NATIONAL BUREAU OF STANDARDS REPORT

7437

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

(Supplement to NBS Reports 6297, 6484, 6645, 6928, 7093, and 7192)

1 January 1962

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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(Supplement to NBS Reports 6297, 6484, 6645, 6928, 7093, and 7192)

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

Reference: ARPA Order No. 20-62

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

ABSTRACT

This is the seventh semi-annual 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. In this connection the chemical elements principally involved are H, Li, Be, B, C, N, O, F, $A\ell$, $C\ell$, and Zr, with more secondary interest in the compounds of Mg, Si, K, Ti, Br, I, W, Hg, and Pb. The emphasis in the NBS work has been on the simpler compounds of these elements.

This report includes some recent NBS measurements under the program: The heat of formation of nitronium perchlorate, and the high-temperature heat capacity of aluminum carbide. As discussed in the report, precise measurements are essentially completed on the heat of combustion of aluminum in fluorine and on the low-temperature heat capacities and absolute entropies of $A\ell_4C_3$, LiH, and $LiA\ell H_4$; however, these data are not yet presented, pending the resolution of small discrepancies needed to put the results on a final basis. Tables of thermodynamic functions are given for four gases omitted from earlier reports (H_2, O_2, H^+, and electron gas), and, on the basis of improved data, for the condensed phases of two substances (BeF_2 and $A\ell_4C_3$). A contribution from those areas in which elaborate apparatus development is still progressing is a description in the report of a new fast-opening large-aperture shutter for high-speed photography. This development will be important in the study of combustions at very high temperatures and pressures.

Also included are several up-to-date literature surveys in the field. One describes recent additions to the literature on the chemistry of numerous light-element compounds. A second describes alloys and intermetallic compounds of aluminum and beryllium with titanium and zirconium; while a third survey covers low-temperature heat capacities and entropies of various substances, particularly the oxides of eight light elements. The fourth report is a comprehensive and critical assembly of the available values for the heats of formation of a large number of compounds.

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

PART A

RECENT EXPERIMENTAL RESULTS AT THE NATIONAL BUREAU OF STANDARDS

Chapter Al

HEAT OF NEUTRALIZATION AND FORMATION OF NITRONIUM PERCHLORATE

by A. A. Gilliland

1. Introduction

Nitronium perchlorate is a white, crystalline material, stable at temperatures up to 120°C. It is extremely hygroscopic, reacting rapidly with water to form nitric and perchloric acids. Aqueous solutions of potassium hydroxide were used in this investigation, as the potassium salts of the acids provided more suitable reference substances. The heats of solution of KNO_3(c) and $KClO_4$(c) in KOH(aq) were also determined.

2. Constants and Conversion Factors

The results of this investigation are given in joules and calories, with 1 cal ≡ 4.1840 joules. All weights are corrected to vacuum. The molecular weights are calculated from the 1957 International Table of Atomic Weights [1]. For NO_2ClO_4(c) an estimated heat capacity of 36 cal/deg mole was used; other auxiliary data were taken where possible from [2].

3. Materials

The KNO_3(c) and $KClO_4$(c) were reagent-grade materials, dried at 120°C and stored in a desiccator. The calorimetric solutions were prepared from reagent-grade KOH and CO_2-free distilled water, and were standardized against potassium acid phthalate. The NO_2ClO_4 was obtained from the Callery Chemical Company. Analyses for total acid by titration with standard base and for NO^+ by oxidation with standard ceric sulfate solution and back titration with standard ferrous ammonium sulfate gave the following results:

Total acid	13.74 ±0.01 millieq/g	(theoret. 13.75)
NO^+	0.06 ±0.01%	

The addition of $AgNO_3$ to the acid solution gave a negative test for chloride ion.

From the measurement of total acid, the purity of the sample was estimated to be 99.93% by weight. The major impurity is probably water, in which case the sample may be taken as 98.84 mole percent NO_2ClO_4 and 0.580 mole percent HNO_3 and $HClO_4$.

4. Apparatus and Procedure

The glass calorimeter, thermometric system, and general calorimetric procedure have been described [3,4,5]. The calorimeter contained 454.6 g of 0.04126 N KOH solution, and the weighed glass ampoule contained about 0.005 moles NO_2ClO_4. The calorimeter assembly was placed in a thermostatically controlled water-bath maintained at 25.0 ±0.002°C. After each run, the calorimeter solution was titrated with standard acid, using a Beckman pH meter, as a check on the mass of sample and completeness of reaction.

The heat of solution of an equimolar mixture of crystalline KNO_3 and $KClO_4$ was measured in the same apparatus containing 454.6 g of 0.02077 N KOH. The sample size was adjusted to give the same final concentration as in the NO_2ClO_4 hydrolysis experiments.

Electrical energy calibration experiments were carried out for the initial conditions of both sets of experiments, using 0.005 moles of NO_2ClO_4, and 0.005 moles each of KNO_3 and $KClO_4$, respectively.

5. Results and Calculations

The results of the two series of electrical calibration experiments are given in tables 1 and 2. ΔRc is the corrected temperature rise, in ohms, of the system [6]. The energy equivalent of the standard calorimetric system, Es, is obtained as the ratio of the quantity of electrical energy, Ee, to the corresponding temperature rise, ΔRc.

The results of the hydrolysis and neutralization experiments on NO_2ClO_4 are given in table 3. Here Δe is the change in the energy equivalent from that of the "standard" system due to deviations in the mass of glass bulb and sample. The term q(dil) represents the correction for the heat of dilution of the individual final solutions to a uniform concentration. This was calculated from the data in [2], assuming that only the KOH(aq) contributed any heat effect. The total energy evolved, q, is calculated by the relation

$$q = \Delta Rc(Es + \Delta e) + q(dil)$$

The results of the heat of solution experiments on the KNO_3-$KClO_4$ mixtures are given in table 4. The term $q(KNO_3)$ is the calculated correction to make the molar quantities of KNO_3 and $KClO_4$ exactly equal.

For the reaction

$$NO_2ClO_4(c) + [4\ KOH + 5300\ H_2O](soln) \longrightarrow [KNO_3 + KClO_4 + 2\ KOH + 5301\ H_2O](soln) \tag{1}$$

$$\Delta H = -199.01 \pm 0.35\ kj/145.465\ g\ sample$$
$$= -47.56 \pm 0.08\ kcal/145.465\ g\ sample.$$

After correcting for the presence of the HNO_3 and $HClO_4$ present as impurities and ignoring slight dilution effects, this equation becomes

$$NO_2ClO_4(c) + [4\ KOH + 5300\ H_2O] \longrightarrow [KNO_3 + KClO_4 + 2\ KOH + 5300\ H_2O] + H_2O(liq) \tag{2}$$

$$\Delta H = -198.78\ kj/mole$$
$$= -47.51\ kcal/mole.$$

From table 4 we have

(3) $KNO_3(c) + KClO_4(c) + [2\ KOH + 5300\ H_2O](soln) \longrightarrow [KNO_3 + KClO_4 + 2\ KOH + 5300\ H_2O](soln)$

$\Delta H = 86.98 \pm 0.07$ kj/mole

$= 20.79 \pm 0.02$ kcal/mole.

Combining equations (2) and (3) we obtain

(4) $NO_2ClO_4(c) + [2\ KOH + 5300\ H_2O](soln) \longrightarrow KNO_3(c) + KClO_4(c) + H_2O(liq)$

$\Delta H = -285.76 \pm 0.36$ kj/mole

$= -68.30 \pm 0.09$ kcal/mole.

If we take the following values for the heats of formation of the other substances in the reaction [7]

Substance	$\Delta Hf^\circ_{298.15}$
$KClO_4(c)$	-103.45 kcal
$KNO_3(c)$	-118.12 kcal
$H_2O(liq)$	-68.314 kcal
$KOH \cdot 2650\ H_2O$	-115.23 kcal

we compute for $NO_2ClO_4(c)$

$\Delta Hf^\circ_{298.15} = 37.15 \pm 1.0$ kj/mole

$= 8.88 \pm 0.25$ kcal/mole.

6. Discussion

Cordes and Fetter [8] measured the heat of reaction of $NO_2ClO_4(c)$ with water and reported a value for the heat of formation of $NO_2ClO_4(c)$ of 8.0 ±0.4 kcal/mole. Recalculating their data with the more recent auxiliary heats of formation used for this work, their value becomes 8.7 ±0.4 kcal/mole, in excellent agreement with our results.

7. References

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Table 1.

Electrical Calibrations of the NO_2ClO_4 System

Expt. No.	ΔRc	Ee	Es
	Ohm	j	j/ohm
1	0.094266	1990.86	21,119.6
2	.097337	2053.87	21,100.6
3	.096767	2042.58	21,108.2
5	.096023	2026.13	21,100.5
6	.095990	2025.34	21,105.6
	Mean		21,106.6
	Standard deviation of the mean		±7.6

Table 2.

Electrical Calibration on $KNO_3/KClO_4$ System

Expt. No.	ΔRc	Ee	Es
	Ohm	j	j/ohm
10	0.092808	1962.35	21,144.1
11	0.085947	1817.33	21,144.8
12	0.095268	2013.70	21,137.2
13	0.093441	1975.56	21,142.3
	Mean		21,142.1
	Standard deviation of the mean		±3.4

Table 3.

Results of the Experiments on the Hydrolysis of NO_2ClO_4

Expt. No.	Δe	ΔR_c	q(dil)	q	weighed NO_2ClO_4	titrated NO_2ClO_4	$\frac{NO_2ClO_4(t)}{NO_2ClO_4(w)}$	$-\Delta H$
	j	ohm	j	j	mole	mole	%	kj/mole
1*	-13.6	0.023575	0.84	498.09	0.0024629	0.00238$^+$	96.7	202.24
2	-10.1	0.042890	0.15	904.94	0.0045364	0.004546	100.2	199.48
3*	-10.2	0.041598	0.15	877.68	0.0044650	0.004434	99.4	196.57
4	-9.7	0.049401	0.00	1042.16	0.0052450	0.005253	100.2	198.69
5	-7.0	0.063000	-0.53	1328.69	0.0066728	0.006603	99.0	199.12
6	-7.7	0.059705	-0.38	1259.28	0.0063211	0.006246	98.8	199.22
7	-9.9	0.046153	-0.04	973.59	0.0049043	0.004901	100.0	198.52
					Mean			199.01
					Standard deviation of the mean			±0.35

*Not included in mean value

$^+$methyl orange end point

Table 4.

Results of the Experiments on the Solution of KNO_3 and $KClO_4$

Expt. No.	Δe	$-\Delta R_c$	KNO_3	$KClO_4$	q_{KNO_3}	q	ΔH
	j	Ohm	mole	mole	j	j	kj/mole
1	-0.47	0.020236	0.0048956	0.0049288	-1.16	428.98	87.03
2	-1.43	0.020453	0.0049324	0.0049920	-2.09	434.48	87.04
3	-1.54	0.020401	0.0049127	0.0049985	-3.00	434.29	86.88
4	-1.32	0.020485	0.0049677	0.0049943	-0.93	434.00	86.90
5	-1.36	0.020450	0.0049381	0.0049863	-1.69	434.02	87.04
			Mean				86.98
			Standard deviation of the mean				±0.07

Chapter A2

FLUORINE-BOMB CALORIMETRY
-- A SUMMARY OF WORK TO DATE

George T. Armstrong, E. S. Domalski, and K. L. Churney

The combustion of metals in fluorine in a bomb calorimeter was undertaken for this contract, with special consideration to be given to metals having relatively non-volatile fluorides. Techniques were developed elsewhere, principally at the Argonne National Laboratory and at the Fullmer Research Institute (England) for burning metals having relatively volatile fluorides. Aluminum was selected for the first material to be studied, to be followed by beryllium.

We found the combustion of aluminum in fluorine to be a process not easily carried out to completion when the free metal was burned either as a foil, shredded foil, fine machine turnings, lumps, or pellets of compressed powder. Spattering of partially burned material, residual unburned shreds, and congealed lumps of aluminum that had melted, were commonly found in the products of combustion of finely shredded or turned aluminum prepared into more or less loosely compacted bundles for burning. Densely compacted bundles, lumps, pellets of compressed powder, and unshredded foil were difficult or impossible to ignite. The difficulties were attributed at least in part to the high thermal conductivity and the relatively low melting point of aluminum. Since procedures have been developed elsewhere which overcome similar difficulties and lead to satisfactory combustion of unadulterated aluminum in oxygen, it is to be presumed that ultimately a satisfactory procedure can be developed for combustion in fluorine. However, in order to obtain heat measurements in the time available, a different approach was adopted.

An agglomeration that we found to burn to a satisfactory degree of completeness, to lead to readily characterizeable products, and to give reproducible heat measurements is a pellet compressed from a mixture of powdered teflon and powdered aluminum. The separation of the aluminum granules by the teflon reduces the thermal conductivity of the pellet to such an extent that it is readily ignited. The energy of combustion of the teflon apparently also sustains the temperature of the reacting materials until combustion is complete.

The further complication of burning a mass of material in fluorine is that the sample-container material may ignite or at least undergo appreciable surface oxidation if allowed to heat to a high temperature by the reaction. A monel or nickel disk, with a shallow recess in the center, which rests on the bottom of the bomb, was found in our experiments to provide a support for the sample allowing complete combustion of the pellet without itself participating in the reaction. This disk, having only moderately good thermal conductivity, loses heat rapidly enough to the bomb to avoid an intolerable temperature rise, without cooling the sample so much as to quench the reaction.

Measurements that we made on the combustion of aluminum-teflon mixtures and of teflon alone have permitted the calculation of the heat of formation of aluminum fluoride. A small discrepancy (0.2 to 0.3 percent) in the energy equivalent of the calorimeter as determined by two different methods precludes further discussion at this time of the actual values found. It is clear, however, that the value that will be derived from the measurements will not differ greatly from values reported by Gross, et al. [1] and by Kolesov, et al. [2].

A full discussion of the experimental measurements, the results, and their relation to other reported measurements will be presented in a later report.

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Chapter A3

ALUMINUM CARBIDE: HIGH-TEMPERATURE THERMODYNAMIC FUNCTIONS BASED ON RECENT MEASUREMENTS OF HEAT CAPACITY AT THE NATIONAL BUREAU OF STANDARDS

Andrew C. Victor, Willis R. Thurber, and Thomas B. Douglas

There is only one well-established solid phase in the $A\ell$-C system, corresponding to the compound $A\ell_4C_3$. No low-temperature heat-capacity data have been found in the literature, but Sato [1] made measurements from 273° to 594°K which Kelley [2] represented by an equation giving a linear variation of heat capacity with temperature in this range. On the basis of an estimated value of $S^\circ_{298} = 25.0 \pm 3$ e.u. (partly on the basis of high-temperature equilibria) and a smooth estimated heat-capacity curve passing thru Sato's data, approximate thermodynamic functions were computed for the range 298°-3000°K and were included in earlier NBS reports of the present series [3,4].

Recently, the heat capacity of an aluminum carbide sample has been measured precisely at the National Bureau of Standards as part of the current program. The measurements at low temperatures are not quite complete, but those from 273° to 1173°K have been finished and are given below. On the basis of these data and the above value of S°_{298}, a new table of the thermodynamic functions has been computed, and appears at the end of this report (Table B-59). The heat capacity in this new, more reliable table shows a maximum difference of -14% from Sato's values and an average difference from earlier tables [3,4] of -10% up to 3000°K. When the NBS low-temperature measurements are completed (probably within the next few months), it will be possible to join smoothly the heat-capacity curves in the low- and high-temperature regions and also to assign a much more definite value of entropy at 298.15°K. For these reasons the present table should be considered tentative, though the changes will probably be small above 400°K.

The sample of aluminum carbide measured at NBS was supplied by the Aluminum Company of America, ALCOA Research Laboratories, through the courtesy of George Long. It had been prepared by heating a stoichiometric mixture of aluminum powder and lampblack in an atmosphere of argon to 1800°C. Specimens of the original sample were analyzed at the National Bureau of Standards. The results by a qualitative spectrochemical method, obtained by the Spectrochemistry Section, are given in Table 1.

Table 1

Spectrochemical Analysis of Sample of $A\ell_4C_3$

Element	%	Element	%	Element	%
Ag	- (?)	Hf	-	Sb	-
$A\ell$	> 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	$T\ell$	-
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.

The chemical analyses were performed by Rolf A. Paulson of the NBS Applied Analytical Research Section. (The results for the small amount of Fe have not been completed and are not included below.) The sample was dissolved in hot acid solution and the evolved gases were burned. The CO_2 found was calculated to $A\ell_4C_3$, and the excess of H_2O over that attributable to CH_4 was calculated to free $A\ell$ (metal). The $A\ell N$ was calculated from a nitrogen analysis. The total aluminum was determined as $A\ell 2O3$, and the excess over that attributable to $A\ell_4C_3$, free $A\ell$, and $A\ell N$ was assumed to be $A\ell_2O_3$ in the original sample. The insoluble residue was weighed, and assumed to be free carbon in the original sample. The results of these chemical analyses on two separate specimens are given in Table 2.

Table 2

Chemical Analysis of Sample of Al_4C_3

Component	Specimen 1 (% by weight)	Specimen 2 (% by weight)
Al_4C_3	94.9	94.8
Free Al	1.2	1.3
Free C	0.9	0.7
AlN	1.4	1.3
Al_2O_3	2.0	2.0
Total	100.4	100.1

The results agree with the usual finding of about 95% Al_4C_3 in samples prepared by the same method [5]. The small discrepancies between the two analyses can be attributed to either uncertainties in the analytical methods or small inhomogeneities in the sample. The approximation to a total of 100% is some indication of the reliability of the analyses.[a]

The enthalpy data, corrected to ideal calorimetric conditions, were further corrected for the impurities according to Table 2 before the preparation of Tables 3 and B-59. The averages for Specimens 1 and 2 were assumed, and each percentage was then multiplied by a constant factor which would reduce their sum to exactly 100%. The corrections were applied additively by subtracting from the measured relative enthalpies the contributions by the impurities as given in their tables of thermodynamic functions in an earlier report [4], with corresponding adjustment of the sample mass. In particular, the elimination of the heat of fusion of the free aluminum present largely eliminated a small hump in the uncorrected enthalpies near the melting point of this element (932°K).

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[a] One possible cause of the fact that the analyses in Table 2 total slightly more than 100% is that a small amount of some aluminum carbide other than Al_4C_3 was present in the sample. All aluminum carbides derived from hydrocarbons other than CH_4 would be richer in carbon than Al_4C_3, and it may be shown that the presence of any of these would lead to too low, not too high, a total analysis as calculated. However, this would not be true in the case of a carbide such as Al_3C, whose existence Baur and Brunner [6] reported.

Although the precision of the enthalpy data indicates a standard deviation from the mean of only several tenths of one percent over most of the temperature range, there are irregularities in the mean heat capacities above 600°K which contribute an uncertainty of ±2% to the tabulated heat capacities in Table B-59. Corresponding uncertainties exist in the other thermal functions.

The enthalpy measurements were made by the "drop" method using a Bunsen ice calorimeter. In brief, the method, which has been described in a previous publication [7], is as follows. The samples, sealed in a container composed of the alloy 80% Ni-20% Cr, is suspended in a furnace until it comes to a constant, known temperature. It is then dropped, with nearly free fall, into a Bunsen ice calorimeter which measures the heat evolved by the sample plus container 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 temperature. The difference between the two values of heat is a measure of the enthalpy change of the sample between 273.15° and the temperature in the furnace. The measured enthalpy values, fully corrected, are given in Table 3.

Table 3

Enthalpy Measurements on Aluminum Carbide(a)

Furnace temp.,T	Relative Enthalpy ($H_T-H_{273.15}$)	
	individual measurement(b)	mean
°K	cal/mole	cal/mole
373.2	2913 2940 2963	2939
473.2	6281 6324 6310	6305
573.2	9992 9989 10020 9989 9988 9987	9994
673.2	13892 13875 13862	13876
773.2	17787 17800	17794
873.2	21895 21873	21884
973.2	25974 25985	25980
1073.2	30299 30277(c)	30288
1173.2	34578(c) 34506(c)	34542

(a) mol. wt. = 143.96g

(b) sample mass = 6.650g except for (c)

(c) sample mass = 6.647g

Because of the scatter of the mean heat capacities $[(C_p)_T$, or $\frac{H_{(T+50)} - H_{(T-50)}}{100}]$ about a smooth curve the authors felt that the data did not warrant a least-squares fit. The mean heat capacities were fitted to the smoothed curve, eq. (1),

$$C_p = 48.66 + 2.67\ (10^{-4})\ T - 6.461\ (10^3)\ T^{-1} \qquad (1)$$

at the temperatures 400, 700 and 1100°K. This equation fits the mean heat capacities with a maximum deviation of about ±2%. Between 350° and 650°K the fit is better than 1% at all temperatures. Above and below this range the agreement is poorer. At and above 723°K the poor quality of the fit is due to the scatter of data about the equation. At and below 350°, the equation seems to give values of heat capacity which are consistently a little too low.

The heat capacities in Table B-59 were obtained from eq. (1) between 400 and 3000°K. Below 400°, values passing through the data were used. These were adjusted to permit smooth joining with eq. (1) at 400°K. The remaining thermal functions were generated by a four-point numerical integration of the heat-capacity values.

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

Chapter A4

LOW-TEMPERATURE CALORIMETRY

George T. Furukawa

The low-temperature calorimetry phase of the program has been concerned with the heat-capacity measurements of substances of interest to the program in the range 15° to 400°K. This work is complemented by a systematic literature survey and data analysis. The data analysis is being performed using a high-speed digital computer. Recently the IBM 704 computer was replaced by the IBM 7090 computer. The data analysis has been interrupted pending the conversion of the analysis coldes for use with the new computer.

Empty and full container heat-capacity measurements on $LiA\ell H_4$ have been completed and the data are now undergoing analysis. At this time a chemical analysis of the sample is needed in order to make adjustments, if any, to the observed heat data.

The empty container measurements on LiH will be completed very soon. As soon as the chemical analysis is completed, thermal functions for this substance will be calculated. Recently V. N. Kostrukov [Zhurnal Fiz. Khim. <u>35</u>, 1759-1762 (1961)] reported heat-capacity measurements on LiH, of 99.8 percent purity based on hydrogen evolution. The value of S^o_{298} calculated from the data is given as 4.79 ±0.005 e.u. Kelley and King (U. S. Bureau of Mines Bulletin 592), using experimental data of limited temperature range, calculated $S^o_{298} = 5.9 \pm 0.5$ e.u. Our measurements on LiH have not progressed sufficiently to make any comparison with the above values of S^o_{298}.

Sample-plus-container heat-capacity measurements have been completed on $A\ell_4C_3$ and the measurements on the empty container are in progress. No unusual effects in the heat capacity has been observed. The chemical analysis on the sample indicates the $A\ell_4C_3$ content to be 94.8 percent. Therefore the observed heat data are expected to require a relatively large adjustment.

A sample of Be_3N_2 of about 97 percent purity has been obtained. Heat measurements on Be_3N_2 will be started as soon as the measurements on LiH are completed. Preparations are being made, also, to synthesize BeC_2 by heating a stoichiometric mixture of high-purity Be metal powder and carbon black in the range 1000° to 1200°C in argon atmosphere or in vacuum.

An exploratory preparation of chrysoberyl, $A\ell_2O_3 \cdot BeO$, was made by another group at the Bureau. A stoichiometric mixture compressed into a pellet was heated for about 1 hour at 1800°C. A petrographic of the chrysoberyl crystallites indicated about 20 percent of what appears to be voids. Sintered samples of BeO from another source were also found to contain similar voids. Efforts will be made to prepare chrysoberyl by melting. A suitable container material is being investigated.

A survey of the literature has been made of the heat-capacity data on Binary metal oxides of Li, Be, Mg, Aℓ, Si, K, Ti, and Zr. Results of this survey are given in another chapter of this report.

Chapter A5

A FAST-OPENING, LARGE-APERTURE SHUTTER FOR HIGH-SPEED PHOTOGRAPHY

by E. C. Cassidy and D. H. Tsai

Abstract

This shutter consists essentially of a metallic foil in a capacitor discharge circuit. The opening action is obtained when the foil is compressed by the electromagnetic forces which accompany the heavy surge current through the circuit, during a transient discharge. A shutter made up of two foils in a loop arrangement may be opened to an area 1 in. x 3 in. in less than 45μ sec. The factors affecting the design and operation of this shutter are analysed. These factors include the circuit parameters, the energy input to the foil, and the materials and the size of the foil. Some experimental results are also given.

Introduction

This paper describes a fast-opening, large-aperture, high-transmittance shutter for high-speed photography. The shutter consists of a piece of metallic foil clamped between two electrodes in a capacitor discharge circuit. The foil is placed in front of a camera so that the camera lens is completely covered. When a heavy current is passed through the foil during the discharge of the capacitor, each current filament in the foil reacts with the magnetic field set up by the other current filaments. The direction of the force is such that the filaments are drawn together[1]. As a result, the edges of the foil are compressed toward the center filament, and the fast-opening action is achieved.

An improved arrangement consists of two foils mounted side by side in the same plane (but insulated from each other along their common edge) and clamped to a common conductor at the top and to two electrodes at the bottom. The foils thus form the two arms of a loop circuit. When current is passed through the foils, each foil is compressed by the electromagnetic forces described above, but in addition, each foil is repelled by the other because they carry current in opposite directions[1]. The opening action is therefore faster.

Typically, a shutter with foils in a loop arrangement opens to an area 1 in. x 3 in. in less than 45μ sec. In conjunction with a high-speed camera and a suitable closing shutter[2], this shutter may be used to observe a high-speed event with full control of the timing and duration of the exposure.

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[1] F. W. Sears, Electricity and Magnetism (Addison-Wesley Press, Inc., Cambridge, Massachusetts, 1951), p. 267.

[2] For examples, see H. E. Edgerton and F. I. Strabola, Rev. Sci. Instr. 27, 162 (1956).

Experiments

Experiments have been made to test the performance of several shutters of both the single- and the looped-foil type with foils of different materials and dimensions. Fig. 1 shows the experimental setup with a looped-foil shutter. In this model, the foils were mounted on opposite sides of a thin piece of transparent plastic. The foils overlapped slightly in order to prevent the passage of light at the center. The plastic piece served to support the clamps at the top and the bottom, and to insulate the two bottom clamps (and the foils) from one another. The clamps were made rather massive in order to reduce distortion when tightened, and to provide good electrical contact with the foils.

The shutter assembly was installed in series with a high-voltage capacitor and a spark gap which served as a switch[3]. The capacitor was charged by means of a power supply. The spark gap was fired by means of a thyratron trigger circuit which supplied a high-voltage pulse to break down the spark gap. With this setup, the timing of the discharge could be controlled to within 1 μsec. The motion of the foils due to the discharge was observed by means of a high-speed framing camera, focussed on the foils.

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[3] E. H. Cullington, W. G. Chace and R. L. Morgan, "Lovotron - a low voltage triggered gap switch", Instrumentation for Geophysical Research No. 5, AFCRC-TR-55-227, September, 1955.

Figs. 2a and 2b show a single-foil shutter before and after the passage of current. With an aluminum foil, 1 in. x 3 in. x 0.0005 in. thick, it was found that the width could be compressed from 1 in. to 1/8 in. in about 100 µsec, under favorable conditions.

Fig. 3 is a portion of a framing camera record which shows the opening action of a looped-foil shutter. The foils were two aluminum foils, 1 in. x 3 in. x 0.001 in. thick each. This particular shutter opened to a width of 1 in. in about 50 µsec.

Results and Discussion

The force on a foil filament of thickness h, width δx, and of unit length, due to current in the other filaments of the foil, may be expressed as:

$$F = \frac{\mu h^2 i^2}{2\pi} \delta x f(x), \tag{1}$$

where

F = force on the foil filament in the plane of the foil,

i = current density in the foil, assumed to be uniform over the width of the foil,

μ = permeability of the medium surrounding the foil filament.

The function $f(x)$ depends on the geometry of the foil, e.g., whether the foil is plane or locally buckled in the process of crumpling. $f(x)$ thus describes the distribution of the force F over the width of the foil, x being measured from a reference position, say from one edge of the foil. As an example, for a single foil of width x_0, thickness h, and unit length, and carrying a current of density i, f(x) has the following form when the foil is plane:

$$f(x) = \ln\left(\frac{x_0 - x}{x}\right) . \tag{2}$$

As the foil crinkles, the form of f(x), of course, will change.

The force F acting on each filament during the discharge is the force which drives the filament toward the center and causes the foil to collapse. The motion of each filament is controlled by the magnitude and the duration of the force F as well as by the mass of the filament, its acceleration, and the forces from the two neighboring (adjacent) filaments. The latter forces are related to what may be called the "stiffness" (or force per unit deflection) of the foil, and may be expressed as

$$\text{stiffness} = KEI, \tag{3}$$

where E is the modulus of elasticity of the material, I is the moment of inertia of the foil with cross-sectional area h for unit length of the foil, and K is some factor related to the mode of buckling of the foil.

The actual solution to the equation of motion for the foil involves rather serious difficulties: for instance, the current in the foil is generally not known, the force F depends on both f(x) and i which are functions of time, the modulus of elasticity E may change due to plastic flow and temperature change, the mode of buckling is not known so that the value of K cannot be fixed, and so on.

The detailed analyses of these problems have not been performed in the present investigation. In the following paragraphs, the qualitative effects of some of the design and operating parameters on the opening speed of the shutter are briefly discussed, and some typical results are presented in support of the discussion.

Optimum Energy Input - The impulse due to force F on the foil filament (cross-sectional area h x δx and unit length) is:

$$\int F dt = \frac{\mu h^2 \delta x}{2\pi} \int i^2 f(x) dt. \tag{4}$$

This is directly related to the electrical energy input e to the foil filament as follows:

$$e = \int R(h\delta x)^2 i^2 dt = \frac{2\pi R \delta x}{\mu \bar{f}(x)} \int F dt = \frac{2\pi\sigma}{\mu \bar{f}(x) h} \int F dt \tag{5}$$

where R is the resistance and σ is resistivity of the filament, and $\bar{f}(x)$ is an averaged value of f(x). In order to obtain a prescribed aperture in the shortest time, the impulse and hence e should be as high as possible. However, the optimum value of e is limited by two considerations: first, e must not be so high as to cause combustion of the foil filament, because the flash from the combustion which is sometimes accompanied by an arc discharge would expose the film, and second, e and hence the impulse or F must not be so high as to cause excessive stresses in the foil, because this could shatter the foil and interrupt the current path, and consequently reduce the force on the filaments. These considerations impose an upper limit to the energy input to a foil.

The optimum energy input depends primarily on the thermochemical and the mechanical (stress-strain relationship) properties of the foil material. For a given material the optimum energy level may be obtained by a trial-and-error method, by adjustment of the initial energy stored in the capacitor. Experience has shown that for a given material the optimum energy (initial stored energy) per unit mass of foil remained approximately constant. Of the three materials tested, copper, aluminum, and monel, it was found that copper and aluminum foils were limited by burning, whereas monel was limited by shattering.

Effect of Circuit Parameters - The capacitance C, resistance R, and inductance L of the circuit affect the current as well as the duration of the discharge. These parameters therefore affect the impulse to the foil and the distribution of the impulse during the discharge. The problem of obtaining the optimum distribution of the impulse is difficult, because the foil is usually in motion during the discharge, so that the force F is affected not only by the changing current but also by the function f(x) in equation (1) as the foil is deformed. Inasmuch as the equation of motion of the foil has not been solved, only a qualitative discussion of the effects of C, R, and L can be given here.

The energy input e to the foil filament in equation (5) may be written as

$$e = a \frac{\delta x}{x_0} (\tfrac{1}{2}CV_0^2),$$

where V_0 is the initial voltage to which the capacitance C is charged, $\frac{1}{2} CV_0^2$ is the initial stored energy in the capacitor, a is the fraction of the stored energy absorbed by the foil (of width x_0), and δx is the width of the filament. Then one may write,

$$\int F dt = \frac{a}{Rx_0} \frac{\mu \bar{f}(x)}{2\pi} (\tfrac{1}{2}CV_0^2).$$

$$= \frac{ah\delta x}{x_0 \sigma} \frac{\mu \bar{f}(x)}{2\pi} (\tfrac{1}{2}CV_0^2). \qquad (6)$$

With a fixed (optimum) energy input to the filament, $\frac{1}{2}CV_0^2$ is also fixed; therefore the impulse delivered to the foil filament is inversely proportional to R, the resistance of the filament, but is independent of C and L, other things being equal.

Curves 1 and 2 in Fig. 4 show the effect of capacitance C on the opening of the shutter with two copper foils in a loop arrangement. These curves were obtained from the framing camera records of the shutter, and show approximately the average distance between the inner edges of the two foils as a function of time. The origin was obtained by extrapolating the curve to zero opening. The dimensions of the foils and other data are given in the caption of the figure. The initial stored energies were very nearly the same for both shutters, but from the appearance of the crumpled foils, it seemed that the energy input to the foils of curve 1 was slightly below the optimum value. With this point taken into consideration, one sees that the change in C had essentially no effect on the opening of the shutter.

The resistance R in the shutter circuit is mainly that of the foils. If the size of the foils is kept the same, then the resistance can be changed only by changing the material (or the resistivity σ) of the foil. This, in general, involves a change in the optimum energy input and in the mass (density) of the foil. Under these conditions, the effect of σ is most readily seen from equation (6), as follows:

$$\int F dt \sim mu \sim \rho u \sim \frac{\frac{1}{2}CV_0^2}{\sigma} \qquad (7)$$

where m is the mass and ρ the density of the foil, u is the velocity, and mu the momentum of the filament due to the impulse. (mu is not equal to $\int F dt$ because the other forces from the neighboring filaments, stiffness, etc., not shown here, also must be taken into account.) From equation (7), one can write for two different materials with subscripts 1 and 2:

$$\frac{u_1}{u_2} = \frac{(\text{energy input})_1}{(\text{energy input})_2} \; \frac{\rho_2 \sigma_2}{\rho_1 \sigma_1}$$

Curves 1 and 3 in Fig. 4 compare ~~with~~ the opening of two shutters, one with copper foils (curve 1) and one with aluminum foils (curve 3), the other conditions are as indicated in the figure caption. For the copper foils, the initial stored energy was 923 joules, the density was 8.9 g/cm^3, and the resistivity was 1.8 x 10^{-6} ohm-cm; for the aluminum foils, these values were 528, 2.7, and 2.8 x 10^{-6}, respectively. Hence,

$$\frac{u_{\text{copper}}}{u_{\text{aluminum}}} = \frac{923}{580} \times \frac{2.7}{8.9} \times \frac{2.8}{1.8} = 0.75. \tag{9}$$

One would therefore conclude that the shutter with copper foils would open more slowly than the shutter with aluminum foils. This is in agreement with the experimental results.

The inductance L of the circuit is determined primarily by the geometry of the circuit, and is not easily adjustable in an actual experiment. The effect of L was therefore not specifically investigated. Generally speaking, a low inductance results in high peak current, and a short duration of discharge, and a high inductance has the opposite effects. If the inductance should be too low, and the peak current too high, the compressive force and the mechanical stresses in the foil migh become excessive and cause shattering of the foil. On the other hand, if the inductance should be too high and the current too low, the duration of the discharge would be long and the opening of the shutter would be slow. The optimum inductance clearly lies between these extremes.

Effect of Size of the Foil - The length of the foil may be considered as fixed by the size of the camera aperture, and was not specifically investigated here. The effects of the width and thickness of the foil may be discussed by examining their influence on the driving force, the mass of the foil filament and the stiffness of the foil.

With the optimum energy input to a foil of a given width, the integral $\int i^2 f(x)dt$ in equation (4) is fixed, therefore the impulse (and the force F) on the foil filament is proportional to h^2. The mass of the filament is directly proportional to h. The stiffness of the foil (per unit length) before buckling is a function of the moment of inertia of the cross-sectional area, and is proportional to h^3. After buckling, the stiffness is greatly reduced, through a change in the value K in equation (3). From the foregoing considerations, one may state that if the force F in equation (1) is sufficient to cause the foil to buckle, then the shutter with foils of larger h would have a higher velocity, because the impulse increases faster than the mass of the filament, and the stiffness does not offer much resistance after the foil buckles. On the other hand, with further increase in h, the stiffness would soon exceed the force F required to buckle the foil, and the foil would not collapse at all.

Curves 3 and 4 in Fig. 4 show the opening of two shutters with aluminum foils of thickness 0.001 in. and 0.0005 in., respectively. The results show that thicker foil, curve 3, opened faster than the thinner foil, curve 4, in agreement with the above conclusion. Curves 3 and 5 show the effect of stiffness on the opening of the shutter. The foils for curve 5 were double thicknesses of 0.0005 in. foils, so that the total thickness was the same as that for curve 3, but the stiffness was lower. The results show that curve 5 initially opened faster than curve 3, apparently because of the lower stiffness for curve 5. Later, curve 5 slowed down more rapidly than did curve 3, but the reason for this is not clear.

If the width of the foil, x_0, alone is changed, f(x) and hence F are affected, but the mass of each foil filament and the stiffness of the foil are unaffected, because the foil thickness is not changed, and because the buckling of the foil is essentially local, as shown by experimental results. f(x) is usually a logarithmic function, equation (2). If x_0 is increased, f(x) generally becomes larger also, and therefore F and the opening speed of the shutter both become larger. Another advantage of a wider x_0 is that as the edge of the foil is torn from the clamping electrodes in the process of opening, the interruption of the current path at the edge is less significant for a wider foil. The maximum value of x_0 is limited by the stored energy available, and by the consideration that f(x) is of the logarithmic type, so that as x_0 becomes larger, the increase in f(x) becomes slower.

Curves 4, 6 and 7 show the effect of foils of three widths, 1 in., 1.5 in., and 2 in., respectively, on the opening of the shutter. The results show that the highest opening speed was obtained with the widest foil. With this foil, the inner edges attained an initial speed of 1.75×10^4 in./sec, and the shutter opened to a width of 1 in. in less than 45 μsec.

Captions for Illustrations

1. Experimental Setup with a Looped-Foil Shutter.

2. A Single Foil Shutter before Discharge (a), after Discharge (b).

3. Opening Action of a Looped-Foil Shutter (20 μsec between frames).

4. Width of Opening versus Time of a Looped-Foil Shutter as Affected by the Capacitance and Resistance of the Circuit and by the Dimensions of the Foil.

Curve	Material	Width (in.)	Thickness (in.)	Capacitance (μfarad)	Stored Energy (joules)
1	Copper	1	0.001	15	924
2	Copper	1	0.001	30	920
3	Aluminum	1	0.001	15	580
4	Aluminum	1	0.0005	15	298
5	Aluminum	1	0.001[a]	15	595
6	Aluminum	1.5	0.0005	15	450
7	Aluminum	2	0.0005	15	580

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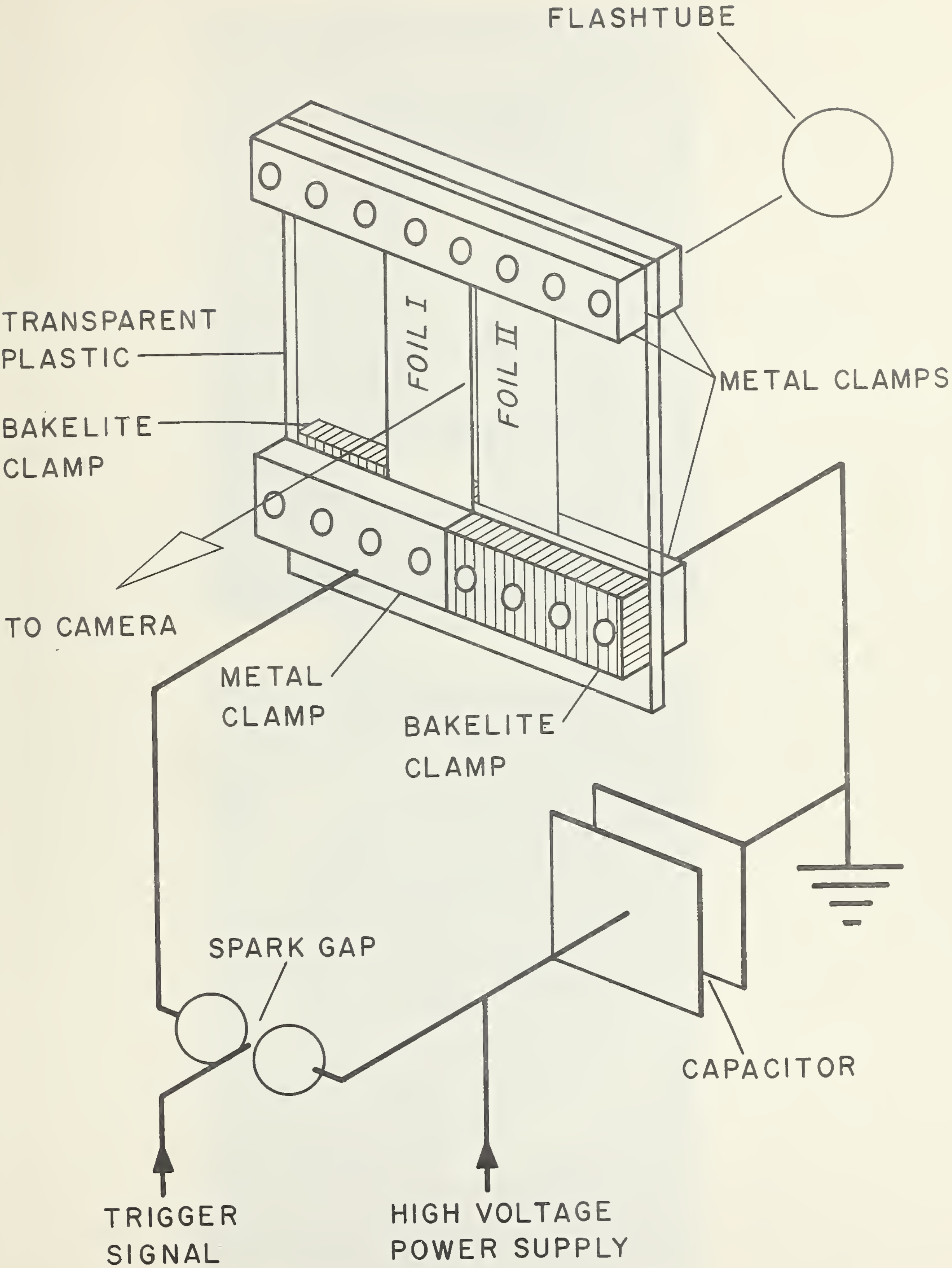
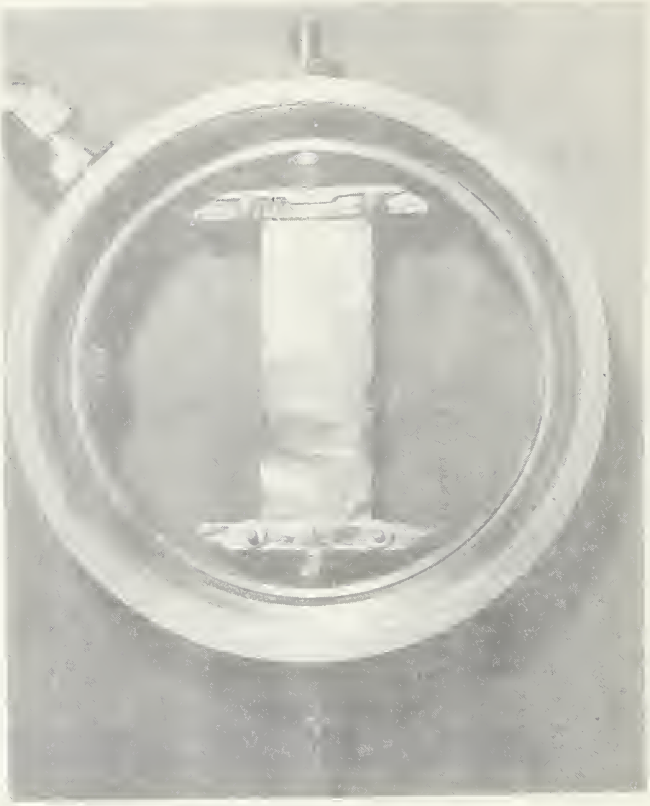
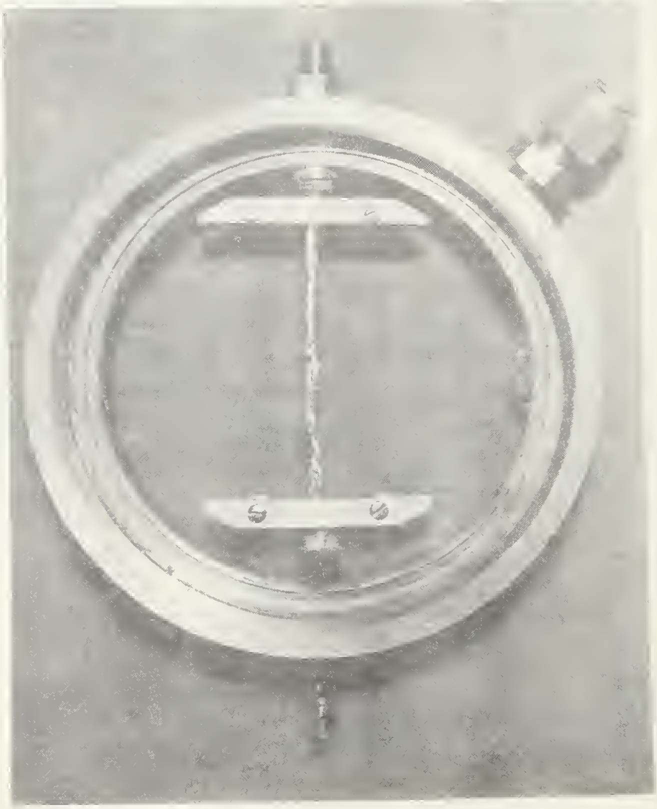
[a] With two thicknesses of 0.0005 in. foils.

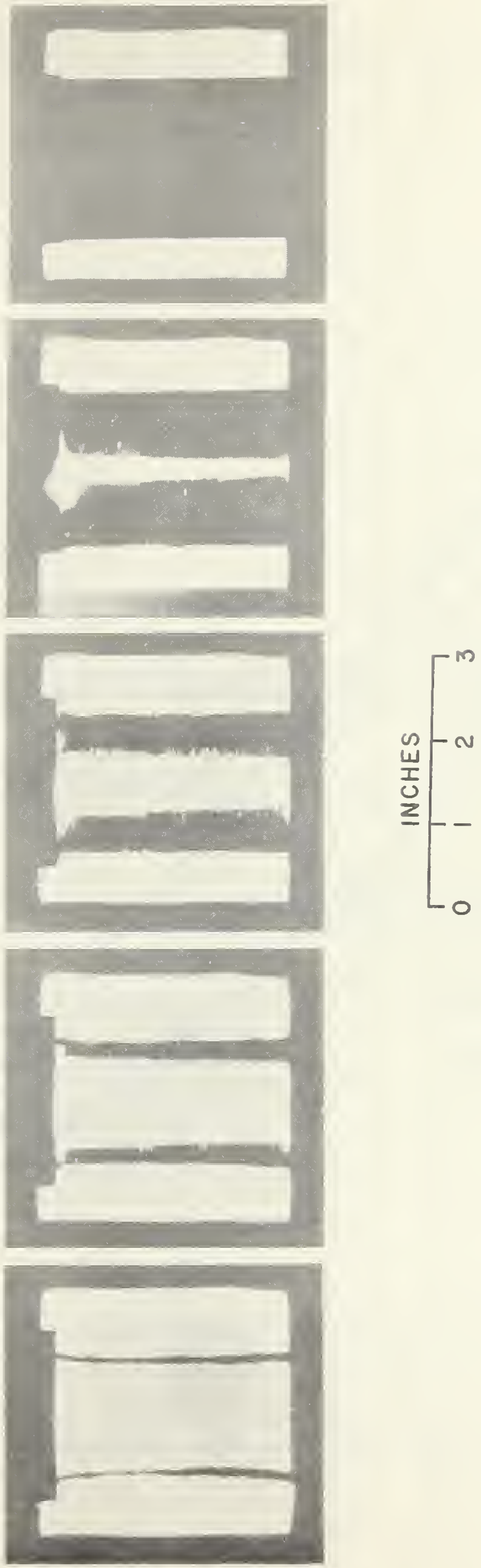

FLASHTUBE
TRANSPARENT PLASTIC
METAL CLAMPS
FOIL I
FOIL II
BAKELITE CLAMP
TO CAMERA
METAL CLAMP
BAKELITE CLAMP
CAPACITOR
SPARK GAP
TRIGGER SIGNAL
HIGH VOLTAGE POWER SUPPLY

(a)



(b)





INCHES
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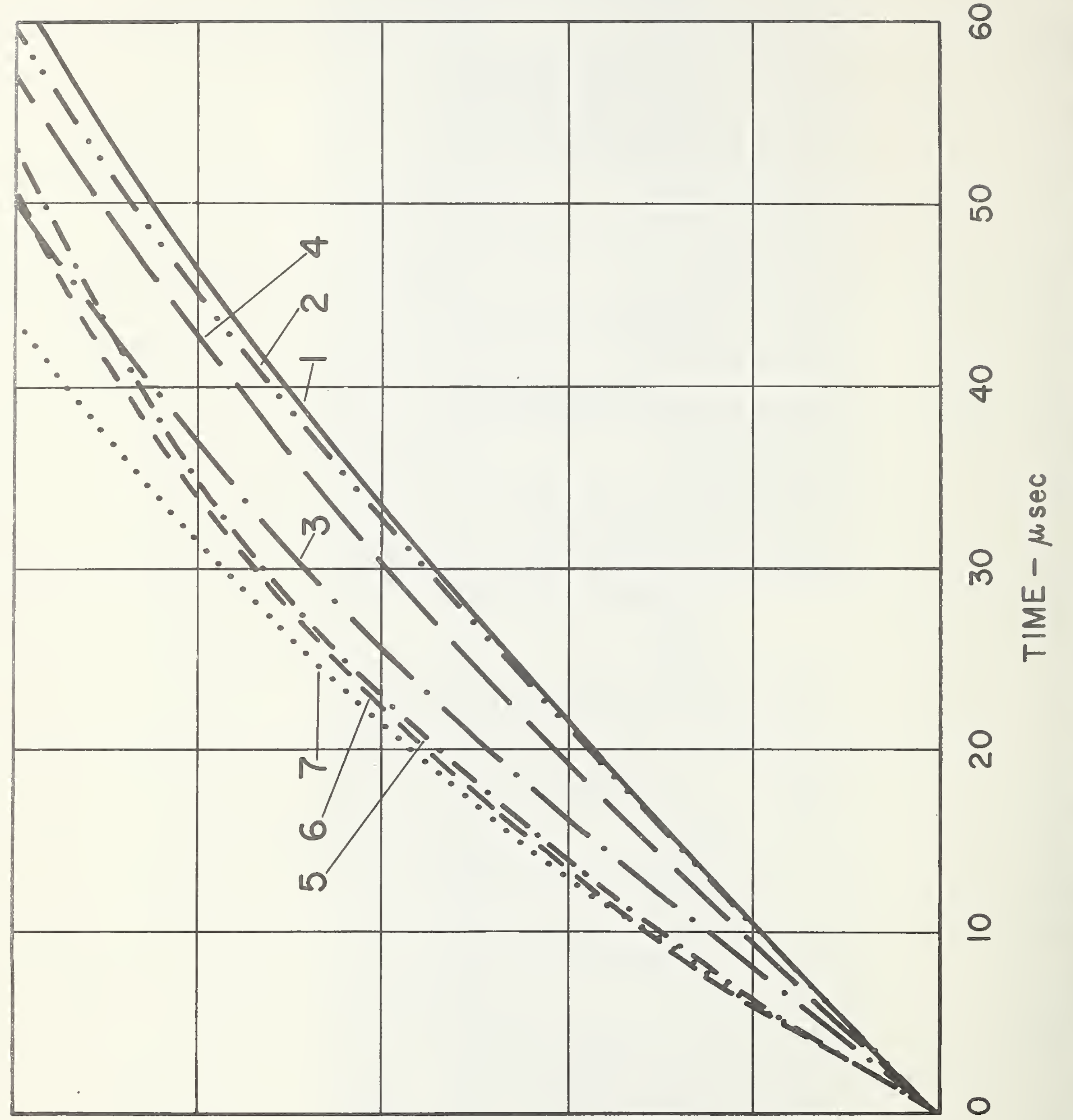
1
2
3


WIDTH OF OPENING – in.
1.0
0.8
0.6
0.4
0.2
0
TIME – μsec
0
10
20
30
40
50
60
1
2
3
4
5
6
7

PART B

RECENT LITERATURE SURVEYS

Chapter B1

RECENT ADDITIONS TO THE LITERATURE ON THE CHEMISTRY OF THE LIGHT ELEMENTS

Leslie A. Krieger and George T. Armstrong

The following articles, classified by element, have appeared in the literature since the last listing of new literature (NBS Report No. 7093).

A. Aluminum Compounds

1. Vapor pressures of cryolitic electrolytes-structure of cryolitic baths as to solids formed and with regard to liquid in equilibrium with the vapor phase. C.A.55, 4127f (1961). A. Vajna and R. Bacchiega, Met. ital. 52, 481-94 (1960).

   Measurements of vapor pressures and of chemical compositions and molecular weights of the vapors of a series of molten mixtures of $A\ell F_3$ and NaF are reported.

2. Effective ionic radii in aqueous solution. C.A.55, 4132c (1961). B. Jakuszewski and S. Taniewska-Osnska. Zeszyty Nauk Uniw. Lodz., Nauki Mat. Przyrod. Ser. II, No. 6, 101-6 (1959).

   Total free energies of solvation of salts such as alkali halides and Be, Mg, and Aℓ chlorides are correlated with an empirical equation.

3. Ionic structure of fused pure cryolite. II. Experimental determination of the binary diagram for cryolite-$A\ell F_3$. C.A.55, 1166i (1961). M. Rolin. Bull. soc. chim. France 1960, 671-7. III. Incompatibility of the different schemes of possible dissociation (save one) with the experimental diagram. Ibid. 677-81. IV. Compatibility of the scheme: $A\ell F_6 \equiv \rightleftharpoons A\ell F_4^- + 2F^-$ with experimental diagram. Ibid. 681-5. See also C.A.55, 7014e (1961).

   The true melting point of pure cryolite is 1009°.

4. Vector hardness properties of boron and aluminum borides. C.A.55, 8233g (1961). A. A. Giardini, J. A. Kohn, L. Toman, and D. W. Eckart. Boron Synthesis, Structure, Properties, Proc. Conf. Asbury Park, N. J., 1959, 140-58 (Pub. 1960).

   Melting points (±50°) were measured as follows:

$A\ell B_2$	1655°	α-$A\ell B_{12}$	2163°
$A\ell B_{10}$	2423°	β-$A\ell B_{12}$	2214°

5. Physicochemical principles of vacuum casting. C.A.55, 12214d (1961), T. F. Fedorov and F. I. Shamrai. Primenenie Vakuuma v Met., Akad. Nauk S.S.S.R., Inst. Met. im. A. A. Baikova 1960, 137-42.

   The equilibrium vapor pressure of Li was measured for the reaction: $3Li_2O \cdot A\ell_2O_3 + 2A\ell(\ell) = 6\ Li(g) + 4A\ell_2O_3$. A ΔH reac. of 27 kcal $mole^{-1}$ and ΔS of 48.5 cal. $mole^{-1}$ deg^{-1} were calculated.

6. Aluminum monofluoride (AℓF). C.A.55, 17326g (1961). S. A. Semenkovich, Trudy, Vsesoyuz. Alyumin.-Magnievyi Inst. 1960, No. 44, 113-19.

   The equilibrium pressure (850-1200°) of AℓF was measured for the reaction: $2A\ell(\ell) + A\ell F_3(s) \rightleftarrows 3A\ell F(g)$. ΔHf°_{298} AℓF(g) determined during experiment is 50.9 kcal. $mole^{-1}$.

7. Hydrazoic acid and the metal azides. C.A.55, 15203h (1961). H. Rosenwasser, U. S. Dept. Comm., Office Tech. Serv., PB Report 144 106, 71 pp. (1958).

   A review of material published since 1934 on the thermochemistry (and other prop.) of the azides of Aℓ, B, Be, Li, Mg, Na and other elements.

8. Thermodynamic properties of aluminum nitride. C.A.55, 18510c (1961). A. D. Mah, E. G. King, W. W. Weller, and A. U. Christensen. U. S. Bur. Mines, Rept. Invest. No. 5716, 8 pp. (1961).

   The high temperature dissociation is discussed.

9. Rate of vaporization of refractory substances. C.A.55, 19393d (1961). R. F. Walker, J. Efimenko, and N. L. Lofgren, Planetary Space Sci. 3, 24-30 (1961).

   The vaporization of $A\ell_2O_3$ (1493-1614°K) was studied by Langmuir evaporation technique and the vapor pressure of AℓO was estimated. Transpiration experiments were carried out on liquid $A\ell_2O_3$ at 2055°C in the presence of H_2O. AℓOH may have been formed.

10. Vapor pressure and velocity of evaporation of some refractory compounds in vacuum at high temperature. C.A.55, 19660g (1961). A. S. Bolgar, T. S. Verkhoglyadova, and G. V. Samsonov. Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk, Met. i Toplivo 1961, No. 1 142-5.

    Vapor pressures and heats of evaporation were determined for:

    $A\ell B_{12}$
    ZrB_2
    ZrC
    TiC
    TiN
    TiB_2

    and other borides, carbides and nitrides.

11. Heats and free energies of formation of gibbsite, kaolinite, halloysite and dickite. C.A.55, 25448e (1961). R. Barany and K. K. Kelley. U. S. Bur. Mines, Rept. Invest. No. 5825, 13 pp. (1961).

The heat of formation of α-$A\ell_2O_3 \cdot 3H_2O$ was determined by HF solution calorimetry.

12. Thermodynamic considerations in the aluminum-producing electrolyte. W. B. Frank. J. Phys. Chem. 65, 2081-87 (1961).

Thermochemical data are reviewed and the following equilibria are discussed:

$$Na_3A\ell F_6(\ell) = NaF(\ell) + NaA\ell F_4(\ell)$$

$$2Na_3A\ell F_6(\ell) + 2A\ell_2O_3(s) = 3NaA\ell O_2(\ell) + 3NaA\ell F_4(\ell)$$

Thermodynamic values for $Na_3A\ell F_6$, $A\ell F_3$, and NaF appearing in the literature are corrected for an apparent error in temperature measurement.

13. (The heat of formation of aluminum fluoride.) V. P. Kolesov, A. M. Martinov, and S. M. Skuratov. Bull. Chem. Thermodynamics No. 4, 26 (1961).

For the reaction, $2A\ell + 3PbF_2 = 2A\ell F_3 + 3Pb$, $\Delta H° = -117.7 \pm 0.6$ kcal mole^{-1} was measured, leading to ΔHf^o_{298} $A\ell F_3(c) = -357.0 \pm 2$ kcal. mole^{-1}.

14. An experimental program for obtaining the thermodynamic properties of propellant combustion products. Final report. D. L. Hildenbrand and L. P. Theard, Ford Motor Co., Newport Beach, Calif., Publication No. U-1274, June 15, 1961.

The vapor pressures were measured and ΔH sub. calcd. for $LiA\ell F_4(c)$, $A\ell F_3(c)$, $ZrF_4(c)$. From the measurements the following were reported (in kcal/mole).

$$\Delta Hf^o_{298}\ A\ell F_3(g) = -285.3 \pm 2$$

$$\Delta Hf^o_{298}\ ZrF_4(g) = -401.1 \pm 3$$

$$\Delta Hf^o_{298}\ LiA\ell F_4(g) = -447 \pm 7 \text{ (estimated)}$$

$$\Delta Hf^o_{298}\ LiA\ell F_4(c) = -512 \pm 5 \text{ (estimated)}$$

Dissociation measurements on $A\ell N(c)$ indicated a heat of formation of about -73 kcal mole^{-1}. Vaporization studies on Mg_3N_2 and on B_2O_3 - MgF_2 mixture are also discussed. OBF and $(OBF)_3$ were identified in the latter studies.

15. Dissociation energies of diatomic molecules. C.A. 55, 16126i (1961). G. R. Somayojulu, J. Chem. Phys. 33, 1541-53 (1960).

Dissociation energies have been calculated for the following molecules and many others:

$A\ell F$	BF	LiF	NaF	BeH	MgH	N_2	F_2	HF
$A\ell C\ell$	$BC\ell$	$LiC\ell$	$NaC\ell$	BeO	MgO	NO	$C\ell_2$	$HC\ell$
$A\ell H$	BH	LiH	NaH			CO	$FC\ell$	NH
		Li_2						CH

16. See reference D. 13, Koehler, et al., $NaA\ell O_2$, $LiA\ell O_2$, $MgA\ell_2O_4$.

17. See reference D. 20, Matlow, $A\ell_2$.

18. See reference E. 4, Grjotheim, et al., $MgA\ell_2O_4$.

19. See reference E. 5, Toguri, $A\ell$-MgO.

20. See reference F. 5, Sokolov and Belyaev, $Na_3A\ell F_6$.

B. Boron Compounds

1. Heterogeneous reactions studied by mass spectrometry. I. Reaction of $B_2O_3(s)$ with $H_2O(g)$. C.A. 55, 4123h (1961). D. J. Meschi, W. A. Chupka, and J. Berkowitz. J. Chem. Phys. 33, 530-3 (1960).

   The equilibrium $\frac{1}{2}B_2O_3(s) + \frac{1}{2}H_2O(g) = HBO_2(g)$ was studied at 1060-1450°K. ΔH_o^o was calcd. to be 47.6 kcal mole^{-1} for the reaction. The heat of formation of $(HBO_2)_3$ was estimated to be -540 kcal mole^{-1}.

2. Degree of dissociation and partial vapor pressure of the oxides of lithium, beryllium, boron, silicon, and lead. C.A. 55, 6086b (1961). L. P. Firsova and A. N. Nesmeyanov. Zhur. Fiz. Khim. 34, 2615-16 (1960).

3. Vapor pressure of lithium, beryllium, boron, silicon, and lead oxides. C.A. 55, 13968f (1961). A. N. Nesmeyanov and L. P. Firsova. Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk, Met. i Toplivo 1959, No. 3, 150-1.

   Vapor pressures were measured by the effusion method in the following temp. ranges.

   B_2O_3 (1299-1515°K) Li_2O (1383-1506°K)

   BeO (2103-2583°K)

4. Determination of the condensation coefficients of lithium, beryllium, boron, silicon, and lead oxides. C.A.55, 13968 (1961). L. P. Firsova and A. N. Nesmeyanov. Zhur. Fiz. Khim. 34, 2719-22 (1960).

   Corrections are made to earlier measurements of the vapor pressures of the oxides on the basis of measurements of condensation coefficients.

5. Measurement of the saturated vapor pressure of boron. C.A.55, 6086d (1961). Yu. A. Priselkov, Yu. A. Sapozhnikov, and A. V. Tseplyaeva. Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk, Met. i Toplivo 1960, No. 1, 134-7.

   The vapor pressure was determined at 1693-1702°K by the Knudson effusion method. The ΔH°_{0} (sub.) calculated is 101 ±2 kcal $mole^{-1}$.

6. The heats of formation of $BF_2C\ell$ and $BFC\ell_2$. C.A.55, 6128g (1961). S. R. Gunn and R. H. Sanborn. J. Chem. Phys. 33, 955-6 (1960).

   The equilibrium constant of the reaction, $BF_3 + BC\ell_3 = BFC\ell_2 + BF_2C\ell$ was determined as a function of temperature. A heat of reaction of 1.1 kcal $mole^{-1}$ was calculated. The heats of formation of $BF_2C\ell$, -211.53, and of $BFC\ell_2$, -153.90 kcal $mole^{-1}$ were estimated.

7. Heat of formation of decaborane. C.A.55, 8026b (1961). W. H. Johnson, M. V. Kilday, and E. J. Prosen. J. Research Natl. Bur. Standards A64, 521-5 (1960).

   The heat of decomposition of decaborane, $B_{10}H_{14}(c) = 10B$ (amorph.) + $7H_2(g)$ was measured. $\Delta Hf^{\circ}_{25^{\circ}C}\ (B_{10}H_{14}) = -66.1$ kj $mole^{-1}$.

8. The reaction between $B_2O_3(\ell)$ and $C(s)$; heat of formation of $B_2O_2(g)$. C.A.55, 15100h (1961). P. Rentzepis, D. White, and P. N. Walsh. J. Phys. Chem. 64, 1784-7 (1960).

   The reactions, $B_2O_3(\ell) + C(s) = B_2O_2(g) + CO(g)$, and $B_2O_3(\ell) + 3C(s) = 3CO(g) + 2B(s)$ were studied and the $P_{CO}/P_{B_2O_2}$ at 1603-56°K. The heat of formation of $B_2O_2(g)$ at 0°K was calculated to be -111.7 kcal $mole^{-1}$.

9. Chemistry of boron hydrides. C.A.55, 15203e (1961). K. F. Lin. Hua Hsueh Tung Pao 1, 11-19 (1960).

   A discussion of the properties of B_2H_6, B_2H_9, B_6H_{10}, B_4H_{10}, and B_5H_{11}.

10. See reference A. 7, Rosenwasser, Boron azide.

11. Vapor pressure of deuteriodiborane. C.A.55, 18227g (1961). J. F. Ditter, J. C. Perrine, and I. Shapiro, J. Chem. Eng. Data 6, 271 (1961).

    The vapor pressures of B_2H_6 and B_2D_6 were measured.

12. Electronic structure of the first row hydrides. III. Predissociation by rotation in the $A^{'}\ II$ state and the dissociation of BH. C.A.55, 19456d (1961). A. C. Hurley, Proc. Phys. Soc. (London) A261, 237-45 (1961).

    D_o (BH) = 3.39 ±0.04 e.u.

13. The heat of chlorination of diboron tetrafluoride. C.A.55, 23023b (1961). S. R. Gunn and L. G. Green. J. Phys. Chem. 65, 178-9 (1961).

    For the reaction: $B_2F_4 + C\ell_2 \rightarrow .92BF_3 + .30BC\ell_3 + .46\ BF_2C\ell + .32\ BC\ell F_2$, ΔH was measured to be -82 kcal mole^{-1}, from which $\Delta H°f$ $B_2F_4(g) = -342.0$ kcal mole^{-1}.

14. Heats of formation of some unstable gaseous hydrides. C.A.55, 23023e (1961). S. R. Gunn and L. G. Green. J. Phys. Chem. 65, 779-83 (1961).

    The heat of decomposition of B_2H_6 was measured, and the $\Delta H°f$ $B_2H_6(g)$ [2B (amorph.) + $3H_2(g)$] was found to be + 5.0 ±0.4 kcal mole^{-1}.

15. The B_5H_{11}-H_2-B_2H_6-B_4H_{10} gas phase equilibrium. C.A.55, 23026a (1961). R. G. Adler and R. D. Stewart. J. Phys. Chem. 65, 172-3 (1961).

    The equilibrium constant was measured for the reaction: $2B_5H_{11}(g) + 2H_2(g) = 2B_4H_{10} + B_2H_6(g)$ at several temperatures, and ΔH reaction was calculated as -7.56 kcal mole^{-1}.

16. Origin of the green bands in the boron-oxygen system. C.A.55, 23038h (1961). W. E. Kaskan, J. D. Mackenzie, and R. C. Millikan. J. Chem. Phys. 34, 570-4 (1961)

    The equilibrium: $\frac{1}{2}B_2O_3(\ell) + \frac{1}{4}O_2(g) = BO_2(g)$ was studied at 1660-1950°K. From the data, ΔH was calculated to be 70 kcal mole^{-1} and from this $\Delta Hf°$ $BO_2 = -74$ kcal mole^{-1}.

17. Studies in molecular structure. I. Scope and summary of the diatomic molecule program. C.A.55, 23029i (1961). B. J. Ransil. Revs. Modern Phys. 32, 239-44 (1960).

    Dissociation energies are calculated for BF, BH, LiF, LiH, Li_2, N_2, F_2, HF, and other molecules. The results are compared with experimental data.

18. Thermodynamic functions for selected compounds. C.A.55, 24215a (1961). C. R. Fuget and J. F. Masi. U. S. Atomic Energy Comm. CCC-1024-TR-263, 23 pp. (1957).

    ΔHf° and other functions were calculated for BN and NaH, $NaBO_2$, $Na_2B_4O_7$ and other compounds.

19. Structures and thermodynamic properties of high-temperature gaseous species in the B_2O_3-H_2O system. C.A.55, 26584d (1961). J. L. Margrave, J. R. Soulen, G. E. Leroi, and S. P. Randall. U. S. Dept. Comm., Office Tech. Serv., PB Rept. 128,540, 7 pp. (1957).

    The vaporization of $B_2O_3(\ell)$, and the $B_2O_3(\ell)$ - $H_2O(g)$ system were studied. The following thermochemical properties were evaluated: ΔH vap, sub. B_2O_3, ΔHf° BO(s,g), $B_2O_2(g)$, $B_2O_3(s,\ell,g)$, $H_3BO_3(s,g)$ $HBO_2(s,g)$.

20. Standard heat of formation of boron oxide. C.A.55, 26637g (1961). G. L. Gal'chenko, A. N. Kornilov, B. I. Timofeev, and S.M. Skuratov. Doklady Akad. Nauk S.S.S.R. 127, 1016-18 (1959).

    The heats of formation of BN, B_2O_3, and $BC\ell_3$ were determined:

    ΔHf°_{298} B_2O_3 (vitreous) $= -301.1 \pm 0.8$ kcal $mole^{-1}$

    ΔHf°_{298} $BC\ell_3(g)$ $= -97.0 \pm 0.7$

    ΔHf°_{298} BN(c) $= -60.7 \pm 0.34$

21. Fluorine bomb calorimetry. III. The heat of formation of boron trifluoride. S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard. J. Phys. Chem. 65, 2157-9 (1961).

    The heat of formation of $BF_3(g)$ was measured by direct combustion of boron in fluorine.

22. Measurements of the heats of formation of inorganic fluorides, especially the elements of atomic number below 20. P. Gross, C. Hayman, D. L. Levi, and M. C. Stuart. Fullmer Research Inst. Report R146/4/23, Nov. 1960.

    The heat of formation of BF_3 was measured by direct combustion of two boron preparations in fluorine. The reported values are:

    ΔHf -270.8 ± 0.15 kcal/mole

    -271.6 ± 0.10 kcal/mole

23. See reference A. 15, Somayajulu, BF, $BC\ell$, BH.

24. Volatility of boron oxide in helium and hydrogen in the presence of water vapor. C.A.55, 11005h (1961). N. Kh. Abrikosov, Ts'un-Wu Liang, and Yu. M. Shaskhov. Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk, Met. i Toplivo 1960, No. 4, 156-9.

    The volatility of B_2O_3 in He or H is greater with H_2O present than in the dry gases over the temperature range 860-1400°.

25. See reference A. 4, Giardini, Kohn, Toman and Eckart, aluminum borides.

26. See reference A. 10, Bolgar, Verkhoglyadova and Samsonov, $A\ell B_{12}$ ZrB_2 and TiB_2.

27. See reference C. 14, Becker, BeB_{12}.

28. See reference C. 15, Hoenig, et al., Be_2B, BeB_2, BeB_6

29. See reference D. 20, Matlow, B_2.

30. See reference E. 2, Hildenbrand and Theard, BN, B_2O_3 - BF_3.

31. See reference G. 11, Lowell and Williams, TiB_2.

32. See reference G. 14, Williams, TiB_2.

33. See reference A. 14, Hildenbrand and Theard, BOF, $(BOF)_3$.

C. Beryllium Compounds

1. Beryllium oxide and its properties. C.A.55, 2228i (1961). P. P. Budnikov and R. A. Belejaev. Zhur. Priklad. Khim. 33, 1921-40 (1960).

    Physicochemical properties of BeO are discussed, analyzed and tabulated.

2. Melting and boiling points of beryllium chloride and an investigation of the sodium chloride-beryllium chloride system. C.A.55, 2254f (1961). E. Fusby and K. L. Wilkinson, J. Inorg. and Nuclear Chem. 14, 123-6 (1960).

    The following properties were measured:

    a) m.p. $BeC\ell_2$ 399°

    b) b.p. " 482.5°

    c) cryst. transition (on cooling) 335°.

3. See reference A. 2, Jakuszewski and Taniewska-Osnska. $BeC\ell_2$.

4. See reference B. 2, Firsova and Nesmeyanov, BeO.

5. See reference B. 3, Nesmeyanov and Firsova, BeO.

6. See reference B. 4, Firsova and Nesmeyanov, BeO.

7. Analogy of the physico chemical properties of BeF_2 and SiO_2. C.A.55, 11986d (1961). R. G. Grebenshchikov. Khim. i Prakt. Primenenie Silikatov, Inst. Khim. Silikatov, Akad. Nauk S.S.S.R. 1960, 18-27.

   A review, giving crystal parameters transition temperatures, and melting point.

8. Mass-spectrometric study of beryllium chloride sublimation. C.A.55, 11988d (1961). L. N. Ryabchikov and G. F. Tikhinskii. Fiz. Metal. i Metalloved. Akad. Nauk S.S.S.R. 10, 635-6 (1960).

   On the basis of studies at 496-578°K values reported are:

$$\Delta H_{sub.} \quad BeC\ell_2 = 34 \pm 1 \text{ kcal mole}^{-1}$$
$$(BeC\ell_2)_2 = 44 \pm 1$$
$$\Delta E_{dissoc.} \quad (BeC\ell_2)_2 = 24 \pm 2$$

9. Heat of formation of beryllium chloride. C.A.55, 12020d (1961). W. H. Johnson and A. A. Gilliland. J. Research Natl. Bur. Standards 65A, 59-61 (1961).

   The heat of formation of $BeC\ell_2(c)$ is -118.03 ±0.56 kcal mole^{-1}, determined by direct combustion of the metal in chlorine.

10. Ionic model and bond energy in the halide molecules of the second group. C.A.55, 15024f (1961). K. S. Krasnov. Izvest. Vyschikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol. 4, No. 1, 38-44 (1961).

    Bond energies were calculated for BeF_2, $BeC\ell_2$, MgF_2, $MgC\ell_2$, and other molecules, and compared with experimental results.

11. Vibrational constants and dissociation energy of the $BeC\ell$ molecule. C.A.55, 15110d (1961). M. M. Novikov and L. N. Turnitskii. Optika i Spektroskopiya 8, 752-60 (1960).

    The most probable value of $D(BeC\ell)$ is 5.9 ±0.5 e.u.

12. See reference A. 7, Rosenwasser, $(Be(N_3)_2)$.

13. Repulsion energy in ionic molecules. C.A. 55, 19385f (1961). K. S. Krasnov. Zhur. Obshchei Khim. 30, 3844-5 (1960).

Bond energies are estimated for BeF_2, $BeCl_2$, LiF, LiCl, MgF_2, $MgCl_2$, NaF, NaCl, and other molecules.

14. Beryllium boride, BeB_{12}, with tetragonal boron structure. C.A. 55, 19570f (1961). H. J. Becker, Z. anorg. u. allgem. Chem. 306, 266-72 (1960).

Preparation and discussion of structure.

15. The system beryllium-boron. C.A. 55, 23021d (1961). C. L. Hoenig, C. F. Cline, and D. E. Sands. J. Am. Ceram. Soc. 44, 385-9 (1961).

Compounds in the system Be-B were investigated. The following values are reported:

m.p. Be_2B = 1400°

m.p. BeB_2 < 1970°

m.p. BeB_6 2020-120.

16. Equilibrium in the reactions for the reduction of beryllium oxide by carbon at high temperatures. C.A. 55, 23234e (1961), F. Sh. Muratov and A. U. Novoselova. Doklady Akad. Nauk S.S.S.R. 129, 334-6 (1959).

The equilibrium in the BeO-C system was studied manometrically. From equilibrium pressure measurement for the reaction: $BeO(s) + 3/2C(s) = 1/2Be_2C(s) + CO(g)$, the ΔH reaction (1700-1950°K) is reported as 50,864 cal $mole^{-1}$.

17. The heat of formation of BeF_2. J. Simmons, Unpublished data, Atlantic Research Corp., April, 1961.

For incomplete combustions of Be in fluorine Simmons has measured $\Delta Hf°_{298} = -258.3, -256.8, -255.9$ for the reaction $Be(c)+F_2=BeF_2(c)$.

18. Thermal reduction of BeF_2 by magnesium. C.A. 55, 4292f (1961), A. I. Evstyukhin. Met. i Metalloved. Chistykh Metal., Sbornik Nauch. Rabot 1959, No. 1, 91-105.

The thermodynamics of Mg reduction of BeF_2 is described. No new data appear to be presented.

19. See reference A. 15, Somayajulu, BeH, BeO.

20. See reference D. 20, Matlow, Be_2.

D. Lithium Compounds

1. Heterogeneous reactions studied by mass spectrometry. II. Reaction of $Li_2O(s)$ with $H_2O(g)$. C.A. 55, 4123i (1961). J. Berkowitz, D. J. Meschi, and W. A. Chupka. J. Chem. Phys. 33, 533-40 (1960).

   $Li_3(OH)_3(g)$ was observed. The following heats of reaction in kcal $mole^{-1}$ were determined:

$$\begin{array}{rll} Li_2O(s) + H_2O(g) & = 2LiOH(g), & \Delta H^{\circ}_{1300} = 79.0 \quad T^{\circ} = K \\ Li_2O(s) + H_2O(g) & = Li_2(OH)_2(g), & \Delta H^{\circ}_{1250} = 15.0 \\ 2LiOH(s) & = Li_2O(s) + H_2O(g), & \Delta H^{\circ}_{500} = 30.4 \\ 2LiOH(s) & = Li_2(OH)_2(g), & \Delta H^{\circ}_{600} = 45.0 \\ Li_2(OH)_2(g) & = 2LiOH(g), & \Delta H^{\circ}_{1300} = 60.0 \end{array}$$

2. Lithium and lithium hydride chemical and physical properties - a literature search. C.A. 55, 4217d (1961). T. F. Davis, U. S. Atomic Energy Comm. TID-3558, 26 pp. (1960).

3. Molecular structure of lithium chloride dimer. Thermodynamic functions of Li_2X_2 ($X = C\ell$, Br, ℓ). C.A. 55, 5072d (1961). S. H. Bauer, T. Jno, and R. F. Porter. J. Chem. Phys. 33, 685-91 (1960).

   From data of Miller and Kusch, heats of vaporization are calculated for the following compounds:

$$\begin{array}{ll} LiC\ell & \Delta H^{\circ}_{1000} = 46 \text{ kcal/mole monomer} \\ (LiC\ell)_2 & \Delta H^{\circ}_{1000} = 40 \text{ kcal/mole dimer} \\ (LiC\ell)_3 & \Delta H^{\circ}_{1000} = 50 \text{ kcal/mole trimer.} \end{array}$$

4. See reference B. 2, Firsova and Nesmeyanov, Li_2O.

5. See reference B. 3, Nesmeyanov and Firsova, Li_2O.

6. See reference B. 4, Firsova and Nesmeyanov, Li_2O.

7. Ionic solvation. III. New theory for calculating heats of hydration of univalent ions at 25°. C.A. 55, 8012d (1961). A. M. Azzam. Can. J. Chem. 38, 2203-16 (1960).

   The heats of hydration of LiF, $LiC\ell$, NaF, $NaC\ell$, and other compounds are calculated and compared to experimental values.

8. See reference A. 5, Fedorov and Shamrai, $Li_2O \cdot A\ell_2O_3$.

9. A survey report on lithium hydride. C.A.55, 12125e (1961). C. E. Messer. U. S. At. Energy Comm. NYO-9470, 58 pp. (1960).

10. Mass spectrometric study of heats of dimerization of alkali chlorides. C.A.55, 15100f (1961). T. A. Milne and H. M. Klein. J. Chem. Phys. 33, 1628-37 (1960).

    The heats of dimerization of $LiC\ell$ 50.1 kcal mole^{-1} (800°K), $NaC\ell$ 44.7 (930°K) and other alkali chlorides are reported.

11. Properties of lithium hydride. I. Single crystals. C.A.55, 15195e (1961). F. E. Pretzel, G. N. Rupert, C. L. Mader, E. K. Storms, G. V. Gritton, and C. C. Rushing. Phys. and Chem. Solids 16, 10-20 (1960).

    Physical properties of LiH, LiD, LiF, and $LiC\ell$ are reviewed and some new results are cited.

12. See reference A. 7, Rosenwasser, lithium azide (LiN_3).

13. Heats and free energies of formation of ferrites and aluminates of calcium, magnesium, sodium, and lithium. C.A.55, 18278e (1961). M. F. Koehler, R. Barany, and K. K. Kelley. U. S. Bur. Mines, Rept. Invest. 5711, 14 pp. (1961).

    ΔHf° for $NaA\ell O_2$, $LiA\ell O_2$, $MgA\ell_2O_4$ and other compounds are tabulated.

14. See reference C. B. Krasnov, LiF, $LiC\ell$.

15. Binding energies of alkali halide molecules. C.A.55, 19386a (1961). G. M. Rothberg. J. Chem. Phys. 34, 2069-78 (1961).

    The ionic binding energies of monomers and dimers and the dissociation energies of the dimers of LiF, $LiC\ell$, NaF, $NaC\ell$ and other alkali halides are calculated.

16. See reference B. 17, Ransil, Li_2, LiF, LiH.

17. The dissociation energies of gaseous alkali halides. C.A.55, 24211i (1961). L. Brewer and E. Brackett. Chem. Revs. 61, 425-32 (1961).

    Tables are given of ΔH for the following reactions:

$$(MX)_2(g) = 2MX(g) \quad (1000^{\circ}K)$$

$$MX(g) = M(g) + X(g) \quad (298^{\circ}K)$$

$$MX(g) = M^{+}(g) + X^{-}(g) \quad (0^{\circ}K)$$

$$MX(c) = MX(g) \quad (298^{\circ}K)$$

$$MX(c) = MX(\ell) \quad (T_{f}^{\circ}K) \text{ where } M = Na, Li, \text{ etc.}$$

$X = F, C\ell$, etc.

also $(LiF)_3(g) = 3LiF(g)$ (1000°K)

18. Melting temperatures of lithium and sodium at pressures up to 30,000 hg./sq. cm. C.A.55, 20555f (1961). E.G. Ponyatovskii. Fiz. Metal. i Metalloved., Akad. Nauk S.S.S.R. 11, 476-7 (1961).

19. See reference A.2, Jakuszewski and Taniewski-Osnska, LiF, $LiC\ell$.

20. Three-dimensional F.E.-M.O. model. I. ΔH dissociation of homonuclear diatomic models. C.A.55, 19456h (1961). S. L. Matlow. J. Chem. Phys. 34, 1187-90 (1961).

    Consistency of the model for calculating heats of dissociation is tested for Li_2, Na_2, Be_2, Mg_2, B_2, $A\ell_2$, O_2, H_2, $C\ell_2$, C_2, N_2, F_2 and other molecules.

21. Standard enthalpy of formation of lithium fluoride. U.P. Kolesov, and S. M. Skuratov. Zhur. Neorg. Khim. 6, 1741-4 (1961).

    The heats of solution of LiF(c) in H_2O, and heat of neutralization of LiOH(aq) and HF(aq) were measured. The ΔHf°_{298} LiF(c) is reported as -146.2 ± 0.3 kcal $mole^{-1}$.

22. See reference A. 15, Somayajulu, Li_2, $LiC\ell$, LiF, LiH.

23. See reference A. 14, Hildenbrand and Theard, $LiA\ell F_4$.

E. Magnesium Compounds

1. See reference A. 2, Jakuszewski and Taniewska-Osnska, $MgC\ell_2$.

2. An experimental program for obtaining the thermodynamic properties of propellant combustion products - Third Quarterly Report. D. L. Hildenbrand and L. P. Theard. Aeronutronic Publication No. U-1187, March 15, 1961. (ASTIA Document AD-253233).

    The vapor pressure of $MgF_2(c)$ was measured and ΔH subl. was calculated. ΔHf°_{298} $MgF_2(g) = -181.2 \pm 2$ kcal $mole^{-1}$ is reported. BN, ZrF_4 and B_2O_3-BF_3 vaporization studies are reported.

3. See reference C. 18, Evstyukhin, MgF_2.

4. The aluminum reduction of magnesium oxide. I. The vapor pressure of magnesium over the system $A\ell$-MgO. C.A.55, 12971g (1961). K. Grjotheim, O. Herstad, and J. M. Togari. Can. J. Chem. 39, 442-50 (1961).

    The vapor pressure of Mg was measured for the temperature range 800-1100°C. The following reaction was reported: $14\ MgO(s) + 2A\ell(\ell) = MgA\ell_2O_4(s) + 3MG(g)$, $\Delta H^\circ_{1280°K} = 133{,}400$ cal. $mole^{-1}$. Thermodynamic functions are also calculated for the reaction: $MgO + A\ell_2O_3 = MgA\ell_2O_4$, $\Delta H^\circ_{298} = +1.1$ kcal $mole^{-1}$.

5. The thermal reduction of magnesium oxide. C.A.55, 13223g (1961), J. M. Toguri. Tidsskr. Kjerni, Bergvesen Met. 20, 211-14 (1960).

   The results of the equilibrium vapor pressure measurements of Mg Over MgO and Aℓ are reported. The abstract is somewhat ambiguous about whether these are new data.

6. See reference C. 10, Krasnov, MgF_2, $MgC\ell_2$.

7. See reference C. 13, Krasnov, MgF_2, $MgC\ell_2$.

8. See reference A. 7, Rosenwasser, $Mg(N_3)_2$.

9. See reference D. 13, Koehler, et al., $MgA\ell_2O_4$.

10. See reference A. 15, Somayajulu, MgH, MgO.

11. See reference D. 20, Matlow, Mg_2.

12. See reference F. 5, Sokolov, et al., $NaMgF_3$.

13. See reference A. 14, Hildenbrand and Theard, Mg_3N_2, MgF_2.

F. Sodium Compounds

1. See reference A. 1, Vajna and Bacchiega, $NaF-A\ell F_3$.

2. The thermodynamics of compounds of changing composition. C.A.55, 6125i (1961). V. I. Korobkov and I. S. Galinker. Zapiski Kharkov. Sel'skokhoz. Inst. im. U.U. Dokuchaeva 14, 33-5 (1957).

   Free energies are determined as a function of temperature (250-400°) and enthalpies are calculated for a series of reactions $NaOH + xH_2O = NaOH \cdot xH_2O$.

3. Thermodynamic properties of sodium. C.A.55, 6127a (1955). M. Makansi, W. A. Selke, and C. F. Bonilla. J. Chem. Eng. Data 5, 441-52 (1960).

   Thermodynamic functions are calculated, and the heat of dimerization of Na vapor is selected as $-16{,}840$ cal mole^{-1} (0°K).

4. See reference D. 7, Azzam, NaF, $NaC\ell$.

5. Free energy of formation of the complex compound $NaMgF_3$. C.A.55, 13218g (1961). O.K. Sokolov and A. I. Belyaev. Izvest. Vysshikh Ucheb. Zavedenii, Tsvetnaya Met. 3, No. 5, 72-8 (1960).

   The free energy (ΔF) and the equilibrium constant (K_p) are tabulated for the following reactions:

$$3NaF + A\ell F_3 = 3NaF \cdot A\ell F_3$$

$$NaF + MgF_2 = NaF \cdot MgF_2$$

$$1/3Na_3A\ell F_6 + MgF_2 = NaMgF_3 + 1/3A\ell F_3$$

6. See reference D. 10, Milne and Klein, $(NaC\ell)_2$.

7. See reference A. 7, Rosenwasser, NaN_3.

8. See reference D. 13, Koehler et al., $NaA\ell O_2$.

9. See reference C. 13, Krasnov, NaF, $NaC\ell$.

10. See reference D. 15, Rothberg, $(NaF)_2$, $(NaC\ell)_2$.

11. Thermodynamics of the principal reactions in chlorinating roasting. C.A.55, 19655a (1961). A. I. Tikhonov and I. T. Sryvalin. Trudy Ural. Politekh. Izvest. im. S. M. Korova. No. 98, 33-40 (1960).

    From literature data calculations were performed for the temperature range 573-973°K to determine the free energy and equilibrium constant for the following reactions among others:

    $$Na + \tfrac{1}{2}C\ell_2 = NaC\ell$$

    $$Na_2O + C\ell_2 = 2NaC\ell + \tfrac{1}{2}O_2$$

12. Heats of vaporization and thermodynamic properties of aqueous solutions of NaOH. C.A.55, 20595a (1961). N. A. Aleksenko, A. G. Bol'shakov, A. V. Kortnev, and G. N. Gasyuk. Nauch. Zapiski Odessk. Politekh. Inst. 20, 12-19 (1960).

    Heats of vaporization were measured for 12 concentrations from 1 to 50 wt. % NaOH. Heats of dilution, vapor pressures, and other thermodynamic properties were calculated for each solution.

13. See reference D. 17, Brewer and Brackett, NaF, $(NaF)_2$, $NaC\ell$, $(NaC\ell)_2$.

14. See reference B. 18, Fuget and Masi, NaH, $NaBO_2$, $Na_2B_4O_7$.

15. See reference D. 18, Ponyatovskii, Na.

16. See reference D. 20, Matlow, Na_2.

17. See reference A. 15, Somoyajulu, $NaC\ell$, NaF, NaH.

18. See reference A. 2, Jakuszewski and Taniewska-Osnska, NaF, $NaC\ell$.

19. Vapor pressure determination of hydrates of sodium chlorite and sodium formate. C.A.55, 5100a (1961). V. Riganti. Gazz. chim. ital. 89, 2275-9 (1959).

    Vapor pressures were measured from 14.7 to 43.8°C.

20. See reference A. 12, Frank, $Na_3A\ell F_6$, $NaA\ell F_4$.

G. Titanium Compounds

1. The thermodynamic properties of the lower chlorides of titanium. C.A. 55, 1169c (1961). R. B. Head, Australian J. Chem. 13, 332-40 (1960).

   The heat of formation (298°K) of $TiC\ell_3$ is -172.3 kcal mole^{-1}, determined by the reduction of $TiC\ell_4$. The heat of formation (298°K) of $TiC\ell_2$ is -122.4 ±3 kcal mole^{-1}, determined by the disproportionation of $TiC\ell_3$.

2. The system titanium-hydrogen. C.A. 55, 2254d (1961). G.A. Melkonian. Z. physik. Chem. (Frankfurt) 17, 120-4 (1958).

   Decomposition pressures are reported for TiH and TiD systems between 400 and 600°. The dissociation enthalpy of $TiH_{1.73}$ is 36.9 kcal mole^{-1}.

3. Melting point and thermal dissociation of titanium dioxide. C.A. 55, 5099f (1961). G. Brauer and W. Littke. J. Inorg. & Nuclear Chem. 16, 67-76 (1960).

   Melting points determined were: TiO_2, 1870°, Ti_2O_3, 1820°. The composition TiO_{2-x} was measured as a function of temperature and pressure of O_2.

4. Complexity of titanium (IV) fluoride solutions. C.A. 55, 5215d (1961). V. Caglioti, L. Ciavatta, and A. Liberti. J. Inorg. & Nuclear Chem. 15, 115-24 (1960).

   From experimental measurements equilibrium constants were calculated for the following:

$$TiOF^+(aq) + F^-(aq) = TiOF_2(aq),$$

$$TiOF_2(aq) + F^-(aq) = TiOF_3^-(aq), \text{ and}$$

$$TiOF_3^-(aq) + F^-(aq) = TiOF_4^=(aq).$$

5. Phase equilibriums of liquid-vapor in systems formed from titanium tetrachloride with chlorides of mono- and trichloracetic acids. C.A. 55, 8009f (1961). G. V. Seryakov, S. A. Vaks, and L. S. Sidoriva, Zhur. Obshchei Khim. 30, 2130-3 (1960).

   The vapor pressure of $TiC\ell_4(\ell)$ is determined and its ΔH vap. calculated.

6. Heat of formation of titanium trichloride. C.A.55, 8026d (1961). W. H. Johnson, A. A. Gillilord, and E. J. Prosen. J. Research Natl. Bur. Standards A64, 515-19 (1960).

   The heat of formation ($\Delta Hf^{o}_{25^{o}}$) is -172.4 ±0.8 kcal $mole^{-1}$, determined from the heat of hydrolysis of $TiC\ell_4$, and the heat of oxidation and hydrolysis of $TiC\ell_3$.

7. The system $Ti-TiC\ell_4$. C.A.55, 13152f (1961). K. Funaki and U. Uchimura. Bull. Tokyo Inst. Technol. Ser. B, No. 3, 191-6 (1960).

   The equilibrium pressure of $TiC\ell_4(g)$ was measured over the reaction $Ti(c) + TiC\ell_4(g) = 2TiC\ell_2(c)$. A heat of reaction of 29.0 kcal was calculated.

8. Dissociation energies of gaseous metal dioxides. C.A.55, 18278d (1961). L. Brewer and G. M. Rosenblatt. Chem. Revs. 61, 257-63 (1961).

   For the reaction $MO_2(g) = M(g) + 2O(g)$, ΔH^{o}_{298} is given for $TiO_2(g)$, 315 ±5, and $ZrO_2(g)$ 347 ±5 kcal $mole^{-1}$, as well as for other metal dioxides.

9. The reaction between titanium tetrachloride and oxygen. C.A.55, 19424h (1961). L. N. Shchegrov, Trudy Ural. Politekh. Inst. im. S. M. Kirova 1960, No 96, 82-92.

   The gas phase reaction: $TiC\ell_4 + O_2 = TiO_2 + 2C\ell_2$ was studied in the temperature range 298-1373°K. ΔF and Kp were calculated and compared with experimental results.

10. See reference A. 10, Bolgar, et al., TiC, TiN, TiB_2.

11. High-temperature calorimeters for the determination of heats of formation of refractory compounds. C. E. Lowell and W. S. Williams. Rev. Sci. Inst. 32, 1120-3 (1961).

    The calorimeter was used to determine the heats of formation of TiB_2 and TiC.

$$\Delta Hf^{o}\ TiB_2 = -50 \pm 5 \text{ kcal mole}^{-1}$$

$$TiC = -45.5 \pm 4.6$$

12. The heats of formation of inorganic fluorides. P. Gross, C. Hayman, and D. L. Levi, XVIIth Int. Congr. Pure and Applied Chem., Abstracts, 1, 90 (1959).

    For the reaction $Ti(c) + 2F_2(g) = TiF_4(c)$ $\Delta H = -392.5 \pm 0.3$ kcal $mole^{-1}$ was measured.

13. W. N. Hubbard, Bull. Chem. Thermodynamics No. 4, 3 (1961), has reported ΔHf TiF_4 from direct combustion of titanium in fluorine.

14. The heat of formation of titanium diboride: experimental and analytical resolution of literature conflict. W. S. Williams. J. Phys. Chem. 65, 2213-16 (1961).

    A discussion involving measurements reported in reference G-11 and other values reported earlier.

H. Zirconium Compounds

1. Equilibriums in the system zirconium-nitrogen at high temperatures and the dependence of the free energy of formation of ZrN_x on composition and structure. C.A. 55, 4123b (1961). E. I. Smagina, V. S. Kutsev, and B. F. Ormont. Trudy Nauch.-Issledovatel. Fiz.-Khim. Inst. im. L. Ya. Karpova 1959, No. 2, 118-31.

    Heats of formation were obtained by burning the nitrides in a bomb calorimeter:

	ΔHf°_{298} kcal/mole
ZrN	-87.9
$ZrN_{0.89}$	-82.4
$ZrN_{0.74}$	-72.2
$ZrN_{0.69}$	-68.7
$ZrN_{0.56}$	-56.1

    The equilibria for dissociation of part of the nitrogen were studied at 1500-1800°K. and 0.1-300 mm Hg pressure of N_2 for the same compositions.

2. Apparatus for measuring vapor pressures of zirconium and hafnium chlorides and iodides. C.A. 55, 17112g (1961). A. I. Evstyukhin and I. P. Barinov. Met. i Metalloved. Chistykh Metal., Moskov. Inzhener.-Fiz. Inst., Sbornik Nauch. Rabot 1960, No. 2, 49-57.

3. See reference G. 8, Brewer and Rosenblatt, ZrO_2.

4. Determination of heat of sublimation of silver, nickel, and zirconium by the method of radioactive indicators. C.A. 55, 18491d (1961). G. B. Fedorov. Met. i Metalloved. Chistykh Metal., Moskov. Inzhener.-Fiz. Inst., Sbornik Nauch. Rabot. 1960, No. 2, 141-7.

    The heat of sublimation of Zr^{95}, 1100-1400°, is 49,000 cal $(g.atom)^{-1}$.

5. Heat capacities and thermodynamic functions of ZrH_2 and ZrD_2 from 5 to 350°K and the hydrogen vibration frequency in ZrH_2. C.A. <u>55</u>, 19449e (1961). H. E. Flotow and D. W. Osborne. J. Chem. Phys. <u>34</u>, 1418-25 (1961).

$$\Delta Ff^\circ_{298} \text{ for } ZrH_2 = -30.9 \pm 2 \text{ kcal mole}^{-1}$$

$$ZrD_2 \cong -31.2$$

6. See reference A. 10, Bolgar, et al., ZrC, ZrB_2.

7. Vaporization of zirconium oxide. C.A. <u>55</u>, 21710a (1961). M.M. Nakata, R. L. McKisson, and B.D. Pollock. U. S. At. Energy Comm. <u>NAA-SR-6095</u>, 10 pp. (1961).

   The vaporization rate of zirconium oxide was measured in the temperature range, 2410 to 2830°K. From the data the following values were calculated:

$$D(ZrO) = 7.8 \pm 0.2 \text{ e.v.}$$

$$D(ZrO_2) = 14.9 \pm 0.2 \text{ e.v.}$$

8. Fluorine bomb calorimetry. I. The heat of formation of zirconium tetrafluoride. C.A.55, 23023c (1961). E. Greenberg, J. L. Settle, H. M. Feder, and W. N. Hubbard. J. Phys. Chem. <u>65</u>, 1168-72 (1961).

   The heat of formation of ZrF_4 was measured by direct combination of the elements in a bomb calorimeter. ΔHf at 25° was -456.80 ±0.25 kcal mole^{-1}.

9. Thermochemistry of zirconium halides. A. G. Turnbull. J. Phys. Chem. <u>65</u>, 1652-4 (1961).

   The heat of reaction of $ZrC\ell_4$(c) with NaOH(aq). For the reaction:

$$ZrC\ell_4(c) + 4NaOH\ (aq,\ 1500\ H_2O \rightarrow ZrO_2\ (\text{hydrous})$$

$$+ 4NaC\ell(aq) + 2H_2O$$

   ΔH was measured as -102.7 kcal mole^{-1}. From this ΔHf°_{298} of ZrO_2 (hydrous) was calculated as -260.3 ±0.6 kcal mole^{-1}.

10. See reference A. 14, Hildenbrand and Theard, ZrF_4.

11. See reference E. 2, Hildenbrand and Theard, ZrF_4.

I. Fluorine

1. See reference B. 17, Ransil, F_2 HF.

2. See reference D. 20, Matlow, F_2.

3. The dissociation energy of fluorine from shock-wave measurements. C.A.55, 16117d (1961). K. L. Wray and D. F. Hornig. U. S. Dept. Com., Office Tech. Serv., PB Rept. 138, 329, 31 pp. (1959).

   $\Delta H_{diss\ 298}$ is reported as 31.6 ±4.3 and upper limit is given as 39.0 kcal $mole^{-1}$.

4. See reference A. 15, Somayajulu, F_2, $FC\ell$, HF.

J. Carbon

1. See reference D. 20, Matlow, C_2.

2. See reference A. 15, Somayajulu, C, CO, CH.

3. Bond dissociation energies in small hydrocarbon molecules. C.A.55, 24211h (1961). B. E. Knox and H. B. Palmer. Chem. Revs. 61, 247-55 (1961).

   A review. "Best" values are given for

$$C_2(g) = 2C(g),\ \Delta H^\circ_0 = 141 \text{ kcal}$$

$$C(c,\text{graphite}) = C(g),\ \Delta H^\circ_0 = 169.6\ (\Delta H^\circ_{298} = 170.2)$$

4. See reference A. 10, Bolgar, et al., TiC, ZrC.

5. See reference B. 8, Rentzepis, White, and Walsh, C, CO.

6. See reference C. 16, Muratov, et al., Be_2C.

7. See reference G. 11, Lowell and Williams, TiC.

K. Chlorine

1. See reference A. 15, Somayajulu, $C\ell_2$, $FC\ell$, $HC\ell$.

2. See reference D. 20, Matlow, $C\ell_2$.

L. Oxygen

1. See reference D. 20, Matlow, O_2.

M. Hydrogen

1. See reference D. 20, Matlow, H_2.

2. Vapor tension of nitrogen and hydrogen at low pressures. C.A. 55, 15025f (1961). E. S. Borovik, S. F. Grishin, and E. Ya. Grisbina, Zhur. Tekh. Fiz. 30, 539-45 (1960).

   The heat of sublimation of hydrogen was determined as 248 cal $mole^{-1}$.

3. Molecular orbital treatment of hydrogen with central potentials and modified boundary conditions. C.A. 55, 16123i (1961). J. M. Peek and E. N. Lassettre. J. Chem. Phys. 33, 1803-7 (1960).

   $D(H_2)$ is calculated as 5.65 e.v.

4. Correlated orbitals for the ground state of the hydrogen molecule. C.A. 55, 23029f (1961). W. Kolos and C. C. J. Roothaan. Revs. Modern Phys. 32, 205-10 (1960).

   The dissociation energy of H_2 is calculated.

5. Accurate electronic wave functions for the hydrogen molecule. C.A. 55, 23029g (1961). W. Kolos and C. C. J. Roothaan. Revs. Modern Phys. 32, 219-32 (1960).

   The dissociation energy of the H_2 molecule is calculated to be 4.7466 e.v.

6. Configuration interaction in the hydrogen molecule. The ground state. C.A. 55, 23029f (1961). A. D. McLean, A. Weiss, and M. Yoshimine. Revs. Modern Phys. 32, 211-18 (1960).

   The binding energy of H_2 is calculated to be 4.54306 e.v.

7. The dissociation energies of the H_2, HD, and D_2 molecules. C.A. 55, 24225e (1961). G. Herzberg and A. Monfile. J. Mol. Spectroscopy 5, 482-98 (1960).

   The far ultraviolet absorption edges of H_2, HD, and D_2 were studied under high resolution. From the precisely measured edges new values for the dissociation energies of H_2, D_2 and HD were determined, which are:

$$D_o^o\ (H_2) = 36{,}113.0 \pm 0.3\ cm^{-1}$$

$$D_o^o\ (HD) = 36{,}399.9 \pm 1.0\ cm^{-1}$$

$$D_o^o\ (D_2) = 36{,}743.6 \pm 0.5\ cm^{-1}$$

8. See reference A. 15, Somayajulu, AℓH, BH, LiH, NaH, BeH, MgH, HF, HCℓ, HC, HN.

9. See reference B. 9, Lin, boron hydrides.

10. See reference B. 11, Ditter, et al., diborane.

11. See reference B. 12, Hurley, BH.

12. See reference B. 14, Gunn and Green, diborane.

13. See reference B. 15, Adler and Stewart, boranes.

14. See reference B. 17, Ransil, BH, LiH, HF.

15. See reference B. 18, Fuget and Masi, NaH.

16. See reference D. 2, Davis, LiH.

17. See reference D. 9, Messer, LiH.

18. See reference D. 11, Pretzel, et al., LiH.

19. See reference G. 2, Melkonian, TiH.

20. See reference H. 5, Flotaw and Osborne, ZrH_2.

N. Nitrogen

1. See reference A. 15, Somayajulu, N_2, NO, NH.

2. See reference D. 20, Matlow, N_2.

3. See reference B. 17, Ransil, N_2.

4. See reference B. 18, Fuget and Masi, BN.

5. See reference A. 10, Bolgar, et al., TiN.

6. See reference A. 7, Rosenwasser, metal azides.

7. See reference B. 20, Gal'chenko, et al., BN.

8. See reference E. 2, Hildenbrand and Theard, BN.

9. See reference H. 1, Smagina, et al., ZrN_x.

10. See reference A. 14, Hildenbrand and Theard, Mg_3N_2, AℓN.

Chapter B2

ALLOYS AND INTERSTITIAL COMPOUNDS OF ALUMINUM AND BERYLLIUM WITH TITANIUM AND ZIRCONIUM

Thomas W. Mears

Very little has appeared in the literature on the alloys or interstitial compounds of these elements since the release of NBS Report No. 7192 (1 July 1961).

Aluminum-Zirconium system

The compound forming peritectically at 1480°C [1] has been characterized as Al_3Zr_2 [2]. It is described as an orthorhombic crystal with lattice constants a = 9.601, b = 13.906 and C = 5.57A. Assuming eight formula units per unit cell, a calculated density of 4.703 g/cm^3 was obtained. Macroscopic determination gave a density of 4.79 g/cm^3.

Beryllium-Titanium system

Conflicting interpretations of data have been reported for $Be_{17}Ti_2$. Payne and Carraline [3] report $Be_{17}Ti_2$ as isomorphous with $Be_{17}Zr_2$ reported earlier. Their lattice constants based on a <u>hexagonal</u> unit cell are a = 7.34a, c = 10.73A. Zalken et al [4] described it in two forms. The α-form of $Be_{17}T_{12}$ is interpreted as a rhombohedral unit cell, and the β-form as a hexagonal unit cell. The following data of Zalkin [4] is very similar to that which he presented in UCRL No. 5876 [5] abstracted in NBS Report No. 7093.

Compound	Structure Type	a	c	Lattice Type	Formula Volume (A^3)
		A°			
Be_3Ti	$NbBe_3$	4.49	21.32	Rhombohed.	
α-$Be_{17}Ti_2$	Nb_2Be_{17}	7.39	10.79	Rhombohed.	170.3
β-$Be_{17}Ti_2$	Th_2Nb_{17}	7.36	7.30	Hexagonal	171.2
$Be_{12}Ti$	$ThMn_{12}$	7.35	4.19	Tetragonal	

Percent increase in volume of alloy or intermetallic as compared to elements

Compound	Density Macro g/cm^3	Density X-ray g/cm^3	Molecular Volume V_M cm^3/mole	Sum of Atomic Volumes ΣV_A cm^3/mole	Percent change on alloying $\frac{V_M - \Sigma V_A}{\Sigma V_A} \times 100$
$A\ell_3Zr_2$	4.79	4.703	55.0	58.0	-5.17
α-$Be_{17}Ti_2$		2.43	102.6	103.65	-1.01
β-$Be_{17}Ti_2$		2.42	103.0	103.65	-0.63

References

[1] D. J. McPherson and M. Hansen, Trans. Am. Soc. Metals 46, 354 (1954).

[2] T. J. Renouf and C. A. Beevers, Acta Cryst. 14, 469 (1961).

[3] R. M. Paine and J. A. Carraline, Acta Cryst. 13, 680 (1960).

[4] A. Zalkin, D. E. Sands, R. J. Bedford, and O. H. Krikorian, Acta Cryst. 14, 63 (1961).

[5] A. Zalkin, D. E. Sands, R. J. Bedford, and O. H. Krikorian, UCRL Report No. 5876 (February 1960).

Chapter B3

LITERATURE SURVEY ON LOW-TEMPERATURE HEAT CAPACITY AND ENTROPY AT 298.15°K OF BINARY METAL OXIDE COMPOUNDS OF Li, Be, Mg, Aℓ, Si, K, Ti, AND Zr AND OF ELEMENTAL Si AND K AND SOME OF THEIR COMPOUNDS

George T. Furukawa

The experimental thermodynamic investigations at low temperatures are being complemented by a systematic literature survey to determine what substances, that are of interest to the program, have already been investigated. The literature data wherever available are being analyzed to obtain tables of thermal functions. In the present report a survey of the heat-capacity data on the various known binary metal oxides of Li, Be, Mg, Aℓ, Si, K, Ti, and Zr are given. A survey of the data on elemental Si and K and their compounds of oxygen and the halogens has not previously been given. Therefore the status of the available data on these substances is given in this report. Tables of thermal functions of the substances discussed in this report will be given at a future date.

In order to determine what binary metal oxides are known, the two books: "Phase Diagrams for Ceramists" by Levin, McMurdie, and Hall [27][a] and "Phase Diagrams for Ceramists. Part II" by Levin and McMurdie [26] were examined. The Bureau of Mines Bulletin 592 [20] and the Ohio State University [3] bibliography were used to locate references to heat-capacity data. The Annual Review of Physical Chemistry, Volumes 10 and 11 [46,30] and the bibliography compilation for 1960 by Zwolinski and Danti [55], that appeared in the Bulletin of Chemical Thermodynamics, No. 4, 1961, in advance of its publication in the 1961 issue of the Annual Review of Physical Chemistry, were examined for references to experimental data. The Bulletin of Chemical Thermodynamics, No. 4, 1961 [5] was consulted for unpublished data.

Table 1 gives a matrix of binary metal oxide compounds that were located in the two books [27,26] previously cited. Aluminum silicates of the composition $A\ell_2O_3 \cdot SiO_2$ (andalusite, kyanite, and sillimanite), which occur in nature, are included in the table although they have not been located in any of the phase diagrams given in the above books. The substances lithium aluminate, $Li_2O \cdot A\ell_2O_3$, and magnesium aluminate, $MgO \cdot A\ell_2O_3$, were discussed in a previous report [35]. Therefore no discussion is given on these compounds in this report.

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[a] Figures in brackets indicate the literature references at the end of this chapter.

As done previously, the substances are discussed separately after listing the low-temperature heat-capacity measurements in chronological order along with the reference and the temperature range of each investigation. Method of preparation, the physical state, and chemical analysis are given whenever available. Tables of adopted values of S°_{298} are given at the end of the discussion. References given in the tables are those from which the adopted values were obtained.

Lithium Disilicate, $Li_2O \cdot 2SiO_2$, 150.0470

Westrum [5] (6° to 350°K) lists lithium disilicate, $Li_2O \cdot 2SiO_2$, among the unpublished heat-capacity data. Both crystalline and vitreous samples were investigated.

Lithium Trisilicate, $Li_2O \cdot 3SiO_2$, 210.1318

Westrum [5] (6° to 350°K) lists lithium trisilicate, $Li_2O \cdot 3SiO_2$, among the unpublished heat-capacity data. A sample in the vitreous state was investigated. A compound having the composition $Li_2O \cdot 3SiO_2$ has not been located in any of the phase diagrams shown in the two books cited [27,26].

Beryllium Orthosilicate, Be_2SiO_4, 110.1080

Kelley [17] (55° to 294°K) reported heat-capacity measurements on beryllium orthosilicate (phenacite), Be_2SiO_4. Natural phenacite samples from two sources, Brazil and Colorado, were mixed and investigated. The sample from Brazil consisted of well formed crystals and, after crushing and washing, analyzed to be 99.9 percent Be_2SiO_4. The sample from Colorado was not well crystallized and contained considerable impurities. After sorting and discarding over 50 percent, the final material analyzed 99.8 percent Be_2SiO_4. These two samples were mixed, the Brazilian sample comprising about 60 percent of the total. Kelley [17] calculated $S^\circ_{298} = 15.4 \pm 0.1$ eu from the data. Kelley and King [20] give $S^\circ_{298} = 15.37 \pm 0.08$ eu.

Magnesium Orthosilicate, Mg_2SiO_4, 140.7076

Kelley [19] (52° to 295°K) measured the heat capacity of magnesium orthosilicate, Mg_2SiO_4. The magnesium orthosilicate sample investigated by Kelley [19] was prepared from c.p. MgO and from a good grade of finely powdered SiO_2, which had been previously digested in 6-N $HC\ell$, washed, and dried. A mixture containing 0.82 percent excess of MgO over the theoretical ratio was heated in a vacuum furnace at 1150 ±20°C for four days. The product was reground and heated for five additional days at 1180 ±10°C. The analysis of the product was 98.6 percent magnesium orthosilicate, 0.8 percent MgO, no free SiO_2, and no magnesium metasilicate. Corrections were applied for the impurities. $S^\circ_{298} = 22.7 \pm 0.2$ eu was reported. Kelley and King [20] give $S^\circ_{298} = 22.75 \pm 0.2$ eu.

Magnesium Metasilicate, $MgSiO_3$, 100.3962

Wagner [50] (21° to 35°K) and Kelley [19] (52° to 296°K) reported heat-capacity measurements on magnesium metasilicate, $MgSiO_3$. The sample of magnesium metasilicate investigated by Kelley [19] was prepared by heating a stoichiometric mixture of MgO and SiO_2 in a furnace at 1300 ±20°C for $13\frac{1}{2}$ days. This initial product contained 27.1 percent magnesium orthosilicate. The product was reground and reheated at 1300°C several times after which the final product analyzed 92.0 percent magnesium metasilicate, 5.6 percent magnesium orthosilicate, and 2.4 percent free SiO_2. Corrections were applied for the impurities present. $S^o_{298} = 16.2 \pm 0.2$ eu was reported. Kelley and King [20] give $S^o_{298} = 16.22 \pm 0.10$ eu.

Aluminum Silicate, $A\ell_2SiO_5$, 162.0460

Aluminum silicate, $A\ell_2SiO_5$, exists in nature in three crystalline forms known as andalusite, kyanite, and sillimanite. Simon and Zeidler [43] and Todd [47] have reported heat-capacity measurements on all three of these substances. The ranges of their measurements are as follows:

	Simon and Zeidler	Todd
Andalusite	24° to 280°K	54° to 297°K
Kyanite	24° to 224°K	54° to 297°K
Sillimanite	17° to 282°K	54° to 297°K

The natural minerals that were investigated by Todd [47] had the following analysis in weight percent:

	Andalusite	Kyanite	Sillimanite
$A\ell_2O_3$	63.15	63.20	61.80
SiO_2	36.84	36.90	36.44
TiO_2	Trace*	None	None
FeO	None	None	0.14
Fe_2O_3	0.11	0.10	0.98
MgO	Trace	None	0.24
CaO	0.02	0.05	0.07
MnO	Trace	None	0.04
Na_2O	None	None	Trace
K_2O	None	None	None
P_2O_5	-	-	0.28
F	-	-	0.04
Total	100.12	100.25	100.03

*Trace = less than 0.01 percent.

The theoretical composition is 62.93 percent $A\ell_2O_3$ and 37.07 percent SiO_2. No corrections were applied to the heat data for deviations of the samples from the theoretical composition. Todd [47] reported the following values of S^o_{298}:

Andalusite	22.28 ±0.10 eu
Kyanite	20.02 ±0.08 eu
Sillimanite	22.97 ±0.10 eu

Kelley and King [20] list the same above values.

Potassium Disilicate, $K_2O \cdot 2SiO_2$, 214.3730

Westrum [5] (6° to 350°K) lists potassium disilicate, $K_2O \cdot 2SiO_2$, among the unpublished heat-capacity data. He has investigated the material in both crystalline and vitreous states.

Potassium Tetrasilicate, $K_2O \cdot 4SiO_2$, 334.5426

Westrum [5] (6° to 350°K) lists potassium tetrasilicate, $K_2O \cdot 4SiO_2$, among the unpublished heat-capacity data. A sample in the vitreous state was investigated.

Lithium Metatitanate, Li_2TiO_3, 109.7762

King [21] (55° to 296°K) reported heat-capacity measurements on lithium metatitanate, Li_2TiO_3, prepared by heating a stoichiometric mixture of lithium carbonate and titania. The mixture was heated six times for a total of 70 hours at 1000° to 1050°C and 30 hours at 1150°C. Between heats, the material was ground and analyzed and the composition adjusted. The analysis of the final product gave 72.70 percent TiO_2, as compared with 72.78 percent theoretical TiO_2 composition. Impurities were 0.03 percent SiO_2 and 0.06 percent Ni and Pt contamination from containers that were used. X-ray diffraction patterns were reported to be in agreement with those given in A.S.T.M. catalog. The value of S^o_{298} reported by King [21] is 21.9 ±0.1 eu. Kelley and King [20] give $S^o_{298} = 21.93 \pm 0.10$ eu.

Magnesium Orthotitanate, Mg_2TiO_4, 160.5216

Todd [48] (52° to 297°K) reported measurements of the heat capacity of magnesium orthotitanate, Mg_2TiO_4. The sample was prepared by compressing into pellets stoichiometric quantities of pure TiO_2 (99.8 percent) and reagent grade MgO and by prolonged heating at approximately 1300° to 1500°C. This material was subsequently ground to -100 mesh, analyzed, adjusted for composition, compressed into pellets, and heated several times until a final product was obtained that analyzed 49.53 percent TiO_2 (theoretical composition of TiO_2 is 49.77 percent) and 0.21 percent SiO_2 impurity. The value of S^o_{298} calculated by Todd [48] from the data is 24.76 ±0.15 eu. Kelley and King [20] give $S^o_{298} = 26.1 \pm 0.2$ eu, with an allowance of $R\ell n2$ for structural randomness.

Magnesium Metatitanate, $MgTiO_3$, 120.2102

Shomate [40] (53° to 296°K) reported measurements of the heat capacity of magnesium metatitanate, $MgTiO_3$, prepared by "prolonged" heating of a stoichiometric mixture of MgO and TiO_2 in vacuum at about 1300°C. X-ray diffraction patterns were reported to be in agreement with those previously published. Chemical analysis of the product gave at least 99 percent $MgTiO_3$, the principal impurity being SiO_2. The SiO_2 was considered to exist in the form of $MgSiO_3$ and a correction for 0.8 percent $MgSiO_3$ was made. Shomate [40] reported S°_{298} to be 17.8 ±0.1 eu. Kelley and King [20] give $S^\circ_{298} = 17.82 \pm 0.10$ eu.

Magnesium Dititanate, $MgTi_2O_5$, 200.1090

Todd [48] (52° to 297°K) measured the heat capacity of magnesium dititanate, $MgTi_2O_5$. In the preparation of the sample stoichiometric quantities of pure TiO_2 (99.8 percent) and reagent grade MgO were compressed into pellets and heated at 1300° to 1500°C. The sample was subsequently ground to -100 mesh, analyzed, adjusted for composition, compressed into pellets, and heated several times until a final product was obtained that analyzed to be 79.63 percent TiO_2 (theoretical composition of TiO_2 is 79.85 percent) and 0.16 percent SiO_2 impurity. X-ray diffraction pattern of the product was reported to be in agreement with that previously published for the substance. Todd [48] calculated S°_{298} to be 30.4 ±0.2 eu from the data. Kelley and King [20] give the same value.

Aluminum Titanate, $A\ell_2TiO_5$, 181.86

King [21] (53° to 296°K) reported heat-capacity measurements on the β form of aluminum titanate prepared by heating a stoichiometric mixture of titania and hydrated alumina. The mixture was pressed into pellets and heated five times for a total of 96 hours between 1400° and 1500°C and 43 hours between 1500° and 1570°C. Between heats, the material was ground and analyzed and the composition adjusted. After each heat the material was quenched to room temperature to minimize the formation of another form of $A\ell_2TiO_5$ in the range 750° to 1300°C [25]. The analysis of the final product gave 43.95 percent TiO_2, as compared with 43.93 percent theoretical TiO_2 composition. The X-ray diffraction pattern was reported to be in agreement with those given in the literature. The value of S°_{298} reported by King [21] is 26.2 ±0.2 eu. Kelley and King [20] give the same value.

Zirconium Silicate, $ZrSiO_4$, 183.3036

Kelley [18] (52° to 295°K) measured the heat capacity of zirconium silicate, $ZrSiO_4$. The $ZrSiO_4$ sample investigated was zircon sand which had been digested in 6N $HC\ell$ and dried. The analysis for ZrO_2, including HfO_2, was 66.3 percent, SiO_2 was 33.6 percent, and Fe_2O_3 was 0.4 percent. The sample was taken to be 98.6 percent $ZrSiO_4$, 0.4 percent Fe_2O_3, and 1.3 percent SiO_2 and corrections were applied accordingly to the heat measurements. The value for S°_{298} was reported to be 20.1 ±0.3 eu. Kelley and King [20] give $S^\circ_{298} = 20.2 \pm 0.2$ eu.

Magnesium Monotungstate, $MgWO_4$, 272.1596

Low-temperature heat-capacity measurements have been reported by King and Weller [22] (53° to 296°K). The magnesium monotungstate sample was prepared by heating a stoichiometric mixture of reagent grade magnesia and tungstic acid 8 times for a total of 5 days at 900°C. Between heats, the material was ground and mixed, chemical analysis was made, and the composition was adjusted as required. The product contained 14.79 percent MgO and 85.24 percent WO_3, the theoretical composition being 14.81 and 85.19 percent, respectively. The X-ray diffraction pattern was reported to have agreed with that given in the literature. King and Weller [22] calculated $S^\circ_{298} = 24.2 \pm 0.2$ eu.

Silicon, Si, 28.086

Measurements of the heat capacity of silicon have been reported by Russell [37] (-191° to 46°C), Dewar [9] (20° to 80°K), Nernst and Schwers [33] (20° to 90°K), Anderson [1] (61° to 296°K), Pearlman and Keesom [34] (12° to 100°K), and Flubacher, Leadbetter, and Morrison [12] (8° to 300°K). Kelley and King [20], using the data reported by Anderson [1], Nernst and Schwers [33], and Pearlman and Keesom [34], calculated $S^\circ_{298} = 4.51 \pm 0.05$ eu. Flubacher, Leadbetter, and Morrison [12] calculated $S^\circ_{298} = 4.497 \pm 0.009$ eu from their data.

Silicon Dioxide, SiO_2, 60.0848

Silica, SiO_2, exists in the three crystalline forms: quartz, cristobalite, and tridymite and these in turn exist in the α and β forms.

Heat measurements on α-quartz have been reported by Koref [23] (-190° to 0°C), Nernst [31] (25° to 233°K), Wietzel [53] (72° to 89°K), Simon [41] (19° to 288°K), Anderson [2] (53° to 297°K), and Jones and Hallett [14] (2° to 4°K). The sample investigated by Anderson [2] was natural quartz of particle sizes between 28 and 35 mesh that was washed with HCℓ and with HNO_3. The analysis gave SiO_2 content to be 99.93 percent. Anderson [2] calculated $S^\circ_{298} = 10.06 \pm 0.1$ eu from the data. Kelley and King [20], using data obtained by Anderson [2], Nernst [31], and Wietzel [53], calculated $S^\circ_{298} = 10.00 \pm 0.10$ eu. Westrum [5] lists as unpublished measurements on the heat capacity of α-quartz in the range 6° to 300°K.

Heat measurements on α-cristobalite have been reported by Wietzel [53] (29° to 198°K), Simon [41] (29° to 117°K), and Anderson [2] (54° to 298°K). The α-cristobalite sample investigated by Anderson [2] was prepared by heating pure vein quartz of -60 mesh sizes at 1600°C for 90 minutes. Petrographic analysis showed complete conversion to α-cristobalite. Chemical analysis gave 99.99 percent SiO_2. Anderson [2] calculated $S^\circ_{298} = 10.34 \pm 0.1$ eu. Kelley and King [20], using all of the above data, calculated $S^\circ_{298} = 10.20 \pm 0.1$ eu. Westrum [5] lists as unpublished measurements on the heat capacity of α-cristobalite in the range 6° to 300°K.

The only known data on α-tridymite are those reported by Anderson [2] (54° to 295°K). The α-tridymite sample investigated was prepared by heating with Na_2WO_4 flux. A mixture containing 6-SiO_2 to 1-Na_2WO_4 was ground to -200 mesh and heated for 4 hours at 1250°C. When reground to -200 mesh and successively washed with HCℓ, boiling water, NH_4OH, and boiling water, the product contained inclusions of Na_2WO_4. After grinding to -400 mesh and washing, the final product that was investigated analyzed 99.46 percent SiO_2. Petrographic analysis showed the material to be α-tridymite. Anderson [2] calculated $S^\circ_{298} = 10.50 \pm 0.2$ eu from the data. Kelley and King [20] calculated $S^\circ_{298} = 10.4 \pm 0.2$ eu from the same data.

Heat measurements on SiO_2 glass have been reported by Nernst [31] (26° to 233°K), Wietzel [53] (19° to 288°K), Simon [41] (19° to 288°K), and Simon and Lange [42] (10° to 13°K). Using the data of Simon [41] and Simon and Lange [42], Kelley and King [20] calculated $S^\circ_{298} - S^\circ_0 = 10.35 \pm 0.10$ eu for SiO_2 glass. Westrum [5] lists as unpublished measurements on the heat capacity of SiO_2 glass in the range 6° to 300°K.

Potassium, K, 39.102

Measurements of the heat capacity of potassium metal have been reported by Schüz [39] (-79° to 0°C); Koref [23] (-191° to 0°C); Dewar [9] (20° to 80°K); Eastman and Rodebush [10] (68° to 287°K); Simon and Zeidler [43] (15° to 277°K); Carpenter and Steward [6] (203° to 610°K); Dauphinee, Martin, and Preston-Thomas [8] (30° to 330°K); Krier, Craig and Wallace [24] (11° to 323°K); Roberts [36] (1.5° to 20°K); and Lien and Phillips [28] (0.17° to 1.1°K). The results of Dauphinee et al. [8], Krier et al. [24], and Roberts [36] are in close agreement. Krier et al. [24] reported $S^\circ_{298} = 15.38 \pm 0.03$ eu. Kelley and King [20], using data reported by Dauphinee et al. [8], Krier, et al. [24], and Simon and Zeidler [43], calculated S°_{298} to be 15.34 ±0.10 eu.

Potassium Superoxide, KO_2, 71.1008

Todd [49] (53° to 297°K) reported heat-capacity measurements on potassium superoxide, KO_2. The sample was 92.4 percent KO_2, 3.5 percent Na_2O_2, 4.1 percent K_2CO_3. Corrections were applied to the heat data for these impurities. Two peaks in the heat capacity were observed at 193° and 231°K. KO_2 is known to be highly colored (orange-yellow) and to be paramagnetic. Therefore these heat-capacity peaks may be associated with color changes that are known to occur in many of the alkali metal oxides and with a magnetic transition. Todd [49] calculated $S^\circ_{298} = 27.9 \pm 0.6$ eu from the data. Kelley and King [20] give 27.9 ±0.3 eu.

Potassium Fluoride, KF, 58.1004

Koref [23] (-190° to 0°C) and Westrum and Pitzer [52] (16° to 530°K) measured the heat capacity of potassium fluoride, KF. Westrum and Pitzer [52] used an adiabatic calorimeter for the range 16° to 323° K and a "drop" calorimeter for the range 298° to 530°K. Their KF sample was prepared by thermal decomposition of KHF_2 first at 300°C and finally at 295°C. The initial KHF_2 sample was analyzed to be 100.03 ±0.06 percent of the theoretical acid and to have 48.5 ±0.2 percent of fluorine (theoretical fluorine content = 48.65 percent). The loss in weight on careful heating of small portions of KHF_2 to constant weight was reported to be 25.60 ±0.04 percent (theoretical loss is 25.62 percent). Westrum and Pitzer [52] calculated S°_{298} = 15.91 ±0.1 eu from the data. Kelley and King [20] give the same value.

Potassium Hydrogen Fluoride, KHF_2, 78.10677

Heat-capacity measurements on potassium hydrogen fluoride, KHF_2, have been reported by Westrum and Pitzer [52] (16° to 523°K) using an adiabatic calorimeter in the range 16° to 316°K and a "drop" calorimeter in the range 298° to 523°K. The KHF_2 sample was prepared by reacting reagent grade anhydrous K_2CO_3 and aqueous HF in platinum ware. The solution was concentrated by boiling and the KHF_2 precipitated by cooling. The material was recrystallized several times and finally dried under vacuum at 40°C. Volumetric, acidimetric analysis of the hydrogen in the final KHF_2 sample gave 100.03 ±0.06 percent of the theoretical amount. Gravimetric analysis of the fluorine gave 48.5 ±0.2 percent fluorine, the theoretical composition being 48.65 percent. Westrum and Pitzer [52] calculated S°_{298} = 24.92 ±0.1 eu. Kelley and King [20] list the same value.

Potassium Chloride, $KC\ell$, 74.5550

Measurements of the heat capacity of potassium chloride have been reported by a number of investigators: Nernst [31] (23° to 86°K); Nernst and Lindemann [32] (23° to 86°K); Koref [23] (-190° to 0°C); Russell [37] (2.1° to 44°C); Lindemann and Schwers [29] (23° to 89°K); Southard and Nelson [44] (17° to 287°K); Keesom and Clark [16] (2.3° to 17°K); Feodosiev [11] (-191° to 25°C); Ziegler and Messer [54] (107° to 320°K); Clusius, Goldmann, and Perlick [7] (11° to 268°K); Sayre and Beaver [38] (69° to 80°K); Keesom and Pearlman [15] (1.5° to 4.3°K); Strelkov, Itskevich, Kostryukov, and Mirskaya [45] (12° to 298°K); Webb and Wilks [51] (1.5° to 4.10°K); and Berg and Morrison [4] (3° to 270°K). S°_{298} calculated by Strelkov <u>et</u> <u>al</u>. [45] from their data is 19.68 ±0.05 eu. Kelley and King [20] give S°_{298} = 19.70 ±0.05 eu.

Potassium Bromide, KBr, 119.0110

Heat measurements on potassium bromide have been reported by Koref [23] (-191° to 0°C); Nernst [31] (79° to 89°K); Nernst and Lindemann [32] (79° to 234°); and Clusius, Goldmann, and Perlick [7] (11° to 270°K). Kelley and King [20], using the above data, calculated $S^\circ_{298} = 23.2 \pm 0.2$ eu.

Potassium Iodide, KI, 166.0064

Heat-capacity measurements on potassium iodide, KI, have been reported by Koref [23] (-191 to 0°C) and by Clusius, Goldmann and Perlick [7] (10° to 270°K). Scales [38a] (2° to 8°K) reported some measurements in graphical form only. Kelley and King [20], using the data reported by Clusius *et al.* [7], calculated $S^\circ_{298} = 24.9 \pm 0.2$ eu.

TABLE 1

Binary Metal Oxide Compounds

	Li	Be	Mg	$A\ell$	Si	K	Ti	Zr
Li								
Be								
Mg								
$A\ell$	$Li_2O \cdot A\ell_2O_3$*	$BeO \cdot A\ell_2O_3$ $BeO \cdot 3A\ell_2O_3$	$MgO \cdot A\ell_2O_3$*					
Si	$2Li_2O \cdot SiO_2$ $Li_2O \cdot SiO_2$ $Li_2O \cdot 2SiO_2$	$2BeO \cdot SiO_2$*	$2MgO \cdot SiO_2$* $MgO \cdot SiO_2$*	$3A\ell_2O_3 \cdot 2SiO_2$ $A\ell_2O_3 \cdot SiO_2$*				
K	$K_2O \cdot TiO_2$			$K_2O \cdot A\ell_2O_3$	$K_2O \cdot SiO_2$ $K_2O \cdot 2SiO_2$* $K_2O \cdot 4SiO_2$*			
Ti	$Li_2O \cdot TiO_2$*		$2MgO \cdot TiO_2$* $MgO \cdot TiO_2$* $MgO \cdot 2TiO_2$*	$A\ell_2O_3 \cdot TiO_2$*	$2SiO_2 \cdot 3Ti_2O_3$	$K_2O \cdot TiO_2$		
Zr					$SiO_2 \cdot ZrO_2$*		$TiO_2 \cdot ZrO_2$	
W	$Li_2O \cdot WO_3$		$MgO \cdot WO_3$*			$K_2O \cdot WO_3$ $K_2O \cdot 2WO_3$ $K_2O \cdot 3WO_3$		

* Substances on which heat-capacity data have been found.

TABLE 2

Entropy of Binary Metal Oxide Compounds of Li, Be, Mg, Aℓ, Si, K, Ti, and Zr and of Elemental Si and K and Some of their Compounds

Chemical Formula	Gram Formula Mass	$S^\circ_{298.15^\circ K}$ cal/deg mole	References
$Li_2O \cdot A\ell_2O_3$	131.8386[†]	12.74 ±0.1	[35]
$MgO \cdot A\ell_2O_3$	142.2726	19.27 ±0.1	[35]
$Li_2O \cdot 2SiO_2$	150.047	*	[5]
$Li_2O \cdot 3SiO_2$	210.1318	*	[5]
$2BeO \cdot SiO_2$	110.108	15.37 ±0.08	[20]
$2MgO \cdot SiO_2$	140.7076	22.75 ±0.2	[20]
$MgO \cdot SiO_2$	100.3962	16.22 ±0.10	[20]
$A\ell_2O_3 \cdot SiO_2$	162.046		
Andalusite		22.28 ±0.10	[47]
Kyanite		20.02 ±0.08	[47]
Sillimanite		22.97 ±0.10	[47]
$K_2O \cdot 2SiO_2$	214.373	*	[5]
$K_2O \cdot 4SiO_2$	334.5426	*	[5]
$Li_2O \cdot TiO_2$	109.7762	21.93 ±0.10	[20]
$2MgO \cdot TiO_2$	160.5216	26.1 ±0.2	[20]
$MgO \cdot TiO_2$	120.2102	17.82 ±0.10	[20]
$MgO \cdot 2TiO_2$	200.109	30.4 ±0.2	[48]
$A\ell_2O_3 \cdot TiO_2$ (β)	181.86	26.2 ±0.2	[21]
$SiO_2 \cdot ZrO_2$	183.3036	20.2 ±0.2	[20]
$MgO \cdot WO_3$	272.1596	24.2 ±0.2	[22]
Si	28.086	4.50 ±0.01	[12]
SiO_2	60.0848		
α Quartz		10.00 ±0.10	[20]
α Cristobalite		10.20 ±0.1	[20]
α Tridymite		10.4 ±0.2	[20]
Glass		10.35 ±0.10 $(S^\circ_{298} - S^\circ_0)$	[20]
K	39.102	15.34 ±0.10	[20]
KO_2	71.1008	27.9 ±0.3	[20]
KF	58.1004	15.91 ±0.1	[52]
KHF_2	78.10677	24.92 ±0.1	[52]
$KC\ell$	74.555	19.70 ±0.05	[20]
KBr	119.011	23.2 ±0.2	[20]
KI	166.0064	24.9 ±0.2	[20]

[†] Atomic weights based on C-12 [13].

[*] Measurements have been made but data are not available as yet.

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Chapter B4

THERMOCHEMICAL DATA FOR SOME SIMPLE HYDRIDES AND INORGANIC OXIDIZERS

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1. Introduction

In connection with a recent survey conducted for the Joint Army-Navy-Air Force Thermochemistry Panel, the available thermochemical data on a number of simple inorganic hydrides and oxidizing agents were evaluated. The results of this survey are presented here as it is believed that many of the substances are of interest to contractors engaged in research in the Light-Element Thermochemistry program. As this review was combined with our current program at the National Bureau of Standards to revise NBS Circular 500, "Selected Values of Chemical Thermodynamic Properties," the values tabulated here have been calculated using new values for the heats of formation of the reference systems and should not be combined with values from Circular 500 without precaution. Thus the recent data on the heats of solution of the alkali metals in water indicate that the value of $\Delta Hf°$ for LiOH(aq) will not be significantly altered from that given in C500, whereas that for NaOH(aq) and KOH(aq) will be more negative by about 0.16 and 0.30 kcal/mole respectively. On the other hand, a slightly more positive value of $\Delta Hf°$ for HCl(aq), resulting from a reevaluation of the data on the heat of solution of HCl(g) to include recent measurements by Gunn [107] reduces somewhat the effect of the changes for the alkali metal ions on the alkali halides, for which the values are derived through measurements of heats of neutralization, solution, and dilution. We have retained the value for HCl(g) used in C500 (corrected for atomic weights); the present discordance in the available values will have to be resolved by additional measurements of the heat of formation of either HCl(g) or AgCl(c). In Table 1 are given some of the values for the reference systems used in the calculations of ΔHf for Tables 2-4. They have been selected from an analysis of all the available data on these substances and represent our present best values for these substances. Values for the heats of formation of some possible reaction products of materials listed in Tables 2 and 4 are also given in Table 1 for use in calculation of reaction heats. Values not significantly altered from those in C500 are not listed. No discussion of the sources of the values in Table 1 will be given in this report.

The symbols and conventions used here are the same as those in C500. The unit of energy is the calorie, equal to 4.1840 joules. The atomic weights are those of the new revised scale based on $C^{12} \equiv 12$, published in [105]. In calculations involving high temperature equilibria, values of $(H°-H_{298})/T$ and $(F°-H_{298})/T$ were taken from the JANAF Tables of Thermal Functions [106] when possible. The uncertainties assigned to the values of $\Delta Hf°$ represent our estimates of over-all probable error of the results.

2. Hydrides

The sources of the values given in Table 2 are as follows:

H(g) The dissociation energy of H_2 has been the subject of a great deal of investigation. The most precise results are obtained spectroscopically. Herzberg and Howe [6] reviewed the data and selected $D_o = 36116 \pm 6$ cm^{-1} as the best value. We have used the factor 1 cm^{-1} = 2.85914 cal and JANAF functions to correct to 298.15°C.

OH(g) Barrow [2] reported the spectroscopic dissociation limit, from which we calculate $\Delta Hf^{\circ}_{298} = 9.37$ kcal. Medvedev, et al [3] measured the heat of explosion of $H_2 + O_2$; Dwyer and Oldenberg [4] and Avramenko, et al [5] studied the H_2O - OH - O_2 equilibrium.

NH(g) See Gaydon [6].

NH_2(g) Foner and Hudson [109] determined the heat of formation from appearance potential measurements on NH_3; Szwarc [110], from measurements of activation energies for dissociation of N_2H_4, obtains for the heat of formation 43. ±2. kcal.

NH_3(g) Stephenson and McMahon [7] review the equilibrium data for N_2 - H_2 - NH_3. These were recalculated with JANAF thermal functions to give $\Delta Hf = -10.97$ kcal. Becker and Roth [8] measured the heats of combustion of oxalic acid and ammonium oxalate and the heat of neutralization of oxalic acid with ammonia. Combining with appropriate heats of solution yields $\Delta Hf = -11.04$ kcal. See also Wittig and Schmatz [9].

NH_3(aq) The heat of solution calculated for the completely unionized system is based on the measurements of Thomsen [59] and Wrewsky and Savaritzky [108].

N_2H_4(liq) Aston, et al [10] and Cole and Gilbert [11] give data on the heat of combustion; Roth [12] measured the heat of chlorination. The heat of vaporization is taken from Scott, et al [13].

HN_3(g) Gunther, et al [14] measured the heat of decomposition obtaining $\Delta Hf = 70.3$ kcal. Dow Chemical Co. [15] reported measurements yielding $\Delta Hf = 71.7$ kcal.

P_xH_y(g) The heats of decomposition of PH_3 and P_2H_4 were measured by Gunn and Green [16]. Ipatiev and Frost [17] studied the equilibrium decomposition of PH_3 at elevated temperatures.

AsH_3(g) Gunn, Jolly, and Green [18] measured the heat of decomposition.

CH_3NH_2(liq) The heat of combustion was measured by Jaffe and Prosen [19].

CH_3NHNH_2(liq) Aston, et al [10] measured the heat of combustion. The value reported is for the bomb process at constant volume and 30°C; the data were corrected to the constant pressure process at 25°C.

$(CH_3)_2NNH_2$(liq) The data of Aston, et al [10] on the heat of combustion were converted to constant pressure and 25°C, yielding $\Delta Hf = 12.71$ kcal; Donovan, et al [20] also measured the heat of combustion, obtaining $\Delta Hf = 11.91$ kcal.

$CH_3NHNHCH_3$(liq) Aston, et al [10] reported only one satisfactory heat combustion measurement; this result has been corrected to 25°C and to constant pressure.

H_2NCH_2(c) Salley and Gray [21] reported the heat of combustion. The d of Lemoult [22] differ by 5.5 kcal and were not used.

$(CH_2)_2NH$(liq) Nelson and Jessup [23] reported the heat of combustion.

$(CH_3)_2N_4(CH_3)_2$(liq) Donovan, et al [20] measured the heat of combustio

SiH_4(g) Gunn and Green [16] measured the heat of decomposition and obt ΔHf = 7.3 kcal. Brimer and Humphreys [24] obtained 7.8 kcal by therm decomposition. The heat of combustion measurements of Ogier [25] are considerable variance with the above.

Si_2H_6(g) See Gunn and Green [16].

B_xH_y The data on heats of formation of BH_3, B_2H_6, B_5H_9, and $B_{10}H_{14}$ ar reviewed in [26]. The other boron hydrides are reported by Gunn and Green [27].

$Al(BH_4)_3$(c) This value is based on the hydrolysis measurements of Rulo and Mason [28]; no weight was assigned to the combustion measurements Because of the uncertainty in the final states of the reaction produc a large uncertainty has been assigned.

BeH_2(c) NBS [29] reported a preliminary value of +1.4 kcal/mole, based heat of hydrolysis in aqueous HCl, but the sample was not of high pur Other unpublished measurements indicate a more negative value. We ha selected -1. ±5. kcal as a probable best value.

MgH_2(c) From measurement of the heat of hydrolysis, Dow [15] reported ΔHf = -19.1 kcal; their decomposition pressure data yield ΔHf = -17.6 kcal. The decomposition pressure measurements of Stampfer, et al [30] and Ellinger, et al [31], combined with appropriate entrop data, yield ΔHf = -16.6 and -16.9 kcal respectively.

LiH(c) The heats of solution of Li(c) and LiH(c) have been measured by Messer, et al [32], Gunn and Green [33], Moers [34], and Guntz [35], yielding ΔHf = -21.34, -21.67, -21.60, and -21.61 kcal, respectively.

$LiBH_4$(c) The heat of hydrolysis was reported by Davis, et al [36].

$LiAlH_4$(c) See Davis, et al [36].

NaH(c) Messer, et al [32] and Gunn and Green [33] determined the heats solution of Na(c) and NaH(c), yielding ΔHf = -13.60 and -13.49 kcal, respectively. The decomposition pressure data of Banus, et al [37] a Sollers and Crenshaw [38], combined with appropriate entropy data, yi ΔHf = -12.5 and -12.6 kcal, respectively.

$NaBH_4$(c) Davis, et al [36] measured the heat of hydrolysis in aqueous

KH(c) The heats of solution of K(c) and KH(c) in H_2O were measured by Messer, et al [32] and Gunn and Green [33] yielding ΔHf = -15.16 and -13.82 kcal, respectively. Decomposition pressure measurements by Ke [39] and Sollers and Crenshaw [41] yield -13.6 kcal.

KBH_4(c) The heat of solution was reported by Johnson, et al [40] and Dow [15].

3. Heavy Metal Hydrides

The heats of formation for the heavy metal hydrides listed in Table 3 are calculated principally from the decomposition pressure data of Mulford [43]. These data yield the molal heat of addition of H_2 to a system in which both solid phases have a variable composition. We have simply made the assumption that this heat can be taken as constant independent of the solid phase compositions and have calculated the heat of the ideal reaction

$$M(c) + x/2\ H_2(g) = MH_x(c).$$

In the case of $UH_3(c)$, Abraham and Flotow [44] and Spedding [45] measured the heat of formation of UH_3 calorimetrically; their data were confirmed by decomposition pressure data. The value for ZrH_2 is calculated by extrapolation from the data in [26].

4. Inorganic Oxidizing Compounds

The values given in Table 4 are based on the following data:

$O(g)$ Brix and Herzberg [46] reviewed the spectroscopic data on the dissociation of O_2.

$O_3(g)$ Gunther, et al [47] measured the heat of decomposition of O_3.

$H_2O_2(liq)$ The heat of decomposition of $H_2O_2(liq)$ was measured by Roth, et al [48] and Giguere, et al [49], yielding $\Delta Hf = -44.84$ and -44.85 kcal respectively.

$H_2O_2(aq)$ The heat of decomposition of $H_2O_2(aq)$ was measured by Fontana [50] and Matheson and Maass [51]; heats of solution and dilution were measured by [48] and [49], all data being quite consistent.

$ClO(g)$ The spectroscopic dissociation energy, 63.33 kcal, was obtained by Durie and Ramsay [52]; Porter and Wright [53] give 63.26 kcal.

$ClO_2(g)$ This is taken from the review by Evans, et al [54].

$Cl_2O(g)$ See [54].

$Cl_2O_7(liq)$ The heat of decomposition of the gas was measured by Goodeve and Marsh [55]; taking the heat of vaporization as 8.3 kcal gives $\Delta Hf = 55.0$ kcal. The heat of solution of the liquid to give $HClO_4(aq)$ was measured by Rosolovskii, et al [56] and by [55]; these data lead to $\Delta Hf = 57.1$ and 56.7 kcal, respectively.

$HClO_4(liq)$ The heats of solution in H_2O of various $HClO_4$ - Cl_2O_7 mixtures was measured by Rosolovskii, et al [56]. Berthelot [57] also measured the heat of solution of $HClO_4$; his value is in good agreement.

$BrCl(g)$ See [54].

$I_2O_5(c)$ Spencer and Hepler [58] measured the heat of solution in aqueous alkali, yielding $\Delta Hf = -42.02$ kcal. Thomsen [59] and Moles and Vitoria [60] measured the heat of solution in H_2O, yielding $\Delta Hf = -42.3$ kcal.

ICl(g) The various equilibrium studies of McMorris and Yost [61] were recomputed, giving ΔHf = 4.13 and 4.00 kcal. The spectroscopic dissociation energy of Brown and Gibson [62] yields ΔHf = 4.06 kcal.

ICl_3(c) Nies and Yost [63] measured the decomposition pressure. Using an estimated entropy for ICl_3 of 45 cal/deg mole, we calculate ΔHf = -19.9 kcal.

NO(g) Berthelot [64] measured the heats of combustion of C_2H_4 and C_2N_2 in O_2 and NO, obtaining ΔHf = 21.4 and 21.8 kcal. Koerner and Daniels [65] burned P(c) in O_2 and NO and obtained, by extrapolation, ΔHf = 21.8 kcal. From a study of the ultraviolet spectrum, Tanaka [111] set the dissociation limit at 6.49 e.v., yielding ΔHf = 21.9 kcal. A recalculation of the high temperature equilibrium data of Nernst [66] yields ΔHf = 22.6 kcal with a definite trend with temperature in the results. The equilibrium data on the various nitrogen oxides are brought into satisfactory agreement with the calorimetric data for HNO_3 if the value selected is ΔHf = 21.80 kcal.

NO_2(g) The equilibrium data of Giauque and Kemp [67] were recalculated.

N_2O_3(g) Beattie and Bell [68] and Verhoek and Daniels [69] measured the equilibrium decomposition of N_2O_3 to NO and NO_2, obtaining ΔHf = 20.28 and 20.32 kcal, respectively.

N_2O_4(g) Gray and Rathbone [70] reviewed and correlated the various data for the NO_2 - N_2O_4 system, from which we calculate the heat of dissociation of N_2O_4 to $2NO_2$ to be 13.68 ±0.03 kcal/mole. See also Jacob [71].

N_2O_5(c) The heat of solution in H_2O to form HNO_3(aq) was measured by Ogg [72] and Berthelot [73], yielding ΔHf = -10.0 and -12.2 kcal. Ray and Ogg [74] measured the heat of reaction of N_2O_5(g) and NO(g) from which we compute ΔHf = -9.6 kcal.

HNO_3(g) Equilibria involving HNO_3 were measured by Jones [75], Feick [76], and Abel, et al [77], yielding ΔHf = -32.06, -32.02, and -32.09 kcal. Becker and Roth [78] and Thomsen [59] measured the heat of neutralization of HNO_3(aq) with NH_3; combining these values with the data for NH_4NO_3 yields ΔHf = -32.27 and -32.07 kcal. Berthelot [79] measured the heat of reaction of N_2O_4 and Cl_2, obtaining ΔHf = -32.10 kcal.

HNO_3(liq) Forsythe and Giauque [80] review the data on the heat of vaporization.

NH_4NO_3(c) The heat of decomposition to N_2, O_2, and H_2O was measured by Becker and Roth [78] and by Medard and Thomas [81], yielding ΔHf = -87.28 and -87.18 kcal, respectively.

NCl_3(liq) Noyes and Tuley [82] measured the heat of reaction of HCl(g) with NCl_3 (in CCl_4). Assuming the heat of solution to be zero, ΔHf = 54.4 kcal.

NOCl(g) Beeson and Yost [83] studied the NOCl - NO - Cl_2 equilibrium from which ΔHf = 12.59 ±0.03 kcal. The calorimetric data of Briner and Pylkoff [84] yield ΔHf = 8.0 kcal.

NO_2Cl(g) Ray and Ogg [85] measured the heat of reaction and equilibrium constant for the reaction of NO and NO_2Cl, from which ΔHf = 3.45 and 2.88 kcal, respectively.

$NOClO_4$(c) Cruse, Hack, and Möller [86] measured the heat of hydrolysis in NaOH(aq).

NO_2ClO_4(c) Cordes and Fetter [87] measured the heat of hydrolysis to HNO_3(aq) and $HClO_4$(aq).

NH_4ClO_4(c) Gilliland and Johnson [88] found the difference in the heats of formation of NH_4ClO_4(c) and NH_4Cl(c) to be 4.64 kcal from which we calculate ΔHf = -70.74 kcal. Birky and Hepler [89] measured the heat of solution; from our data on the ions, we calculate ΔHf = -70.59 kcal.

$N_2H_4 \cdot HClO_4$(c) We have estimated the heat of neutralization of $HClO_4$(aq) with N_2H_4 by analogy with the data for $N_2H_4 \cdot HCl$. Gilbert and Cobb [90] measured the heat of solution.

Li_2O(c) Kolesov, et al [91] and deForcrand [92] measured the heat of solution of Li_2O, obtaining ΔHf = -142.7 and -142.5 kcal, respectively.

Li_2O_2(c) deForcrand [93] measured the heats of the reactions of Li_2O_2 with HCl(aq) and LiOH(aq) with H_2O_2(aq).

LiO_3(c) The heat of formation was estimated by Nikolskii, et al [94].

$LiClO_4$(c) The data of [88] yield ΔHf = -90.93 kcal; those of [89] yield -91.19 kcal.

NaO_2(c) Gilles and Margrave [95] measured the heat of decomposition in H_2O.

NaO_3(c) Estimated by [94].

Na_2O(c) The heat of solution was measured by Rengade [96], Roth and Kaule [97], and Matsui and Oka [98] yielding ΔHf = -99.45, -100.10, and -99.70 kcal, respectively.

Na_2O_2(c) Gilles and Margrave [95] and Roth and Kaule [97] measured the heat of solution, yielding ΔHf = -122.5 and -120.9 kcal, respectively.

$NaClO_4$(c) See [88].

KO_2(c) The heat of decomposition in H_2O was measured by Gilles and Margrave [95]; Kazarnovskaya and Kazarnovskii [99] and deForcrand [100] determined the heat of solution in H_2SO_4(aq). The resulting values of ΔHf are -67.9, -67.9, and -68.0 kcal.

KO_3(c) The heat of solution was measured by Nikolskii, et al [101].

K_2O(c) Rengade [102] measured the heats of solution of K(c) and K_2O(c) in H_2O.

K_2O_2(c) Centnerzwer and Blumenthal [103] measured the decomposition pressure as a function of temperature.

K_2O_3(c) deForcrand [100] measured the heat of solution in H_2SO_4(aq).

$KClO_4$(c) The heat of decomposition to KCl(c) and O_2(g) was measured by Gilliland and Johnson [104]. Previous measurements are reviewed in this article.

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Table 1.

Reference Values of Heats of Formation Used in the Calculations

Formula	State	$\Delta Hf^\circ_{298.15}$ kcal/mole
OH^-	aq, std	-54.954
H_2O	liq	-68.314
HF	g	-64.4
Cl	g	+28.92
HCl	g	-22.062
HCl	aq, std	-39.96
N	g	+113.0
HNO_3	aq, std	-49.44
CO_2	g	-94.050
B_2O_3	c	-305.34
H_3BO_3	c	-262.16
BN	c	-60.3
$BeCl_2$	c	-118.0
NaOH	aq, std	-112.40
NaCl	c	-98.32
KOH	aq, std	-115.30
KCl	c	-104.41

Table 2.

Selected Values of Heats of Formation
of Some Inorganic Hydrides

Formula	State	$\Delta Hf^{\circ}_{298.15}$ kcal/mole	
H_2	g	0	
H	g	52.099	±0.020
OH	g	9.37	±0.3
NH	g	78.9	±5.
NH_2	g	42.8	±4.
NH_3	g	-11.00	±0.05
	aq	-19.29	±0.07
N_2H_4	liq	12.05	±0.05
	g	22.75	±0.10
HN_3	g	71.7	±1.0
PH_3	g	1.6	±0.5
P_2H_4	g	5.0	±1.0
AsH_3	g	15.87	±0.25
CH_3NH_2	liq	-11.3	±0.1
CH_3NHNH_2	liq	13.10	±0.30
$(CH_3)_2NNH_2$	liq	12.2	±0.4
$CH_3NHNHCH_3$	liq	13.5	±1.0
H_2NCN	c	14.65	±0.13
$(CH_2)_2NH$ (ethylenimine)	liq	21.96	±0.14
$(CH_3)_2N_4(CH_3)_2$ (tetramethyltetrazene)	liq	55.36	±0.21
SiH_4	g	7.3	±0.3
Si_2H_6	g	17.1	±0.3
BH_3	g	18.	±3.
B_2H_6	g	7.53	±0.25
B_4H_{10}	g	13.8	±1.0
B_5H_9	liq	7.74	±0.42
B_5H_{11}	g	22.2	±1.0
B_6H_{10}	g	19.6	±2.0
$B_{10}H_{14}$	c	-15.8	±1.5

Table 2 - Continued.

Formula	State	$\Delta Hf^{\circ}_{298.15}$ kcal/mole	
$Al(BH_4)_3$	c	-74.7	±7.
BeH_2	c	-1.	±5.
MgH_2	c	-17.5	±2.0
LiH	c	-21.63	±0.07
$LiBH_4$	c	-46.44	±0.05
$LiAlH_4$	c	-25.74	±0.40
NaH	c	-13.52	±0.05
$NaBH_4$	c	-45.65	±0.12
KH	c	-13.82	±0.05
KBH_4	c	-55.00	±0.55

Table 3.

Heats of Formation of Some Heavy Metal Hydrides

Formula	State	ΔH^{+} kcal/mole
ZrH_2	c	-42.4
LaH_2	c	-46.6
CeH_2	c	-30.4
PrH_2	c	-47.8
NdH_2	c	-44.8
GdH_2	c	-46.9
UH_3	c	-30.4

[+] The values of ΔH are the heats of addition of H_2 to a two-solid-phase system consisting of metal plus dissolved H_2 and the metal hydride containing somewhat less than the indicated amount of H, extrapolated to the formula listed.

Table 4.

Selected Values of Heats of Formation of Some Inorganic Oxidizers

Formula	State	$\Delta Hf^\circ_{298.15}$ kcal/mole
O_2	g	0.
O	g	59.554 ± 0.040
O_3	g	33.93 ± 0.5
H_2O_2	liq	-44.87 ± 0.05
	aq	-45.67
ClO	g	24.17 ± 0.2
ClO_2	g	25.0 ± 1.5
Cl_2O	g	18.1 ± 0.3
Cl_2O_7	liq	56.9 ± 0.5
$HClO_4$	liq	-9.8 ± 0.3
* BrCl	g	3.48 ± 0.05
* I_2O_5	c	-42.10 ± 0.2
* ICl	g	4.10 ± 0.05
* ICl_3	c	-19.9 ± 1.0
NO	g	21.80 ± 0.20
NO_2	g	8.15 ± 0.20
N_2O_3	g	20.30 ± 0.20
N_2O_4	g	2.62 ± 0.20
N_2O_5	c	-10.0 ± 0.3
HNO_3	g	-32.10 ± 0.10
	liq	-41.47
NH_4NO_3	c	-87.23 ± 0.05
NCl_3	liq	54.4 ± 2.0
NOCl	g	12.59 ± 0.03
NO_2Cl	g	3.2 ± 0.5
$NOClO_4$	c	-36.83
NO_2ClO_4	c	8.7 ± 0.5
NH_4ClO_4	c	-70.67 ± 0.05
$N_2H_4 \cdot HClO_4$	c	-43.6 ± 2.0

*Br_2(liq) and I_2(c) are taken as the standard reference states for these elements.

Table 4 - Continued.

Formula	State	$\Delta Hf^\circ_{298.15}$ kcal/mole	
Li_2O	c	-142.6	± 0.1
Li_2O_2	c	-151.7	± 2.
LiO_3 (lithium ozonide)	c	-36.	±10.
$LiClO_4$	c	-91.05	± 0.2
NaO_2	c	-62.3	± 0.7
NaO_3	c	-45.	±10.
Na_2O	c	-99.9	± 0.1
Na_2O_2	c	-122.0	± 0.7
$NaClO_4$	c	-91.57	± 0.2
KO_2	c	-67.9	± 0.5
KO_3	c	-63.3	± 3.
K_2O	c	-86.4	± 0.5
K_2O_2	c	-118.5	± 1.
K_2O_3	c	-126.0	± 1.
$KClO_4$	c	-103.45	± 0.15

Chapter B5

DERIVATION OF TABLES OF THERMODYNAMIC FUNCTIONS FOR CRYSTALLINE AND LIQUID BERYLLIUM FLUORIDE

C. W. Beckett, W. G. Goodson, and T. B. Douglas

If good heat-capacity measurements over the whole temperature range were available on the condensed states of BeF_2, the generation of thermodynamic tables would be simple. But so far as we know, no such measurements have been made. We, as others, have arrived at tables by treating the vaporization data on this substance in conjunction with tables for the gas functions, and then, by analogy with similar substances, constructing reasonable enthalpy-temperature functions for the solid and liquid. Pending the time when direct thermal data are available, this indirect procedure seems to give reasonable results. And since different people tend to assume different values for the parameters that have to be estimated (see, e.g., [2] and [4]), a comparison of tables from different sources often gives an idea of how sensitive the results are to the assumptions.

It may be noted that an accurate experimental determination of the heat capacity and heat of fusion of BeF_2 presents one problem near the melting point. Even if the reported polymorphic transitions [11] prove reversible, the liquid is not likely to crystallize and give a reliable heat of fusion by drop calorimetry unless the resulting glass can be related energetically to the crystalline state by a separate experiment such as solution calorimetry.

Our procedure in deriving the tables for crystalline and liquid BeF_2 appearing at the end of this report was as follows.

Four series of vapor-pressure measurements were originally available to us, three by the transpiration method (1019°-1241°K [5], 1040°-1376°K [7], and 1075°-1298°K [8]) and one by the Knudsen effusion method (846°-950°K [6]). (Before we finished using these data, a fifth series of measurements appeared [1].) On the basis of a critical discussion of the melting point in a recent report [1], we assumed this to be 816°K. The vapor-pressure data are all in the liquid range. The vapor was assumed to be wholly monomeric in these temperature ranges. It has been reported from mass-spectrometric results [9] that in the case of BeF_2 the ratio of dimer to monomer is approximately 0.001, but no temperature was stated. If one assumes this ratio to hold at 800°K, the corresponding ratio at 1300°K may be estimated from the thermodynamic relation

$$(p_2/p_1)_{1300}/(p_2/p_1)_{800} = 10^{0.105(\Delta H_1 - \Delta H_D)\,\mathrm{kcal}} \qquad (1)$$

if the heat of vaporization to the monomer ΔH_1 and the heat of dissociation of the dimer ΔH_D can be approximated. Equation (1) gives the values

$(\Delta H_1 - \Delta H_D)$ (kcal)	$(p_2/p_1)_{1300}$
0	0.001
10	0.01
20	0.1
30	0.6

ΔH_1 is approximately 50 kcal. For $BeC\ell_2$ ΔH_D is approximately 30 kcal, and by analogy with the aluminum halides one might guess that for BeF_2 it is at least 35 kcal, in which case the saturated vapor would be less than 4% dimerized at 1300°K and correspondingly less at lower temperatures. This figure is essentially within the experimental error of the vapor-pressure data.

On a log P-vs. 1/T plot of the vapor-pressure data, the effusion-method results were temporarily discounted as being subject to the errors of low pressures, and a tangent was drawn to the other three sets at a mean temperature of 1150°K. From the slope, ordinate, and S°(gas) [reference 10, Table A-51] at this temperature S°_{1150} (liquid) was found to be 35.046 cal/deg K-mole. By assuming per gram atom the reasonable estimate of a constant heat capacity of 8 cal/deg K of liquid and, agreeing with Brewer [3], a heat of fusion of 2 cal/deg K, the entropy of the crystal at the melting point was readily evaluated. While this entropy of fusion does not allow for entropies of the reported transitions below the melting point [11], it is true in many cases that the sum of the entropies of transition and fusion approximates the entropy of fusion expected if transitions are assumed absent. Since our table does not allow for any transitions, it may thus be assumed as an estimate for the low-temperature crystal form over the whole temperature region below the melting point.

The heat capacity of the crystal was estimated by analogy with accurately measured values for the analogous substances $A\ell F_3$, MgF_2, and $MgC\ell_2$ [reference 10:Tables B-5, B-14, and B-15]. As shown in Fig. 1, the heat capacities of these three salts were plotted on reduced temperature scales so as to make the entropy of each equal at 816°K to that arrived at for $BeF_2(c)$ at this temperature. The three curves nearly coincide (particularly those of the two polyvalent fluorides), and an average curve was drawn to represent BeF_2.

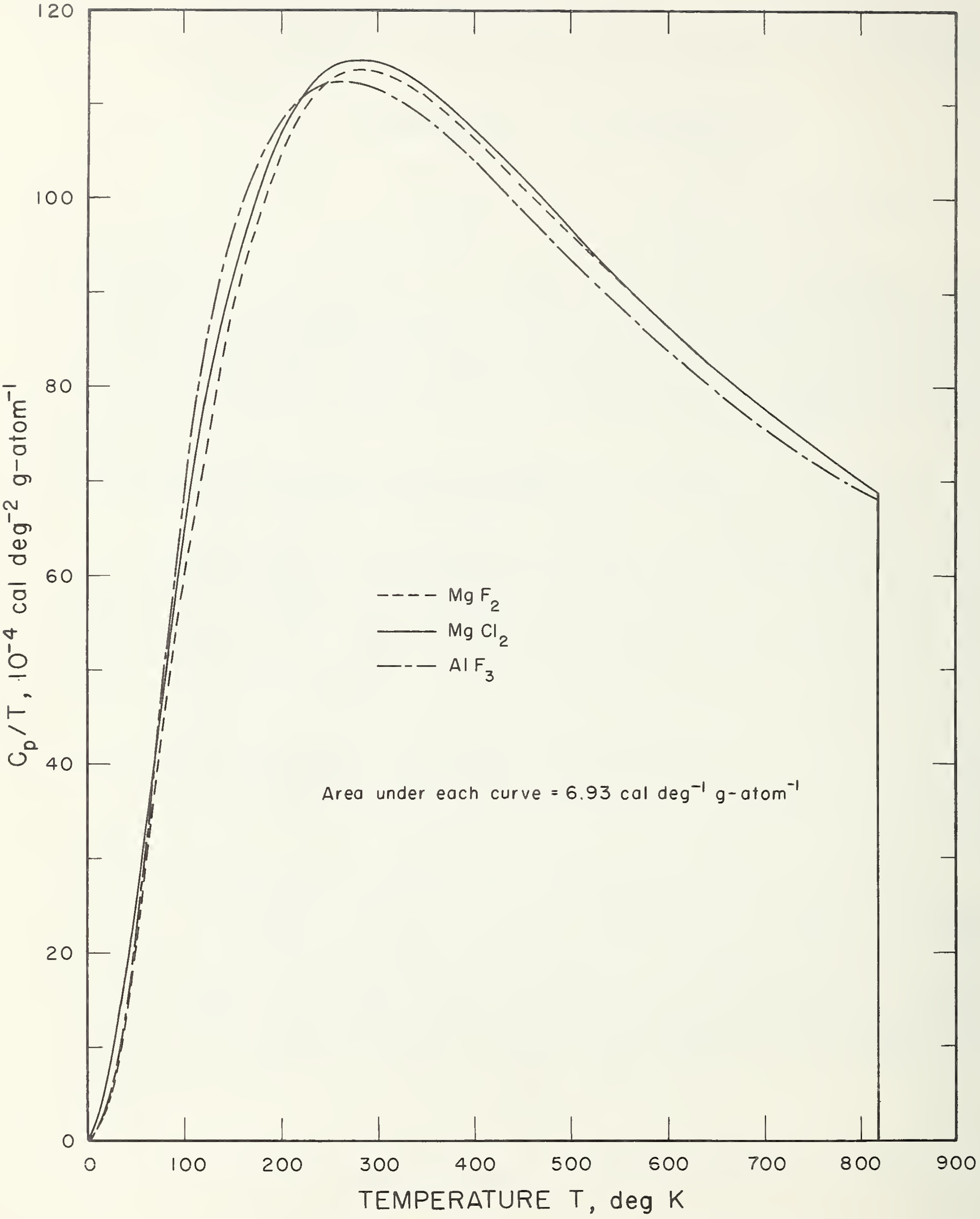

Fig. I: Entropy Plot of three Substances Analogous to BeF_2

The resulting thermodynamic functions for BeF_2 gave $\Delta H_0^\circ = 57.29$ kcal/mole for the heat of vaporization at 0°K. Reference [6] cites values varying from 54.8 to 59.1 and classified according to derivation from spectroscopic data or the Third Law, a distinction which seems to imply independently determined heat capacities of the condensed states. It may be noted that in our procedure it was necessary to combine the results of spectroscopic data (on which our tables for the gas are partly based), the Second Law, and the Third Law, and our table for the condensed phase is thus consistent with the single value of ΔH_0° stated above.

The individual measurements of the vapor pressure of BeF_2 are compared with those interpolated from our tables in Fig. 2. The values of [1] are higher, and those of [6] lower. The curve represents values computed from recently issued tables of thermodynamic functions generated elsewhere [2].

The situation regarding $BeC\ell_2$ is similar to that for BeF_2 in that, so far as we know, no heat-capacity data are available for the solid and liquid. We understand that the Thermal Laboratory of the Dow Chemical Co., Midland, Michigan, has undertaken such measurements on $BeC\ell_2$. We have carried out an extensive correlation of the available data and have arrived at a basis for generating a consistent set of thermodynamic functions for the solid, liquid, and dimer gas. However, we are aware of only one set of vapor-pressure measurements on $BeC\ell_2$; and besides, unlike that of BeF_2, the saturated vapor of $BeC\ell_2$ is known to contain large proportions of both monomer and dimer. Others have previously estimated and issued condensed-state tables for $BeC\ell_2$. The most promising way to improve the existing tables for this substance is undoubtedly through access to new data.

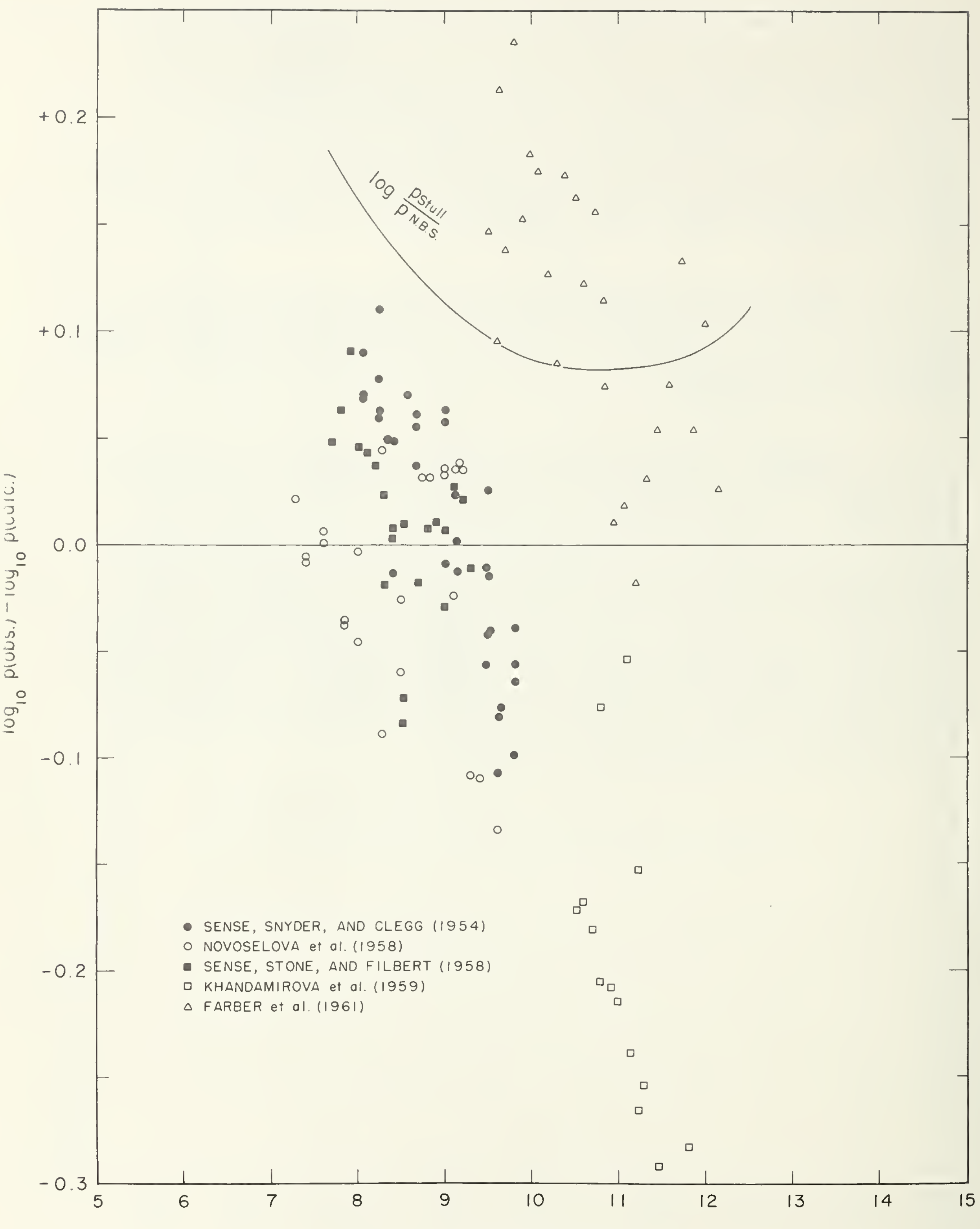

Fig. 2: Observed vs. Calculated Vapor Pressure of BeF_2 (ℓ)

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APPENDIX A

IDEAL-GAS THERMODYNAMIC FUNCTIONS

APPENDIX A

IDEAL GAS THERMODYNAMIC FUNCTIONS

by

Joseph Hilsenrath and William H. Evans

The thermodynamic functions are given for H^+, e^-, H_2, and O_2. The tables for the proton and the electron are newly computed. Those for H_2 and O_2 were converted and extrapolated from existing NBS tables [1,2].

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Table A-1-1 Thermodynamic Functions for H^+

T °K	$\frac{-(F^\circ - H^\circ_0)}{T}$	$\frac{H^\circ - H^\circ_0}{T}$	S°	C°_p	$H^\circ - H^\circ_0$
273.15	20.6102	4.9681	25.5783	4.9681	1357.1
298.15	21.0453	4.9681	26.0134	4.9681	1481.3
1000.	27.0575	4.9681	32.0257	4.9681	4968.1
1100.	27.5310	4.9681	32.4992	4.9681	5465.0
1200.	27.9633	4.9681	32.9315	4.9681	5961.8
1300.	28.3610	4.9681	33.3291	4.9681	6458.6
1400.	28.7292	4.9681	33.6973	4.9681	6955.4
1500.	29.0719	4.9681	34.0401	4.9681	7452.2
1600.	29.3926	4.9681	34.3607	4.9681	7949.0
1700.	29.6938	4.9681	34.6619	4.9681	8445.9
1800.	29.9777	4.9681	34.9459	4.9681	8942.7
1900.	30.2463	4.9681	35.2145	4.9681	9439.5
2000.	30.5012	4.9681	35.4693	4.9681	9936.3
2100.	30.7436	4.9681	35.7117	4.9681	10433.1
2200.	30.9747	4.9681	35.9428	4.9681	10929.9
2300.	31.1955	4.9681	36.1637	4.9681	11426.7
2400.	31.4070	4.9681	36.3751	4.9681	11923.6
2500.	31.6098	4.9681	36.5779	4.9681	12420.4
2600.	31.8046	4.9681	36.7728	4.9681	12917.2
2700.	31.9921	4.9681	36.9603	4.9681	13414.0
2800.	32.1728	4.9681	37.1410	4.9681	13910.8
2900.	32.3472	4.9681	37.3153	4.9681	14407.6
3000.	32.5156	4.9681	37.4837	4.9681	14904.4
3100.	32.6785	4.9681	37.6466	4.9681	15401.3
3200.	32.8362	4.9681	37.8044	4.9681	15898.1
3300.	32.9891	4.9681	37.9572	4.9681	16394.9
3400.	33.1374	4.9681	38.1056	4.9681	16891.7
3500.	33.2814	4.9681	38.2496	4.9681	17388.5
3600.	33.4214	4.9681	38.3895	4.9681	17885.3
3700.	33.5575	4.9681	38.5257	4.9681	18382.2
3800.	33.6900	4.9681	38.6581	4.9681	18879.0
3900.	33.8190	4.9681	38.7872	4.9681	19375.8
4000.	33.9448	4.9681	38.9130	4.9681	19872.6
4100.	34.0675	4.9681	39.0357	4.9681	20369.4
4200.	34.1872	4.9681	39.1554	4.9681	20866.2
4300.	34.3041	4.9681	39.2723	4.9681	21363.0
4400.	34.4183	4.9681	39.3865	4.9681	21859.9
4500	34.5300	4.9681	39.4981	4.9681	22356.7
4600.	34.6392	4.9681	39.6073	4.9681	22853.5
4700.	34.7460	4.9681	39.7142	4.9681	23350.3
4800.	34.8506	4.9681	39.8188	4.9681	23847.1
4900.	34.9531	4.9681	39.9212	4.9681	24343.9
5000.	35.0534	4.9681	40.0216	4.9681	24840.7
5100.	35.1518	4.9681	40.1200	4.9681	25337.6
5200.	35.2483	4.9681	40.2164	4.9681	25834.4
5300.	35.3429	4.9681	40.3111	4.9681	26331.2
5400.	35.4358	4.9681	40.4039	4.9681	26828.0
5500.	35.5270	4.9681	40.4951	4.9681	27324.8
5600.	35.6165	4.9681	40.5846	4.9681	27821.6
5700.	35.7044	4.9681	40.6726	4.9681	28318.5
5800.	35.7908	4.9681	40.7590	4.9681	28815.3
5900.	35.8757	4.9681	40.8439	4.9681	29312.1
6000.	35.9592	4.9681	40.9274	4.9681	29808.9

The tables are in units of calories, moles and °K. See reverse side for conversion factors to other units. The atomic weight = 1.0075

Table A-1-1 Thermodynamic Functions for H^+ - Continued

T °K	$-\frac{(F^\circ - H^\circ_0)}{T}$	$\frac{H^\circ - H^\circ_0}{T}$	S°	C°_p	$H^\circ - H^\circ_0$
6100.	36.0414	4.9681	41.0095	4.9681	30305.7
6200.	36.1221	4.9681	41.0903	4.9681	30802.5
6300.	36.2016	4.9681	41.1698	4.9681	31299.3
6400.	36.2799	4.9681	41.2480	4.9681	31796.2
6500.	36.3569	4.9681	41.3251	4.9681	32293.0
6600.	36.4328	4.9681	41.4009	4.9681	32789.8
6700.	36.5075	4.9681	41.4756	4.9681	33286.6
6800.	36.5811	4.9681	41.5492	4.9681	33783.4
6900.	36.6536	4.9681	41.6218	4.9681	34280.2
7000.	36.7251	4.9681	41.6932	4.9681	34777.0
7100.	36.7956	4.9681	41.7637	4.9681	35273.9
7200.	36.8650	4.9681	41.8332	4.9681	35770.7
7300.	36.9336	4.9681	41.9017	4.9681	36267.5
7400.	37.0012	4.9681	41.9693	4.9681	36764.3
7500.	37.0679	4.9681	42.0360	4.9681	37261.1
7600.	37.1337	4.9681	42.1018	4.9681	37757.9
7700.	37.1986	4.9681	42.1668	4.9681	38254.8
7800.	37.2627	4.9681	42.2309	4.9681	38751.6
7900.	37.3260	4.9681	42.2941	4.9681	39248.4
8000.	37.3885	4.9681	42.3566	4.9681	39745.2
8100.	37.4502	4.9681	42.4184	4.9681	40242.0
8200.	37.5112	4.9681	42.4793	4.9681	40738.8
8300.	37.5714	4.9681	42.5395	4.9681	41235.6
8400.	37.6309	4.9681	42.5990	4.9681	41732.5
8500.	37.6897	4.9681	42.6578	4.9681	42229.3
8600.	37.7478	4.9681	42.7159	4.9681	42726.1
8700.	37.8052	4.9681	42.7734	4.9681	43222.9
8800.	37.8620	4.9681	42.8302	4.9681	43719.7
8900.	37.9181	4.9681	42.8863	4.9681	44216.5
9000.	37.9737	4.9681	42.9418	4.9681	44713.3
9100.	38.0286	4.9681	42.9967	4.9681	45210.2
9200.	38.0828	4.9681	43.0510	4.9681	45707.0
9300.	38.1366	4.9681	43.1047	4.9681	46203.8
9400.	38.1897	4.9681	43.1578	4.9681	46700.6
9500.	38.2423	4.9681	43.2104	4.9681	47197.4
9600.	38.2943	4.9681	43.2624	4.9681	47694.2
9700.	38.3458	4.9681	43.3139	4.9681	48191.1
9800.	38.3967	4.9681	43.3649	4.9681	48687.9
9900.	38.4472	4.9681	43.4153	4.9681	49184.7
10000.	38.4971	4.9681	43.4653	4.9681	49681.5

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal g^{-1} °K^{-1} (or °C^{-1})	.99256
joules g^{-1} °K^{-1} (or °C^{-1})	4.1529
Btu lb^{-1} °R^{-1} (or °F^{-1})	.99191

Table A-81 Thermodynamic Functions for e^- (Electron Gas)

T °K	$\frac{-(F^\circ-H^\circ_0)}{T}$	$\frac{H^\circ - H^\circ_0}{T}$	S°	C°_p	$H^\circ - H^\circ_0$
273.15	-0.4147	4.9681	4.5534	4.9681	1357.1
298.15	0.0204	4.9681	4.9885	4.9681	1481.3
1000.	6.0326	4.9681	11.0008	4.9681	4968.1
1100.	6.5061	4.9681	11.4743	4.9681	5465.0
1200.	6.9384	4.9681	11.9066	4.9681	5961.8
1300.	7.3361	4.9681	12.3042	4.9681	6458.6
1400.	7.7043	4.9681	12.6724	4.9681	6955.4
1500.	8.0470	4.9681	13.0152	4.9681	7452.2
1600.	8.3677	4.9681	13.3358	4.9681	7949.0
1700.	8.6689	4.9681	13.6370	4.9681	8445.9
1800.	8.9528	4.9681	13.9210	4.9681	8942.7
1900.	9.2215	4.9681	14.1896	4.9681	9439.5
2000.	9.4763	4.9681	14.4444	4.9681	9936.3
2100.	9.7187	4.9681	14.6868	4.9681	10433.1
2200.	9.9498	4.9681	14.9180	4.9681	10929.9
2300.	10.1706	4.9681	15.1388	4.9681	11426.7
2400.	10.3821	4.9681	15.3502	4.9681	11923.6
2500.	10.5849	4.9681	15.5531	4.9681	12420.4
2600.	10.7798	4.9681	15.7479	4.9681	12917.2
2700.	10.9673	4.9681	15.9354	4.9681	13414.0
2800.	11.1479	4.9681	16.1161	4.9681	13910.8
2900.	11.3223	4.9681	16.2904	4.9681	14407.6
3000.	11.4907	4.9681	16.4589	4.9681	14904.4
3100.	11.6536	4.9681	16.6218	4.9681	15401.3
3200.	11.8113	4.9681	16.7795	4.9681	15898.1
3300.	11.9642	4.9681	16.9324	4.9681	16394.9
3400.	12.1125	4.9681	17.0807	4.9681	16891.7
3500.	12.2565	4.9681	17.2247	4.9681	17388.5
3600.	12.3965	4.9681	17.3647	4.9681	17885.3
3700.	12.5326	4.9681	17.5008	4.9681	18382.2
3800.	12.6651	4.9681	17.6333	4.9681	18879.0
3900.	12.7942	4.9681	17.7623	4.9681	19375.8
4000.	12.9199	4.9681	17.8881	4.9681	19872.6
4100.	13.0426	4.9681	18.0108	4.9681	20369.4
4200.	13.1623	4.9681	18.1305	4.9681	20866.2
4300.	13.2792	4.9681	18.2474	4.9681	21363.0
4400.	13.3935	4.9681	18.3616	4.9681	21859.9
4500.	13.5051	4.9681	18.4733	4.9681	22356.7
4600.	13.6143	4.9681	18.5825	4.9681	22853.5
4700.	13.7212	4.9681	18.6893	4.9681	23350.3
4800.	13.8258	4.9681	18.7939	4.9681	23847.1
4900.	13.9282	4.9681	18.8963	4.9681	24343.9
5000.	14.0286	4.9681	18.9967	4.9681	24840.7
5100.	14.1269	4.9681	19.0951	4.9681	25337.6
5200.	14.2234	4.9681	19.1916	4.9681	25834.4
5300.	14.3180	4.9681	19.2862	4.9681	26331.2
5400.	14.4109	4.9681	19.3791	4.9681	26828.0
5500.	14.5021	4.9681	19.4702	4.9681	27324.8
5600.	14.5916	4.9681	19.5597	4.9681	27821.6
5700.	14.6795	4.9681	19.6477	4.9681	28318.5
5800.	14.7659	4.9681	19.7341	4.9681	28815.3
5900.	14.8509	4.9681	19.8190	4.9681	29312.1
6000.	14.9344	4.9681	19.9025	4.9681	29808.9

The tables are in units of calories, moles and °K. See reverse side for conversion factors to other units. The atomic weight = .00054876

Table A-81 Thermodynamic Functions for e^- (Electron Gas) - Continued

T °K	$\frac{-(F^\circ - H_0^\circ)}{T}$	$\frac{H^\circ - H_0^\circ}{T}$	S°	C_p°	$H^\circ - H_0^\circ$
6100.	15.0165	4.9681	19.9846	4.9681	30305.7
6200.	15.0973	4.9681	20.0654	4.9681	30802.5
6300.	15.1768	4.9681	20.1449	4.9681	31299.3
6400.	15.2550	4.9681	20.2231	4.9681	31796.2
6500.	15.3320	4.9681	20.3002	4.9681	32293.0
6600.	15.4079	4.9681	20.3760	4.9681	32789.8
6700.	15.4826	4.9681	20.4507	4.9681	33286.6
6800.	15.5562	4.9681	20.5243	4.9681	33783.4
6900.	15.6287	4.9681	20.5969	4.9681	34280.2
7000.	15.7002	4.9681	20.6684	4.9681	34777.0
7100.	15.7707	4.9681	20.7388	4.9681	35273.9
7200.	15.8402	4.9681	20.8083	4.9681	35770.7
7300.	15.9087	4.9681	20.8768	4.9681	36267.5
7400.	15.9763	4.9681	20.9444	4.9681	36764.3
7500.	16.0430	4.9681	21.0111	4.9681	37261.1
7600.	16.1088	4.9681	21.0769	4.9681	37757.9
7700.	16.1737	4.9681	21.1419	4.9681	38254.8
7800.	16.2378	4.9681	21.2060	4.9681	38751.6
7900.	16.3011	4.9681	21.2693	4.9681	39248.4
8000.	16.3636	4.9681	21.3318	4.9681	39745.2
8100.	16.4253	4.9681	21.3935	4.9681	40242.0
8200.	16.4863	4.9681	21.4544	4.9681	40738.8
8300.	16.5465	4.9681	21.5147	4.9681	41235.6
8400.	16.6060	4.9681	21.5742	4.9681	41732.5
8500.	16.6648	4.9681	21.6330	4.9681	42229.3
8600.	16.7229	4.9681	21.6911	4.9681	42726.1
8700.	16.7803	4.9681	21.7485	4.9681	43222.9
8800.	16.8371	4.9681	21.8053	4.9681	43719.7
8900.	16.8933	4.9681	21.8614	4.9681	44216.5
9000.	16.9488	4.9681	21.9169	4.9681	44713.3
9100.	17.0037	4.9681	21.9718	4.9681	45210.2
9200.	17.0580	4.9681	22.0261	4.9681	45707.0
9300.	17.1117	4.9681	22.0798	4.9681	46203.8
9400.	17.1648	4.9681	22.1330	4.9681	46700.6
9500.	17.2174	4.9681	22.1855	4.9681	47197.4
9600.	17.2694	4.9681	22.2376	4.9681	47694.2
9700.	17.3209	4.9681	22.2890	4.9681	48191.1
9800.	17.3718	4.9681	22.3400	4.9681	48687.9
9900.	17.4223	4.9681	22.3904	4.9681	49184.7
10000.	17.4722	4.9681	22.4404	4.9681	49681.5

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal g^{-1} °K^{-1} (or °C^{-1})	1822.3
joules g^{-1} °K^{-1} (or °C^{-1})	7624.4
Btu lb^{-1} °R^{-1} (or °F^{-1})	1821.1

Table A-82 Thermodynamic Functions for H_2

T °K	$\frac{-(F^\circ - H^\circ_0)}{T}$	$\frac{H^\circ - H^\circ_0}{T}$	S°	C°_p	$H^\circ - H^\circ_0$
50.	10.7988	10.0496	20.8483	4.9781	502.5
100.	16.7983	7.5893	24.3877	5.3934	758.9
150.	19.7335	6.9733	26.7068	6.0671	1046.0
200.	21.7128	6.8084	28.5212	6.5182	1361.7
250.	23.2271	6.7785	30.0056	6.7706	1694.6
300.	24.4632	6.7885	31.2517	6.8938	2036.5
350.	25.5124	6.8084	32.3208	6.9514	2382.9
400.	26.4226	6.8282	33.2508	6.9753	2731.3
450.	27.2274	6.8441	34.0716	6.9872	3079.9
500.	27.9488	6.8600	34.8088	6.9932	3430.0
550.	28.6046	6.8719	35.4766	7.0011	3779.6
600.	29.2008	6.8839	36.0847	7.0091	4130.3
650.	29.7533	6.8938	36.6471	7.0210	4481.0
700.	30.2660	6.9018	37.1677	7.0369	4831.2
750.	30.7409	6.9117	37.6526	7.0568	5183.8
800.	31.1881	6.9216	38.1097	7.0806	5537.3
850.	31.6074	6.9316	38.5389	7.1104	5891.8
900.	32.0028	6.9435	38.9463	7.1422	6249.1
950.	32.3784	6.9554	39.3338	7.1800	6607.6
1000.	32.7341	6.9673	39.7015	7.2197	6967.3
1050.	33.0760	6.9793	40.0552	7.2614	7328.2
1100.	33.4019	6.9932	40.3950	7.3091	7692.5
1150.	33.7119	7.0091	40.7209	7.3568	8060.4
1200.	34.0120	7.0230	41.0349	7.4065	8427.6
1250.	34.2961	7.0409	41.3370	7.4582	8801.1
1300.	34.5743	7.0568	41.6311	7.5118	9173.8
1350.	34.8426	7.0746	41.9173	7.5635	9550.8
1400.	35.1010	7.0925	42.1935	7.6172	9929.5
1450.	35.3474	7.1124	42.4598	7.6688	10313.0
1500.	35.5898	7.1323	42.7221	7.7205	10698.4
1550.	35.8243	7.1521	42.9765	7.7722	11085.8
1600.	36.0509	7.1720	43.2229	7.8219	11475.2
1650.	36.2715	7.1919	43.4634	7.8695	11866.6
1700.	36.4861	7.2138	43.6998	7.9192	12263.4
1750.	36.6967	7.2336	43.9304	7.9669	12658.8
1800.	36.8994	7.2555	44.1549	8.0146	13059.9
1850.	37.1002	7.2754	44.3755	8.0623	13459.4
1900.	37.2929	7.2972	44.5901	8.1080	13864.7
1950.	37.4837	7.3191	44.8028	8.1517	14272.2
2000.	37.6685	7.3409	45.0095	8.1955	14681.9
2050.	37.8513	7.3608	45.2122	8.2372	15089.7
2100.	38.0282	7.3827	45.4109	8.2769	15503.6
2150.	38.2011	7.4045	45.6056	8.3167	15919.7
2200.	38.3740	7.4244	45.7984	8.3544	16333.7
2250.	38.5389	7.4463	45.9852	8.3922	16754.1
2300.	38.7039	7.4661	46.1700	8.4280	17172.1
2350.	38.8648	7.4880	46.3528	8.4618	17596.8
2400.	39.0238	7.5079	46.5317	8.4975	18018.9
2450.	39.1768	7.5297	46.7066	8.5313	18447.8
2500.	39.3299	7.5496	46.8795	8.5651	18874.0
2600.	39.6280	7.5893	47.2173	8.6287	19732.3
2700.	39.9141	7.6291	47.5432	8.6903	20598.5
2800.	40.1923	7.6688	47.8612	8.7479	21472.7
2900.	40.4626	7.7066	48.1692	8.8036	22349.1
3000.	40.7229	7.7444	48.4673	8.8592	23233.1

This table is in units of calories, moles and °K.

Table A-82 Thermodynamic Functions for H_2 - Continued

T °K	$\frac{-(F^o-H^o_0)}{T}$	$\frac{H^o - H^o_0}{T}$	S^o	C^o_p	$H^o - H^o_0$
3100.	40.9773	7.7821	48.7594	8.9148	24124.5
3200.	41.2257	7.8179	49.0436	8.9685	25017.2
3300.	41.4662	7.8537	49.3198	9.0222	25917.0
3400.	41.7027	7.8874	49.5901	9.0738	26817.3
3500.	41.9312	7.9232	49.8544	9.1235	27731.2
3600.	42.1538	7.9570	50.1107	9.1692	28645.2
3700.	42.3724	7.9908	50.3631	9.2149	29565.9
3800.	42.5870	8.0226	50.6095	9.2567	30485.8
3900.	42.7976	8.0544	50.8520	9.3004	31412.0
4000.	43.0003	8.0862	51.0865	9.3421	32344.6
4100.	43.2010	8.1180	51.3190	9.3858	33283.6
4200.	43.3958	8.1478	51.5436	9.4276	34220.6
4300.	43.5866	8.1796	51.7661	9.4713	35172.1
4400.	43.7754	8.2094	51.9847	9.5110	36121.2
4500.	43.9622	8.2372	52.1994	9.5528	37067.4
4600.	44.1430	8.2670	52.4100	9.5945	38028.2
4700.	44.3219	8.2948	52.6167	9.6342	38985.7
4800.	44.4948	8.3246	52.8194	9.6720	39958.2
4900.	44.6676	8.3525	53.0201	9.7117	40927.0
5000.	44.8366	8.3803	53.2168	9.7495	41901.4
5200.	45.1261	8.3149	53.4411	9.4036	43237.5
5300.	45.2847	8.3356	53.6204	9.4234	44178.5
5400.	45.4407	8.3560	53.7968	9.4427	45122.6
5500.	45.5942	8.3759	53.9702	9.4616	46067.5
5600.	45.7453	8.3954	54.1408	9.4801	47014.1
5700.	45.8940	8.4147	54.3088	9.4983	47963.5
5800.	46.0406	8.4335	54.4741	9.5161	48914.5
5900.	46.1849	8.4520	54.6370	9.5336	49866.9
6000.	46.3271	8.4701	54.7973	9.5507	50820.6
6100.	46.4672	8.4880	54.9553	9.5676	51776.7
6200.	46.6054	8.5055	55.1111	9.5842	52733.9
6300.	46.7416	8.5228	55.2645	9.6005	53693.4
6400.	46.8760	8.5399	55.4159	9.6166	54655.1
6500.	47.0085	8.5565	55.5651	9.6325	55617.5
6600.	47.1393	8.5730	55.7123	9.6481	56582.1
6700.	47.2683	8.5891	55.8575	9.6635	57547.2
6800.	47.3957	8.6050	56.0007	9.6787	58514.2
6900.	47.5214	8.6205	56.1421	9.6937	59481.7
7000.	47.6456	8.6360	56.2817	9.7085	60452.2
273.15	23.8261	6.7811	30.6022	6.8398	1852.3
298.15	24.4208	6.7877	31.2087	6.8908	2023.7

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal g^{-1} $°K^{-1}$ (or $°C^{-1}$)	.49603
joules g^{-1} $°K^{-1}$ (or $°C^{-1}$)	2.0754
Btu lb^{-1} $°R^{-1}$ (or $°F^{-1}$)	.49571

Table A-83 Thermodynamic Functions for O_2

T °K	$\frac{-(F^\circ-H_0^\circ)}{T}$	$\frac{H^\circ - H_0^\circ}{T}$	S°	C_p°	$H^\circ - H_0^\circ$
50.	29.6797	6.9089	36.5886	6.9612	345.4
100.	34.4710	6.9332	41.4042	6.9582	693.3
150.	37.2830	6.9425	44.2255	6.9580	1041.4
200.	39.2802	6.9473	46.2274	6.9618	1389.5
250.	40.8322	6.9502	47.7825	6.9797	1737.6
300.	42.1001	6.9584	49.0585	7.0238	2087.5
350.	43.1732	6.9733	50.1465	7.0979	2440.7
400.	44.1052	6.9952	51.1004	7.1963	2798.1
450.	44.9319	7.0226	51.9545	7.3105	3160.2
500.	45.6732	7.0578	52.7309	7.4316	3528.9
550.	46.3469	7.0981	53.4450	7.5532	3904.0
600.	46.9669	7.1404	54.1073	7.6706	4284.3
650.	47.5412	7.1845	54.7258	7.7811	4670.0
700.	48.0738	7.2322	55.3060	7.8839	5062.6
750.	48.5746	7.2787	55.8533	7.9779	5459.1
800.	49.0456	7.3254	56.3710	8.0637	5860.4
850.	49.4907	7.3715	56.8623	8.1418	6265.8
900.	49.9140	7.4157	57.3297	8.2127	6674.1
950.	50.3154	7.4600	57.7754	8.2773	7087.0
1000.	50.7010	7.5007	58.2017	8.3362	7500.7
1050.	51.0666	7.5430	58.6097	8.3900	7920.2
1100.	51.4184	7.5828	59.0012	8.4397	8341.1
1150.	51.7562	7.6211	59.3773	8.4852	8764.3
1200.	52.0821	7.6571	59.7392	8.5277	9188.5
1250.	52.3961	7.6921	60.0882	8.5675	9615.1
1300.	52.6982	7.7269	60.4250	8.6048	10044.9
1350.	52.9903	7.7603	60.7505	8.6404	10476.3
1400.	53.2725	7.7928	61.0653	8.6746	10910.0
1450.	53.5467	7.8236	61.3704	8.7072	11344.3
1500.	53.8130	7.8531	61.6661	8.7390	11779.6
1550.	54.0714	7.8817	61.9530	8.7698	12216.6
1600.	54.3218	7.9103	62.2320	8.8000	12656.5
1650.	54.5642	7.9389	62.5031	8.8296	13099.2
1700.	54.8027	7.9645	62.7672	8.8588	13539.7
1750.	55.0332	7.9912	63.0244	8.8878	13984.5
1800.	55.2597	8.0154	63.2752	8.9164	14427.7
1850.	55.4783	8.0416	63.5200	8.9449	14877.0
1900.	55.6930	8.0659	63.7589	8.9731	15325.2
1950.	55.9036	8.0887	63.9924	9.0013	15773.1
2000.	56.1083	8.1122	64.2205	9.0293	16224.4
2050.	56.3090	8.1348	64.4439	9.0571	16676.4
2100.	56.5058	8.1567	64.6625	9.0848	17129.1
2150.	56.6985	8.1780	64.8765	9.1124	17582.6
2200.	56.8853	8.2010	65.0863	9.1400	18042.3
2250.	57.0701	8.2219	65.2920	9.1672	18499.3
2300.	57.2510	8.2428	65.4937	9.1945	18958.3
2350.	57.4298	8.2620	65.6919	9.2217	19415.8
2400.	57.6027	8.2835	65.8862	9.2487	19880.4
2500.	57.9425	8.3224	66.2650	9.3020	20806.1
2600.	58.2684	8.3622	66.6306	9.3542	21741.7
2700.	58.5864	8.3984	66.9848	9.4053	22675.6
2800.	58.8924	8.4351	67.3276	9.4552	23618.3
2900.	59.1886	8.4717	67.6602	9.5039	24567.9
3000.	59.4767	8.5067	67.9834	9.5512	25520.0
3100.	59.7549	8.5422	68.2972	9.5967	26480.9

This table is in units of calories, moles and °K.

Table A-83 Thermodynamic Functions for O_2 - Continued

T °K	$\frac{-(F^\circ - H^\circ_0)}{T}$	$\frac{H^\circ - H^\circ_0}{T}$	S°	C°_p	$H^\circ - H^\circ_0$
3200.	60.0272	8.5754	68.6026	9.6406	27441.4
3300.	60.2915	8.6084	68.8999	9.6827	28407.8
3400.	60.5498	8.6398	69.1896	9.7235	29375.4
3500.	60.8002	8.6718	69.4720	9.7624	30351.3
3600.	61.0447	8.7030	69.7477	9.7996	31330.8
3700.	61.2831	8.7334	70.0165	9.8351	32313.6
3800.	61.5176	8.7616	70.2793	9.8691	33294.2
3900.	61.7442	8.7918	70.5360	9.9015	34288.2
4000.	61.9687	8.8183	70.7870	9.9321	35273.1
4100.	62.1853	8.8475	71.0328	9.9613	36274.7
4200.	62.4000	8.8731	71.2731	9.9890	37267.1
4300.	62.6086	8.8999	71.5086	10.0152	38269.8
4400.	62.8133	8.9258	71.7391	10.0398	39273.4
4500.	63.0140	8.9510	71.9650	10.0631	40279.6
4600.	63.2108	8.9757	72.1864	10.0845	41288.0
4700.	63.4055	8.9979	72.4034	10.1046	42290.2
4800.	63.5943	9.0222	72.6165	10.1237	43306.4
4900.	63.7811	9.0442	72.8253	10.1406	44316.7
5000.	63.9639	9.0665	73.0304	10.1567	45332.4
5200.	64.3053	9.1511	73.4565	10.2450	47585.9
5300.	64.4821	9.1742	73.6562	10.2780	48623.2
5400.	64.6565	9.1966	73.8531	10.3116	49661.9
5500.	64.8284	9.2189	74.0473	10.3457	50703.9
5600.	64.9976	9.2410	74.2386	10.3801	51749.4
5700.	65.1640	9.2630	74.4270	10.4147	52799.2
5800.	65.3278	9.2849	74.6126	10.4496	53852.3
5900.	65.4888	9.3065	74.7953	10.4849	54908.6
6000.	65.6471	9.3282	74.9753	10.5206	55969.2
6100.	65.8030	9.3497	75.1527	10.5568	57032.9
6200.	65.9565	9.3709	75.3275	10.5937	58099.7
6300.	66.1078	9.3922	75.4999	10.6314	59170.8
6400.	66.2570	9.4131	75.6700	10.6699	60243.5
6500.	66.4043	9.4335	75.8378	10.7093	61317.9
6600.	66.5501	9.4536	76.0037	10.7502	62393.7
6700.	66.6941	9.4735	76.1675	10.7916	63472.2
6800.	66.8364	9.4929	76.3293	10.8333	64552.0
6900.	66.9769	9.5120	76.4890	10.8749	65632.9
7000.	67.1157	9.5309	76.6466	10.9160	66716.3
273.15	41.4463	6.9540	48.4003	6.9965	1899.5
298.15	42.0564	6.9582	49.0146	7.0218	2074.6

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal g^{-1} $°K^{-1}$ (or $°C^{-1}$)	.031250
joules g^{-1} $°K^{-1}$ (or $°C^{-1}$)	.13075
Btu lb^{-1} $°R^{-1}$ (or $°F^{-1}$)	.031230

APPENDIX B

THERMODYNAMIC FUNCTIONS FOR SOLIDS AND LIQUIDS

(For discussions, see Chapter A3 (page 13) and Chapter B5 (page 96).)

TABLE B-58

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM FLUORIDE (BeF_2)

SOLID AND LIQUID PHASES

GRAM MOLECULAR WEIGHT = 47.013

1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

(SOLID)

T DEG K	$-(F_T^0-H_0^0)/T$ CAL/DEG	$(H_T^0-H_0^0)/T$ CAL/DEG	S_T^0 CAL/DEG	$(H_T^0-H_0^0)$ CAL	C_P^0 CAL/DEG	$-(F_T^0-H_0^0)$ CAL	Log P (calc.) P in mm. Hg
0.00	0.0000	0.0000	0.000	0.000	0.000	0.000	
5.00	0.0001	0.0004	0.000	0.002	0.001	0.001	
10.00	0.0007	0.0015	0.002	0.015	0.005	0.007	
15.00	0.0016	0.0034	0.005	0.051	0.011	0.024	
20.00	0.0031	0.0070	0.010	0.140	0.026	0.061	
25.00	0.0052	0.0131	0.018	0.327	0.050	0.131	
30.00	0.0084	0.0216	0.030	0.648	0.081	0.251	
35.00	0.0125	0.0331	0.046	1.160	0.126	0.438	
40.00	0.0179	0.0480	0.066	1.921	0.181	0.715	
45.00	0.0226	0.0665	0.091	2.992	0.250	1.016	
50.00	0.0327	0.0891	0.122	4.456	0.339	1.635	-240.481
75.00	0.0991	0.2687	0.367	20.16	0.972	7.431	-156.411
100.00	0.2134	0.5587	0.771	55.87	1.922	21.34	-114.265
125.00	0.3771	0.9373	1.313	117.2	2.998	47.14	- 88.921
150.00	0.5858	1.375	1.960	206.2	4.134	87.86	- 71.996
175.00	0.8330	1.851	2.684	324.0	5.287	145.8	- 59.890
200.00	1.113	2.351	3.463	470.2	6.406	222.5	- 50.803
225.00	1.419	2.862	4.280	643.9	7.474	319.2	- 43.731
250.00	1.747	3.373	5.120	843.2	8.461	436.7	- 38.073
273.15	2.066	3.840	5.906	1049.	9.292	564.3	- 33.757
275.00	2.092	3.877	5.968	1066.	9.355	575.3	- 33.443
298.15	2.424	4.332	6.755	1292.	10.11	722.6	- 29.850
300.00	2.450	4.368	6.818	1310.	10.16	735.1	- 29.587
350.00	3.194	5.300	8.494	1855.	11.57	1118.	- 23.531
400.00	3.959	6.156	10.11	2462.	12.69	1584.	- 18.997
450.00	4.730	6.934	11.66	3120.	13.59	2128.	- 15.478
500.00	5.497	7.637	13.13	3818.	14.31	2749.	- 12.668
550.00	6.255	8.271	14.53	4549.	14.89	3440.	- 10.376
600.00	7.000	8.844	15.84	5306.	15.38	4200.	- 8.470
650.00	7.729	9.363	17.09	6086.	15.80	5024.	- 6.863
700.00	8.440	9.836	18.28	6885.	16.16	5908.	- 5.489
750.00	9.134	10.27	19.40	7701.	16.48	6850.	- 4.302
800.00	9.809	10.67	20.48	8534.	16.81	7847.	- 3.266
816.00	10.02	10.79	20.81	8803.	16.90	8176.	- 2.962

(LIQUID)

T DEG K	$-(F_T^0-H_0^0)/T$ CAL/DEG	$(H_T^0-H_0^0)/T$ CAL/DEG	S_T^0 CAL/DEG	$(H_T^0-H_0^0)$ CAL	C_P^0 CAL/DEG	$-(F_T^0-H_0^0)$ CAL	Log P (calc.) P in mm. Hg
816.	10.0200	16.7900	26.8100	13699.	24.00	8176.	- 2.9632
850.	10.7133	17.0775	27.7908	14516.	24.00	9106.	- 2.4096
900.	11.7003	17.4621	29.1624	15716.	24.00	10530.	- 1.6788
950.	12.6537	17.8063	30.4600	16916.	24.00	12019.	- 1.0315
1000.	13.5752	18.1160	31.6912	18116.	24.00	13575.	- 0.4550
1050.	14.4660	18.3962	32.8622	19316.	24.00	15189.	0.0061
1100.	15.3275	18.6510	33.9785	20516.	24.00	16860.	0.5255
1150.	16.1620	18.8836	35.0456	21716.	24.00	18586.	0.9451
1200.	16.9701	19.0968	36.0669	22916.	24.00	20364.	1.3257
1250.	17.7537	19.2930	37.0467	24116.	24.00	22192.	1.6723
1300.	18.5137	19.4741	37.9878	25316.	24.00	24068.	1.9890
1350.	19.2518	19.6417	38.8935	26516.	24.00	25990.	2.2792
1400.	19.9693	19.7974	39.7667	27716.	24.00	27957.	2.5454
1450.	20.6665	19.9424	40.6089	28916.	24.00	29966.	2.7910
1500.	21.3447	20.0777	41.4224	30117.	24.00	32017.	3.0176
1550.	22.0051	20.2042	42.2093	31317.	24.00	34108.	3.2276
1600.	22.6485	20.3229	42.9714	32517.	24.00	36238.	3.4220
1650.	23.2754	20.4343	43.7097	33717.	24.00	38404.	3.6027
1700.	23.8872	20.5392	44.4264	34917.	24.00	40608.	3.7709
1750.	24.4841	20.6381	45.1222	36117.	24.00	42847.	3.9278
1800.	25.0664	20.7316	45.7980	37317.	24.00	45120.	4.0744
1850.	25.6358	20.8199	46.4557	38517.	24.00	47426.	4.2114
1900.	26.1920	20.9036	47.0956	39717.	24.00	49765.	4.3396
1950.	26.4164	20.9830	47.3994	40917.	24.00	51512.	4.5300
2000.	27.2683	21.0585	48.3268	42117.	24.00	54537.	4.5731
2050.	27.7890	21.1303	48.9193	43317.	24.00	56967.	4.6793
2100.	28.2993	21.1986	49.4979	44517.	24.00	59429.	4.7792
2150.	28.7988	21.2638	50.0626	45717.	24.00	61917.	4.8734
2200.	29.2882	21.3260	50.6142	46917.	24.00	64434.	4.9624
2250.	29.7681	21.3854	51.1535	48117.	24.00	66978.	5.0461
2300.	30.2390	21.4423	51.6813	49317.	24.00	69550.	5.1253
2350.	30.7007	21.4967	52.1974	50517.	24.00	72147.	5.2001
2400.	31.1536	21.5489	52.7025	51717.	24.00	74769.	5.2711
2450.	31.5987	21.5991	53.1978	52918.	24.00	77417.	5.3382
2500.	32.0353	21.6470	53.6823	54118.	24.00	80088.	5.4018

TABLE B-59

THERMODYNAMIC FUNCTIONS FOR ALUMINUM CARBIDE (AL_4C_3)
SOLID PHASE

GRAM MOLECULAR WT.= 143.96 GRAMS 1 CAL=4.1840 ABS J
T DEG K = 273.15 + T DEG C

T	$-(F_T^0-H_{298}^0)/T$	$(H_T^0-H_{298}^0)/T$	$(S_T^0-S_0^0)$	$(H_T^0-H_{298}^0)$	C_P^0	$-(F_T^0-H_{298}^0)$
DEG K	CAL / DEG MOLE	CAL / DEG MOLE	CAL / DEG MOLE	CAL / MOLE	CAL / DEG MOLE	CAL / MOLE
298.15	25.000	0.	25.000	0.	28.335	7453.7
300.00	25.000	0.1750	25.176	52.511	28.420	7500.1
310.00	25.021	1.0933	26.115	338.93	28.860	7756.6
320.00	25.070	1.9676	27.038	629.64	29.280	8022.4
330.00	25.143	2.8016	27.945	924.54	29.700	8297.3
340.00	25.239	3.5990	28.838	1223.6	30.120	8581.2
350.00	25.354	4.3627	29.717	1526.9	30.540	8874.0
360.00	25.487	5.0956	30.583	1834.3	30.950	9175.5
370.00	25.636	5.8000	31.437	2145.9	31.370	9485.6
380.00	25.800	6.4784	32.279	2461.7	31.790	9804.2
390.00	25.977	7.1327	33.110	2781.7	32.200	10131.
400.00	26.166	7.7646	33.931	3105.8	32.620	10466.
425.00	26.682	9.2581	35.940	3934.6	33.570	11339.
450.00	27.250	10.625	37.876	4781.4	34.180	12262.
475.00	27.859	11.891	39.751	5648.5	35.190	13233.
500.00	28.499	13.076	41.576	6538.2	35.870	14249.
550.00	29.848	15.204	45.053	8362.4	37.060	16416.
600.00	31.252	17.068	48.321	10240.	38.050	18751.
650.00	32.685	18.715	51.401	12164.	38.890	21245.
700.00	34.127	20.183	54.310	14128.	39.620	23888.
750.00	35.565	21.500	57.066	16125.	40.250	26673.
800.00	36.991	22.689	59.681	18151.	40.790	29593.
850.00	38.400	23.769	62.169	20203.	41.290	32639.
900.00	39.786	24.754	64.542	22279.	41.720	35808.
950.00	41.149	25.658	66.808	24375.	42.110	39092.
1000.00	42.487	26.489	68.977	26489.	42.470	42487.
1050.00	43.798	27.258	71.057	28621.	42.790	45988.
1100.00	45.083	27.971	73.055	30768.	43.080	49591.
1150.00	46.341	28.634	74.976	32929.	43.350	53292.
1200.00	47.573	29.252	76.826	35102.	43.600	57088.
1250.00	48.779	29.830	78.610	37288.	43.820	60974.
1300.00	49.960	30.373	80.333	39485.	44.040	64948.
1350.00	51.116	30.882	81.999	41691.	44.230	69006.
1400.00	52.247	31.362	83.611	43907.	44.410	73147.
1450.00	53.356	31.815	85.172	46133.	44.590	77366.
1500.00	54.442	32.244	86.687	48366.	44.750	81663.
1550.00	55.506	32.650	88.156	50607.	44.900	86034.
1600.00	56.549	33.035	89.584	52856.	45.050	90478.
1650.00	57.571	33.401	90.973	55112.	45.180	94992.
1700.00	58.573	33.749	92.323	57374.	45.310	99575.
1750.00	59.556	34.082	93.639	59643.	45.440	104224.
1800.00	60.521	34.399	94.920	61918.	45.550	108938.
1850.00	61.468	34.701	96.170	64198.	45.660	113715.
1900.00	62.397	34.991	97.389	66484.	45.770	118554.
1950.00	63.309	35.269	98.579	68775.	45.870	123454.
2000.00	64.206	35.535	99.742	71071.	45.960	128412.
2050.00	65.086	35.791	100.87	73371.	46.060	133427.
2100.00	65.952	36.036	101.98	75676.	46.140	138499.
2150.00	66.803	36.272	103.07	77985.	46.220	143626.
2200.00	67.639	36.499	104.13	80298.	46.310	148806.
2250.00	68.462	36.718	105.18	82616.	46.390	154039.
2300.00	69.271	36.929	106.20	84937.	46.460	159324.
2350.00	70.067	37.133	107.20	87262.	46.540	164659.
2400.00	70.851	37.329	108.18	89591.	46.610	170044.
2450.00	71.623	37.519	109.14	91923.	46.670	175477.
2500.00	72.383	37.703	110.08	94258.	46.750	180958.
2600.00	73.868	38.053	111.92	98939.	46.870	192059.
2700.00	75.311	38.382	113.69	103632.	46.990	203340.
2800.00	76.712	38.691	115.40	108337.	47.100	214795.
2900.00	78.075	38.983	117.05	113052.	47.200	226419.
3000.00	79.402	39.259	118.66	117777.	47.300	238206.

S_0^0 APPLIES TO THE REFERENCE STATE OF THE SOLID AT ZERO DEG K

H_{298}^0 APPLIES TO THE REFEERENCE STATE OF THE SOLID AT 298.15 DEG K

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U. S. DEPARTMENT OF COMMERCE
Luther H. Hodges, *Secretary*

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

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