15°K.

APPENDIX B

THERMODYNAMIC FUNCTIONS FOR SOLIDS AND LIQUIDS

(For the sources of the data, see Chapters 3, 4, 5, 6, 9, 10, and 14.)

Table B-46 Revised

Thermodynamic functions for zirconium, Zr

T in deg K, thermodynamic functions in cal (deg K)$^{-1}$ mole^{-1}. Subscript 1 refers to Zr(α). Subscript 2 refers to H_2(g).

$(\overline{C}_p)_1 = C_p°$ $\overline{S}_1 = S°$ $\overline{S}_2 = -(\overline{G}_2 - G_2^\circ)/T = \infty$

T	Phases present	$\frac{H°-H°_{298.15}}{T}$	C_p°	$S°$	$\frac{G°-H°_{298.15}}{T}$	$\frac{\overline{H}_1^\circ-H°_1}{T}$	$\frac{\overline{G}_1-G_1^\circ}{T}$	$\frac{\overline{H}_2-H_2^\circ}{T}$	$(\overline{C}_p)_2$
298.15	α	0	6.197	9.290	−9.290	0	0	−86.12	1.16
300	α	0.038	6.205	9.329	−9.291	0	0	−85.62	1.20
350	α	.934	6.404	10.301	−9.367	0	0	−74.13	2.18
400	α	1.628	6.572	11.167	−9.539	0	0	−65.39	3.10
450	α	2.186	6.712	11.949	−9.763	0	0	−58.49	3.97
500	α	2.644	6.830	12.663	−10.019	0	0	−52.90	4.78
550	α	3.030	6.931	13.319	−10.289	0	0	−48.25	5.52
600	α	3.359	7.020	13.926	−10.567	0	0	−44.32	6.21
650	α	3.643	7.102	14.491	−10.848	0	0	−40.95	6.84
709	α	3.893	7.182	15.020	−11.127	0	0	−38.02	7.40
750	α	4.115	7.265	15.519	−11.404	0	0	−35.44	7.91
791.5	α	4.282	7.340	15.912	−11.629	0	0	−33.53	8.29
800	α	4.315	7.357	15.990	−11.675	0	0	−33.16	8.36
820	α	4.390	7.396	16.172	−11.782	0	0	−32.32	8.53
845.6	α	4.482	7.451	16.400	−11.919	0	0	−31.30	8.64
850	α	4.497	7.461	16.439	−11.942	0	0	−31.13	8.66
865.3	α	4.550	7.496	16.573	−12.023	0	0	−30.55	8.73
891.5	α	4.637	7.561	16.797	−12.160	0	0	−29.60	8.85
900	α	4.665	7.584	16.869	−12.204	0	0	−29.31	8.89
950	α	4.822	7.729	17.283	−12.461	0	0	−27.67	9.11
956.6	α	4.842	7.751	17.337	−12.494	0	0	−27.46	9.14
1000	α	4.972	7.904	17.684	−12.712	0	0	−26.18	9.34
1050	α	5.116	8.111	18.074	−12.958	0	0	−24.83	9.56
1080.9	α	5.204	8.258	18.312	−13.108	0	0	−24.05	9.70
1100	α	5.258	8.357	18.457	−13.199	0	0	−23.59	9.79
1136	α	5.359	8.560	18.729	−13.370	0	0	−22.76	9.95
1136	β	6.18	7.76	19.55	−13.37	0.82	0	−28.66	4.29
1150	β	6.20	7.76	19.65	−13.45	.80	−0.01	−28.35	4.29
1200	β	6.27	7.76	19.98	−13.71	.73	− .04	−27.29	4.29

Table B-47 Revised

Thermodynamic functions for $ZrH_{0.25}$

T in deg K, thermodynamic functions in cal (deg K)$^{-1}$ mole^{-1}. Subscript 1 refers to Zr(α). Subscript 2 refers to H_2(g).

T	Phases present	$\frac{H°-H_{298.15}^\circ}{T}$	C_p°	$S°$	$\frac{G°-H_{298.15}^\circ}{T}$	$\frac{\overline{H}_1-H_1^\circ}{T}$	$(\overline{C}_p)_1$	$\overline{S}_1$	$\frac{\overline{G}_1-G_1^\circ}{T}$	$\frac{\overline{H}_2-H_2^\circ}{T}$	$(\overline{C}_p)_2$	$\overline{S}_2$	$\frac{\overline{G}_2-}{T}$
298.15	$\alpha+\delta$	0	6.54	9.27	−9.27	0.02	6.32	9.31	−0.00	−139.12	1.71	−0.29	−107.
300	$\alpha+\delta$	0.04	6.54	9.31	−9.27	.02	6.32	9.34	− .00	−138.29	1.74	− .28	−106.
350	$\alpha+\delta$	.98	6.78	10.33	−9.35	.02	6.42	10.33	− .00	−119.20	2.86	+.07	−86.
400	$\alpha+\delta$	1.73	7.11	11.26	−9.53	.02	6.58	11.19	− .00	−104.73	4.24	.54	−72.02
450	$\alpha+\delta$	2.35	7.51	12.12	−9.77	.03	6.81	11.98	− .00	−93.32	5.57	1.12	−60.36
500	$\alpha+\delta$	2.89	7.94	12.93	−10.05	.04	7.12	12.71	− .00	−84.07	6.56	1.76	−51.
550	$\alpha+\delta$	3.37	8.39	13.71	−10.35	.08	7.51	13.41	− .01	−76.44	7.05	2.41	−43.
600	$\alpha+\delta$	3.80	8.85	14.46	−10.66	.13	7.97	14.08	− .02	−70.06	7.03	3.03	−37.
650	$\alpha+\delta$	4.21	9.32	15.19	−10.98	.21	8.48	14.74	− .04	−64.69	6.75	3.58	−31.
700	$\alpha+\delta$	4.59	9.86	15.90	−11.30	.31	9.01	15.39	− .06	−60.09	6.76	4.08	−27.00
750	$\alpha+\delta$	4.97	10.53	16.60	−11.63	.43	9.53	16.03	− .08	−56.07	8.00	4.58	−23.
800	$\alpha+\delta$	5.34	11.48	17.31	−11.97	.55	10.00	16.66	− .11	−52.41	11.86	5.20	−19.
820	$\alpha+\delta$	5.50	11.99	17.60	−12.10	.61	10.17	16.91	− .13	−50.98	14.54	5.52	−18.
820	$\alpha+\beta$	6.49	9.99	18.59	−12.10	.26	7.56	16.56	− .13	−40.26	19.43	16.24	−18.
850	$\alpha+\beta$	6.64	11.60	18.97	−12.34	.24	6.88	16.82	− .14	−38.15	37.74	17.19	−16.81
900	$\alpha+\beta$	7.18	17.32	19.90	−12.73	+.07	3.96	17.09	− .15	−31.22	106.89	22.53	−14.
950	$\alpha+\beta$	7.61	14.82	20.74	−13.13	− .08	5.26	17.35	− .15	−25.53	76.49	27.08	−13.
956.6	$\alpha+\beta$	7.66	14.94	20.84	−13.18	− .10	5.29	17.39	− .15	−24.86	77.14	27.62	−13.
956.6	β	7.66	8.53	20.84	−13.18	+1.23	7.20	18.72	− .15	−35.49	10.61	16.99	−13.
1000	β	7.70	8.53	21.22	−13.52	1.15	7.20	19.04	− .20	−33.80	10.61	17.46	−11.56
1050	β	7.74	8.53	21.64	−13.90	1.06	7.20	19.39	− .25	−32.03	10.61	17.98	−9.96
1100	β	7.77	8.53	22.03	−14.26	0.96	7.20	19.72	− .30	−30.42	10.61	18.47	−8.
1136	β	7.80	8.53	22.31	−14.51	.89	7.20	19.95	− .33	−29.35	10.61	18.82	−7.
1150	β	7.80	8.53	22.41	−14.61	.86	7.20	20.04	− .34	−28.96	10.61	18.95	−7.
1200	β	7.84	8.53	22.77	−14.94	.76	7.20	20.35	− .38	−27.61	10.61	19.40	−5.

Table B-48 Revised

Thermodynamic functions for $ZrH_{0.50}$

T in deg K, thermodynamic functions in cal (deg K)$^{-1}$ mole^{-1}. Subscript 1 refers to Zr(α). Subscript 2 refers to H_2(g).

T	Phases present	$\frac{H^\circ-H^\circ_{298.15}}{T}$	C_p°	S°	$\frac{G^\circ-H^\circ_{298.15}}{T}$	$\frac{\bar{H}_1-H_1^\circ}{T}$	$(\bar{C}_p)_1$	$\bar{S}_1$	$\frac{\bar{G}_1-G_1^\circ}{T}$	$\frac{\bar{H}_2-H_2^\circ}{T}$	$(\bar{C}_p)_2$	$\bar{S}_2$	$\frac{\bar{G}_2-G_2^\circ}{T}$
298.15	$\alpha+\delta$	0	6.75	9.23	−9.23	0.02	6.32	9.31	−0.00	−139.12	1.71	−0.29	−107.62
300	$\alpha+\delta$	0.04	6.76	9.28	−9.23	.02	6.32	9.34	−.00	−138.29	1.74	−.28	−106.76
350	$\alpha+\delta$	1.03	7.14	10.34	−9.32	.02	6.42	10.33	−.00	−119.20	2.86	+.07	−86.95
400	$\alpha+\delta$	1.82	7.64	11.33	−9.51	.02	6.58	11.19	−.00	−104.73	4.24	.54	−72.02
450	$\alpha+\delta$	2.50	8.21	12.26	−9.76	.03	6.81	11.98	−.00	−93.32	5.57	1.12	−60.36
500	$\alpha+\delta$	3.10	8.76	13.15	−10.06	.04	7.12	12.71	−.00	−84.07	6.56	1.76	−51.03
550	$\alpha+\delta$	3.64	9.27	14.01	−10.38	.08	7.51	13.41	−.01	−76.44	7.05	2.41	−43.38
600	$\alpha+\delta$	4.12	9.73	14.84	−10.72	.13	7.97	14.08	−.02	−70.06	7.03	3.03	−37.01
650	$\alpha+\delta$	4.57	10.17	15.64	−11.06	.21	8.48	14.74	−.04	−64.69	6.75	3.58	−31.62
700	$\alpha+\delta$	4.99	10.70	16.41	−11.42	.31	9.01	15.39	−.06	−60.09	6.76	4.08	−27.00
750	$\alpha+\delta$	5.40	11.53	17.17	−11.78	.43	9.53	16.03	−.08	−56.07	8.00	4.58	−23.00
800	$\alpha+\delta$	5.82	12.97	17.96	−12.14	.55	10.00	16.66	−.11	−52.41	11.86	5.20	−19.49
820	$\alpha+\delta$	6.00	13.80	18.29	−12.28	.61	10.17	16.91	−.13	−50.98	14.54	5.52	−18.22
820	$\alpha+\beta$	8.34	12.42	20.62	−12.28	.26	7.56	16.56	−.13	−40.26	19.43	16.24	−18.22
850	$\alpha+\beta$	8.54	16.32	21.12	−12.59	.24	6.88	16.82	−.14	−38.15	37.74	17.19	−16.81
865.3	$\alpha+\beta$	8.72	22.57	21.46	−12.74	.22	5.74	16.94	−.14	−36.72	67.33	18.09	−16.14
865.3	β	8.72	10.51	21.46	−12.74	2.55	6.68	19.26	−.14	−46.02	15.35	8.78	−16.14
900	β	8.79	10.51	21.87	−13.08	2.41	6.68	19.52	−.24	−43.93	15.35	9.39	−14.37
950	β	8.88	10.51	22.44	−13.56	2.24	6.68	19.88	−.37	−41.19	15.35	10.22	−12.07
1000	β	8.96	10.51	22.98	−14.02	2.07	6.68	20.23	−.48	−38.72	15.35	11.00	−10.02
	β												
1050		9.04	10.51	23.49	−14.46	1.91	6.68	20.55	−.57	−36.49	15.35	11.75	−8.19
1100	β	9.10	10.51	23.98	−14.88	1.75	6.68	20.86	−.66	−34.46	15.35	12.47	−6.54
1136	β	9.15	10.51	24.32	−15.17	1.64	6.68	21.08	−.71	−33.11	15.35	12.97	−5.45
1150	β	9.16	10.51	24.45	−15.29	1.59	6.68	21.16	−.73	−32.61	15.35	13.16	−5.05
1200	β	9.22	10.51	24.90	−15.68	1.44	6.68	21.44	−.80	−30.92	15.35	13.81	−3.70

Table B-48a

Thermodynamic functions for $ZrH_{0.57}$

T in deg K, thermodynamic functions in cal (deg K)$^{-1}$ mole^{-1}. Subscript 1 refers to Zr(α). Subscript 2 refers to H_2(g).

T	Phases present	$\frac{H^\circ-H^\circ_{298.15}}{T}$	C_p°	S°	$\frac{G^\circ-H^\circ_{298.15}}{T}$	$\frac{\bar{H}_1-H_1^\circ}{T}$	$(\bar{C}_p)_1$	$\bar{S}_1$	$\frac{\bar{G}_1-G_1^\circ}{T}$	$\frac{\bar{H}_2-H_2^\circ}{T}$	$(\bar{C}_p)_2$	$\bar{S}_2$	$\frac{\bar{G}_2-G_2^\circ}{T}$
298.15	$\alpha+\delta$	0	6.81	9.22	−9.22	0.02	6.32	9.31	−0.00	−139.12	1.71	−0.29	−107.62
300	$\alpha+\delta$	0.04	6.82	9.26	−9.22	.02	6.32	9.34	−.00	−138.29	1.74	−.28	−106.76
350	$\alpha+\delta$	1.04	7.24	10.34	−9.31	.02	6.42	10.33	−.00	−119.20	2.86	+.07	−86.95
400	$\alpha+\delta$	1.85	7.79	11.35	−9.50	.02	6.58	11.19	−.00	−104.73	4.24	.54	−72.02
450	$\alpha+\delta$	2.54	8.40	12.30	−9.76	.03	6.81	11.98	−.00	−93.32	5.57	1.12	−60.36
500	$\alpha+\delta$	3.16	8.99	13.22	−10.06	.04	7.12	12.71	−.00	−84.07	6.56	1.76	−51.03
550	$\alpha+\delta$	3.71	9.52	14.10	−10.39	.08	7.51	13.41	−.01	−76.44	7.05	2.41	−43.38
600	$\alpha+\delta$	4.22	9.98	14.95	−10.73	.13	7.97	14.08	−.02	−70.06	7.03	3.03	−37.01
650	$\alpha+\delta$	4.68	10.40	15.76	−11.09	.21	8.48	14.74	−.04	−64.69	6.75	3.58	−31.62
700	$\alpha+\delta$	5.10	10.94	16.55	−11.45	.31	9.01	15.39	−.06	−60.09	6.76	4.08	−27.00
750	$\alpha+\delta$	5.52	11.81	17.33	−11.82	.43	9.53	16.03	−.08	−56.07	8.00	4.58	−23.00
800	$\alpha+\delta$	5.96	13.38	18.14	−12.18	.55	10.00	16.66	−.11	−52.41	11.86	5.20	−19.49
820	$\alpha+\delta$	6.15	14.31	18.48	−12.34	.61	10.17	16.91	−.13	−50.98	14.54	5.52	−18.22
820	β	8.85	10.89	21.19	−12.34	2.21	9.66	18.51	−.13	−47.10	4.29	9.41	−18.22
850	β	8.93	10.89	21.58	−12.65	2.21	9.66	18.86	−.21	−45.53	4.29	9.56	−16.55
900	β	9.04	10.89	22.20	−13.17	2.20	9.66	19.41	−.34	−43.16	4.29	9.80	−14.02
950	β	9.13	10.89	22.79	−13.66	2.19	9.66	19.93	−.45	−41.04	4.29	10.03	−11.74
1000	β	9.22	10.89	23.35	−14.13	2.18	9.66	20.42	−.56	−39.14	4.29	10.25	−9.69
1050	β	9.30	10.89	23.88	−14.58	2.15	9.66	20.90	−.67	−37.41	4.29	10.46	−7.82
1100	β	9.37	10.89	24.39	−15.02	2.12	9.66	21.35	−.77	−35.85	4.29	10.66	−6.12
1136	β	9.42	10.89	24.74	−15.32	2.09	9.66	21.66	−.84	−34.80	4.29	10.80	−4.98
1150	β	9.44	10.89	24.87	−15.43	2.08	9.66	21.78	−.86	−34.42	4.29	10.86	−4.56
1200	β	9.50	10.89	25.33	−15.84	2.03	9.66	22.19	−.95	−33.11	4.29	11.04	−3.12

Table B-49 Revised

Thermodynamic functions for $ZrH_{0.75}$

T in deg K, thermodynamic functions in cal (deg K)$^{-1}$ mole^{-1}. Subscript 1 refers to Zr(α). Subscript 2 refers to H_2(g).

T	Phases present	$\frac{H^\circ-H^\circ_{298.15}}{T}$	C°_p	S°	$\frac{G^\circ-H^\circ_{298.15}}{T}$	$\frac{\overline{H}_1-H^\circ_1}{T}$	$(\overline{C}_p)_1$	$\overline{S}_1$	$\frac{\overline{G}_1-G^\circ_1}{T}$	$\frac{\overline{H}_2-H^\circ_2}{T}$	$(\overline{C}_p)_2$	$\overline{S}_2$	$\frac{\overline{G}_2-G^\circ_2}{T}$
298.15	$\alpha+\delta$	0	6.97	9.20	−9.20	0.02	6.32	9.31	−0.00	−139.12	1.71	−0.29	−107.62
300	$\alpha+\delta$	0.04	6.98	9.24	−9.20	.02	6.32	9.34	− .00	−138.29	1.74	− .28	−106.76
350	$\alpha+\delta$	1.07	7.49	10.35	−9.28	.02	6.42	10.33	− .00	−119.20	2.86	+ .07	−86.95
400	$\alpha+\delta$	1.91	8.17	11.40	−9.48	.02	6.58	11.19	− .00	−104.73	4.24	.54	−72.02
450	$\alpha+\delta$	2.65	8.90	12.40	−9.75	.03	6.81	11.98	− .00	−93.32	5.57	1.12	−60.36
500	$\alpha+\delta$	3.31	9.58	13.37	−10.06	.04	7.12	12.71	− .00	−84.07	6.56	1.76	−51.03
550	$\alpha+\delta$	3.91	10.16	14.32	−10.41	.08	7.51	13.41	− .01	−76.44	7.05	2.41	−43.38
600	$\alpha+\delta$	4.45	10.61	15.22	−10.77	.13	7.97	14.08	− .02	−70.06	7.03	3.03	−37.01
650	$\alpha+\delta$	4.94	11.01	16.08	−11.15	.21	8.48	14.74	− .04	−64.69	6.75	3.58	−31.62
700	$\alpha+\delta$	5.39	11.55	16.92	−11.53	.31	9.01	15.39	− .06	−60.09	6.76	4.08	−27.00
750	$\alpha+\delta$	5.83	12.53	17.74	−11.92	.43	9.53	16.03	− .08	−56.07	8.00	4.58	−23.00
800	$\alpha+\delta$	6.30	14.45	18.61	−12.31	.55	10.00	16.66	− .11	−52.41	11.86	5.20	−19.49
820	$\alpha+\delta$	6.51	15.62	18.98	−12.47	.61	10.17	16.91	− .13	−50.98	+14.54	+5.52	−18.22
820	$\beta+\delta$	8.41	23.55	20.87	−12.47	5.88	33.12	22.19	− .13	−60.00	−25.52	−3.50	−18.22
850	$\beta+\delta$	8.98	25.08	21.76	−12.78	6.56	31.21	23.35	− .35	−58.86	−16.36	−4.24	−16.08
891.5	$\beta+\delta$	9.71	23.77	22.93	−13.22	7.25	26.40	24.73	− .68	−56.99	−7.03	−4.79	−13.32
891.5	β	9.71	11.27	22.93	−13.22	2.20	9.66	19.68	− .68	−43.55	+4.29	+8.65	−13.32
900	β	9.72	11.27	23.04	−13.32	2.20	9.66	19.78	− .70	−43.16	4.29	8.69	−12.91
950	β	9.80	11.27	23.65	−13.84	2.19	9 66	20.30	− .82	−41.04	4.29	8.92	−10.63
1000	β	9.88	11 27	24.22	−14.35	2.18	9.66	20.80	− .94	−39.14	4.29	9.14	−8.58
1050	β	9.94	11.27	24.78	−14.83	2.15	9.66	21.27	−1.04	−37.41	4.29	9.35	−6.71
1100	β	10.00	11.27	25.30	−15.30	2.12	9.66	21.72	−1.14	−35.85	4.29	9.55	−5.00
1136	β	10.04	11.27	25.66	−15.62	2.09	9.66	22.03	−1.21	−34.80	4.29	9.69	−3.87
1150	β	10.06	11.27	25.80	−15.74	2.08	9.66	22.15	−1.23	−34.42	4.29	9.75	−3.44
1200	β	10.11	11.27	26.28	−16.17	2.03	9.66	22.56	−1.32	−33.11	4.29	9.93	−2.01

Table B-50 Revised

Thermodynamic functions for $ZrH_{1.00}$

T in deg K, thermodynamic functions in cal (deg K)$^{-1}$ mole^{-1}. Subscript 1 refers to Zr(α). Subscript 2 refers to H_2(g).

T	Phases present	$\frac{H^\circ-H^\circ_{298.15}}{T}$	C°_p	S°	$\frac{G^\circ-H^\circ_{298.15}}{T}$	$\frac{\overline{H}_1-H^\circ_1}{T}$	$(\overline{C}_p)_1$	$\overline{S}_1$	$\frac{\overline{G}_1-G^\circ_1}{T}$	$\frac{\overline{H}_2-H^\circ_2}{T}$	$(\overline{C}_p)_2$	$\overline{S}_2$	$\frac{\overline{G}_2-G^\circ_2}{T}$
298.15	$\alpha+\delta$	0	7.18	9.16	−9.16	0.02	6.32	9.31	−0.00	−139.12	1.71	−0.29	−107.62
300	$\alpha+\delta$	0.04	7.20	9.20	−9.16	.02	6.32	9.34	− .00	−138.29	1.74	− .28	−106.76
350	$\alpha+\delta$	1.11	7.85	10.36	−9.25	.02	6.42	10.33	− .00	−119.20	2.86	+ .07	−86.95
400	$\alpha+\delta$	2.00	8.70	11.46	−9.46	.02	6.58	11.19	− .00	−104.73	4.24	.54	−72.02
450	$\alpha+\delta$	2.80	9.60	12.54	−9.74	.03	6.81	11.98	− .00	−93.32	5.57	1.12	−60.36
500	$\alpha+\delta$	3.52	10.40	13.59	−10.07	.04	7.12	12.71	− .00	−84.07	6.56	1.76	−51.03
550	$\alpha+\delta$	4.18	11.04	14.62	−10.44	.08	7.51	13.41	− .01	−76.44	7.05	2.41	−43.38
600	$\alpha+\delta$	4.77	11.49	15.60	−10.83	.13	7.97	14.08	− .02	−70.06	7.03	3.03	−37.01
650	$\alpha+\delta$	5.30	11.85	16.53	−11.23	.21	8.48	14.74	− .04	−64.69	6.75	3.58	−31.62
700	$\alpha+\delta$	5.78	12.39	17.43	−11.64	.31	9.01	15.39	− .06	−60.09	6.76	4.08	−27.00
750	$\alpha+\delta$	6.26	13.53	18.32	−12.06	.43	9.53	16.03	− .08	−56.07	8.00	4.58	−23.00
800	$\alpha+\delta$	6.78	15.93	19.26	−12.48	.55	10.00	16.66	− .11	−52.41	11.86	5.20	−19.49
820	$\alpha+\delta$	7.02	17.44	19.67	−12.65	.61	10.17	16.91	− .13	−50.98	+14.54	+5.52	−18.22
820	$\beta+\delta$	7.79	20.36	20.44	−12.65	5.88	33.12	22.19	− .13	−60.00	−25.52	−3.50	−18.22
850	$\beta+\delta$	8.29	23.04	21.23	−12.94	6.56	31.21	23.35	− .35	−58.86	−16.36	−4.24	−16.08
900	$\beta+\delta$	9.11	22.60	22.55	−13.44	7.35	25.37	24.97	− .75	−56.58	−5.52	−4.85	−12.78
950	$\beta+\delta$	9.77	20.60	23.72	−13.95	7.75	20.07	26.19	−1.16	−54.08	+1.07	−4.96	−9.79
1000	$\beta+\delta$	10.27	19.04	24.73	−14.46	7.89	16.68	27.13	−1.56	−51.58	4.72	−4.80	−7.08
1050	$\beta+\delta$	10.66	17.99	25.63	−14.97	7.88	14.76	27.89	−1.94	−49.20	6.47	−4.52	−4.62
1080.9	$\beta+\delta$	10.86	17.46	26.15	−15.28	7.83	13.97	28.31	−2.17	−47.80	6.98	−4.32	−3.22
1080.9	β	10.86	11.81	26.15	−15.28	2.13	9.66	22.62	−2.17	−36.43	4.29	+7.06	−3.22
1100	β	10.88	11.81	26.36	−15.48	2.12	9.66	22.79	−2.21	−35.85	4.29	7.14	−2.59
1136	β	10.91	11.81	26.74	−15.83	2.09	9.66	23.10	−2.28	−34.80	4.29	7.28	−1.45
1150	β	10.92	11.81	26.88	−15.96	2.08	9.66	23.22	−2.30	−34.42	4.29	7.33	−1.03
1200	β	10.96	11.81	27.38	−16.42	2.03	9.66	23.63	−2.39	−33.11	4.29	7.52	+0.41

Table B-51 Revised

Thermodynamic functions for $ZrH_{1.25}$

T in deg K, thermodynamic functions in cal (deg K)$^{-1}$ mole^{-1}. Subscript 1 refers to Zr(α). Subscript 2 refers to H_2(g).

T	Phases present	$\frac{H^\circ-H^\circ_{298.15}}{T}$	C°_p	S°	$\frac{G^\circ-H^\circ_{298.15}}{T}$	$\frac{\overline{H}_1-H^\circ_1}{T}$	$(\overline{C}_p)_1$	$\overline{S}_1$	$\frac{\overline{G}_1-G^\circ_1}{T}$	$\frac{\overline{H}_2-H^\circ_2}{T}$	$(\overline{C}_p)_2$	$\overline{S}_2$	$\frac{\overline{G}_2-G^\circ_2}{T}$
298.15	$\alpha+\delta$	0	7.39	9.12	−9.12	0.02	6.32	9.31	−0.00	−139.12	1.71	−0.29	−107.62
300	$\alpha+\delta$	0.05	7.42	9.17	−9.12	.02	6.32	9.34	−.00	−138.29	1.74	−.28	−106.76
350	$\alpha+\delta$	1.15	8.21	10.37	−9.22	.02	6.42	10.33	−.00	−119.20	2.86	+.07	−86.95
400	$\alpha+\delta$	2.10	9.23	11.53	−9.34	.02	6.58	11.19	−.00	−104.73	4.24	.54	−72.02
450	$\alpha+\delta$	2.95	10.29	12.68	−9.73	.03	6.81	11.98	−.00	−93.32	5.57	1.12	−60.36
500	$\alpha+\delta$	3.73	11.23	13.81	−10.08	.04	7.12	12.71	−.00	−84.07	6.56	1.76	−51.03
550	$\alpha+\delta$	4.45	11.92	14.92	−10.47	.08	7.51	13.41	−.01	−76.44	7.05	2.41	−43.38
600	$\alpha+\delta$	5.09	12.37	15.98	−10.89	.13	7.97	14.08	−.02	−70.06	7.03	3.30	−37.01
650	$\alpha+\delta$	5.66	12.70	16.98	−11.32	.21	8.48	14.74	−.04	−64.69	6.75	3.58	−31.62
700	$\alpha+\delta$	6.18	13.24	17.94	−11.76	.31	9.01	15.39	−.06	−60.09	6.76	4.08	−27.00
750	$\alpha+\delta$	6.69	14.53	18.89	−12.20	.43	9.53	16.03	−.08	−56.07	8.00	4.58	−23.00
791.5	$\alpha+\delta$	7.15	16.77	19.73	−12.57	.53	9.93	16.55	−.11	−53.02	10.94	5.08	−20.05
791.5	δ	7.15	13.12	19.73	−12.57	2.91	13.12	18.94	−.11	−56.82	0.00	1.26	−20.05
800	δ	7.22	13.12	19.87	−12.65	2.94	13.12	19.08	−.15	−56.29	.00	1.26	−19.44
820	δ	7.36	13.12	20.19	−12.83	3.01	13.12	19.40	−.22	−55.09	.00	1.26	−18.07
845.6	δ	7.53	13.12	20.59	−13.06	3.09	13.12	19.80	−.32	−53.64	.00	+1.26	−16.39
845.6	$\beta+\delta$	7.53	20.64	20.59	−13.06	6.49	31.62	23.18	−.32	−59.05	−17.56	−4.16	−16.39
850	$\beta+\delta$	7.60	20.99	20.70	−13.10	6.56	31.21	23.35	−.35	−58.86	−16.36	−4.24	−16.08
900	$\beta+\delta$	8.39	21.91	21.94	−13.55	7.35	25.37	24.97	−.75	−56.58	−5.52	−4.85	−12.78
950	$\beta+\delta$	9.07	20.74	23.10	−14.02	7.75	20.07	26.19	−1.16	−54.08	+1.07	−4.96	−9.79
1000	$\beta+\delta$	9.63	19.63	24.13	−14.50	7.89	16.68	27.13	−1.56	−51.58	4.72	−4.80	−7.08
1050	$\beta+\delta$	10.08	18.80	25.07	−14.99	7.88	14.76	27.89	−1.94	−49.20	6.47	−4.52	−4.62
1100	$\beta+\delta$	10.46	18.03	25.93	−15.46	7.78	13.56	28.55	−2.31	−46.98	7.15	−4.20	−2.38
1136	$\beta+\delta$	10.69	17.45	26.50	−15.81	7.68	12.87	28.98	−2.56	−45.49	7.32	−3.97	−0.89
1150	$\beta+\delta$	10.77	17.22	26.71	−15.94	7.64	12.62	29.13	−2.66	−44.94	7.35	−3.88	−.34
1200	$\beta+\delta$	11.02	16.39	27.42	−16.40	7.47	11.76	29.65	−2.98	−43.06	7.41	−3.56	+1.53

Table A-82 Adapted

Ideal-gas thermodynamic functions for normal hydrogen, H_2 *(25 percent para, 75 percent ortho)*

T in deg K, thermodynamic functions in cal (deg K)$^{-1}$ mole^{-1}

T	$\frac{H^\circ-H^\circ_{298.15}}{T}$	C_p°	S°	$\frac{G^\circ-H^\circ_{298.15}}{T}$	T	$\frac{H^\circ-H^\circ_{298.15}}{T}$	C_p°	S°	$\frac{G^\circ-H^\circ_{298.15}}{T}$
298.15	0	6.891	31.209	−31.209	845.6	4.537	7.108	38.502	−33.965
300	0.043	6.894	31.252	−31.209	850	4 551	7.110	38.539	−33.988
350	1.026	6.951	32.321	−31.295	865.3	4.596	7.120	38.666	−34.070
400	1.769	6.975	33.251	−31.482	891.5	4.671	7.136	38.879	−34.208
450	2.347	6.987	34.072	−31.725	900	4.695	7.142	38.946	−34.251
500	2.813	6.993	34.809	−31.996	950	4.825	7.180	39.334	−34.509
550	3.192	7.001	35.477	−32.285	956.6	4.841	7.185	39.384	−34.543
600	3.511	7.009	36.085	−32.574	1000	4.944	7.220	39.702	−34.758
650	3.780	7.021	36.647	−32.867	1050	5.052	7.261	40.055	−35.003
700	4.011	7.037	37.168	−33.157	1080.9	5.116	7.291	40.267	−35.151
750	4.214	7.057	37.653	−33.439	1100	5.154	7.309	40.395	−35.241
791.5	4.363	7.077	38.034	−33.671	1136	5.223	7.343	40.631	−35.408
800	4.392	7.081	38.110	−33.718	1150	5.249	7.357	40.721	−35.472
820	4.458	7.092	38.285	−33.827	1200	5.337	7.406	41.035	−35.698

REVISED REVISED

TABLE B-58

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM FLUORIDE (BE F_2)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=47.0090 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

(QUARTZ 1)

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG MOLE	S^0_T CAL/DEG MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.001	0.001	0.004	0.004	0.001
10.00	0.003	0.009	0.012	0.091	0.041	0.027
15.00	0.011	0.037	0.048	0.559	0.164	0.163
20.00	0.029	0.095	0.124	1.901	0.387	0.575
25.00	0.059	0.180	0.239	4.497	0.655	1.466
30.00	0.100	0.283	0.383	8.485	0.942	3.010
35.00	0.152	0.398	0.551	13.935	1.239	5.336
40.00	0.214	0.522	0.735	20.871	1.536	8.545
45.00	0.282	0.651	0.934	29.295	1.834	12.712
50.00	0.358	0.784	1.142	39.209	2.132	17.897
55.00	0.439	0.920	1.359	50.617	2.431	24.148
60.00	0.525	1.059	1.584	63.518	2.729	31.503
65.00	0.615	1.199	1.814	77.911	3.028	39.995
70.00	0.709	1.340	2.049	93.794	3.326	49.651
75.00	0.807	1.482	2.289	111.16	3.622	60.494
80.00	0.907	1.625	2.532	130.01	3.914	72.545
85.00	1.010	1.768	2.778	150.30	4.200	85.818
90.00	1.115	1.911	3.026	172.00	4.479	100.33
95.00	1.222	2.053	3.275	195.08	4.752	116.08
100.00	1.331	2.195	3.526	219.50	5.018	133.08
105.00	1.441	2.336	3.777	245.25	5.279	151.34
110.00	1.553	2.475	4.029	272.29	5.535	170.85
115.00	1.666	2.614	4.280	300.59	5.785	191.62
120.00	1.780	2.751	4.532	330.13	6.030	213.65
125.00	1.896	2.887	4.783	360.88	6.269	236.94
130.00	2.011	3.022	5.033	392.82	6.504	261.48
135.00	2.128	3.155	5.283	425.91	6.733	287.27
140.00	2.245	3.287	5.532	460.14	6.958	314.31
145.00	2.363	3.417	5.780	495.48	7.178	342.59
150.00	2.481	3.546	6.027	531.91	7.393	372.10
155.00	2.599	3.674	6.273	569.41	7.605	402.85
160.00	2.718	3.800	6.517	607.95	7.812	434.83
165.00	2.837	3.924	6.761	647.52	8.015	468.02
170.00	2.955	4.048	7.003	688.10	8.214	502.43
175.00	3.075	4.169	7.244	729.66	8.410	538.05
180.00	3.194	4.290	7.484	772.19	8.602	574.87
185.00	3.313	4.409	7.722	815.67	8.790	612.89
190.00	3.432	4.527	7.959	860.08	8.975	652.09
195.00	3.551	4.643	8.194	905.42	9.157	692.47
200.00	3.670	4.758	8.428	951.65	9.336	734.03
205.00	3.789	4.872	8.661	998.77	9.512	776.75
210.00	3.908	4.985	8.892	1046.8	9.685	820.64
215.00	4.026	5.096	9.122	1095.6	9.855	865.68
220.00	4.145	5.206	9.351	1145.3	10.023	911.86
225.00	4.263	5.315	9.578	1195.8	10.189	959.18
230.00	4.381	5.423	9.804	1247.2	10.352	1007.6
235.00	4.499	5.529	10.028	1299.4	10.513	1057.2
240.00	4.616	5.635	10.251	1352.3	10.672	1107.9
245.00	4.734	5.739	10.473	1406.1	10.829	1159.7
250.00	4.851	5.842	10.693	1460.6	10.984	1212.6
255.00	4.967	5.945	10.912	1515.9	11.138	1266.6
260.00	5.084	6.046	11.130	1572.0	11.291	1321.8
265.00	5.200	6.146	11.346	1628.8	11.442	1377.9
270.00	5.316	6.246	11.562	1686.4	11.592	1435.2
273.15	5.388	6.308	11.697	1723.1	11.686	1471.8
275.00	5.431	6.344	11.776	1744.7	11.741	1493.6
280.00	5.546	6.442	11.988	1803.8	11.888	1553.0
285.00	5.661	6.539	12.200	1863.6	12.034	1613.4
290.00	5.776	6.635	12.411	1924.1	12.179	1675.0
295.00	5.890	6.730	12.620	1985.4	12.322	1737.5
298.15	5.962	6.790	12.752	2024.4	12.412	1777.5
300.00	6.004	6.825	12.828	2047.4	12.464	1801.2

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

THIS TABLE SUPERSEDES TABLE B-58 OF NBS REPORT 7437.

TABLE B-58(CONT.)

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM FLUORIDE (BE F_2) SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=47.0090 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG MOLE	S^0_T CAL/DEG MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
			(QUARTZ 1)			
300.00	6.004	6.825	12.828	2047.4	12.464	1801.2
310.00	6.230	7.011	13.241	2173.4	12.735	1931.3
320.00	6.456	7.194	13.650	2302.1	12.996	2065.8
330.00	6.680	7.374	14.053	2433.3	13.245	2204.3
340.00	6.903	7.550	14.452	2566.9	13.480	2346.9
350.00	7.124	7.722	14.846	2702.8	13.701	2493.4
360.00	7.344	7.891	15.235	2840.9	13.908	2643.8
370.00	7.562	8.057	15.619	2980.9	14.101	2798.0
373.15	7.631	8.108	15.739	3025.5	14.159	2847.4
380.00	7.779	8.218	15.997	3122.9	14.280	2956.1
390.00	7.995	8.376	16.370	3266.5	14.445	3118.0
400.00	8.209	8.529	16.738	3411.7	14.597	3283.5
425.00	8.737	8.896	17.633	3780.8	14.922	3713.2
450.00	9.255	9.238	18.494	4157.2	15.176	4164.9
475.00	9.764	9.556	19.320	4539.2	15.371	4637.6
500.00	10.261	9.851	20.112	4925.4	15.523	5130.6
			(QUARTZ 2)			
500.00	10.261	10.251	20.512	5125.4	15.523	5130.6
550.00	11.262	10.742	22.004	5908.0	15.776	6194.0
600.00	12.215	11.172	23.388	6703.4	16.051	7329.2
650.00	13.125	11.560	24.685	7514.2	16.388	8531.3
700.00	13.995	11.919	25.914	8343.0	16.780	9796.5
750.00	14.829	12.258	27.087	9193.5	17.242	11122.
800.00	15.631	12.585	28.216	10068.	17.745	12504.
825.00	16.020	12.745	28.766	10515.	18.010	13217.
			(LIQUID)			
825.00	16.021	14.042	30.063	11585.	18.272	13217.
850.00	16.442	14.171	30.613	12045.	18.557	13975.
900.00	17.259	14.431	31.690	12988.	19.146	15533.
950.00	18.046	14.695	32.741	13960.	19.759	17144.
1000.00	18.807	14.964	33.771	14964.	20.392	18807.
1050.00	19.544	15.238	34.782	16000.	21.042	20521.
1100.00	20.259	15.517	35.776	17069.	21.707	22285.
1150.00	20.955	15.801	36.756	18171.	22.384	24098.
1200.00	21.633	16.089	37.723	19307.	23.073	25960.

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

THIS TABLE SUPERSEDES TABLE B-58 OF NBS REPORT 7437.

REVISED REVISED

TABLE B-83

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM ALUMINATE ($BE\ O.AL_2O_3$)
SOLID PHASE

GRAM MOLECULAR WT.=126.9728 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G^0_T-H^C_0)/T$	$(H^0_T-H^C_0)/T$	S^0_T	$(H^0_T-H^C_0)$	C^0_P	$-(G^0_T-H^C_0)$
DEG K	CAL/DEG MOLE	CAL/DEG MOLE	CAL/DEG MOLE	CAL/MOLE	CAL/DEG MOLE	CAL/MOLE
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.000	0.000	0.001	0.000	0.000
10.00	0.000	0.001	0.001	0.008	0.003	0.003
15.00	0.001	0.003	0.004	0.040	0.011	0.013
20.00	0.002	0.006	0.009	0.128	0.025	0.043
25.00	0.004	0.012	0.017	0.311	0.050	0.104
30.00	0.007	0.022	0.029	0.649	0.088	0.215
35.00	0.011	0.035	0.046	1.218	0.143	0.400
40.00	0.017	0.053	0.070	2.119	0.221	0.689
45.00	0.025	0.077	0.102	3.474	0.327	1.115
50.00	0.034	0.109	0.143	5.440	0.466	1.724
55.00	0.047	0.149	0.196	8.198	0.644	2.567
60.00	0.062	0.199	0.261	11.942	0.860	3.703
65.00	0.080	0.259	0.339	16.863	1.115	5.197
70.00	0.102	0.331	0.432	23.151	1.407	7.120
75.00	0.127	0.413	0.541	30.994	1.737	9.547
80.00	0.157	0.507	0.664	40.589	2.108	12.552
85.00	0.191	0.613	0.804	52.144	2.519	16.216
90.00	0.229	0.731	0.960	65.822	2.956	20.621
95.00	0.272	0.861	1.133	81.748	3.419	25.848
100.00	0.320	1.001	1.320	100.06	3.911	31.973
105.00	0.372	1.151	1.524	120.90	4.430	39.077
110.00	0.429	1.313	1.742	144.40	4.972	47.235
115.00	0.492	1.484	1.975	170.65	5.533	56.523
120.00	0.558	1.665	2.223	199.76	6.112	67.013
125.00	0.630	1.854	2.485	231.79	6.705	78.777
130.00	0.707	2.053	2.759	266.83	7.310	91.881
135.00	0.788	2.259	3.047	304.91	7.924	106.39
140.00	0.874	2.472	3.346	346.07	8.544	122.37
145.00	0.965	2.692	3.657	390.36	9.170	139.87
150.00	1.060	2.918	3.978	437.77	9.797	158.95
155.00	1.159	3.151	4.310	488.33	10.425	179.67
160.00	1.263	3.388	4.651	542.02	11.052	202.07
165.00	1.371	3.629	5.000	598.85	11.676	226.19
170.00	1.483	3.875	5.358	658.78	12.296	252.08
175.00	1.599	4.125	5.723	721.80	12.911	279.78
180.00	1.718	4.377	6.096	787.88	13.520	309.33
185.00	1.842	4.632	6.474	856.99	14.122	340.75
190.00	1.969	4.890	6.859	929.09	14.715	374.08
195.00	2.099	5.149	7.249	1004.1	15.300	409.34
200.00	2.233	5.410	7.643	1082.1	15.876	446.57
205.00	2.370	5.673	8.042	1162.9	16.443	485.78
210.00	2.510	5.936	8.445	1246.5	17.000	527.00
215.00	2.652	6.199	8.852	1332.9	17.546	570.24
220.00	2.798	6.463	9.261	1421.9	18.083	615.52
225.00	2.946	6.727	9.673	1513.7	18.610	662.86
230.00	3.097	6.991	10.088	1608.0	19.127	712.26
235.00	3.250	7.255	10.505	1704.9	19.633	763.74
240.00	3.405	7.518	10.924	1804.3	20.130	817.31
245.00	3.563	7.780	11.344	1906.2	20.617	872.98
250.00	3.723	8.042	11.765	2010.5	21.094	930.75
255.00	3.885	8.302	12.187	2117.1	21.561	990.63
260.00	4.049	8.562	12.610	2226.1	22.019	1052.6
265.00	4.214	8.820	13.034	2337.3	22.466	1116.7
270.00	4.381	9.077	13.458	2450.7	22.903	1183.0
273.15	4.488	9.238	13.725	2523.3	23.173	1225.8
275.00	4.550	9.332	13.882	2566.3	23.330	1251.3
280.00	4.721	9.586	14.306	2684.0	23.746	1321.8
285.00	4.893	9.838	14.730	2803.8	24.153	1394.4
290.00	5.066	10.088	15.154	2925.5	24.550	1469.1
295.00	5.240	10.336	15.577	3049.2	24.938	1545.9
298.15	5.351	10.492	15.843	3128.2	25.177	1595.4
300.00	5.416	10.583	15.999	3174.9	25.316	1624.9

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

THIS TABLE SUPERSEDES TABLE B-83 OF NBS REPORT 7587.

TABLE B-83(CONT.)

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM ALUMINATE (BE O•AL$_2$O$_3$)
SOLID PHASE

GRAM MOLECULAR WT.=126.9728 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG-MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG-MOLE	S^0_T CAL/DEG-MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG-MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
300.00	5.416	10.583	15.999	3174.9	25.316	1624.9
310.00	5.771	11.070	16.841	3431.7	26.048	1789.1
320.00	6.130	11.549	17.679	3695.7	26.748	1961.7
330.00	6.493	12.020	18.513	3966.6	27.415	2142.6
340.00	6.859	12.482	19.341	4243.9	28.053	2331.9
350.00	7.227	12.936	20.163	4527.5	28.664	2529.4
360.00	7.598	13.381	20.979	4817.2	29.256	2735.1
370.00	7.970	13.818	21.788	5112.6	29.831	2949.0
373.15	8.088	13.954	22.042	5206.9	30.008	3018.0
380.00	8.344	14.247	22.591	5413.7	30.381	3170.9
390.00	8.720	14.667	23.387	5720.1	30.887	3400.8
400.00	9.096	15.078	24.175	6031.3	31.340	3638.6
425.00	10.040	16.064	26.105	6827.2	32.312	4267.2
450.00	10.985	16.991	27.976	7645.9	33.165	4943.3
475.00	11.927	17.862	29.790	8484.6	33.917	5665.5
500.00	12.865	18.682	31.547	9341.1	34.589	6432.3
550.00	14.717	20.182	34.900	11100.	35.746	8094.4
600.00	16.532	21.521	38.053	12913.	36.721	9919.0
650.00	18.303	22.724	41.026	14770.	37.569	11897.
700.00	20.027	23.811	43.838	16668.	38.324	14019.
750.00	21.704	24.802	46.506	18602.	39.010	16278.
800.00	23.334	25.710	49.044	20568.	39.644	18667.
850.00	24.918	26.547	51.466	22565.	40.237	21181.
900.00	26.458	27.324	53.782	24591.	40.799	23812.
950.00	27.955	28.047	56.002	26645.	41.336	26557.
1000.00	29.411	28.725	58.135	28725.	41.853	29411.
1050.00	30.828	29.362	60.190	30830.	42.353	32369.
1100.00	32.208	29.963	62.171	32960.	42.840	35429.
1150.00	33.552	30.534	64.086	35114.	43.316	38585.
1200.00	34.864	31.076	65.939	37291.	43.782	41836.
1250.00	36.143	31.593	67.736	39492.	44.240	45178.
1300.00	37.392	32.088	69.480	41715.	44.692	48609.
1350.00	38.612	32.563	71.175	43961.	45.137	52126.
1400.00	39.804	33.020	72.825	46229.	45.578	55726.
1450.00	40.971	33.461	74.432	48518.	46.015	59407.
1500.00	42.112	33.887	75.999	50830.	46.447	63168.
1550.00	43.230	34.299	77.529	53163.	46.877	67007.
1600.00	44.325	34.699	79.024	55518.	47.304	70920.
1650.00	45.399	35.087	80.486	57893.	47.728	74908.
1700.00	46.452	35.465	81.917	60290.	48.150	78969.
1750.00	47.485	35.833	83.319	62708.	48.570	83100.
1800.00	48.500	36.193	84.693	65147.	48.988	87300.
1850.00	49.496	36.544	86.041	67607.	49.405	91568.
1900.00	50.476	36.888	87.364	70088.	49.820	95904.
1950.00	51.438	37.225	88.663	72589.	50.234	100304.
2000.00	52.385	37.556	89.940	75111.	50.647	104770.
2050.00	53.316	37.880	91.196	77654.	51.059	109298.
2100.00	54.233	38.199	92.431	80217.	51.470	113889.
2150.00	55.135	38.512	93.647	82801.	51.880	118541.

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

THIS TABLE SUPERSEDES TABLE B-83 OF NBS REPORT 7587.

TABLE B-106

THERMODYNAMIC FUNCTIONS FOR LITHIUM ALUMINUM FLUORIDE ($LI_3AL\ F_6$)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=161.7889 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$\frac{-(G^\circ_T-H^\circ_{298})}{T} - S^\circ_{298}$	$\frac{(H^\circ_T-H^\circ_{298})}{T}$	$(S^\circ_T-S^\circ_{298})$	$(H^\circ_T-H^\circ_{298})$	C°_p	$-(G^\circ_T-H^\circ_{298})-TS^\circ_{298}$
			(SOLID--ALPHA)			
298.15	0.000	0.000	0.000	0.000	48.442	0.000
300.00	0.001	0.299	0.300	89.753	48.590	0.278
310.00	0.037	1.870	1.906	579.57	49.367	11.332
320.00	0.120	3.366	3.485	1077.0	50.106	38.311
330.00	0.245	4.793	5.038	1581.6	50.808	80.949
340.00	0.409	6.156	6.565	2093.0	51.477	138.98
350.00	0.606	7.460	8.066	2611.0	52.116	212.16
360.00	0.834	8.709	9.543	3135.2	52.726	300.22
370.00	1.089	9.907	10.996	3665.4	53.312	402.94
373.15	1.175	10.274	11.448	3833.7	53.492	438.29
380.00	1.369	11.056	12.425	4201.4	53.875	520.06
390.00	1.670	12.161	13.831	4742.9	54.415	651.36
400.00	1.992	13.224	15.216	5289.6	54.936	796.61
425.00	2.869	15.714	18.583	6678.5	56.159	1219.4
450.00	3.833	17.993	21.826	8096.8	57.285	1724.7
475.00	4.862	20.089	24.951	9542.1	58.330	2309.7
500.00	5.943	22.025	27.968	11013.	59.305	2971.4
550.00	8.209	25.497	33.706	14023.	61.086	4514.8
600.00	10.560	28.531	39.091	17118.	62.687	6336.1
650.00	12.952	31.215	44.167	20290.	64.149	8418.7
700.00	15.355	33.616	48.971	23531.	65.504	10748.
743.15	17.422	35.500	52.922	26382.	66.602	12947.
			(SOLID--BETA)			
743.15	17.422	36.531	53.953	27148.	66.313	12947.
750.00	17.759	36.804	54.562	27603.	66.530	13319.
800.00	20.195	38.712	58.907	30969.	68.140	16156.
850.00	22.596	40.491	63.087	34417.	69.788	19207.
900.00	24.958	42.165	67.124	37949.	71.469	22463.
950.00	27.281	43.752	71.033	41565.	73.176	25917.
1000.00	29.564	45.267	74.831	45267.	74.906	29564.

The subscript "298" refers to the temperature 298.15°K.

TABLE B-107

THERMODYNAMIC FUNCTIONS FOR LITHIUM BERYLLIUM FLUORIDE (LI$_2$BE F$_4$) SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=98.8838 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$\frac{-(G^\circ_T-H^\circ_{298})}{T} - S^\circ_{298}$	$\frac{(H^\circ_T-H^\circ_{298})}{T}$	$(S^\circ_T-S^\circ_{298})$	$(H^\circ_T-H^\circ_{298})$	C°_p	$-(G^\circ_T-H^\circ_{298})-TS^\circ_{298}$
			(SOLID)			
298.15	0.000	0.000	0.000	0.000	32.326	0.000
300.00	0.001	0.200	0.200	59.865	32.392	0.183
310.00	0.024	1.244	1.268	385.57	32.749	7.543
320.00	0.080	2.234	2.313	714.84	33.106	25.470
330.00	0.163	3.175	3.338	1047.7	33.464	53.743
340.00	0.271	4.071	4.342	1384.1	33.821	92.157
350.00	0.401	4.926	5.328	1724.1	34.178	140.52
360.00	0.552	5.744	6.295	2067.7	34.535	198.65
370.00	0.720	6.527	7.246	2414.8	34.892	266.37
373.15	0.776	6.766	7.543	2524.9	35.005	289.66
380.00	0.904	7.278	8.182	2765.5	35.250	343.52
390.00	1.102	8.000	9.102	3119.8	35.607	429.96
400.00	1.314	8.694	10.008	3477.7	35.964	525.52
425.00	1.891	10.325	12.215	4387.9	36.857	803.47
450.00	2.524	11.823	14.347	5320.5	37.750	1135.6
475.00	3.201	13.211	16.412	6275.4	38.643	1520.3
500.00	3.911	14.505	18.417	7252.7	39.536	1955.7
550.00	5.407	16.862	22.269	9274.1	41.322	2973.7
600.00	6.966	18.975	25.941	11385.	43.108	4179.6
650.00	8.562	20.900	29.462	13585.	44.894	5565.3
700.00	10.177	22.678	32.854	15874.	46.680	7123.7
745.00	11.636	24.176	35.812	18011.	48.287	8669.0
			(LIQUID)			
745.00	11.636	38.412	50.048	28617.	55.500	8668.9
750.00	11.894	38.526	50.420	28895.	55.500	8920.1
800.00	14.415	39.587	54.001	31670.	55.500	11532.
850.00	16.843	40.523	57.366	34445.	55.500	14317.
900.00	19.183	41.355	60.538	37220.	55.500	17265.
950.00	21.440	42.100	63.539	39995.	55.500	20368.
1000.00	23.616	42.770	66.386	42770.	55.500	23616.
1050.00	25.718	43.376	69.094	45545.	55.500	27004.
1100.00	27.749	43.927	71.676	48320.	55.500	30524.
1150.00	29.713	44.430	74.143	51095.	55.500	34170.
1200.00	31.613	44.891	76.505	53870.	55.500	37936.
1250.00	33.455	45.316	78.770	56645.	55.500	41818.
1300.00	35.240	45.707	80.947	59420.	55.500	45812.
1350.00	36.972	46.070	83.042	62195.	55.500	49912.
1400.00	38.653	46.407	85.060	64970.	55.500	54115.
1450.00	40.287	46.720	87.008	67745.	55.500	58417.
1500.00	41.876	47.013	88.889	70520.	55.500	62814.

The subscript "298" refers to the temperature 298.15°K.

TABLE B-108

THERMODYNAMIC FUNCTIONS FOR LITHIUM BOROHYDRIDE (LI B H_4)
SOLID PHASE

GRAM MOLECULAR WT.=21.78188 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G_T^0-H_0^C)/T$	$(H_T^0-H_0^C)/T$	S_T^0	$(H_T^0-H_0^C)$	C_P^0	$-(G_T^0-H_0^C)$
DEG K	$\frac{CAL}{DEG\ MOLE}$	$\frac{CAL}{DEG\ MOLE}$	$\frac{CAL}{DEG\ MOLE}$	$\frac{CAL}{MOLE}$	$\frac{CAL}{DEG\ MOLE}$	$\frac{CAL}{MOLE}$
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.001	0.001	0.004	0.004	0.001
10.00	0.003	0.008	0.011	0.085	0.037	0.026
15.00	0.010	0.032	0.042	0.479	0.129	0.147
20.00	0.024	0.073	0.097	1.452	0.274	0.483
25.00	0.046	0.133	0.179	3.314	0.470	1.162
30.00	0.077	0.206	0.283	6.188	0.696	2.308
35.00	0.115	0.298	0.413	10.426	1.010	4.038
40.00	0.162	0.408	0.570	16.335	1.361	6.486
45.00	0.217	0.536	0.754	24.127	1.765	9.785
50.00	0.281	0.682	0.963	34.082	2.224	14.066
55.00	0.354	0.844	1.197	46.398	2.704	19.456
60.00	0.435	1.019	1.453	61.122	3.186	26.074
65.00	0.523	1.204	1.727	78.268	3.675	34.019
70.00	0.620	1.399	2.018	97.906	4.183	43.376
75.00	0.723	1.602	2.325	120.13	4.707	54.228
80.00	0.833	1.812	2.645	144.98	5.230	66.647
85.00	0.949	2.028	2.978	172.41	5.740	80.700
90.00	1.072	2.248	3.320	202.35	6.234	96.441
95.00	1.199	2.471	3.670	234.73	6.717	113.91
100.00	1.332	2.695	4.027	269.51	7.191	133.15
105.00	1.468	2.920	4.389	306.63	7.655	154.19
110.00	1.609	3.146	4.755	346.04	8.105	177.04
115.00	1.754	3.371	5.125	387.66	8.540	201.74
120.00	1.903	3.595	5.498	431.42	8.961	228.30
125.00	2.054	3.818	5.872	477.25	9.370	256.72
130.00	2.208	4.039	6.247	525.10	9.767	287.02
135.00	2.364	4.259	6.623	574.91	10.154	319.20
140.00	2.523	4.476	6.999	626.62	10.530	353.25
145.00	2.684	4.691	7.375	680.18	10.893	389.19
150.00	2.847	4.904	7.750	735.53	11.244	427.00
155.00	3.011	5.114	8.124	792.61	11.583	466.69
160.00	3.177	5.321	8.497	851.35	11.912	508.24
165.00	3.343	5.526	8.869	911.71	12.232	551.66
170.00	3.511	5.727	9.239	973.65	12.544	596.93
175.00	3.680	5.926	9.607	1037.1	12.848	644.04
180.00	3.850	6.123	9.973	1102.1	13.146	692.99
185.00	4.020	6.317	10.337	1168.6	13.437	743.77
190.00	4.191	6.508	10.699	1236.5	13.719	796.36
195.00	4.363	6.696	11.059	1305.8	13.991	850.75
200.00	4.535	6.882	11.417	1376.4	14.255	906.94
205.00	4.707	7.065	11.772	1448.3	14.510	964.92
210.00	4.879	7.245	12.124	1521.5	14.758	1024.7
215.00	5.052	7.423	12.474	1595.9	15.001	1086.2
220.00	5.225	7.598	12.822	1671.5	15.243	1149.4
225.00	5.397	7.770	13.167	1748.3	15.486	1214.4
230.00	5.570	7.941	13.510	1826.3	15.735	1281.1
235.00	5.742	8.109	13.852	1905.7	15.991	1349.5
240.00	5.915	8.276	14.191	1986.3	16.257	1419.6
245.00	6.087	8.442	14.529	2068.2	16.532	1491.4
250.00	6.259	8.606	14.866	2151.6	16.819	1564.9
255.00	6.432	8.770	15.202	2236.4	17.114	1640.0
260.00	6.603	8.934	15.537	2322.8	17.417	1716.9
265.00	6.775	9.097	15.872	2410.6	17.724	1795.4
270.00	6.947	9.259	16.206	2500.0	18.033	1875.6
273.15	7.055	9.362	16.416	2557.1	18.228	1927.0
275.00	7.118	9.422	16.540	2590.9	18.342	1957.5
280.00	7.289	9.584	16.873	2683.4	18.647	2041.0
285.00	7.460	9.745	17.206	2777.4	18.945	2126.2
290.00	7.631	9.906	17.538	2872.9	19.235	2213.1
295.00	7.802	10.067	17.869	2969.7	19.516	2301.6
298.15	7.909	10.168	18.077	3031.5	19.687	2358.2
300.00	7.972	10.227	18.199	3068.0	19.785	2391.7

H_0^C IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-109

THERMODYNAMIC FUNCTIONS FOR SODIUM FLUORIDE (NA F)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=41.9882 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

(SOLID)

T DEG K	$-(G_T^0-H_0^C)/T$ CAL/DEG MOLE	$(H_T^0-H_0^C)/T$ CAL/DEG MOLE	S_T^0 CAL/DEG MOLE	$(H_T^0-H_0^C)$ CAL/MOLE	C_P^0 CAL/DEG MOLE	$-(G_T^0-H_0^C)$ CAL/MOLE
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.000	0.000	0.002	0.001	0.001
10.00	0.001	0.003	0.004	0.030	0.012	0.010
15.00	0.003	0.010	0.013	0.150	0.040	0.050
20.00	0.008	0.024	0.032	0.473	0.095	0.158
25.00	0.015	0.046	0.062	1.154	0.185	0.385
30.00	0.027	0.079	0.106	2.391	0.318	0.798
35.00	0.042	0.126	0.168	4.413	0.500	1.476
40.00	0.063	0.187	0.250	7.477	0.735	2.513
45.00	0.089	0.263	0.352	11.853	1.024	4.009
50.00	0.121	0.356	0.477	17.796	1.361	6.075
55.00	0.160	0.464	0.624	25.527	1.738	8.820
60.00	0.206	0.587	0.793	35.223	2.145	12.355
65.00	0.258	0.723	0.981	47.006	2.571	16.783
70.00	0.317	0.871	1.188	60.945	3.006	22.199
75.00	0.382	1.027	1.410	77.061	3.440	28.687
80.00	0.454	1.192	1.646	95.338	3.869	36.321
85.00	0.531	1.362	1.893	115.73	4.287	45.163
90.00	0.614	1.535	2.149	138.19	4.692	55.265
95.00	0.702	1.712	2.414	162.62	5.080	66.670
100.00	0.794	1.890	2.684	188.96	5.451	79.411
105.00	0.891	2.068	2.958	217.10	5.804	93.514
110.00	0.991	2.245	3.236	246.97	6.138	109.00
115.00	1.095	2.421	3.516	278.46	6.456	125.88
120.00	1.201	2.596	3.797	311.50	6.757	144.16
125.00	1.311	2.768	4.079	346.00	7.042	163.85
130.00	1.423	2.938	4.360	381.89	7.311	184.95
135.00	1.537	3.104	4.641	419.09	7.564	207.45
140.00	1.653	3.268	4.920	457.51	7.802	231.36
145.00	1.770	3.428	5.198	497.08	8.024	256.65
150.00	1.889	3.585	5.474	537.73	8.233	283.33
155.00	2.009	3.738	5.747	579.38	8.428	311.39
160.00	2.130	3.887	6.017	621.99	8.612	340.80
165.00	2.252	4.033	6.285	665.48	8.784	371.56
170.00	2.374	4.175	6.550	709.81	8.946	403.64
175.00	2.497	4.314	6.811	754.93	9.099	437.05
180.00	2.621	4.449	7.070	800.79	9.244	471.75
185.00	2.745	4.580	7.325	847.35	9.380	507.74
190.00	2.868	4.708	7.577	894.58	9.509	545.00
195.00	2.992	4.833	7.825	942.43	9.631	583.50
200.00	3.116	4.954	8.071	990.88	9.747	623.24
205.00	3.240	5.073	8.313	1039.9	9.857	664.20
210.00	3.364	5.188	8.551	1089.4	9.961	706.36
215.00	3.487	5.300	8.787	1139.5	10.061	749.71
220.00	3.610	5.409	9.019	1190.0	10.156	794.23
225.00	3.733	5.516	9.249	1241.0	10.246	839.90
230.00	3.855	5.620	9.475	1292.5	10.332	886.71
235.00	3.977	5.721	9.698	1344.4	10.414	934.64
240.00	4.099	5.819	9.918	1396.6	10.492	983.68
245.00	4.220	5.915	10.135	1449.3	10.567	1033.8
250.00	4.340	6.009	10.349	1502.3	10.638	1085.0
255.00	4.460	6.101	10.561	1555.7	10.706	1137.3
260.00	4.579	6.190	10.769	1609.3	10.770	1190.6
265.00	4.698	6.277	10.975	1663.4	10.832	1245.0
270.00	4.816	6.362	11.178	1717.7	10.891	1300.4
273.15	4.890	6.414	11.304	1752.0	10.927	1335.8
275.00	4.934	6.445	11.378	1772.3	10.948	1356.8
280.00	5.051	6.525	11.576	1827.1	11.003	1414.2
285.00	5.167	6.605	11.771	1882.3	11.055	1472.5
290.00	5.282	6.682	11.964	1937.7	11.106	1531.9
295.00	5.397	6.757	12.154	1993.3	11.155	1592.2
298.15	5.469	6.804	12.273	2028.5	11.185	1630.6
300.00	5.511	6.831	12.342	2049.2	11.202	1653.4

H_0^C IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-109(CONT.)

THERMODYNAMIC FUNCTIONS FOR SODIUM FLUORIDE (NA F)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=41.9882 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G_T^0-H_0^C)/T$	$(H_T^0-H_0^C)/T$	S_T^0	$(H_T^0-H_0^C)$	C_P^0	$-(G_T^0-H_0^C)$
DEG K	CAL / DEG MOLE	CAL / DEG MOLE	CAL / DEG MOLE	CAL / MOLE	CAL / DEG MOLE	CAL / MOLE
			(SOLID)			
300.00	5.511	6.831	12.342	2049.2	11.202	1653.4
310.00	5.738	6.973	12.711	2161.7	11.292	1778.7
320.00	5.961	7.110	13.071	2275.0	11.374	1907.6
330.00	6.182	7.240	13.422	2389.2	11.451	2040.1
340.00	6.400	7.365	13.765	2504.0	11.521	2176.0
350.00	6.615	7.484	14.100	2619.6	11.585	2315.3
360.00	6.828	7.599	14.427	2735.7	11.644	2458.0
370.00	7.037	7.709	14.747	2852.4	11.699	2603.8
373.15	7.103	7.743	14.846	2889.3	11.715	2650.4
380.00	7.244	7.815	15.059	2969.7	11.750	2752.9
390.00	7.449	7.916	15.365	3087.4	11.797	2905.0
400.00	7.650	8.014	15.664	3205.6	11.842	3060.2
425.00	8.143	8.242	16.386	3503.0	11.946	3460.9
450.00	8.620	8.451	17.071	3802.9	12.043	3879.1
475.00	9.082	8.642	17.725	4105.1	12.136	4314.1
500.00	9.530	8.819	18.350	4409.7	12.229	4765.1
550.00	10.386	9.138	19.525	5025.9	12.425	5712.5
600.00	11.194	9.421	20.615	5652.4	12.636	6716.4
650.00	11.958	9.676	21.634	6289.5	12.844	7772.8
700.00	12.684	9.910	22.594	6936.8	13.049	8878.8
750.00	13.375	10.126	23.501	7594.3	13.251	10031.
800.00	14.035	10.327	24.362	8261.9	13.452	11228.
850.00	14.667	10.517	25.184	8939.5	13.652	12467.
900.00	15.273	10.697	25.970	9627.1	13.851	13746.
950.00	15.856	10.868	26.724	10325.	14.049	15063.
1000.00	16.418	11.032	27.450	11032.	14.247	16418.
1050.00	16.960	11.190	28.150	11749.	14.444	17808.
1100.00	17.484	11.342	28.826	12476.	14.641	19232.
1150.00	17.991	11.490	29.481	13213.	14.837	20690.
1200.00	18.484	11.633	30.117	13960.	15.033	22180.
1250.00	18.961	11.773	30.735	14717.	15.229	23702.
1285.00	19.288	11.869	31.157	15252.	15.366	24785.
			(LIQUID)			
1285.00	19.288	18.118	37.406	23282.	16.400	24785.
1300.00	19.498	18.098	37.596	23528.	16.400	25347.
1350.00	20.180	18.036	38.215	24348.	16.400	27243.
1400.00	20.835	17.977	38.812	25168.	16.400	29168.
1450.00	21.464	17.923	39.387	25988.	16.400	31123.
1500.00	22.071	17.872	39.943	26808.	16.400	33107.
1550.00	22.656	17.825	40.481	27628.	16.400	35117.
1600.00	23.222	17.780	41.002	28448.	16.400	37155.
1650.00	23.768	17.738	41.506	29268.	16.400	39217.
1700.00	24.297	17.699	41.996	30088.	16.400	41305.
1750.00	24.810	17.662	42.471	30908.	16.400	43417.
1800.00	25.307	17.627	42.933	31728.	16.400	45552.
1850.00	25.789	17.594	43.383	32548.	16.400	47710.
1900.00	26.258	17.562	43.820	33368.	16.400	49890.

H_0^C IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-110

THERMODYNAMIC FUNCTIONS FOR SODIUM CHLORIDE (NA CL)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=58.4428 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G_T^0-H_0^C)/T$	$(H_T^0-H_0^C)/T$	S_T^0	$(H_T^0-H_0^C)$	C_P^0	$-(G_T^0-H_0^C)$
DEG K	CAL / DEG MOLE	CAL / DEG MOLE	CAL / DEG MOLE	CAL / MOLE	CAL / DEG MOLE	CAL / MOLE
			(SOLID)			
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.001	0.001	0.005	0.004	0.002
10.00	0.003	0.008	0.011	0.082	0.034	0.026
15.00	0.009	0.030	0.039	0.444	0.124	0.141
20.00	0.023	0.074	0.098	1.488	0.314	0.467
25.00	0.048	0.153	0.201	3.835	0.652	1.193
30.00	0.086	0.274	0.360	8.241	1.132	2.572
35.00	0.140	0.439	0.579	15.359	1.730	4.896
40.00	0.211	0.641	0.852	25.651	2.393	8.453
45.00	0.300	0.873	1.173	39.301	3.068	13.499
50.00	0.405	1.127	1.532	56.338	3.745	20.248
55.00	0.525	1.395	1.920	76.726	4.405	28.866
60.00	0.658	1.672	2.330	100.32	5.023	39.482
65.00	0.803	1.952	2.755	126.87	5.590	52.189
70.00	0.958	2.230	3.188	156.12	6.100	67.044
75.00	1.121	2.504	3.625	187.78	6.555	84.075
80.00	1.291	2.770	4.061	221.60	6.967	103.29
85.00	1.467	3.028	4.495	257.41	7.350	124.68
90.00	1.647	3.279	4.926	295.07	7.712	148.24
95.00	1.831	3.521	5.352	334.49	8.052	173.93
100.00	2.017	3.756	5.773	375.55	8.368	201.75
105.00	2.206	3.982	6.188	418.13	8.657	231.65
110.00	2.397	4.201	6.597	462.08	8.921	263.62
115.00	2.588	4.411	6.999	507.30	9.162	297.61
120.00	2.780	4.614	7.394	553.67	9.382	333.60
125.00	2.972	4.809	7.781	601.09	9.583	371.54
130.00	3.165	4.996	8.161	649.47	9.766	411.40
135.00	3.357	5.176	8.532	698.72	9.933	453.13
140.00	3.548	5.348	8.896	748.78	10.086	496.71
145.00	3.738	5.514	9.253	799.56	10.226	542.08
150.00	3.928	5.673	9.602	851.02	10.356	589.22
155.00	4.117	5.826	9.943	903.10	10.475	638.09
160.00	4.304	5.973	10.277	955.76	10.586	688.64
165.00	4.490	6.115	10.605	1008.9	10.689	740.85
170.00	4.675	6.251	10.925	1062.6	10.784	794.68
175.00	4.858	6.382	11.239	1116.8	10.872	850.09
180.00	5.039	6.507	11.547	1171.3	10.954	907.06
185.00	5.219	6.629	11.848	1226.3	11.028	965.55
190.00	5.398	6.745	12.143	1281.6	11.097	1025.5
195.00	5.574	6.858	12.432	1337.3	11.160	1087.0
200.00	5.749	6.966	12.715	1393.2	11.218	1149.8
205.00	5.922	7.070	12.993	1449.4	11.272	1214.1
210.00	6.094	7.171	13.265	1505.9	11.322	1279.8
215.00	6.264	7.268	13.532	1562.7	11.369	1346.8
220.00	6.432	7.362	13.794	1619.6	11.414	1415.1
225.00	6.599	7.452	14.051	1676.8	11.458	1484.7
230.00	6.763	7.540	14.303	1734.2	11.500	1555.6
235.00	6.926	7.625	14.551	1791.8	11.541	1627.7
240.00	7.088	7.707	14.794	1849.6	11.581	1701.1
245.00	7.248	7.786	15.034	1907.6	11.620	1775.6
250.00	7.406	7.863	15.269	1965.8	11.658	1851.4
255.00	7.562	7.938	15.500	2024.2	11.696	1928.3
260.00	7.717	8.011	15.727	2082.7	11.732	2006.4
265.00	7.870	8.081	15.951	2141.5	11.768	2085.6
270.00	8.022	8.150	16.172	2200.4	11.803	2165.9
273.15	8.117	8.192	16.309	2237.6	11.825	2217.1
275.00	8.172	8.216	16.388	2259.5	11.837	2247.3
280.00	8.321	8.281	16.602	2318.8	11.870	2329.8
285.00	8.468	8.345	16.812	2378.2	11.903	2413.3
290.00	8.613	8.406	17.020	2437.8	11.934	2497.9
295.00	8.758	8.466	17.224	2497.6	11.965	2583.5
298.15	8.848	8.503	17.351	2535.3	11.984	2638.0
300.00	8.900	8.525	17.425	2557.5	11.995	2670.1

H_0^C IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-110(CONT.)

THERMODYNAMIC FUNCTIONS FOR SODIUM CHLORIDE (NA CL)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=58.4428 GRAMS　　　　1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G^0_T-H^C_0)/T$	$(H^0_T-H^C_0)/T$	S^0_T	$(H^0_T-H^C_0)$	C^0_P	$-(G^0_T-H^C_0)$
DEG K	CAL / DEG MOLE	CAL / DEG MOLE	CAL / DEG MOLE	CAL / MOLE	CAL / DEG MOLE	CAL / MOLE
			(SOLID)			
300.00	8.900	8.525	17.425	2557.5	11.995	2670.1
310.00	9.182	8.638	17.820	2677.7	12.053	2846.4
320.00	9.458	8.745	18.203	2798.5	12.109	3026.5
330.00	9.728	8.848	18.577	2919.9	12.164	3210.4
340.00	9.994	8.946	18.941	3041.8	12.217	3398.0
350.00	10.255	9.041	19.295	3164.2	12.269	3589.2
360.00	10.511	9.131	19.642	3287.2	12.320	3783.9
370.00	10.762	9.218	19.980	3410.6	12.370	3982.0
373.15	10.840	9.245	20.085	3449.6	12.386	4045.1
380.00	11.009	9.301	20.311	3534.6	12.419	4183.4
390.00	11.252	9.382	20.634	3659.0	12.466	4388.2
400.00	11.490	9.460	20.950	3783.9	12.511	4596.1
425.00	12.069	9.642	21.712	4098.0	12.618	5129.4
450.00	12.625	9.810	22.436	4414.7	12.717	5681.4
475.00	13.160	9.966	23.126	4733.8	12.814	6251.0
500.00	13.675	10.111	23.786	5055.4	12.913	6837.4
550.00	14.651	10.375	25.026	5706.3	13.125	8058.1
600.00	15.564	10.613	26.177	6367.9	13.337	9338.5
650.00	16.422	10.829	27.251	7039.1	13.515	10674.
700.00	17.232	11.028	28.260	7719.7	13.710	12062.
750.00	17.999	11.213	29.213	8410.1	13.905	13499.
800.00	18.728	11.388	30.116	9110.2	14.100	14983.
850.00	19.424	11.553	30.977	9820.1	14.295	16510.
900.00	20.089	11.711	31.799	10540.	14.490	18080.
950.00	20.726	11.862	32.588	11269.	14.685	19690.
1000.00	21.338	12.008	33.346	12008.	14.880	21338.
1050.00	21.927	12.150	34.077	12757.	15.075	23024.
1073.00	22.191	12.213	34.405	13105.	15.165	23811.
			(LIQUID)			
1073.00	22.191	18.597	40.789	19955.	16.000	23811.
1100.00	22.653	18.534	41.186	20387.	16.000	24918.
1150.00	23.474	18.423	41.897	21187.	16.000	26995.
1200.00	24.256	18.322	42.578	21987.	16.000	29107.
1250.00	25.002	18.229	43.232	22787.	16.000	31253.
1300.00	25.715	18.144	43.859	23587.	16.000	33430.
1350.00	26.399	18.064	44.463	24387.	16.000	35638.
1400.00	27.054	17.991	45.045	25187.	16.000	37876.
1450.00	27.684	17.922	45.606	25987.	16.000	40142.
1500.00	28.291	17.858	46.149	26787.	16.000	42436.
1550.00	28.875	17.798	46.673	27587.	16.000	44757.
1600.00	29.440	17.742	47.181	28387.	16.000	47103.
1650.00	29.985	17.689	47.674	29187.	16.000	49475.
1700.00	30.512	17.639	48.151	29987.	16.000	51870.

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-111

THERMODYNAMIC FUNCTIONS FOR SODIUM BOROHYDRIDE ($NA\,B\,H_4$)
SOLID PHASE

GRAM MOLECULAR WT.=37.83268 GRAMS　　1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG-MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG-MOLE	S^0_T CAL/DEG-MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG-MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.001	0.002	0.006	0.005	0.002
10.00	0.003	0.010	0.014	0.103	0.043	0.033
15.00	0.012	0.039	0.051	0.579	0.167	0.179
20.00	0.030	0.099	0.129	1.977	0.412	0.609
25.00	0.062	0.197	0.259	4.914	0.784	1.557
30.00	0.110	0.335	0.445	10.057	1.303	3.291
35.00	0.175	0.517	0.692	18.111	1.927	6.110
40.00	0.257	0.732	0.989	29.281	2.545	10.294
45.00	0.357	0.971	1.328	43.682	3.224	16.070
50.00	0.473	1.232	1.705	61.604	3.944	23.637
55.00	0.603	1.509	2.112	83.015	4.612	33.169
60.00	0.747	1.794	2.541	107.64	5.233	44.794
65.00	0.902	2.083	2.984	135.37	5.862	58.600
70.00	1.067	2.375	3.442	166.25	6.485	74.659
75.00	1.240	2.669	3.909	200.15	7.067	93.033
80.00	1.422	2.961	4.383	236.84	7.604	113.76
85.00	1.610	3.249	4.859	276.16	8.118	136.86
90.00	1.804	3.534	5.337	318.02	8.625	162.35
95.00	2.003	3.815	5.817	362.40	9.127	190.24
100.00	2.205	4.093	6.298	409.27	9.617	220.53
105.00	2.412	4.367	6.779	458.54	10.087	253.22
110.00	2.621	4.637	7.258	510.11	10.537	288.31
115.00	2.833	4.903	7.736	563.88	10.970	325.80
120.00	3.047	5.165	8.212	619.79	11.390	365.67
125.00	3.263	5.422	8.686	677.78	11.805	407.92
130.00	3.481	5.676	9.157	737.83	12.217	452.53
135.00	3.700	5.926	9.625	799.95	12.630	499.48
140.00	3.920	6.172	10.092	864.13	13.042	548.78
145.00	4.141	6.416	10.557	930.36	13.452	600.40
150.00	4.362	6.658	11.020	998.64	13.857	654.34
155.00	4.584	6.896	11.481	1068.9	14.253	710.60
160.00	4.807	7.132	11.939	1141.2	14.637	769.15
165.00	5.030	7.365	12.395	1215.3	15.004	829.98
170.00	5.254	7.595	12.849	1291.2	15.352	893.10
175.00	5.477	7.821	13.298	1368.8	15.681	958.46
180.00	5.700	8.044	13.745	1447.9	15.990	1026.1
185.00	5.924	8.263	14.187	1528.6	16.281	1095.9
189.90	6.143	8.473	14.616	1609.1	16.550	1166.5
189.90	6.143	9.749	15.891	1851.3	16.550	1166.5
190.00	6.148	9.752	15.900	1852.9	16.555	1168.1
195.00	6.403	9.930	16.333	1936.3	16.814	1248.7
200.00	6.657	10.105	16.762	2021.0	17.062	1331.4
205.00	6.909	10.278	17.186	2106.9	17.301	1416.3
210.00	7.158	10.448	17.606	2194.0	17.532	1503.3
215.00	7.406	10.615	18.021	2282.3	17.758	1592.3
220.00	7.652	10.780	18.432	2371.6	17.980	1683.5
225.00	7.896	10.942	18.839	2462.1	18.197	1776.6
230.00	8.138	11.102	19.241	2553.6	18.411	1871.9
235.00	8.379	11.260	19.639	2646.2	18.620	1969.1
240.00	8.618	11.416	20.033	2739.8	18.824	2068.2
245.00	8.855	11.569	20.424	2834.4	19.022	2169.4
250.00	9.090	11.720	20.810	2930.0	19.213	2272.5
255.00	9.323	11.869	21.192	3026.5	19.397	2377.5
260.00	9.555	12.015	21.570	3123.9	19.573	2484.4
265.00	9.786	12.159	21.945	3222.2	19.741	2593.2
270.00	10.014	12.301	22.315	3321.3	19.900	2703.8
273.15	10.157	12.389	22.547	3384.2	19.996	2774.5
275.00	10.241	12.441	22.682	3421.2	20.051	2816.3
280.00	10.467	12.578	23.044	3521.8	20.194	2930.6
285.00	10.690	12.713	23.403	3623.1	20.330	3046.8
290.00	10.913	12.845	23.758	3725.1	20.460	3164.7
295.00	11.133	12.975	24.109	3827.7	20.583	3284.3
298.15	11.272	13.056	24.328	3892.7	20.658	3360.6
300.00	11.352	13.103	24.456	3930.9	20.701	3405.7

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-111(CONT.)

THERMODYNAMIC FUNCTIONS FOR SODIUM BOROHYDRIDE (NA B H_4)
SOLID PHASE

GRAM MOLECULAR WT.=37.83268 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G_T^0-H_0^C)/T$ CAL / DEG-MOLE	$(H_T^0-H_0^C)/T$ CAL / DEG-MOLE	S_T^0 CAL / DEG-MOLE	$(H_T^0-H_0^C)$ CAL / MOLE	C_P^0 CAL / DEG-MOLE	$-(G_T^0-H_0^C)$ CAL / MOLE
300.00	11.352	13.103	24.456	3930.9	20.701	3405.7
310.00	11.786	13.352	25.138	4139.1	20.924	3653.7
320.00	12.214	13.592	25.806	4349.4	21.134	3908.4
330.00	12.636	13.823	26.459	4561.7	21.335	4169.8
340.00	13.052	14.047	27.099	4776.0	21.528	4437.6
350.00	13.462	14.264	27.726	4992.3	21.715	4711.7
360.00	13.867	14.473	28.340	5210.3	21.896	4992.1
370.00	14.266	14.676	28.942	5430.2	22.072	5278.5
373.15	14.391	14.739	29.130	5499.8	22.127	5369.9
380.00	14.660	14.873	29.533	5651.7	22.244	5570.9
390.00	15.049	15.064	30.113	5875.0	22.411	5869.1
400.00	15.433	15.250	30.683	6100.0	22.576	6173.1
425.00	16.371	15.693	32.064	6669.5	22.990	6957.5
450.00	17.280	16.110	33.390	7249.7	23.429	7775.8
475.00	18.161	16.508	34.669	7841.3	23.902	8626.6
500.00	19.018	16.890	35.908	8444.9	24.390	9508.9
550.00	20.662	17.606	38.268	9683.2	25.153	11364.
600.00	22.222	18.268	40.491	10961.	25.963	13333.
650.00	23.709	18.891	42.600	12279.	26.761	15411.
700.00	25.131	19.481	44.613	13637.	27.549	17592.

H_0^C IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-112

THERMODYNAMIC FUNCTIONS FOR POTASSIUM FLUORIDE (K F)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=58.1004 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG-MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG-MOLE	S^0_T CAL/DEG-MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG-MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
			(SOLID)			
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.000	0.001	0.001	0.004	0.003	0.001
10.00	0.002	0.006	0.008	0.063	0.028	0.020
15.00	0.008	0.029	0.037	0.439	0.148	0.119
20.00	0.023	0.081	0.104	1.621	0.312	0.460
25.00	0.048	0.146	0.194	3.655	0.536	1.193
30.00	0.082	0.243	0.325	7.290	0.936	2.470
35.00	0.129	0.374	0.503	13.077	1.387	4.523
40.00	0.189	0.531	0.720	21.240	1.887	7.565
45.00	0.262	0.712	0.974	32.044	2.442	11.786
50.00	0.347	0.914	1.262	45.715	3.028	17.362
55.00	0.445	1.133	1.577	62.313	3.608	24.449
60.00	0.553	1.362	1.915	81.745	4.160	33.173
65.00	0.671	1.598	2.269	103.87	4.687	43.628
70.00	0.798	1.837	2.635	128.58	5.189	55.885
75.00	0.933	2.076	3.009	155.71	5.661	69.994
80.00	1.075	2.314	3.389	185.12	6.098	85.988
85.00	1.222	2.549	3.771	216.63	6.501	103.89
90.00	1.374	2.779	4.153	250.09	6.875	123.70
95.00	1.531	3.004	4.534	285.34	7.222	145.42
100.00	1.690	3.223	4.913	322.26	7.543	169.04
105.00	1.853	3.436	5.288	360.73	7.842	194.54
110.00	2.017	3.642	5.660	400.65	8.121	221.91
115.00	2.184	3.843	6.027	441.92	8.382	251.13
120.00	2.351	4.037	6.388	484.45	8.626	282.17
125.00	2.520	4.225	6.745	528.15	8.852	315.01
130.00	2.689	4.407	7.097	572.94	9.061	349.61
135.00	2.859	4.583	7.442	618.73	9.252	385.96
140.00	3.029	4.753	7.782	665.44	9.428	424.03
145.00	3.198	4.917	8.116	712.99	9.590	463.77
150.00	3.368	5.075	8.443	761.32	9.741	505.17
155.00	3.537	5.228	8.765	810.38	9.880	548.20
160.00	3.705	5.376	9.081	860.11	10.011	592.81
165.00	3.873	5.518	9.391	910.48	10.134	638.99
170.00	4.039	5.656	9.695	961.44	10.250	686.71
175.00	4.205	5.788	9.994	1013.0	10.358	735.93
180.00	4.370	5.917	10.287	1065.0	10.461	786.64
185.00	4.534	6.041	10.575	1117.6	10.558	838.80
190.00	4.697	6.161	10.858	1170.6	10.648	892.38
195.00	4.858	6.277	11.135	1224.0	10.733	947.36
200.00	5.019	6.390	11.408	1277.9	10.813	1003.7
205.00	5.178	6.498	11.676	1332.2	10.887	1061.4
210.00	5.336	6.604	11.939	1386.8	10.956	1120.5
215.00	5.492	6.706	12.198	1441.7	11.020	1180.8
220.00	5.647	6.804	12.452	1497.0	11.080	1242.4
225.00	5.801	6.900	12.701	1552.5	11.136	1305.3
230.00	5.954	6.993	12.947	1608.3	11.189	1369.5
235.00	6.106	7.082	13.188	1664.4	11.238	1434.8
240.00	6.256	7.170	13.425	1720.7	11.285	1501.3
245.00	6.404	7.254	13.658	1777.2	11.329	1569.0
250.00	6.552	7.336	13.888	1834.0	11.372	1637.9
255.00	6.698	7.415	14.113	1890.9	11.414	1707.9
260.00	6.842	7.493	14.335	1948.1	11.455	1779.0
265.00	6.986	7.568	14.554	2005.5	11.494	1851.3
270.00	7.128	7.641	14.769	2063.1	11.534	1924.6
273.15	7.217	7.686	14.903	2099.4	11.558	1971.3
275.00	7.269	7.712	14.981	2120.8	11.572	1998.9
280.00	7.408	7.781	15.190	2178.8	11.610	2074.4
285.00	7.547	7.849	15.396	2236.9	11.648	2150.8
290.00	7.684	7.915	15.599	2295.3	11.685	2228.3
295.00	7.820	7.979	15.799	2353.8	11.721	2306.8
298.15	7.905	8.019	15.923	2390.7	11.744	2356.8
300.00	7.954	8.042	15.996	2412.5	11.757	2386.3

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-112(CONT.)

THERMODYNAMIC FUNCTIONS FOR POTASSIUM FLUORIDE (K F)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=58.1004 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG-MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG-MOLE	S^0_T CAL/DEG-MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG-MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
			(SOLID)			
300.00	7.954	8.042	15.996	2412.5	11.757	2386.3
310.00	8.220	8.163	16.383	2530.4	11.826	2548.2
320.00	8.481	8.278	16.759	2649.0	11.892	2713.9
330.00	8.737	8.389	17.126	2768.2	11.954	2883.3
340.00	8.989	8.494	17.484	2888.1	12.014	3056.4
350.00	9.237	8.596	17.833	3008.5	12.070	3233.0
360.00	9.481	8.693	18.174	3129.5	12.124	3413.0
370.00	9.720	8.786	18.507	3251.0	12.176	3596.4
373.15	9.795	8.815	18.610	3289.3	12.192	3654.9
380.00	9.956	8.876	18.832	3373.0	12.225	3783.1
390.00	10.187	8.963	19.150	3495.5	12.273	3973.1
400.00	10.415	9.046	19.461	3618.4	12.318	4166.1
425.00	10.970	9.242	20.211	3927.7	12.423	4662.1
450.00	11.503	9.421	20.924	4239.5	12.518	5176.4
475.00	12.017	9.586	21.603	4553.6	12.608	5708.0
500.00	12.513	9.740	22.252	4869.8	12.694	6256.3
550.00	13.432	10.016	23.448	5508.5	12.863	7387.9
600.00	14.315	10.259	24.574	6155.5	13.012	8588.8
650.00	15.145	10.476	25.621	6809.6	13.152	9843.9
700.00	15.928	10.672	26.600	7470.6	13.287	11150.
750.00	16.671	10.851	27.522	8138.2	13.417	12503.
800.00	17.376	11.015	28.392	8812.2	13.543	13901.
850.00	18.049	11.168	29.216	9492.5	13.667	15341.
900.00	18.691	11.310	30.001	10179.	13.789	16822.
950.00	19.306	11.444	30.750	10871.	13.909	18341.
1000.00	19.896	11.570	31.466	11570.	14.028	19896.
1050.00	20.464	11.690	32.154	12274.	14.146	21487.
1100.00	21.010	11.804	32.814	12984.	14.262	23111.
1130.00	21.329	11.870	33.199	13413.	14.332	24102.
			(LIQUID)			
1130.00	21.329	17.844	39.172	20163.	16.000	24102.
1150.00	21.642	12.811	39.453	20483.	16.000	24888.
1200.00	22.398	17.736	40.134	21283.	16.000	26878.
1250.00	23.121	17.667	40.787	22083.	16.000	28901.
1300.00	23.812	17.603	41.415	22883.	16.000	30956.
1350.00	24.475	17.543	42.019	23683.	16.000	33042.
1400.00	25.112	17.488	42.601	24483.	16.000	35157.
1450.00	25.725	17.437	43.162	25283.	16.000	37302.
1500.00	26.316	17.389	43.704	26083.	16.000	39473.
1550.00	26.885	17.344	44.229	26883.	16.000	41672.
1600.00	27.435	17.302	44.737	27683.	16.000	43896.
1650.00	27.967	17.263	45.229	28483.	16.000	46145.
1700.00	28.482	17.225	45.707	29283.	16.000	48419.
1750.00	28.980	17.190	46.171	30083.	16.000	50716.
1800.00	29.464	17.157	46.622	30883.	16.000	53035.

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-113

THERMODYNAMIC FUNCTIONS FOR POTASSIUM CHLORIDE (K CL)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=74.5550 GRAMS   1 CAL=4.1840 ABS J
T DEG K = 273.15 + T DEG C

T	$-(G_T^0-H_0^C)/T$	$(H_T^0-H_0^C)/T$	S_T^0	$(H_T^0-H_0^C)$	C_P^0	$-(G_T^0-H_0^C)$
DEG K	CAL/DEG MOLE	CAL/DEG MOLE	CAL/DEG MOLE	CAL/MOLE	CAL/DEG MOLE	CAL/MOLE
			(SOLID)			
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.001	0.002	0.003	0.011	0.009	0.004
10.00	0.006	0.019	0.026	0.194	0.080	0.062
15.00	0.022	0.070	0.092	1.054	0.293	0.334
20.00	0.055	0.172	0.227	3.441	0.693	1.101
25.00	0.109	0.333	0.442	8.314	1.285	2.739
30.00	0.189	0.550	0.738	16.494	2.004	5.658
35.00	0.293	0.814	1.106	28.476	2.796	10.243
40.00	0.420	1.112	1.533	44.486	3.606	16.818
45.00	0.570	1.433	2.003	64.476	4.381	25.641
50.00	0.738	1.764	2.501	88.178	5.088	36.891
55.00	0.921	2.095	3.017	115.23	5.726	50.681
60.00	1.118	2.423	3.541	145.37	6.320	67.071
65.00	1.325	2.744	4.069	178.38	6.879	86.094
70.00	1.539	3.058	4.598	214.08	7.389	107.76
75.00	1.761	3.362	5.123	252.16	7.832	132.06
80.00	1.987	3.653	5.641	292.28	8.205	158.98
85.00	2.217	3.931	6.148	334.11	8.520	188.45
90.00	2.449	4.193	6.643	377.41	8.795	220.44
95.00	2.683	4.442	7.125	422.02	9.048	254.86
100.00	2.917	4.679	7.595	467.87	9.288	291.67
105.00	3.150	4.904	8.054	514.89	9.520	330.80
110.00	3.384	5.119	8.502	563.05	9.741	372.19
115.00	3.616	5.324	8.940	612.28	9.948	415.80
120.00	3.846	5.521	9.367	662.49	10.135	461.57
125.00	4.076	5.709	9.784	713.59	10.301	509.45
130.00	4.303	5.888	10.191	765.47	10.444	559.40
135.00	4.529	6.059	10.588	818.01	10.569	611.35
140.00	4.752	6.222	10.974	871.12	10.677	665.26
145.00	4.973	6.378	11.351	924.75	10.773	721.08
150.00	5.192	6.526	11.717	978.84	10.861	778.75
155.00	5.408	6.667	12.075	1033.3	10.943	838.23
160.00	5.622	6.802	12.423	1088.3	11.021	899.48
165.00	5.833	6.931	12.764	1143.6	11.096	962.45
170.00	6.042	7.054	13.096	1199.2	11.167	1027.1
175.00	6.248	7.173	13.421	1255.2	11.235	1093.4
180.00	6.452	7.286	13.738	1311.6	11.298	1161.3
185.00	6.653	7.396	14.048	1368.2	11.357	1230.8
190.00	6.851	7.501	14.352	1425.1	11.412	1301.8
195.00	7.048	7.602	14.649	1482.3	11.463	1374.3
200.00	7.241	7.699	14.940	1539.7	11.511	1448.3
205.00	7.433	7.792	15.225	1597.4	11.558	1523.7
210.00	7.621	7.882	15.504	1655.3	11.603	1600.5
215.00	7.808	7.970	15.777	1713.4	11.648	1678.7
220.00	7.992	8.054	16.046	1771.8	11.692	1758.3
225.00	8.174	8.135	16.309	1830.4	11.737	1839.1
230.00	8.354	8.214	16.567	1889.2	11.783	1921.3
235.00	8.531	8.290	16.821	1948.2	11.828	2004.8
240.00	8.706	8.364	17.071	2007.5	11.874	2089.5
245.00	8.880	8.436	17.316	2066.9	11.918	2175.5
250.00	9.051	8.507	17.557	2126.6	11.961	2262.7
255.00	9.220	8.575	17.795	2186.5	12.002	2351.1
260.00	9.387	8.641	18.028	2246.6	12.041	2440.6
265.00	9.552	8.705	18.258	2306.9	12.077	2531.4
270.00	9.716	8.768	18.484	2367.4	12.111	2623.2
273.15	9.818	8.807	18.624	2405.6	12.130	2681.7
275.00	9.877	8.829	18.706	2428.0	12.141	2716.2
280.00	10.037	8.889	18.925	2488.8	12.169	2810.3
285.00	10.195	8.946	19.141	2549.7	12.194	2905.4
290.00	10.351	9.003	19.353	2610.8	12.217	3001.7
295.00	10.505	9.057	19.562	2671.9	12.236	3099.0
298.15	10.601	9.091	19.692	2710.5	12.248	3160.8
300.00	10.658	9.110	19.768	2733.1	12.254	3197.3

H_0^C IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-113(CONT.)

THERMODYNAMIC FUNCTIONS FOR POTASSIUM CHLORIDE (K CL)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=74.5550 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG MOLE	S^0_T CAL/DEG MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
			(SOLID)			
300.00	10.658	9.110	19.768	2733.1	12.254	3197.3
310.00	10.958	9.212	20.170	2855.8	12.284	3397.0
320.00	11.252	9.309	20.561	2978.8	12.308	3600.7
330.00	11.540	9.400	20.940	3102.0	12.328	3808.2
340.00	11.822	9.486	21.308	3225.3	12.345	4019.4
350.00	12.098	9.568	21.666	3348.9	12.362	4234.3
360.00	12.369	9.646	22.015	3472.6	12.378	4452.7
370.00	12.634	9.720	22.354	3596.4	12.395	4674.6
373.15	12.716	9.743	22.459	3635.5	12.401	4745.1
380.00	12.894	9.791	22.685	3720.5	12.414	4899.8
390.00	13.149	9.858	23.008	3844.7	12.434	5128.2
400.00	13.400	9.923	23.323	3969.2	12.456	5359.9
425.00	14.006	10.074	24.080	4281.4	12.522	5952.5
450.00	14.586	10.212	24.798	4595.4	12.603	6563.5
475.00	15.141	10.340	25.482	4911.6	12.696	7192.1
500.00	15.675	10.461	26.135	5230.3	12.798	7837.4
550.00	16.682	10.682	27.364	5875.3	13.004	9175.1
600.00	17.620	10.885	28.505	6531.0	13.224	10572.
650.00	18.499	11.074	29.573	7197.8	13.452	12024.
700.00	19.326	11.252	30.578	7876.3	13.687	13528.
750.00	20.108	11.422	31.531	8566.6	13.927	15081.
800.00	20.851	11.586	32.437	9269.0	14.170	16681.
850.00	21.558	11.746	33.304	9983.7	14.417	18324.
900.00	22.234	11.901	34.135	10711.	14.665	20010.
950.00	22.881	12.053	34.934	11450.	14.915	21737.
1000.00	23.503	12.202	35.706	12202.	15.167	23503.
1043.00	24.020	12.329	36.349	12859.	15.384	25053.
			(LIQUID)			
1043.00	24.020	18.178	42.197	18959.	16.000	25053.
1050.00	24.140	18.162	42.304	19071.	16.000	25348.
1100.00	24.984	18.065	43.049	19871.	16.000	27482.
1150.00	25.785	17.975	43.760	20671.	16.000	29653.
1200.00	26.548	17.893	44.441	21471.	16.000	31858.
1250.00	27.277	17.817	45.094	22271.	16.000	34096.
1300.00	27.974	17.747	45.722	23071.	16.000	36367.
1350.00	28.643	17.682	46.325	23871.	16.000	38668.
1400.00	29.285	17.622	46.907	24671.	16.000	40999.
1450.00	29.902	17.566	47.469	25471.	16.000	43358.
1500.00	30.497	17.514	48.011	26271.	16.000	45746.

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-114

THERMODYNAMIC FUNCTIONS FOR POTASSIUM BROMIDE (K BR)
SOLID PHASE

GRAM MOLECULAR WT.=119.0110 GRAMS　　　1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL/DEG MOLE	$(H^0_T-H^C_0)/T$ CAL/DEG MOLE	S^0_T CAL/DEG MOLE	$(H^0_T-H^C_0)$ CAL/MOLE	C^0_P CAL/DEG MOLE	$-(G^0_T-H^C_0)$ CAL/MOLE
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.003	0.010	0.014	0.052	0.041	0.017
10.00	0.025	0.067	0.092	0.669	0.239	0.248
15.00	0.073	0.197	0.271	2.962	0.747	1.100
20.00	0.160	0.435	0.595	8.703	1.580	3.204
25.00	0.291	0.759	1.050	18.973	2.548	7.269
30.00	0.462	1.144	1.607	34.331	3.600	13.872
35.00	0.670	1.567	2.237	54.849	4.599	23.457
40.00	0.908	2.006	2.914	80.248	5.543	36.322
45.00	1.170	2.445	3.615	110.01	6.337	52.639
50.00	1.449	2.867	4.317	143.36	6.989	72.469
55.00	1.742	3.271	5.012	179.88	7.608	95.795
60.00	2.043	3.655	5.698	219.31	8.147	122.58
65.00	2.350	4.017	6.367	261.11	8.554	152.75
70.00	2.660	4.353	7.013	304.68	8.864	186.21
75.00	2.971	4.663	7.634	349.69	9.139	222.84
80.00	3.281	4.951	8.232	396.06	9.407	262.51
85.00	3.590	5.221	8.810	443.75	9.668	305.13
90.00	3.895	5.475	9.370	492.71	9.914	350.59
95.00	4.198	5.714	9.912	542.85	10.139	398.80
100.00	4.497	5.941	10.438	594.06	10.341	449.68
105.00	4.792	6.155	10.947	646.23	10.523	503.15
110.00	5.083	6.357	11.440	699.26	10.686	559.12
115.00	5.370	6.548	11.918	753.06	10.830	617.52
120.00	5.652	6.729	12.382	807.54	10.958	678.28
125.00	5.931	6.901	12.832	862.61	11.070	741.32
130.00	6.204	7.063	13.268	918.22	11.170	806.57
135.00	6.474	7.217	13.691	974.29	11.258	873.97
140.00	6.739	7.363	14.102	1030.8	11.340	943.46
145.00	7.000	7.501	14.501	1087.7	11.416	1015.0
150.00	7.256	7.633	14.889	1144.9	11.488	1088.5
155.00	7.509	7.758	15.267	1202.5	11.556	1163.8
160.00	7.757	7.878	15.635	1260.5	11.621	1241.1
165.00	8.001	7.992	15.994	1318.8	11.682	1320.2
170.00	8.241	8.102	16.343	1377.3	11.739	1401.0
175.00	8.478	8.206	16.684	1436.1	11.790	1483.6
180.00	8.710	8.307	17.017	1495.2	11.837	1567.9
185.00	8.939	8.403	17.342	1554.5	11.879	1653.8
190.00	9.165	8.495	17.659	1614.0	11.916	1741.3
195.00	9.386	8.583	17.969	1673.6	11.949	1830.3
200.00	9.605	8.667	18.272	1733.5	11.980	1920.9
205.00	9.820	8.748	18.568	1793.4	12.007	2013.0
210.00	10.032	8.826	18.858	1853.5	12.034	2106.6
215.00	10.240	8.901	19.141	1913.8	12.059	2201.6
220.00	10.446	8.973	19.419	1974.1	12.084	2298.0
225.00	10.648	9.043	19.691	2034.6	12.108	2395.8
230.00	10.847	9.110	19.957	2095.2	12.132	2494.9
235.00	11.044	9.174	20.218	2155.9	12.157	2595.4
240.00	11.238	9.237	20.475	2216.8	12.181	2697.1
245.00	11.429	9.297	20.726	2277.7	12.205	2800.1
250.00	11.617	9.355	20.973	2338.8	12.229	2904.3
255.00	11.803	9.412	21.215	2400.0	12.253	3009.8
260.00	11.986	9.467	21.453	2461.4	12.276	3116.5
265.00	12.167	9.520	21.687	2522.8	12.299	3224.3
270.00	12.346	9.572	21.917	2584.3	12.322	3333.4
273.15	12.457	9.603	22.060	2623.2	12.337	3402.6
275.00	12.522	9.622	22.144	2646.0	12.345	3443.5
280.00	12.696	9.671	22.366	2707.8	12.367	3554.8
285.00	12.867	9.718	22.586	2769.7	12.389	3667.2
290.00	13.037	9.764	22.801	2831.7	12.411	3780.6
295.00	13.204	9.809	23.014	2893.8	12.432	3895.2
298.15	13.308	9.837	23.146	2933.0	12.444	3967.9
300.00	13.369	9.853	23.223	2956.0	12.452	4010.8

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-114(CONT.)

THERMODYNAMIC FUNCTIONS FOR POTASSIUM BROMIDE (K BR)
SOLID PHASE

GRAM MOLECULAR WT.=119.0110 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(G^0_T-H^C_0)/T$ CAL DEG-MOLE	$(H^0_T-H^C_0)/T$ CAL DEG-MOLE	S^0_T CAL DEG-MOLE	$(H^0_T-H^C_0)$ CAL MOLE	C^0_P CAL DEG-MOLE	$-(G^0_T-H^C_0)$ CAL MOLE
300.00	13.369	9.853	23.223	2956.0	12.452	4010.8
310.00	13.694	9.938	23.632	3080.7	12.491	4245.0
320.00	14.010	10.018	24.029	3205.8	12.527	4483.4
330.00	14.320	10.095	24.415	3331.2	12.560	4725.6
340.00	14.622	10.168	24.790	3457.0	12.591	4971.6
350.00	14.918	10.237	25.155	3583.1	12.620	5221.4
360.00	15.207	10.304	25.511	3709.4	12.647	5474.7
370.00	15.491	10.368	25.858	3836.0	12.674	5731.5
373.15	15.579	10.387	25.966	3875.9	12.683	5813.2
380.00	15.768	10.429	26.197	3962.9	12.701	5991.8
390.00	16.040	10.487	26.527	4090.0	12.729	6255.5
400.00	16.306	10.544	26.850	4217.5	12.758	6522.3
425.00	16.949	10.676	27.625	4537.4	12.837	7203.4
450.00	17.563	10.799	28.362	4859.4	12.927	7903.3
475.00	18.150	10.913	29.063	5183.8	13.024	8621.1
500.00	18.712	11.021	29.734	5510.6	13.120	9356.2
550.00	19.773	11.220	30.993	6170.9	13.298	10875.
600.00	20.757	11.401	32.158	6840.8	13.498	12454.
650.00	21.676	11.570	33.247	7520.8	13.704	14090.
700.00	22.540	11.730	34.270	8211.2	13.914	15778.
750.00	23.354	11.883	35.237	8912.2	14.127	17516.
800.00	24.126	12.030	36.156	9624.0	14.343	19301.
850.00	24.859	12.172	37.032	10347.	14.560	21130.
900.00	25.559	12.311	37.870	11080.	14.778	23003.
950.00	26.228	12.447	38.675	11824.	14.998	24917.
1000.00	26.870	12.580	39.450	12580.	15.219	26870.

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-115

THERMODYNAMIC FUNCTIONS FOR POTASSIUM BOROHYDRIDE ($K\ B\ H_4$)
SOLID PHASES

GRAM MOLECULAR WT.=53.94488 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G^0_T-H^C_0)/T$	$(H^0_T-H^C_0)/T$	S^0_T	$(H^0_T-H^C_0)$	C^0_P	$-(G^0_T-H^C_0)$
DEG K	CAL/DEG-MOLE	CAL/DEG-MOLE	CAL/DEG-MOLE	CAL/MOLE	CAL/DEG-MOLE	CAL/MOLE
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	0.001	0.002	0.003	0.011	0.009	0.004
10.00	0.006	0.017	0.023	0.173	0.069	0.058
15.00	0.019	0.058	0.078	0.877	0.234	0.292
20.00	0.046	0.138	0.184	2.756	0.553	0.921
25.00	0.090	0.267	0.357	6.675	1.034	2.244
30.00	0.153	0.442	0.595	13.257	1.609	4.598
35.00	0.237	0.653	0.890	22.853	2.236	8.289
40.00	0.339	0.891	1.230	35.645	2.882	13.572
45.00	0.459	1.147	1.606	51.631	3.542	20.653
50.00	0.594	1.421	2.015	71.047	4.228	29.694
55.00	0.743	1.708	2.451	93.933	4.929	40.846
60.00	0.904	2.007	2.911	120.42	5.673	54.240
65.00	1.077	2.319	3.396	150.76	6.475	69.997
70.00	1.261	2.646	3.906	185.20	7.282	88.245
75.00	1.455	2.978	4.432	223.34	7.949	109.09
77.16	1.541	3.121	4.662	240.79	8.201	118.91
77.16	1.541	3.818	5.359	294.56	8.200	118.91
80.00	1.682	3.979	5.661	318.29	8.505	134.56
85.00	1.932	4.259	6.190	361.99	8.973	164.19
90.00	2.183	4.533	6.716	408.01	9.435	196.45
95.00	2.435	4.803	7.239	456.33	9.891	231.34
100.00	2.688	5.069	7.757	506.91	10.340	268.83
105.00	2.942	5.331	8.273	559.72	10.781	308.91
110.00	3.196	5.588	8.784	614.71	11.215	351.55
115.00	3.450	5.842	9.292	671.84	11.636	396.75
120.00	3.704	6.092	9.796	731.05	12.044	444.47
125.00	3.958	6.338	10.296	792.26	12.440	494.70
130.00	4.211	6.580	10.791	855.43	12.825	547.42
135.00	4.464	6.818	11.282	920.49	13.199	602.60
140.00	4.716	7.053	11.769	987.39	13.560	660.23
145.00	4.967	7.283	12.251	1056.1	13.911	720.28
150.00	5.218	7.510	12.728	1126.5	14.255	782.73
155.00	5.468	7.733	13.201	1198.6	14.595	847.56
160.00	5.717	7.953	13.670	1272.4	14.932	914.74
165.00	5.965	8.169	14.134	1347.9	15.262	984.25
170.00	6.212	8.383	14.595	1425.1	15.586	1056.1
175.00	6.458	8.593	15.051	1503.8	15.912	1130.2
180.00	6.703	8.801	15.504	1584.2	16.238	1206.6
185.00	6.947	9.006	15.954	1666.2	16.564	1285.2
190.00	7.190	9.210	16.400	1749.8	16.887	1366.1
195.00	7.432	9.410	16.842	1835.0	17.209	1449.2
200.00	7.673	9.609	17.282	1921.9	17.532	1534.5
205.00	7.912	9.807	17.719	2010.4	17.859	1622.0
210.00	8.151	10.002	18.153	2100.5	18.190	1711.7
215.00	8.389	10.197	18.585	2192.3	18.520	1803.6
220.00	8.625	10.389	19.015	2285.7	18.845	1897.6
225.00	8.861	10.581	19.442	2380.7	19.175	1993.7
230.00	9.096	10.771	19.867	2477.4	19.497	2092.0
235.00	9.329	10.960	20.290	2575.7	19.810	2192.4
240.00	9.562	11.148	20.710	2675.5	20.121	2294.9
245.00	9.794	11.334	21.128	2776.9	20.428	2399.5
250.00	10.025	11.519	21.544	2879.8	20.726	2506.1
255.00	10.255	11.702	21.957	2984.1	21.014	2614.9
260.00	10.484	11.884	22.368	3089.9	21.292	2725.7
265.00	10.712	12.064	22.776	3197.0	21.559	2838.6
270.00	10.939	12.242	23.181	3305.5	21.811	2953.5
273.15	11.081	12.354	23.435	3374.4	21.963	3026.9
275.00	11.165	12.419	23.584	3415.1	22.049	3070.4
280.00	11.390	12.593	23.983	3525.9	22.272	3189.3
285.00	11.615	12.764	24.379	3637.8	22.481	3310.2
290.00	11.838	12.934	24.772	3750.7	22.674	3433.1
295.00	12.061	13.100	25.161	3864.5	22.853	3557.9
298.15	12.200	13.204	25.404	3936.7	22.958	3637.6
300.00	12.282	13.264	25.546	3979.2	23.016	3684.7

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

TABLE B-115(CONT.)

THERMODYNAMIC FUNCTIONS FOR POTASSIUM BOROHYDRIDE $(K\ B\ H_4)$
SOLID PHASES

GRAM MOLECULAR WT.=53.94488 GRAMS　　1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G^0_T-H^C_0)/T$	$(H^0_T-H^C_0)/T$	S^0_T	$(H^0_T-H^C_0)$	C^0_P	$-(G^0_T-H^C_0)$
DEG K	CAL/DEG MOLE	CAL/DEG MOLE	CAL/DEG MOLE	CAL/MOLE	CAL/DEG MOLE	CAL/MOLE
300.00	12.282	13.264	25.546	3979.2	23.016	3684.7
310.00	12.722	13.583	26.304	4210.6	23.295	3943.7
320.00	13.158	13.890	27.047	4444.7	23.519	4210.4
330.00	13.590	14.184	27.774	4680.8	23.694	4484.6
340.00	14.017	14.466	28.483	4918.4	23.818	4765.9
350.00	14.440	14.734	29.175	5157.0	23.893	5054.2
360.00	14.859	14.989	29.849	5396.2	23.945	5349.3
370.00	15.273	15.232	30.505	5635.9	24.001	5651.1
373.15	15.403	15.306	30.709	5711.5	24.018	5747.5
380.00	15.683	15.464	31.146	5876.2	24.052	5959.4
390.00	16.087	15.684	31.771	6116.9	24.093	6274.0
400.00	16.487	15.895	32.382	6358.0	24.125	6594.7
425.00	17.465	16.381	33.846	6961.9	24.186	7422.8
450.00	18.414	16.816	35.230	7567.2	24.238	8286.4
475.00	19.334	17.208	36.542	8174.0	24.306	9183.7
500.00	20.226	17.565	37.791	8782.7	24.403	10113.
550.00	21.931	18.201	40.131	10010.	24.742	12062.
600.00	23.539	18.769	42.308	11261.	25.341	14123.
650.00	25.063	19.307	44.370	12550.	26.256	16291.
700.00	26.513	19.847	46.360	13893.	27.531	18559.

H^C_0 IS THE ENTHALPY OF THE SOLID AT 0 DEG K AND 1 ATM PRESSURE.

☆ U. S. GOVERNMENT PRINTING OFFICE : 1964 O - 732-779