Thermodynamic Properties of the Group IIA Elements

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The thermodynamic properties of the alkaline earth metals in the condensed state have been critically reassessed, and recommended values for all of the relevant thermodynamic properties are given. These values are compared with those published in recent reviews by the staff at the Institute for High Temperatures (Moscow) and the National Bureau of Standards (Washington, DC), and the reasons for any differences are discussed in detail. A direct result of this review is a set of recommendations for experimental studies which should enhance the reliability of the thermodynamic results.

The properties considered are: temperatures and enthalpies of phase transformations and fusion, heat capacities from 0 K to 2000 K, the Debye temperatures, and electronic heat capacity coefficients at absolute zero temperature.

Key words: elements; enthalpy; function; fusion; Gibbs energy; heat capacity; phase transition; thermodynamics.

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1. Introduction

The thermodynamic properties of the alkaline earth metals in the condensed phase have been reassessed. The need for this activity was the existence of new data since the time of the more recent reviews. However, the study still suffers from the insufficient data available for these metals.

The principal difficulty in this analysis centers on the lack of definitive information on (1) the high temperature heat capacities and (2) enthalpies of transformation and fusion. This situation arises from the high chemical activity of these elements. They can readily form oxides, nitrides, hydrides and other compounds with non-metallic elements at room and elevated temperatures, and therefore can be easily contaminated in an atmosphere containing non-metallic elements. Preparation of the pure elements is difficult, and even the best materials available for Ca, Sr and Ba usually contain appreciable amounts of impurities.

The measurements of the thermodynamic properties of these elements have gone through several stages of evolution. Seventy to one hundred years ago the experimental methods and materials were of poor quality from the point of view of modern standards. Commercial materials were often used without additional purification and chemical analysis, and as a result the data exhibited significant scatter.

With time, experimental techniques improved and some measurements, made on less reactive materials 40–70 years ago, agreed satisfactorily with modern data. The importance of the purity of samples for the elements of the IIA group was well understood, and in order to obtain better specimens, purification by distillation and sublimation was often applied to commercial material. Attention was paid to chemical analysis of samples, whereas the content of separate metals and non-metallic impurities was rarely checked. Very often only the general level of the impurities was given. The measures taken did not necessarily improve the quality of data.

Before the 1950's it was not clear how many allotropic modifications each element had, but progress was steadily made. Teitel and Cohen [49TEI/COH] and Buzzard [53BUZ] established the existence of the second modification in Be. Good materials were prepared in the King Laboratories, Syracuse, NY, where the metals were passed through multi-step distillation and sublimation. This led to a decrease in the level of oxygen and nitrogen and, in turn, helped to establish that only one allotropic modification existed in Ba [49SHE]. King *et al.* investigated their purest samples of Ca and Sr carefully, and found in them three allotropic modifications: fcc, hcp and bcc [58SCH/KIN]. However, at this time, another source of error, hydrogen, was not understood. The hydrogen content rarely had been checked in previous studies, and furthermore the accuracy of such analyses was low.

An essential contribution to the understanding of the crystal modifications of Ca and Sr and the role of hydrogen was made in the Ames Laboratory (Iowa State University) by Peterson and his colleagues [61PET/FAT],[66PET/COL]. It was shown that very small amounts of hydrogen in Ca and Sr converted the pure phase to a two-phase system containing solid solutions with a hexagonal structure. This latter phase was taken by King and his colleagues [58SCH/KIN] and by many other scientists to be a third modification, hcp, in Ca and Sr. Peterson removed the dissolved hydrogen by vacuum treatment of samples in Ta capsules. The materials still contained about 100 ppm hydrogen, but showed no sign of the hexagonal phase. Since these investigations, hydrogen has been included in the list of impurities to be controlled.

Currently there is considerable confidence in our knowledge of the crystal modification of each element, as summarized in Table 1–1. However, the transitions between modifications are not unambiguously established. Much of this stems from the difficulty not only in obtaining but also in maintaining pure metallic samples. Recently, very pure samples of Ca, Sr and Ba were prepared in the Ames Laboratory. These materials are considered the best available [87PET]. The use of the Ames materials does not guarantee the best results even with perfect measuring techniques. These metals could easily be contaminated during handling and measuring procedures. Even exposure to an inert gas not sufficiently purified or to a low vacuum can lead to the contamination of good specimens. Such "slightly" contaminated materials can produce results no better than older data obtained with materials containing considerable amounts of oxides. Therefore, at the present time, heat capacities of acceptable accuracy do not exist for Ca, Sr, and Ba above 373 K.

The separate review for each element consists of brief descriptions of experimental studies with emphasis on the measured property, temperature range, the technique used, the chemical analysis, the results obtained and accuracy of the data. The literature includes several sources which are difficult to access. Some studies have never been published and exist only in the form of private communications. The important information is often missing

TABLE 1-1. Crystal Structure and Lattice Parameters of the Elements of the IIA Group [85VIL/CAL]

Phase	Temperature interval of stability (K)	Structure		Lattice	Parameters (nm)	Temperature measurement (K)
α-Be	0–1543	hcp		$a = 0.22858$,	$c = 0.35843$	298
β-Be	1543–1563		bcc	$a = 0.25515$		1543
Mg	0–923	hcp		$a = 0.32089$,	$c = 0.52101$	298
α-Ca	0–716	fcc		$a = 0.55884$		298
β-Ca	716–1115		bcc	$a = 0.448$		716
α-Sr	0–820	fcc		$a = 0.6084$		298
β-Sr	820–1041		bcc	$a = 0.4434$		820
Ba	0–1000		bcc	$a = 0.5013$		298

in the original studies; chemical analysis was frequently not given or carried out for some metallic impurities. Sometimes data are given in the form of small-scale graphs, smoothed values, or fitted equations. It is very difficult to assign accuracy to a given study when details are absent about material handling and measuring procedures, and tables of original data are often omitted. These defects influence the value of a given study, and as a result it is difficult to estimate accuracy for most of the studies. The most reliable data sets selected from the literature are reproduced in the Appendix.

The data on separate properties are combined, screened and the best values selected. The selected heat capacity and enthalpy data are fitted with up to five-term polynomials for well-defined selected temperature ranges. The resulting equations are used to calculate the entropy and enthalpy at different temperatures. The standard entropy, $S°(298.15\ K)$, and the enthalpy difference, $H°(298.15\ K) - H°(0)$, are also calculated. The results of these calculations are tabulated in Sec. 8 for each element. The standard entropy is rounded to 0.01 $J·K^{-1}·mol^{-1}$ and the enthalpy difference to 1 $J·mol^{-1}$ which is $<5\%$ of the estimated uncertainty. Such a treatment makes the entropy and enthalpy values calculated below and above 298.15 K more consistent. The selected and calculated values are compared with similar quantities in other reviews: [73HUL], [77KEY], [81GUR], [85JAN], [86SHP/KAG], [87GAR/PAR], [89COX/WAG], and [89DIN]. It should be mentioned that [89COX/WAG] extended the [77KEY] study and reproduced values for Be from [81GUR] and values for Mg and Ca from [85JAN]. [89DIN] reproduced values for Be from [85JAN], for Mg and Ca from [87GAR/PAR], for Sr from [85JAN] and for Ba from [81GUR]. In addition, [89DIN] estimated Gibbs energies of phases which are unstable at atmospheric pressure: hcp – for Ba, Ca and Sr; fcc – Be and Mg; bcc of Mg.

The recommended values sometimes are tentative due to the lack of reliable data. The quantities which are least well known are summarized in the Conclusion (Chapter 7) to encourage further investigations.

General comments:

1. The units used throughout the text are temperature in K, enthalpy and Gibbs energy in $J·mol^{-1}$, entropy and heat capacity in $J·K^{-1}·mol^{-1}$.
2. The heat capacity data below $T = 5$ K are normally represented in terms of a two-term equation:

$$C_p^\circ = \gamma T + 1943\ (T/\Theta_D)^3$$

where γ is the electronic contribution to the heat capacity and the lattice term with the Debye temperature Θ_D is given for each study when appropriate.

3. In general, the literature coverage extends from the 1930's to 1991. Although there are earlier data reported in the literature, it does not add to this review as the samples tended to be less pure or defined, but there were some exceptions which have been included.
4. The temperature scale used for the recommended values is ITS-90. Many of the reported data are given in terms of earlier temperature scales. Oftentimes the scale used is not mentioned, so that we must guess as to the appropriate corrections to make. It should be noted that below $T = 1000$ K, the corrections between all temperature scales are less than 1 K, while above this temperature (up to 2000 K) the corrections are always less than 2 K. These corrections are well within the uncertainty of the measured temperatures for these condensed phases.
5. The relative atomic masses for these alkaline earth metals have been reassessed through the years. The recommended thermodynamic values are based on the following relative atomic masses (1988 data):

   Be, 9.012182; Mg, 24.305; Ca, 40.078; Sr, 87.62; and Ba, 137.327

   Since the 1930's, these values have changed by +0.01 for all elements except Ba which has changed by 0.03.

6. The heat capacity data themselves are given in two forms: in this article and in an electronic database. The electronic package, written for an IBM PC compatible computer, contains references, brief descriptions of studies, and assessed data. The program retrieves and plots stored data from one or several sources and makes it possible to add new data. The data can be searched by author's name or by type of data required (Heat Capacity/Enthalpy, Transformation and Fusion). A facility for fitting data to a six-term polynomial is also provided. This database is available from the Standard Reference Data Program (NIST).
7. In each appendix, the values for heat capacity and enthalpy are reported. The discription "experimental" values are self explanatory. The term "calculated" values refers to the fact that an equation is available from which we can currently calculate heat capacity values at any temperature. "Smoothed" values refer to the fact that the original authors do not report any experimental values but only list (or graph) values at a selected set of temperatures.
8. The thermodynamic properties of the alkaline earth metals in the condensed state have been critically reassessed, and recommended values are given. These values are compared with those published in recent reviews by the staff at the Institute for High Temperatures (Moscow) [81GUR],[86SHP/KAG] and the National Bureau of Standards (Washington, DC) [85JAN], and the reasons for any differences are discussed in detail.
9. A direct result of this review is a set recommendations for experimental studies which should enhance the reliability of the thermodynamic results as given in Sec. 7.2.

1.1. References for the Introduction

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87PET Peterson, D. T., J. Metals **5**, 20–23 (1987); Materials preparation.

89COX/WAG Cox, J. D., Wagman, D. D., and Medvedev, V. A., "CODATA Key Values for Thermodynamics," Hemisphere Publ. Corp., New York, (1989); Review.

89DIN Dinsdale, A. T., SGTE Data for Pure Elements, NPL Report DMA(A)195, (1985); Review.

2. Beryllium

2.1. Introduction

At ambient pressure, beryllium exists in two stable crystalline modifications, hcp and bcc (T_{trs}/K = 1543). The information on the temperature and enthalpy of the transformation and fusion is conflicting. This gives rise to the largest uncertainty in our understanding of the thermodynamic properties of this element. The analysis of the data for this element is also weakened by the lack of detailed information on the experimental data for heat capacity and enthalpy. Often in the studies of prime interest, only smoothed heat capacities or enthalpy were reported. As a result, each of the various studies cannot be analyzed in detail or combined into a completely satisfactory heat capacity picture. This defect is common for all elements of the IIA Group. The heat capacity values for β–Be and the separate enthalpies of fusion and transformation have never been measured by a calorimetric technique. This absence of data has given rise to numerous speculations.

2.2. Heat Capacity and Enthalpy Measurements

2.2.1. Temperatures below 298.15 K

[34CRI/SIM]

Cristescu and Simon measured the heat capacity of Be using a sample of 99% purity at temperatures from 10 K to 300 K. The authors gave their experimental results in the form of a small graph from 10 to 23 K (40 points) and a table of smoothed values from 10 to 300 K. They noticed an anomaly in the heat capacity between 10 and 14 K. The anomaly was not confirmed in later publications. These results are listed in Table 2-8 and shown in Figs. 2-2 and 2–3. This study is not considered to be very accurate.

[53HIL/SMI]

Hill and Smith measured the heat capacity of Be in an adiabatic calorimeter from 4 to 300 K. The commercial sample of beryllium contained 0.15 wt. % chlorine and 0.1 wt. % oxygen. Over 150 experimental points were shown in two graphs from 4 to 20 K and above 20 K. Smoothed heat capacity values were listed, and they are reproduced in the Appendix (Sec. 2.9.). The data below 20 K were fitted to the equation

$$C_p^\circ/\mathrm{J\cdot K^{-1}\ mol^{-1}} = 2.26\times10^{-4}T + 1943.7(T/1160)^3$$

This equation corresponds to $\gamma = 0.226\ \mathrm{mJ\cdot K^{-2}\ mol^{-1}}$ and $\Theta_D = 1160$ K. The authors did not notice the anomaly observed by Cristescu and Simon [34CRI/SIM]. The data above 40 K were read from a line drawn through experimental points in a small graph. They are listed in the Table 2-12 and shown in Figs. 2–1, 2–2, and 2–3. The data are considered reasonably reliable.

[64GME]

Gmelin measured the heat capacity of a zone-refined single crystal containing less than 100 ppm metallic impurities in the temperature range 1.2–4.4 K. The sample had a residual resistance ratio, $\rho(300\ \mathrm{K})/\rho(20\ \mathrm{K}) = 220$. All experimental points, given only in a graphical form, were fitted to the equation

$$C_p^\circ/\mathrm{mJ\cdot K^{-1}\ mol^{-1}} = (0.184 \pm 0.002)T + (0.716 \pm 0.05)\times10^{-3}T^3$$

The smoothed heat capacities calculated from the above equation are shown in Figs. 2–1 and 2-2 and are listed in the Table 2-18. The equation corresponds to $\gamma = 0.184 \pm 0.002\ \mathrm{mJ\cdot K^{-2}mol^{-1}}$ and $\Theta_D = 1390 \pm 30$ K.

[66AHL]

Ahlers measured the heat capacity of high purity Be in an adiabatic vacuum calorimeter from 1.4 to 30 K. Two samples were prepared by seven zone-refining passes of a vacuum distilled starting material. One of the samples was a single crystal with an excellent residual resistance ratio, $\rho(300\ \mathrm{K})/\rho(4.2\ \mathrm{K}) = 1100$. The sample was not analyzed chemically, but this high ratio indicates that the sample was very pure. Ahlers did not list the experimental values, and presented the data only in terms of an equation:

$$C_p^\circ/\mathrm{mJ\cdot K^{-1}\ mol^{-1}} = (0.1714 \pm 0.0008)T + (0.598 \pm 0.02)\times10^{-3}T^3 + (0.185 \pm 0.04)\times10^{-6}T^5$$

This equation represents the measured heat capacity values in the temperature range of 1.4 to 30 K, yielding $\Theta_D = 1481 \pm 16$ K and $\gamma = (1.714 \pm 0.008)\times10^{-4}\ \mathrm{J\cdot K^{-2}\ mol^{-1}}$. A graph of the differences between these measured and calculated values is also given. The smoothed heat capacities calculated from the above equation are shown in Figs. 2–1, 2–2 and 2-3 and are listed in Table 2-19. Judging by the description of this study, these are the most reliable low-temperature measurements of Be.

[69GME]

Gmelin prepared three Be samples of different purity containing 100 ppm, 500–800 ppm, and 1000–1200 ppm impurities. The heat capacity was measured from 1 to 80 K. Gmelin reported the electronic specific heat and the Debye temperature for the best sample as being the same as those given in an earlier study [64GME]. He found that when the concentration of impurities increased, the Debye temperature decreased, and the electronic heat capacity increased. The calculated Debye temperature was found to decrease rapidly as the temperature of measurement was increased.

2.2.2. Temperatures Above 298.15 K

[34JAE/ROS]

Jaeger and Rosenbohm measured the enthalpy of Be by drop calorimetry from 373 to 1338 K. Two Be samples of U.S. and German origin were used. The samples were not analyzed for impurities. The authors suggested the presence of a considerable amount of oxygen in their samples. Some heat effects found at about 779 and 911 K can be taken to show the effects of impurities in the samples. Jaeger and Rosenbohm noticed a small increase in the heat capacity after a sample was heated to higher temperatures. This could be the result of oxidation which occurred during the previous heating. Jaeger and Rosenbohm expressed their data by a complex five-term equation:

$$C_p^\circ/\mathrm{J\cdot K^{-1}\ mol^{-1}} = 15.625 + 2.717\times10^{-2}(T-273) - 0.838\times10^{-5}\,(T-273)^2 - 0.542\times10^{-7}\,(T-273)^3 + 0.591\times10^{-10}\,(T-273)^4$$

The measured enthalpy values are listed in the Table 2-9 and shown in Fig. 2–5. These data are considered to be of low accuracy due to the presumed oxygen impurity.

[51GIN/DOU]

Ginnings *et al*. measured the enthalpy of two Be samples in a Bunsen ice calorimeter up to 1173 K. The first sample had 0.3% metallic impurities, 0.3% oxygen, 0.1% water, and more than 99% Be. The second sample had the same amount of oxygen and water but a greater amount of Mg (0.4%), with other metallic impurities totalling ~0.1%. The authors made 51 measurements with the first sample and 15 with the second. The difference between the results obtained with these two samples does not exceed 1%. The average measured enthalpy values (Fig. 2–5) and the derived heat capacity values (Fig. 2–4) are listed in the Tables 2-10 and 2-11. Ginnings and Douglas noticed an inflection point near 773 K, which might indicate some reaction of the sample with impurities or the container. Judging by results shown in Figs. 2–4 and 2–5, this study has satisfactory accuracy.

[59MIT]

Mit'kina used a calorimeter in which the temperature increase was measured when a wire sample, used as an-

anode, was heated by a current of electrons from a tungsten cathode in a vacuum system. The beryllium sample contained 0.2% metallic impurities. Four heat capacity points between 623 and 773 K were determined (see the Table 2-14 and Fig. 2–4). Two more values at 323 and 373 K were determined by quantitative thermal analysis. The accuracy of these data is considered to be low.

[60KAN/KRA]

Kantor *et al*. measured the enthalpy of Be by means of a drop calorimeter from 600 to 2200 K. Specimens were prepared by double distillation of a material originally containing about 99.8 wt. % Be (no detail about the composition of the final product is given). The containers were made of Pt for measurements below 1200 K and of BeO for the higher temperatures. The results of measurements (30 points; 13 in the crystal region and 17 in the liquid region) are given in a graph and reproduced in Fig. 2–5 and in the Table 2-16. These data were expressed by two equations:

solid Be (600–1560 K)

$$H°(T) - H°(298.15\ \text{K})/\text{J·mol}^{-1} = -6234 + 18.08T + 4.56\times10^{-3}T^2,$$

liquid Be (1560–2200 K)

$$H°(T) - H°(298.15\ \text{K})/\text{J·mol}^{-1} = 5552 + 25.43T + 1.075\times10^{-3}T^2.$$

The authors listed the smoothed values of the heat capacity of Be reproduced in the Table 2-15 and shown in Fig. 2–4. This investigation is considered very reliable. It should be noted there are no measured enthalpy points in the region of the β-phase.

[62WAL/EWI]

Walker *et al*. measured the enthalpy of five Be samples by means of a drop-calorimetric method from 303 to 1073 K. The samples contained 98–99.3% Be, 0.2–0.4% metallic impurities, and 0.5–1.3% oxygen. The authors reported only the smoothed heat capacity values which are listed in the Table 2-17 and shown in Fig. 2–4. The accuracy of these data is considered low.

[70TYE/BRA]

Tye and Brazel measured the enthalpy of 13 hot pressed Be samples by drop calorimetry from 570 to 1110 K and the heat capacity by adiabatic calorimetry between 300 and 670 K (Fig. 2–4 and 2–5). The samples contained 98.2–98.5% Be, 0.3–0.5% metallic impurities, 0.15% C, and 1.0–1.2% oxygen. The thermal conductivity and electrical resistivity of the samples were also measured. The experimental heat capacity and enthalpy $[H°(T) - H°(297.5\ \text{K})]$ values are listed in Tables 2-20 and 2-21, with the heat capacity values also being shown in Fig. 2–4. The accuracy of these data is considered low because of the use of impure materials.

2.3. Discussion of Heat Capacity and Enthalpy Data

2.3.1. α-Be below 298.15 K

Figures 2–1 and 2–2 show the low-temperature data (0 – 20 K) of [53HIL/SMI], [64GME], and [66AHL]. In these studies the electronic contribution to the heat capacity and the Debye temperature were determined, as shown in Table 2-1. The electronic heat capacity was estimated also in [67FAL].

The values of $C_p°$, γ and Θ_D, obtained in [64GME] and [66AHL], are close, between 1.5 and 5 K. The data of Ahlers [66AHL] were preferred because he used better materials than [64GME]. The same selection was previously made in [73HUL]. The data of [66AHL] and the error limits were rounded. The heat capacity below 30 K was described in [66AHL]:

$$C_p°/\text{J·K}^{-1}\ \text{mol}^{-1} = 1.714\times10^{-4}T + 0.598\times10^{-6}T^3 + 0.185\times10^{-9}T^5 \quad (2\text{–}1)$$

The heat capacity between 30 and 300 K was studied in [34CRI/SIM] and [53HIL/SMI]. On comparing these studies, preference was given to the more recent investigation [53HIL/SMI]. Figs. 2–2 and 2–3 show that the heat capacity values given in both studies below 30 K are greater than the more accurate data of [66AHL]. To cover a considerable gap at 30 K, a spline was introduced between the data of [66AHL] and [53HIL/SMI]. Between 30 and 40 K the calculated cubic spline satisfies four conditions: at 30 K it has the same heat capacity value and its temperature derivative as Eq. 2–1 and at 40 K the same value and derivative as Eq. 2–3. The spline can be expressed:

$$C_p°/\text{J·K}^{-1}\ \text{mol}^{-1} = -0.99077 + 9.7344\times10^{-2}\text{T} - 3.1856\times10^{-3}T^2 + 3.5677\times10^{-5}T^3 \quad (2\text{–}2)$$

Above 40 K two equations were derived from the data of [53HIL/SMI]. For the interval 40–100 K

$$C_p°/\text{J·K}^{-1}\ \text{mol}^{-1} = 2.946 - 8.064\times10^{-2}\text{T} - 1.215\times10^{3}T^{-2} + 7.052\times10^{-4}T^2\ \text{J·K}^{-1}\ \text{mol}^{-1}; \quad (2\text{–}3)$$

and for the interval 100 – 298.15 K

$$C_p°/\text{J·K}^{-1}\ \text{mol}^{-1} = -15.195 + 0.1576T + 2.937\times10^{4}T^{-2} - 1.764\times10^{-4}T^2 \quad (2\text{–}4)$$

The $C_p°$, $H°(T) - H°(0)$ and $S°(T)$ values at different temperatures calculated from Eqs. 2–1 to 2–4 are given in the Appendix (Sec. 2.9.). At standard temperature the following values were calculated:

$$C_p°(298.15\ \text{K}) = 16.443\ \text{J·K}^{-1}\ \text{mol}^{-1}$$
$$S°(298.15\ \text{K}) = 9.503\ \text{J·K}^{-1}\ \text{mol}^{-1}$$
$$H°(298.15\ \text{K}) - H°(0) = 1942.07\ \text{J·mol}^{-1}$$

These values are compared with those given in other reviews in Table 2–2.

The calculated values of $H°(298.15\ K) - H°(0)$ and $S°(298.15\ K)$ were rounded. The adopted values are close to [73HUL] and [81GUR]. The uncertainty limit was increased mainly because the studies [34CRI/SIM] and [53HIL/SMI] are not very accurate. [85JAN] used the same original studies, but gave smaller values for the standard entropy and enthalpy difference, which seems reasonable.

Figure 2–2 shows that the heat capacity values below 20 K measured in [53HIL/SMI] are higher than more accurate data [66AHL]. It can be assumed that above 20 K the data at [53HIL/SMI] were also overestimated. Therefore present calculations based on [53HIL/SMI] can lead to overestimated values of the standard entropy and enthalpy increment $H°(298.15\ K) - H°(0)$. New measurements are desirable.

2.3.2. α–Be above 298.15 K

Figure 2–5 shows the enthalpy $H°(T) - H°(298.15\ K)$ measured in [34JAE/ROS], [51GIN/DOU], [60KAN/KRA] and [70TYE/BRA]. The data agree satisfactorily except for several points of [34JAE/ROS]. Figure 2 4 shows heat capacities derived from the measured enthalpies [51GIN/DOU], [60KAN/KRA], [62WAL/EWI], [70TYE/BRA], experimental heat capacity values of [59MIT]. The data of [51GIN/DOU] seem to be the most accurate. Between 600 and 1100 K they are very close to the data of [60KAN/KRA], which form a smooth continuation above 1100 K up to the transformation temperature 1543 K. Such a selection was made in [73HUL], [73SPE] and [85JAN]. Spencer [73SPE] derived the equation

$$C_p°/J{\cdot}K^{-1}\ mol^{-1} = 21.205 + 5.694\times10^{-3}\,T - 5.874\times10^{5}T^{-2} + 0.962\times10^{-6}T^{2} \quad (2\text{–}5)$$

This equation was adopted here. It describes the experimental data for α–Be very well and is consistent with the low-temperature data (Eq. 2–4). Gurvich *et al.* [81GUR] derived a three-term equation on the basis of [34JAE/ROS], [51GIN/DOU], [60KAN/KRA], [62WAL/EWI].

$$C_p°/J{\cdot}K^{-1}\ mol^{-1} = 18.736 + 9.293\times10^{-3}T - 4.501\times10^{5}T^{-2}$$

The values calculated from this equation at high temperatures, however, exceed the experimental values of [60KAN/KRA] by 2%, and the equation is less accurate than Eq. 2–5.

2.3.3. β–Be

No heat capacity data are available for the narrow 20 K region of stability of β–Be. [73HUL] and [73SPE] selected for this interval a constant heat capacity $32.22\ J{\cdot}K^{-1}\ mol^{-1}$, while [81GUR] and [85JAN] chose the value of $30\ J{\cdot}K^{-1}\ mol^{-1}$. In the absence of data, a constant value $30\ J{\cdot}K^{-1}mol^{-1}$ was adopted from [81GUR] and [85JAN]. The accuracy of this value should be about 10%. For the temperature range 1543 – 1563 K:

$$C_p°/J{\cdot}K^{-1}\ mol^{-1} = 30 \quad (2\text{–}6)$$

2.3.4. Liquid Be

The only available set of measured enthalpy values [60KAN/KRA] was treated differently in reviews. [73HUL] and [73SPE] adopted an average constant value $29.5\ J{\cdot}K^{-1}\ mol^{-1}$, [81GUR] used a rounded value $30\ J{\cdot}K^{-1}\ mol^{-1}$ and [85JAN] – the original equation of Kantor *et al.* (see below). All attempts to improve on the measured values can be understood, but there appears to be no reason to deviate from the original equation of [60KAN/KRA] based on 17 points in a 690 K interval (Fig. 2–5). The approach of the authors of [85JAN] was adopted here. For the temperature range 1563–2200 K

$$C_p°/J{\cdot}K^{-1}\ mol^{-1} = 25.435 + 2.150\times10^{-3}T \quad (2\text{–}7)$$

$C_p°(T)$, $H°(T) - H°(298\ K)$ and $S°(T)$ values calculated by Eqs. 2–5 to 2–7 are shown in Table 2-7.

2.4. Phase Equilibrium Data

At atmospheric pressure beryllium has two crystal phases: hcp (α) and bcc (β). The bcc phase was established in [59MAR/MOO].

[39LOS]

Losano determined $T_{fus} = 1557$ K for a sintered sample containing 99.96% Be. Losano noticed a second thermal effect about 20 K below the melting point but attributed it to impurities in the Be sample.

[49TEI/COH]

Teitel and Cohen suggested the existence of a second modification of Be while studying the Be–Fe system. The vacuum melted Be contained about 0.3 wt. % metallic impurities, 0.02 wt. % carbon, 0.015 wt. % nitrogen, and 0.035 wt. % oxygen. The thermal analysis of Be revealed a second thermal effect slightly below the fusion temperature which was suggested to be due to an allotropic transformation. The fusion temperature was determined as 1551 K on heating and 1548 K on cooling, and the transformation point 1536 K on heating and 1534 K on cooling. Teitel and Cohen were the first to propose the existence of a second allotrope in Be.

[53BUZ]

Buzzard studied the Be–U system by thermal analysis. Beryllium had 0.05 wt. % impurities and a fusion temperature of 1556 ± 3 K. The author observed a second arrest at 1523 ± 10 K, which was assumed to be a polymorphic transformation. Buzzard mentioned four previous studies back to 1916 where a thermal effect below the fusion point was observed, but not identified as a phase transformation.

[59MAR/MOO]

Martin and Moore studied Be by high-temperature x-ray and thermal analysis and electrical resistance measurements. Five samples of different purity were examined; the purest sample contained about 0.04 wt. % metallic impurities, 0.008 wt. % oxygen and 0.4 cm^3/g hydrogen. The x-ray analysis showed that above 1523 K a bcc structure was present. A poor specimen was prepared for this experiment, and the obtained temperature is not reliable. According to thermal analyses of different samples, the fusion temperature varied from 1555 to 1565 K and the transformation temperature from 1528 to 1548 K. The average of all measurements can be calculated as 1540 K for the transformation and 1560 K for the fusion. However, the authors selected 1523 K as the transformation temperature and 1563 K as the fusion temperature. Their choice for T_{trs} was poor because the sample used for x-ray analysis probably contained more impurities than the samples used for thermal analysis. The value of T_{fus}, which was selected, was probably based on measurements of a zone-refined sample; however, the results for four other samples do not deviate essentially from those for the selected specimen. The DTA curves showed that the enthalpy of the transformation was about 75 % of that of fusion. The measurements were well performed, and the results of this study are relatively reliable.

[60GEL/PIC]

Gelles and Pickett investigated the bcc phase of Be and some of its alloys by thermal and x-ray analysis. The authors used a commercial, impure, beryllium containing about 400 ppm metallic impurities, 700 ppm chlorine, 155 ppm carbon and 3100 ppm BeO. The fusion temperature of Be was determined as 1555 ± 5 K and the transformation point as 1538 ± 5 K. This study is considered rather inaccurate due to the use of impure samples.

[60KAN/KRA]

Kantor *et al.* in their enthalpy measurements determined the fusion temperature of Be (>99.8 wt. %) as 1560 ± 3 K. The authors were evidently not aware of the existence of β–Be; their enthalpy measurements did not detect a separate effect of transformation. The combined enthalpy of the hcp-bcc transformation and enthalpy of fusion was determined as 14.77 ± 0.33 $kJ \cdot mol^{-1}$.

[61AMO/IVA] and [62SIN/IVA]

Amonenko *et al.* in two papers described one investigation of the phase transformation in Be. The beryllium sample was condensed in a vacuum, and had 99.96–99.97% purity (0.03% metallic impurities, 0.01% O_2 and C), and the residual resistance ratio, ρ(293 K)/ ρ(4.2 K), was about 100. The specimens were studied by electrical resistivity measurements and high-temperature x-ray structural analysis. According to both methods, the phase transformation occurred at 1527 ± 5 K [61AMO/IVA]. In [62SIN/IVA] this transition was reported as 1531 ± 5 K. The different results reported for the same investigation indicate that the temperature control in the study was probably not adequate. The results are considered to be of low accuracy.

[65FRA/CON]

Francois and Contre studied the temperatures of transformation and fusion at different pressures. At ambient pressure they obtained 1533 K for transformation and 1558 K for the fusion temperature. When the pressure was increased, the temperature of fusion increased at a rate 40 ± 20 K GPa^{-1}, and the temperature of transformation decreased at a rate -40 ± 20 K GPa^{-1}. The authors used their results to estimate an enthalpy of transformation, $\Delta_{trs}H = 7.5$ $kJ \cdot mol^{-1}$, which is probably correct. However, the enthalpy of fusion estimated from their data, 14.7 $kJ \cdot mol^{-1}$, is very high. The accuracy of these data is therefore considered low.

[67FAL]

Falge observed superconductivity in pure Be with 3 ppm Fe, 1 ppm Ni, 5 ppm Mn, 10 ppm Si, 15 ppm Al, and 5 ppm N. For zero field the transition temperature was determined as 0.026 K. A slope of 68 ± 2 Oe K^{-1} was determined for the initial slope of the critical magnetic field. From this slope, the electronic specific heat was found as $\gamma = 0.21 \pm 0.02$ $mJ \cdot K^{-2} mol^{-1}$; this value is less accurate than those obtained by calorimetric experiment.

[72RAD/BER]

Radenac and Berthaut measured the enthalpy of fusion of Be by differential thermal analysis. The material used contained about 300 ppm metallic impurities. The temperature of fusion was reported as 1550 K and of transformation as 1527 K, while the illustration provided in the paper for the sample test with heating/cooling rate 50 K/h indicates that the observed temperature of fusion was 1570 K on heating and 1561 K on cooling (average 1565 K), and the temperature of transformation was found to be 1550 K on heating and 1540 K on cooling (average 1545 K). The enthalpy of fusion was estimated as 9050 $J \cdot mol^{-1}$. The values given in [72RAD/BER] should be treated as approximate.

[77LOA/DEA]

Loasby and Dearden determined the temperatures of transformation and fusion and estimated the enthalpies of these transitions. Four samples were prepared by different methods, the purest of which contained about 400 ppm metallic impurities and 1400 ppm BeO. The temperatures of transformation and fusion were determined very accurately by differential thermal analysis. The average temperature of transformation of several samples was found from the data tabulated in [77LOA/DEA] to be 1545 K, and of fusion, 1565 K, while Loasby and Dearden recommended 1552 and 1563 K, respectively. The enthalpy of transformation was roughly estimated as 2094 $J \cdot mol^{-1}$ and of fusion as 2527 $J \cdot mol^{-1}$, their ratio being about 0.83. These enthalpy values are much lower than those reported by other investigators. However, the magnitude of the ratio of the two effects appears to be quite

reliable. An accurate value of this ratio is important for partition of the combined effect (transformation plus fusion) which was measured by Kantor *et al.* [60KAN/KRA] (see below).

[79ALD/PET]

Aldinger and Petzow determined temperatures of transformation 1534 ± 3 K and fusion 1552 ± 5 K by thermal analysis. No information on the materials and procedure was given. The authors compared areas under the DTA curves corresponding to transformation and fusion, their ratio being about 0.8. They divided the combined effect, measured by [60KAN/KRA], into $\Delta_{trs}H°$ = 6560 J·mol^{-1} and $\Delta_{fus}H°$ = 8220 J·mol^{-1}.

[84ABE]

Abey studied the effect of hydrostatic pressure of up to 6 GPa on the transformation and fusion temperatures using thermal analysis. At ambient pressure, the temperature of transformation was 1538 K, and it decreased with pressure at a rate $dT/dP = -43 \pm 7$ K GPa^{-1}. The temperature of fusion, 1558 K, increases with pressure at a rate $\Delta T_{fus} = 35 \pm 7$ K GPa^{-1}. These values are more accurate than those of [65FRA/CON]. The enthalpies of transformation and fusion were determined by quantitative thermal analysis, by comparing areas under DTA curves for Be and for a silver standard sample. The author obtained 7950 ± 800 J·mol^{-1} for the transformation and 9200 ± 800 J·mol^{-1} for the fusion (the ratio being about 0.86). The combined transformation and fusion effects 17.15 kJ·mol^{-1} exceed the value measured in [60KAN/KRA] by about 15% which is in reasonable agreement taking into consideration the low accuracy of the DTA experiments. Unfortunately, Abey did not check the precision of his apparatus by calibrating with a substance of well established enthalpy. The work of Abey is an important contribution to establishing the correct enthalpies of transformation and fusion.

2.5. Discussion of Phase Equilibrium Data

2.5.1. Superconductivity

According to [67FAL] Be becomes a superconductor at 0.026 K.

2.5.2. Temperature of the α–β Phase Transformation of Be

The experimental values in the Table 2–3 are scattered from 1525 to 1545 K; most of the studies can be rated only as poor because of the use of impure samples. The average value, T_{trs}/K = 1543 ± 6, is adopted from studies [59MAR/MOO] and [77LOA/DEA], which were performed more carefully than others. Reviews [73HUL], [74SPE], [85JAN] were based on the x-ray analysis of [59MAR/MOO] and [61AMO/IVA] which do not provide accurate temperatures. The temperature of transformation requires further investigation.

All measured temperatures have been converted to ITS–90. At 1550 K the correction terms are $T_{90} - T_{27}$ = 1 K; $T_{90} - T_{48}$ = 2 K; $T_{90} - T_{68}$ = 0 where T_{27}, T_{48}, T_{68} corresond to temperature scales ITS–27, IPTS–48, IPTS–68, respectively. These terms are estimated as the difference in scales in °C plus 0.15 kelvins omitted in previous conversion from °C to kelvins; the result is rounded to the nearest one degree.

2.5.3. Temperature of Fusion of Be

The fusion temperature, T_{fus}/K = 1563 ± 4, is adopted on the basis of studies [59MAR/MOO], [60KAN/KRA] and [77LOA/DEA]. It is slightly higher than the temperature recommended in previous reviews. The studies are summarized in Table 2-4. The fusion temperature, which is adopted here, is based on relatively old and not very accurate measurements. No precise measurements have been carried out recently. All experimentally measured temperatures of fusion are corrected to ITS–90.

2.5.4. Enthalpy of Transformation and Fusion of Be

A separate enthalpy of transformation and enthalpy of fusion were determined roughly by thermal analysis [72RAD/BER], [77LOA/DEA], [79ALD/PET], and [84ABE] (Table 2-5). Kantor *et al.* [60KAN/KRA] obtained an accurate combined (fusion plus transformation) enthalpy of 14.77 kJ·mol^{-1}. Several attempts were made to separate this value into its constituent parts using different considerations as a guide to the partition.

Gschneidner [75GSC] compared the entropies of transformation and fusion of different elements as a function of structure and the number of valence electrons. For Be the entropies were determined as 2.134 J·K^{-1} mol^{-1} for transformation and 7.74 J·K^{-1} mol^{-1} for fusion. If we use the adopted temperatures of phase transformation and fusion, then the enthalpy of transformation and fusion can be estimated as 3.3 and 12.1 kJ·mol^{-1}, respectively. Kaufman [84KAU], [86KAU] and Miodownik [86MIO] have recommended the enthalpy of transformation of Be to be about 4.4–4.8 kJ·mol^{-1}. Kaufman analyzed several beryllium phase diagrams and recommended two expressions for the Gibbs energy of transformation

$$\Delta_{trs}G\,/\text{J·mol}^{-1} = 4602 - 3.012T \text{ [84KAU], and}$$
$$\Delta_{trs}G\,/\text{J·mol}^{-1} = 4450 - 2.91\,T \text{ [86KAU].}$$

Miodownik used the results of a first principle calculation by Lam *et al.* [84LAM/CHO] together with a number of assumptions. One of the assumptions is that the entropy of fusion for beryllium should be consistent with those for other elements. The Gibbs energy of the α–β transformation was described in [86MIO] by equation

$$\Delta_{trs}G\,/\text{J·mol}^{-1} = 4770 - 3.14T.$$

The values recommended in [75GSH], [84KAU], [86KAU], [86MIO] are either theoretical or based on phase boundaries, which have not been determined with

the precision necessary to obtain accurate energies of transformation.

Aldinger and Petzow [79ALD/PET] used a ratio of enthalpies of transformation and fusion, obtained by thermal analysis. The total effect measured by Kantor *et al.* [60KAN/KRA] was divided between transformation, 6.56 kJ·mol^{-1}, and fusion, 8.22 kJ·mol^{-1} (ratio 0.8). The authors of [85JAN] developed this approach and used the more accurate ratio of Abey [84ABE]. The treatment of data made in [85JAN] is adopted here; the values are rounded. The total effect of [60KAN/KRA] is divided into the enthalpy of transformation, 6700 ± 500 J·mol^{-1} and fusion, 8000 ± 500 J·mol^{-1}. Reliable calorimetric measurements of enthalpy of transformation and enthalpy of fusion are still absent.

2.6. References for Be

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34JAE/ROS Jaeger, F. M. and Rosenbohm, E., Recueil Trav. Chim. **53**, 451–63 (1934); C_p°, 566–685 K; ΔH°(373–1338 K).

39LOS Losana, L., Alluminio **8**, 67–75 (1939); T_{fus}, C_p°, $\Delta_{fus}H^\circ$.

49TEI/COH Teitel, R. J. and Cohen, M., J. Metals **1**(4), 285–296 (1949); T_{trs}, T_{fus}.

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84LAM/CHO Lam, P. K., Chou, M. Y., and Cohen, M. L., J. Phys. C. **17**, 2065–2073 (1984); Estimation: $\Delta_{trs}G$, $\Delta_{fus}G$.

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87GAR/PAR Editors Garvin, D., Parker, V. B., and White, H. J., Jr., "CODATA Thermochemical Tables," Hemisphere Publ. Corp., NY, (1987); Review.

89COX/WAG Cox, J. D., Wagman, D. D., and Medvedev, V. A., "CODATA Key Values for Thermodynamics," Hemisphere Publ. Corp., New York (1989); Review.

2.7. Adopted Values

Electronic contribution to C_p°: $\gamma = 0.1714 \pm 0.01$ mJ·K^{-2} mol^{-1}

Debye temperature at 0 K: $\Theta_D = 1480 \pm 20$ K

Heat Capacity Equations

α-Be

Temperature range 0–30 K:

$$C_p^\circ/\text{J·K}^{-1}\,\text{mol}^{-1} = 1.714\times10^{-4}T + 0.598\times10^{-6}T^3 + 0.185\times10^{-9}T^5$$

Temperature range 30–40 K:

$$C_p^\circ/\text{J·K}^{-1}\,\text{mol}^{-1} = -0.99077 + 9.7344\times10^{-2}\text{T} - 3.1856\times10^{-3}T^2 + 3.5677\times10^{-5}T^3$$

Temperature range 40–100 K

C_p°/J·K^{-1} mol^{-1} = 2.946 − 8.064×10^{-2}T − 1.215×10$^{3}T^{-2}$ + 7.052×10$^{-4}T^{2}$

Temperature range 100–298.15 K

C_p°/J·K^{-1} mol^{-1} = −15.195 + 0.1576T + 2.937×10$^{4}T^{-2}$ − 1.764×10$^{-4}T^{2}$

Temperature range 298.15–1543 K

C_p°/J·K^{-1} mol^{-1} = 21.205 + 5.694×10^{-3}T − 5.874×10$^{5}T^{-2}$ + 0.962×10$^{-6}T^{2}$

β-Be

Temperature range 1543–1563 K

C_p°/J·K^{-1} mol^{-1} = 30.0

Liquid Be

Temperature range 1563–2200 K

C_p°/J·K^{-1} mol^{-1} = 25.435 + 2.150×10^{-3}T

Values at 298.15 K

C_p°(298.15 K) = 16.44 ± 0.08 J·K^{-1} mol^{-1}

S°(298.15 K) = 9.50 ± 0.1 J·K^{-1} mol^{-1}

H°(298.15 K) − H°(0) = 1942 ± 20 J·mol^{-1}

Phase Equilibrium Data

Superconductivity: T_c/K = 0.026 K

Temperature of α–β transformation: T_{trs}/K = 1543 ± 6

Enthalpy of α–β transformation: $\Delta_{trs}H^\circ$/J·mol^{-1} = 6700 ± 500

Temperature of fusion: T_{fus}/K = 1563 ± 4

Enthalpy of fusion: $\Delta_{fus}H^\circ$/J·mol^{-1} = 8000 ± 500

2.8. Calculated Thermodynamic Functions of Be

The thermodynamic functions presented in Tables 2–6 and 2–7 are calculated using the equations presented in the previous section. Values in brackets are calculated by using the equation for the next higher adjacent temperature interval.

2.9. Appendix

Experimental Results of Be

Tables 2–8 to 2–21 present heat capacity or enthalpy data as they were presented in the original article. As a result, the numerical values listed in this Appendix are the actual experimental values, tabular smoothed values, values calculated from equations, or values extracted from a graph. Where necessary, values are converted to joules (from calories). In all cases, the table heading indicates the type of data listed.

TABLE 2–1. Electronic contribution to the heat capacity and Debye temperature of Be

Reference	γ, mJ·K^{-2} mol^{-1}	Θ_D, K	T/K range
Original Studies			
53HIL/SMI	0.226	1160	4–20
64GME	0.184 ± 0.002	1390	1.2–4.4
66AHL	0.1714 ± 0.0008	1481 ± 16	1.4–30
67FAL	0.21 ± 0.02		0–0.4
Review			
73HUL	0.1714 ± 0.0008		Based on [66AHL]
Adopted			
This study	0.1714 ± 0.001	1480 ± 20	Based on [66AHL]

TABLE 2–2. Comparison of the heat capacity, enthalpy, and entropy values for Be at 298.15 K

Reference	C_p°(298.15 K) J·K^{-1} mol^{-1}	S°(298.15 K) J·K^{-1} mol^{-1}	H°(298.15 K) − H°(0) J·mol^{-1}
73HUL	16.443	9.498 ± 0.04	1950
73SPE	16.380	9.498	–
77KEY	–	9.500 ± 0.08	1950 ± 20
81GUR	16.443	9.500 ± 0.08	1950 ± 20
85JAN	16.380	9.440 ± 0.15	1932
89COX/WAG	16.443	9.500 ± 0.08	1950 ± 20
Adopted:	16.443	9.50 ± 0.1	1942 ± 20

TABLE 2–3. Temperature of phase transformation of Be

Reference	T/K	Comments
Original Studies		
49TEI/COH	1537	Thermal analysis
53BUZ	1525	Thermal analysis
59MAR/MOO	1542	Thermal analysis, average value
	1525	x-ray analysis
60GEL/PIC	1540	Thermal analysis
61AMO/IVA	1529	x-ray analysis
62SIN/IVA	1533	x-ray analysis
65FRA/CON	1535	Thermal analysis
72RAD/BER	1545	Thermal analysis
77LOA/DEA	1545	Thermal analysis, average value
79ALD/PET	1534	Thermal analysis
84ABE	1538	Thermal anlysis
Reviews		
73HUL	1527 ± 5	Based on 61AMO/IVA
73SPE	1527 ± 5	Based on 61AMO/IVA
81GUR	1550 ± 5	Based on 59MAR/MOO and 77LOA/DEA
85JAN	1525 ± 25	Based on 61AMO/IVA
Adopted		
This study	1543 ± 6 K	Based on 59MAR/MOO and 77LOA/DEA

TABLE 2–4. Temperature of fusion of Be

Reference	T/K	Comments
Original Studies		
39LOS	1556	Thermal analysis
49TEI/COH	1552	Thermal analysis
53BUZ	1558	Thermal analysis
59MAR/MOO	1562	Thermal analysis, average value
60GEL/PIC	1557	Thermal anlysis
60KAN/KRA	1562	Enthalpy analysis
65FRA/CON	1560	Thermal analysis
72RAD/BER	1565	Thermal analysis
77LOA/DEA	1565	Thermal analysis, average value
79ALD/PET	1552	Thermal analysis
84ABE	1558	Thermal analysis
Reviews		
73HUL	1560 ± 5	Based on 59MAR/MOO, 60KAN/KRA
73SPE	1560 ± 5	Based on 59MAR/MOO, 60KAN/KRA
81GUR	1560 ± 5	Based on 59MAR/MOO, 60KAN/KRA and 77LOA/DEA
85JAN	1560 ± 5	Based on 59MAR/MOO, 60KAN/KRA and 77LOA/DEA
Adopted		
This study	1563 ± 4	

TABLE 2–5. Enthalpy of transformation and fusion of Be

Reference	$\Delta_{trs}H°$ J·mol^{-1}	$\Delta_{fus}H°$ J·mol^{-1}	$\Delta_{trs}H° + \Delta_{fus}H°$ J·mol^{-1}	Comments
Original Studies				
39LOS	–	10000	–	Thermal analysis
60KAN/KRA	–	–	14770	Enthalpy meas.
65FRA	7500	14700		Temp. pres. meas
72RAD/BER	–	9050	–	Thermal analysis
77LOA/DEA	2100	2500	4600	Thermal analysis
79ALD/PET	6560	8220	14780	Thermal analysis
84ABE	7950	9200	17150	Thermal analysis
Reviews				
73HUL	(2556)	(12213)	(14769)	Based on 60KAN/KRA & 75GSC
73SPE	2100 ± 200	12600 ± 300	14700	Based on 60KAN/KRA & 75GSC

TABLE 2–5. Enthalpy of transformation and fusion of Be – Continued

Reference	$\Delta_{trs}H°$ J·mol^{-1}	$\Delta_{fus}H°$ J·mol^{-1}	$\Delta_{trs}H° + \Delta_{fus}H°$ J·mol^{-1}	Comments
81GUR	2100 ± 200	12600 ± 300	14700	Based on 60KAN/KRA & 77LOA/DEA
85JAN	6849 ± 500	7895 ± 500	14744	Based on 60KAN/KRA & ratio from 77LOA/DEA & 84ABE
Adopted				
This study	6700 ± 500	8000 ± 500	14700	Based on 60KAN/KRA & ratio from 77LOA/DEA & 84ABE

TABLE 2–6. Thermodynamic functions of Be below 298.15 K

T/K	$C_p°(T)$ J·K^{-1} mol^{-1}	$H°(T)-H°(0)$ J·mol^{-1}	$S°(T)$ J·K^{-1} mol^{-1}
5	0.000932	0.00224	0.000882
10	0.00233	0.01010	0.001917
15	0.00473	0.02720	0.003272
20	0.00880	0.06017	0.005141
25	0.0154	0.1195	0.007761
30	0.0258(0.0258)	0.2207	0.01142
35	0.0436	0.3880	0.01655
40	0.0894(0.0894)	0.7040	0.02492
45	0.145	1.299	0.03885
50	0.191	2.140	0.5652
60	0.309	4.589	0.1009
70	0.509	8.594	0.1622
80	0.818	15.130	0.2490
90	1.251	25.368	0.3691
100	1.813(1.738)	40.573	0.5288
120	3.216	89.537	0.9710
140	4.910	170.620	1.5926
160	6.652	286.246	2.3620
180	8.364	436.505	3.2449
200	10.003	620.323	4.2118
220	11.546	835.991	5.2384
240	12.978	1081.427	6.3053
260	14.291	1354.323	7.3967
280	15.478	1652.223	8.5000
298.15	16.443(16.380)	1942.068	9.5027

TABLE 2–7. Thermodynamic functions of Be above 298.15 K

T/K	$C_p°(T)$ J·K^{-1} mol^{-1}	$H°(T)-H°(298.15\ K)$ J·mol^{-1}	$S°(T)$ J·K^{-1} mol^{-1}
298.15	16.38	0	9.50
300	16.47	30.39	9.60
400	19.97	1872.54	14.88
500	21.94	3975.14	19.56
600	23.34	6242.19	23.69
700	24.46	8633.66	27.37
800	25.46	11130.51	30.71
900	26.38	13723.00	33.76
1000	27.27	16406.07	36.59
1100	28.15	19177.18	39.23
1200	29.01	22035.29	41.71
1300	29.89	24980.28	44.07
1400	30.76	28012.60	46.32
1500	31.65	31133.10	48.47
1543 (α)	32.03	32502.30	49.37
1543 (β)	30.00	39202.30	53.71
1563 (β)	30.00	39802.30	54.10

TABLE 2–7. Thermodynamic functions of Be above 298.15 K – Continued

T/K	$C_p^\circ(T)$ J·K^{-1} mol^{-1}	$H^\circ(T)-H^\circ(298.15\ K)$ J·mol^{-1}	$S^\circ(T)$ J·K^{-1} mol^{-1}
1563 (liq)	28.80	47802.30	59.22
1600	28.88	48869.20	59.89
1800	29.31	54687.20	63.32
2000	29.74	60591.20	66.43
2200	30.17	66581.20	69.28

TABLE 2–8. SMOOTHED heat capacity values of Be [34CRI/SIM]

T/K	$C_p^\circ(T)$ / J·K^{-1} mol^{-1}
10	0.0025
20	0.0155
30	0.0502
40	0.11
50	0.22
60	0.38
70	0.61
80	0.90
90	1.28
100	1.73
110	2.28
120	2.77
130	3.60
160	6.19
180	8.12
190	9.04
200	9.92
210	10.79
240	13.31
270	15.73
280	16.48
300	17.91

TABLE 2–9. EXPERIMENTAL enthalpy values $[H^\circ(T)-H^\circ(273\ K)]$ of Be [34JAE/ROS]

T/K	$H^\circ(T)-H^\circ(273\ K)$
373	1689
373	1690
471	3560
570	5685
579	5720
666	7850
666	7860
691	8415
713	8930
724	9200
773	10370
823	11580
905	13220
1075	18120
1338	(24870)

TABLE 2–10. EXPERIMENTAL enthalpy values $[H^\circ(T)-H^\circ(273\ K)]$ of Be [51GIN/DOU]

T / K	$H^\circ(T)-H^\circ(273\ K)$, J·mol^{-1}	
	Sample I	Sample II
367.0	1609	1608
468.8	3683	...
571.3	5970	5952
667.6	8256	...
770.8	10800	10760
870.6	13350	...
972.7	16065	15990
1069.9	18740	...
1169.4	21580	21490

TABLE 2–11. CALCULATED heat capacity values of Be [51GIN/DOU]

T/K	$C_p^\circ(T)$, J·K^{-1} mol^{-1}	T/K	$C_p^\circ(T)$, J·K^{-1} mol^{-1}
373	19.20	873	26.05
473	21.49	973	27.02
573	23.05	1073	28.02
673	24.17	1173	29.12
773	25.07		

TABLE 2–12. SMOOTHED heat capacity values of Be [53HIL/SMI]

T / K	$C_p^\circ(T)$, J·K^{-1} mol^{-1}
5	0.0013
10	0.0035
20	0.0145
40	0.0904
60	0.307
80	0.816
100	1.83
120	3.19
150	5.73
200	10.04
250	13.85
300	16.53

TABLE 2–13. GRAPHICAL heat capacity values of Be [53HIL/SMI]

T/K	$C_p^\circ(T)$, J·K^{-1} mol^{-1}	T/K	$C_p^\circ(T)$, J·K^{-1} mol^{-1}
40	0.095	100	1.83
45	0.140	120	3.30
50	0.185	140	4.90
55	0.245	160	6.60
60	0.310	180	8.25
65	0.395	200	10.00
70	0.520	220	11.50
75	0.660	240	13.05
80	0.815	260	14.40
85	1.015	280	15.60
90	1.245	300	16.50
95	1.500		

TABLE 2–14. EXPERIMENTAL heat capacity values of Be [59MIT]

T/K	$C_p^\circ(T)$ / J·K^{-1} mol^{-1}
323	17.53
373	18.48
623	23.19
673	23.94
723	24.70
773	25.34

TABLE 2–15. EXPERIMENTAL enthalpy values $[H^\circ(T) - H^\circ(298.15\ K)]$ of Be [60KAN/KRA]

T/K	$H^\circ(T) - H^\circ(298.15\ K)$ J·mol^{-1} Solid Be	T/K	$H^\circ(T) - H^\circ(298.15\ K)$ J·mol^{-1} Liquid Be
625	6850	1550	47600
685	8100	1575	47800
815	11700	1585	49000
905	14400	1610	49900
1020	17700	1610	48700
1100	19800	1635	49400
1160	21400	1650	49900
1290	25000	1700	52100
1390	27400	1780	54600
1485	30800	1820	55500
1545	32300	1830	56500
1550	33900	1880	58200
1550	35900	1960	59700
		1965	60700
		2050	62900
		2080	63100
		2150	65400

TABLE 2–16. CALCULATED heat capacity values of Be [60KAN/KRA]

T/K	$C_p^\circ(T)$ / J·K^{-1} mol^{-1}
600	23.64
700	24.48
800	25.36
900	26.28
1000	27.15
1100	28.07
1200	29.00
1300	29.95
1400	30.88
1500	31.84
1560 (sol)	32.30
1560 (liq)	28.78
1600	28.87
1700	29.09
1800	29.30
1900	29.52
2000	29.73

TABLE 2–17. SMOOTHED heat capacity values of Be [62WAL/EWI]

T/K	$C_p^\circ(T)$ / J·K^{-1} mol^{-1}
303	16.48
373	18.78
473	20.85
573	22.28
673	23.38
773	24.40
873	25.41
973	26.43
1073	27.49

TABLE 2–18. SMOOTHED heat capacity values of Be [64GME]

T/K	$C_p^\circ(T)$, mJ·K^{-1} mol^{-1}
1	0.185
2	0.374
3	0.571
4	0.782
5	1.0095

TABLE 2–19. SMOOTHED heat capacity values of Be [66AHL]

T/K	$C_p^\circ(T)$, mJ·K^{-1}mol^{-1}
1	0.172
2	0.348
3	0.530
4	0.724
5	0.932
10	2.33
15	4.73
20	8.80
25	15.43
30	25.78

TABLE 2–20. EXPERIMENTAL enthalpy values [$H°(T) - H°(297.5$ K)] of Be [70TYE/BRA]

T/K	$H°(T) - H°(297.5$ K), J·mol^{-1}
532.3	4623
589.1	6011
650.4	7408
696.6	8570
752.9	9913
810.2	11400
871.0	13075
913.1	14200
971.2	15780
1025.7	16870
1077.0	18725
1110.5	19550

TABLE 2–21. SMOOTHED heat capacity values of Be [70TYE/BRA]

T/K	$C_p^\circ(T)$, J·K^{-1} mol^{-1}
323	17.46
373	19.13
423	20.66
473	21.85
523	22.75
573	23.44
623	23.85

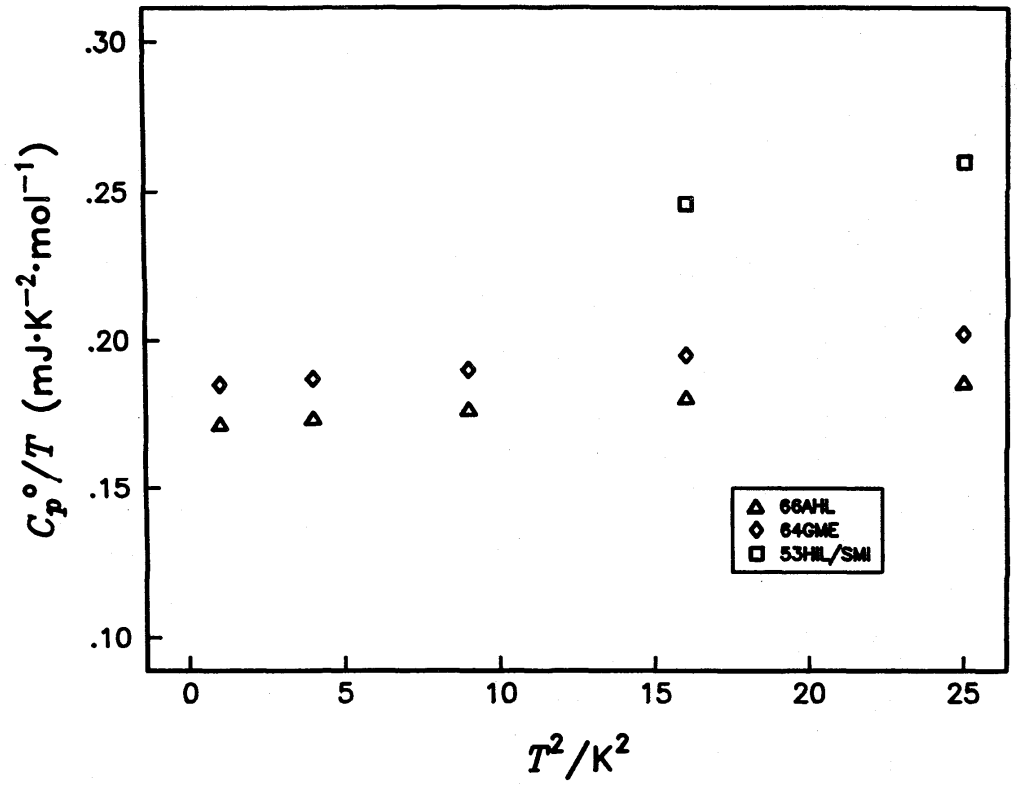

FIG. 2–1. C_p°/T versus T^2 for Be below 5 K.

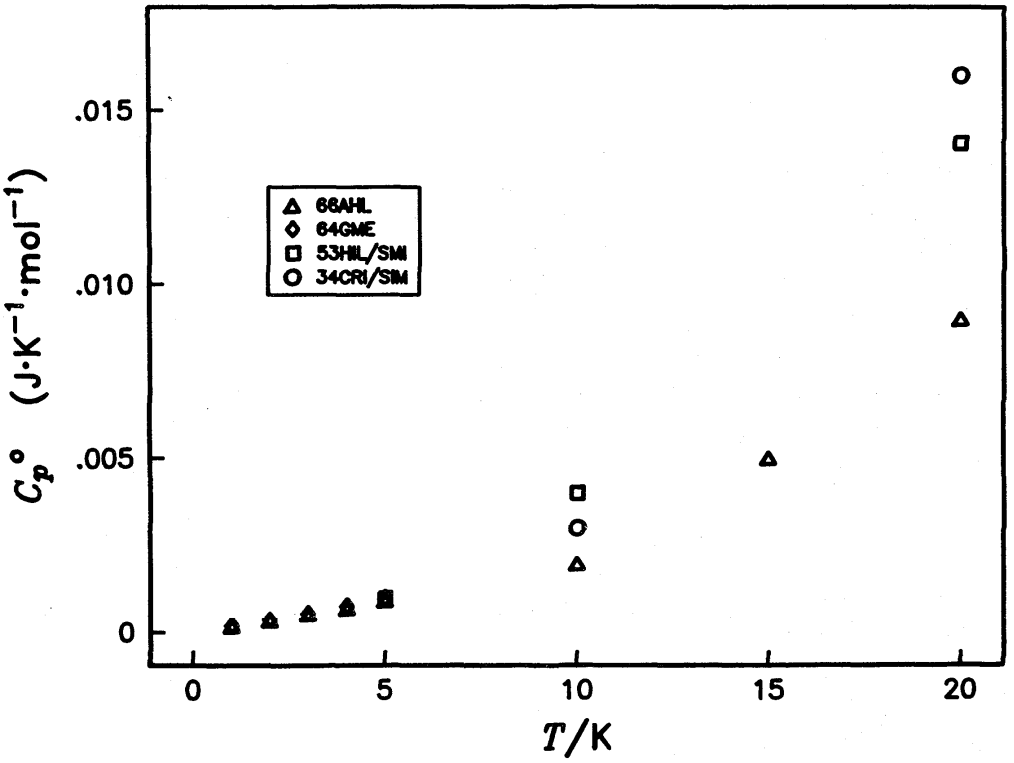

FIG. 2–2. Heat Capacity of Be below 20 K.

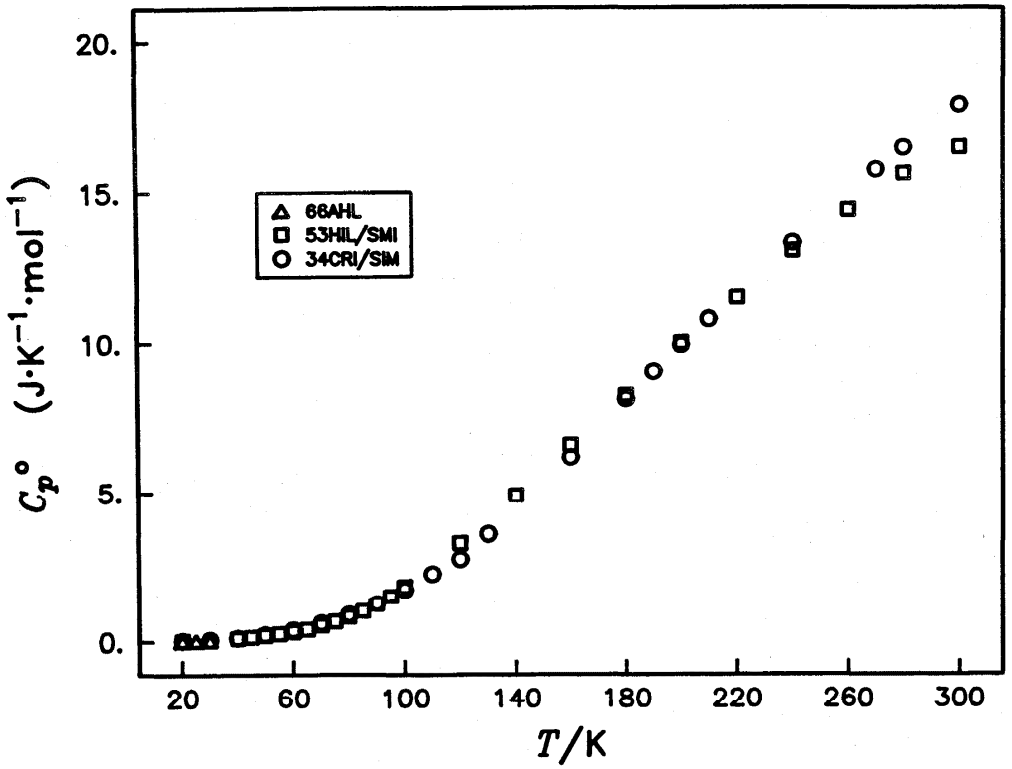

FIG. 2–3. Heat Capacity of Be at 20–300 K.

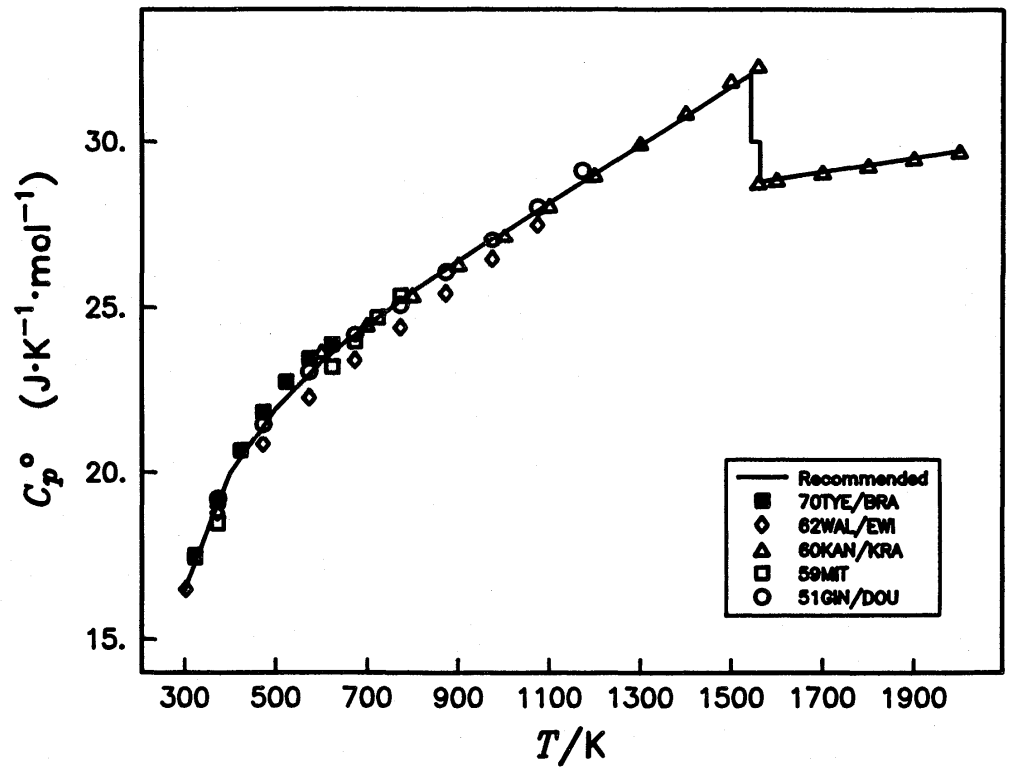

FIG. 2–4. Heat Capacity of Be at 300–2000 K.

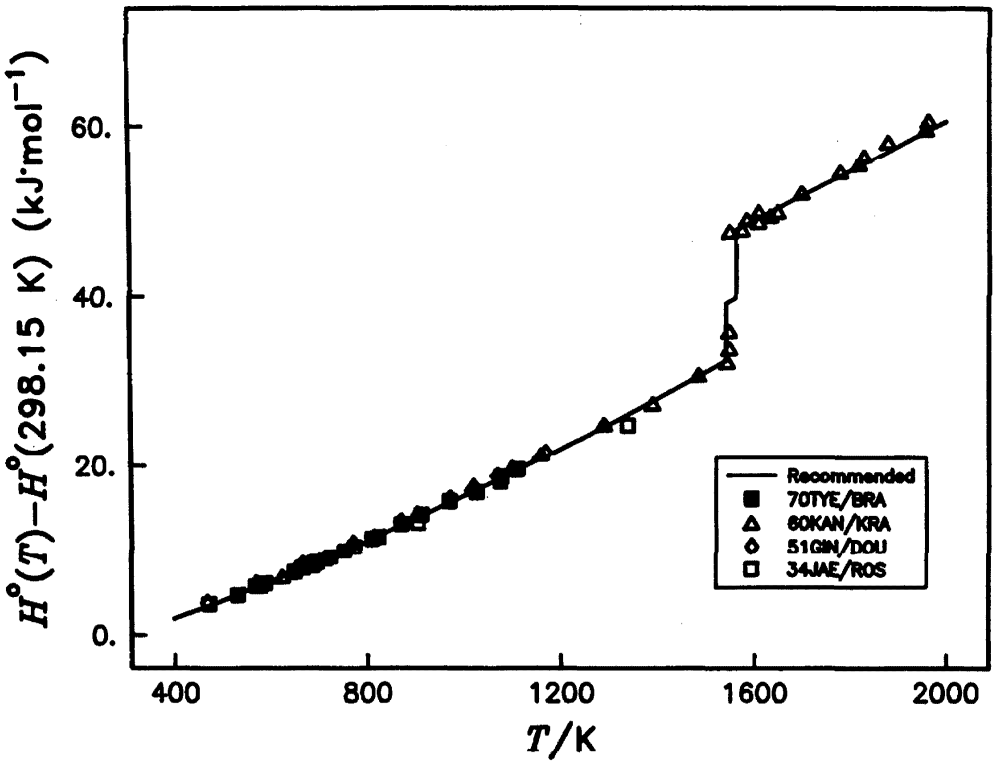

FIG. 2–5. $H^\circ(T)-H^\circ(298.15\ K)$ for solid and liquid Be.

3. Magnesium

3.1. Introduction

At ambient pressure, magnesium has one stable crystalline modification, hcp. The temperature of fusion was established in the thirties. The measured values for the enthalpy of fusion vary from 8240 to 9200 J·mol^{-1}. The heat capacity and enthalpy data for solid Mg agree satisfactorily; however, discrepancies are observed for liquid magnesium. Despite some deficiencies, the thermodynamic properties of Mg are known better than any other element of the IIA Group.

3.2. Heat Capacity and Enthalpy Measurements

3.2.1. Temperatures below 298.15 K

[30CLU/VAU]

Clusius and Vaughen measured the heat capacity of Mg from 11 to 228 K in an adiabatic vacuum calorimeter. The sample was the purest available at that time and contained about 0.13 wt. % metallic impurities. The reported heat capacity values are listed in the Table 3-12 and shown in Figs. 3-1, 3–2 and 3–3. This early study gave relatively accurate values which do not deviate much from more modern results (Fig. 3–3).

[52EST/FRI]

Estermann *et al.* measured the heat capacity of commercial Mg (99.96% pure) in a vacuum Nernst calorimeter between 2 and 3.7 K. Eighteen experimental points are shown in graphical form in this study; the authors also derived $\gamma = 1.36\times10^{-3}$ J·K^{-2} mol^{-1} and $\Theta_D = 342$ K. These values were used to calculate the heat capacity at 2, 3, and 4 K, and are listed in the Table 3-14. Figure; 3–1 shows that these values are higher than any others; therefore the accuracy of this study is considered to be low.

[54CRA/KRI]

Craig *et al.* measured the heat capacity of Mg in the temperature interval from 12 K to 320 K. The purity of the samples was not given in the paper. Only the smoothed results were reported and these are shown in Figs. 3-1, 3–2 and 3–3 and are listed in the Table 3-15. These values agree well with [30CLU/VAU], [55SMI], and [66MAN/WOL] and they appear to be very reliable.

[55SMI]

Smith measured the heat capacity of Mg from 1.3 to 18 K. The composition of the material used for the samples was not given. The experimental points were shown in two graphs from 1 to 4 K (14 points) and from 5 to 18 K (14 points). The data below 4 K were fitted to the equation:

$$C_p^\circ/\text{mJ·K}^{-1}\,\text{mol}^{-1} = 1.318T + 2.904\times10^{-2}T^3$$

From this equation, Smith derived $\gamma = 1.318$ mJ·K^{-2} mol^{-1} and $\Theta_D = 406 \pm 10$ K. The heat capacities, calculated by the above equation, and the values above 4 K, taken from the graph, are shown in Figs. 3–1 and 3–2 and are listed in the Table 3-16. These results appear to be very reliable.

[57LOG/CLE]

Logan *et al.* measured the heat capacity of two Mg samples with 0.043% Mn in one and 0.013% Fe in the other specimen from 3 to 13 K. The results for these two samples agree within 5%. The experimental values are listed in the Table 3-19 and shown in Figs. 3-1 and 3–2. From the data, Logan *et al.* derived $\gamma = 1.28 \pm 0.06$ mJ·K^{-2} mol^{-1} and $\Theta_D = 390 \pm 7$ K. The heat capacity values obtained in this study are very close to those of [55SMI].

[58RAY]

Rayne measured the heat capacities of Mg and four dilute Mg-Al alloys with up to 3.9 at wt. % Al in the temperature range 1.5–4.0 K. The Mg sample (Johnson Matthey) was 99.99 wt. % pure. From this study, Rayne derived, for pure Mg, $\gamma = 1.265 \pm 0.01$ mJ·K^{-2} mol^{-1} and $\Theta_D = 403 \pm 4$ K. These values can be used to calculate the heat capacities between 1 and 4 K which are shown in Figs. 3–1 and 3-2 and listed in the Table 3-21. These values are very close to those of [55SMI] and are of good accuracy.

[59MAN/BOR], [66MAN/WOL]

Mannchen and Bornkessel [59MAN/BOR] measured the heat capacity of two Mg samples at temperatures from 12 K to 300 K. The impurity content of samples was not given in the paper except for hydrogen. One sample contained 21 ml hydrogen per 100 g metal (0.046 at.% H). The other sample of the same origin was held in vacuum at 520°C for 20 h. After this treatment no hydrogen was found in the sample. The authors [59MAN/BOR] gave only a small-scale graph with 48 experimental points for the hydrogen-free sample and 82 points for the sample with hydrogen. Some experimental data points were extracted from this graph. These values were assumed to have an accuracy of about 1.5% and are given in the Table 3–22. The heat capacity values for both samples are in good agreement below 100 K. Above this temperature the heat capacity values for the sample with hydrogen are higher than those for the vacuum treated sample. The difference increases with temperature and reaches 3% at 300 K. The values obtained for a hydrogen-free sample agree with [54CRA/KRI] within 0.5%.

In a following study, Mannchen and Wolf [66MAN/WOL] measured the heat capacities of four Mg samples containing different amounts of Si (0.005 and 0.1 wt. %) and H (from 0.76 to 25.7 ml/100 g metal) from 20 to 300 K. Smoothed values were tabulated for the four samples. Three samples with low Si content released heat during measurements because of a reaction which developed between 150 and 250 K. The reaction was explained by the liberation of hydrogen bound to the crystal lattice and its imperfections. Surprisingly, a sample containing a

considerable amount of hydrogen 15.1 ml/100 g and silicon (0.1 wt. % Si), did not show this phenomenon. The heat capacity values obtained for this sample may represent pure magnesium with an accuracy of about 1.5%. They are also reproduced in the Table 3-24 and shown in Fig. 3–3. The values obtained in [59MAN/BOR] and [66MAN/WOL] are less accurate than those of [54CRA/KRA] because of the impurities.

[61MAR]

Martin measured the heat capcity of Mg in a narrow range of temperatures, 0.4–1.5 K. The sample had about 0.03 wt. % metallic impurities, and a residual resistivity ratio $\rho(300\ K)/\rho(4.2\ K) = 278$. Eighty experimental points were shown in a graph and are represented by the equation:

$$C_p^\circ/\text{mJ}\cdot\text{K}^{-1}\ \text{mol}^{-1} = 1.224T + 2.282\times10^{-2}T^3\ .$$

Martin obtained values of $\gamma = 1.224 \pm 0.01$ mJ·K^{-2} mol^{-1} and $\Theta_D = 440 \pm 60$ K. Despite the use of relatively pure samples and a good technique, a considerable scatter of data was observed, which decreases the value of this study. The heat capacity values were calculated from the above equation. These values are shown in Fig. 3–1 and 3-2 and are listed in the Table 3–23.

[65PAN/SAM]

Panova and Samoilov measured the heat capacities of Mg and a Mg alloy containing 2.8 at.% Pb between 1.2 and 20 K in an adiabatic calorimeter. The purity of the Mg samples was not given. The 26 experimental points were given in a graphical form. The authors obtained $\gamma = 1.31$ mJ·K^{-2} mol^{-1} and $\Theta_D = 311 \pm 10$ K, from which smoothed heat capacities were calculated for temperatures in the range of 1 – 5 K. The C_p° values for 10, 15 and 18 K were taken from the graph. These values are given in the Table 3-25 and are also shown in Figs. 3–1 and 3–2. It is evident from these two figures that the heat capacity values differ from the results of other investigators. It is concluded that the samples used by Panova and Samoilov were impure and that the technique was not accurate.

3.2.2. Temperatures Above 298.15 K

[24EAS/WIL]

Eastman *et al.* measured the enthalpy of commercial magnesium in a mixing calorimeter from 373 to 888 K. The twenty experimental points were not listed in the paper; the authors only gave the equation:

$$H^\circ(T) - H^\circ(293\ K)\ /\ \text{J}\cdot\text{mol}^{-1} = -6948.15 + 22.113T + 5.464\times10^{-3}T^2\ .$$

The heat capacities calculated from this equation are listed in the Table 3-9 and are shown in Fig. 3–4.

[26AWB/GRI]

Awbery and Griffith measured the enthalpy of Mg in a drop calorimeter from 525 to 1023 K. The magnesium sample contained 0.05% Si and 0.02% Fe. The reported melting point of Mg, 917 K, appears low and would indicate that the amount of impurities was probably greater than was reported. The measured enthalpy is listed in the Table 3-11 and shown in Fig. 3–5. Shpil'rain *et al.* [86SHP/KAG] analyzed the results of this study and derived the following enthalpy expressions:

solid Mg (525 – 917 K)

$$H^\circ(T) - H^\circ(289\ K)\ /\ \text{J}\cdot\text{mol}^{-1} = -6601 + 21.46T + 4.9\times10^{-3}T^2\ ,$$

liquid Mg (917 – 1023 K)

$$H^\circ(T) - H^\circ(289\ K)\ /\ \text{J}\cdot\text{mol}^{-1} = -11819 + 36.56T,$$

The heat capacity values calculated from these equations are listed in the Table 3-10 and shown in Fig. 3–4. The authors also obtained the enthalpy of fusion, $\Delta_{fus}H = 4730$ J·mol^{-1}, which is low in comparison with more modern measurements. This study is therefore not considered to be reliable.

[31SEE]

Seekamp measured the heat capacity of Mg with 0.08% impurities in a calorimeter calibrated with copper. The twelve experimental points were measured between room temperature and 773 K and were given in a graphical form; they show considerable scatter in the values (5%). Seekamp also gave smoothed values which are reproduced in the Table 3-13 and shown in Fig. 3–4. These data are considered to have low accuracy.

[45REI]

Reinartz (discussed in [50KUB]) used a 99.6% pure Mg sample and measured the heat capacity of liquid Mg from 923 to 1133 K. Reinartz determined a constant value of 34.18 J·K^{-1} mol^{-1}.

[55STU/MCD]

Stull and McDonald measured the enthalpy of doubly sublimed magnesium of 99.95 to 99.98 wt. % pure in a drop calorimeter from 700 to 1100 K. The experimental points are shown in a graph in the paper; they are reproduced in Fig. 3–5 and the Table 3-17. These points are described by two equations:

solid Mg (298.15 – 923 K)

$$H^\circ(T) - H^\circ(298.15\ K)\ /\ \text{J}\cdot\text{mol}^{-1} = 18.66T + 7.734\times10^{-3}T^2 - 1.384\times10^5/T - 5788,$$

liquid Mg (923 – 1100 K)

$$H^\circ(T) - H^\circ(298.15\ K)\ /\ \text{J}\cdot\text{mol}^{-1} = 22.13T + 5.44\times10^{-3}T^2 + 4.928\times10^4/T + 1714\ .$$

The maximum deviation of the observations from these equations is 0.7%. The enthalpy of melting was found to be 8950 J·mol^{-1}. The smoothed heat capacity values are listed in the Table 3-18.

In a subsequent publication [67MCD], McDonald reveals that the reported enthalpy of fusion and heat capacity of liquid Mg are in error because of a mistake in correcting a contribution related to the magnetic transformation in the stainless steel container. This study is therefore considered as having a 1% systematic error.

[57SAB/STE]

Saba *et al.* measured the heat capacity of Mg in an adiabatic calorimeter at temperatures from 293 to 548 K. The purity of the samples was not stated in the paper. These authors obtained thirty-seven experimental points, but only smoothed values are given in the paper. The deviation of the smoothed values from experiment does not exceed 0.4% and was on average 0.1%. The smoothed values are shown in Fig. 3–4 and listed in the Table 3-20. The authors found that their results from 300 to 320 K are consistently 0.2% lower than those in a previous investigation made in the same laboratory [54CRA/KRI]. They explained the difference as being due to the combined systematic error of the two different methods employed. These values can be considered as relatively accurate.

[67MCD]

McDonald redetermined the enthalpy of Mg from 400 to 1260 K. The material and apparatus were about the same as in [55STU/MCD]. The amount of metallic impurities in the sample was less than 0.02 wt. %. Some improvements were made to the container, which consisted of two parts: the inner shell was made of Pt-10% Rh and the outer shell of tantalum. The calorimeter was calibrated by the use of an alumina standard. The 11 measured enthalpy values are listed in the Table 3–26 and shown in Fig. 3–5. They were used to derive the equation and to calculate heat capacity values reproduced in the Table 3-27 and shown in Fig. 3–4. The enthalpy of fusion was determined as 8480 ± 200 J·mol^{-1}, and the heat capacity of liquid Mg as a constant value 34.3 J·K^{-1} mol^{-1}. These results are accurate and reliable, and the study can be considered as the best available at the present time.

[84SHP/KAG]

Shpil'rain *et al.* measured the heat capacity of solid and liquid Mg by a pulse-differential calorimetry which is based on measuring and comparing the rates of temperature increase during pulse heating of the sample to be investigated and a standard specimen with a well-defined heat capacity. The material had about 0.1 wt. % of metallic impurities. The 26 measurements were made from 350 to 1540 K. The experimental heat capacity values, tabulated in the paper, are listed in the Table 3-28 and shown in Fig. 3–4. The data were fitted to the equations:

solid Mg (400–923 K)

$$C_p^\circ / \text{J·K}^{-1}\,\text{mol}^{-1} = 24.5607 + 2.10915\times10^{-3}T + 3.13382\times10^{-6}T^2$$

liquid Mg (923–1600 K)

$$C_p^\circ / \text{J·K}^{-1}\,\text{mol}^{-1} = -34.69344 + 0.20418T - 1.90247\times10^{-4}T^2 + 5.4392\times10^{-8}T^3$$

As Fig. 3–4 shows, the experimental results deviate considerably (up to 10%) from the results obtained by a very accurate drop calorimetric technique. This considerable discrepancy leads to the general conclusion that the pulse-differential method which requires precise knowledge of several correction factors is not accurate and can be a source of considerable systematic errors if these factors are ill-defined. All information obtained by this method should be regarded as potentially unreliable and subject to some inaccuracy. Therefore, the results of this study are considered as of low accuracy. The authors also determined the temperature of fusion, T_{fus} = 923 ± 1 K and enthalpy of fusion, $\Delta_{fus}H$ = 9200 ± 120 J·mol^{-1}.

3.3. Discussion of Heat Capacity and Enthalpy Data

3.3.1. Mg below 298.15 K

For temperatures below 5 K, the heat capacity was measured in [52EST/FRI], [55SMI], [57LOG/CLE], [58RAY], [61MAR], [65PAN/SAM] (Fig. 3–1). In each study γ and Θ_D were calculated. These values for each study are listed in Table 3-1. The values depend on the method, the temperature of measurement, and the purity of samples.

The study [61MAR] seems to have been carefully performed; however, the scatter of the experimental points is considerable. The study [58RAY] was selected as the most accurate, and the values of γ and Θ_D, determined in it, were used to derive the heat capacity equation for the temperature range from 0 to 4 K:

$$C_p^\circ / \text{mJ·K}^{-1}\,\text{mol}^{-1} = 1.265T + 2.97\times10^{-2}T^3 \quad (3\text{–}1)$$

Between 4 and 20 K heat capacity measurements were made in [30CLU/VAU] (above 11 K), [54CRA/KRI] (above 12 K), [55SMI] (1–20 K) and [57LOG/CLE] (3–13 K). These data agree satisfactorily, as shown in Fig. 3–2. The values from [55SMI] (mostly) and [54CRA/KRI], listed in Table 3-2, were used to derive an equation for the temperature range 4–20 K:

$$C_p^\circ / \text{J·K}^{-1}\,\text{mol}^{-1} = -0.02637 + 0.01052T + 0.06691T^{-2} - 1.115\times10^{-3}T^2 + 7.763\times10^{-5}T^3 \quad (3\text{–}2)$$

Above 20 K the data of [54CRA/KRI], [30CLU/VAU], [59MAN/BOR] and [66MAN/WOL] agree satisfactorily(Fig. 3–3). Preference was given to [54CRA/KRI] as being the most carefully performed. The heat capacity values of [54CRA/KRI] are fitted to two equations:

for 20 K $\geq T \leq$ 100 K

$$C_p^\circ / \text{J·K}^{-1}\,\text{mol}^{-1} = -5.153 + 0.1258T + 858.320\text{T}^{-2} + 0.00257T^2 - 1.756\times10^{-5}T^3 \quad (3\text{–}3)$$

for 100 K $\geq T \leq$ 298.15 K

$$C_p^\circ / \text{J·K}^{-1}\,\text{mol}^{-1} = 12.124 + 0.1106\text{T} - 4.5\times10^{4}\text{T}^{-2} - 3.408\times10^{-4}T^2 + 3.953\times10^{-7}T^3 \quad (3\text{–}4)$$

Equations 1–4 were used to calculate $C_p^\circ(T)$, $H^\circ(T)-H^\circ(0)$ and $S^\circ(T)$. The calculated values are shown in the Table 3–7. At the standard temperature the heat capacity, enthalpy and entropy were calculated as

C_p°(298.15 K) = 24.775 J·K^{-1} mol^{-1}
S°(298.15 K) = 32.535 J·K^{-1} mol^{-1}
H°(298.15 K) − H°(0) = 4979.16 J·mol^{-1}.

These values are compared with those recommended in other reviews in Table 3–3.

The difference between the values listed in reviews and those adopted here is mostly due to the various selections of data below 20 K. The accuracies are 30 J·mol^{-1} for H°(298.15 K) − H°(0) and 0.2 J·K^{-1} mol^{-1} for S°(298.15 K) which reflect the uncertainties in the published studies, the proper selection of the best studies and any error in the mathematical description of the experimental data.

3.3.2. Splines

One probable source of error is due to the fact that four different equations are used to describe the heat capacity between 0 and 298 K. At the node points at 4, 20, 100 and 298 K, the heat capacities have two different values and two different derivatives, dC_p°/dT, which are calculated from the two adjacent equations (Table 3–4).

An attempt was made to join adjacent sections of Eqs. 1–4 by intermediate short cubic splines which have at the edges the same heat capacity values and the same derivatives as the neighboring main equations. Such splines were calculated for the intervals 3 to 5, 18 to 25, 90 to 110, and 180 to 320 K. The values of S°(298.15 K) and H°(298.15 K) − H°(0) were recalculated using Equations 1–4 and four splines. The difference between the variance of the splines and the separate equations was small: about +0.7 J·mol^{-1} for the enthalpy and +0.004 J·K^{-1} mol^{-1} for the standard entropy. As the splines do not change the calculated thermodynamic quantities significantly, the application of splines was abandoned.

3.3.3. Mg above 298.15 K

Figure 3–5 shows the enthalpy $H^\circ(T)-H^\circ$(298.15 K) measured in [26AWB/GRI], [55STU/MCD] and [67MCD]. The results for solid Mg agree satisfactorily. Heat capacities measured [31SEE], [57SAB/STE], [84SHP/KAG] and derived from enthalpy measurements [24EAS/WIL], [26AWB/GRI], [55STU/MCD], [67MCD] are shown in Fig. 3–4. The data agree satisfactorily except for those of [84SHP/KAG] which deviate considerably from the other results and evidently contain errors. The best measurements were made by McDonald [67MCD]. His values were fitted to the heat capacity equation from 298 to 923 K.

$$C_p^\circ = 28.260 - 6.023\times10^{-3}\text{T} - 2.378\times10^{5}\text{T}^{-2} + 11.684\times10^{-6}T^2 \text{ J·K}^{-1}\,\text{mol}^{-1} \quad (3\text{–}5)$$

The three reviews – [73HUL], [81GUR], and [85JAN] – used several sources and different treatments to derive the heat capacity values. The values given in [85JAN] were used in [87GAR/PAR] and [89COX/WAG]. The heat capacities recommended in the above reviews differ by less than 1%. [81GUR] recommended for solid Mg the equation (298–923 K):

$$C_p^\circ = 22.030 + 10.226\times10^{-3}\text{T} - 0.202\times10^{5}T^{-2} + 0.544\times10^{-6}T^2 \text{ J·K}^{-1}\,\text{mol}^{-1}.$$

Shpil'rain *et al.* [86SHP/KAG] derived another equation for solid Mg combining their data [84SHP/KAG] with a statistical weight of 5 and the data of McDonald [67MCD] (298–923 K):

$$C_p^\circ = 22.335 + 9.201\times10^{-3}\text{T} - 0.020\times10^{6}T^{-2} + 0.544\times10^{-6}T^2 \text{ J·K}^{-1}\,\text{mol}^{-1}$$

As the data of [84SHP/KAG] are less reliable than [67MCD], the recommendation of [86SHP/KAG] is considered inaccurate.

3.3.4. Liquid Mg

Several heat capacity measurements were made for liquid Mg: [45REI], [55STU/MCD], [67MCD] and [84SHP/KAG]. See Sec. 3.2.2 for the description of these studies. Enthalpy measurements [26AWB/GRI], [55STU/MCD], [67MCD] are shown in Fig. 3–5. The results of [26AWB/GRI] are much lower than the mutually consistent data of [55STU/MCD] and [67MCD]. The heat capacities derived from enthalpy measurements [26AWB/GRI], [55STU/MCD], [67MCD] and directly measured heat capacity values [84SHP/KAG] are given in Tables 3–10, 3–18, 3–27, and 3–28. Near the melting point, the best value 34.3 J·K^{-1} mol^{-1} was obtained in [67MCD]. This agrees with the constant value 33.9 ± 1.2 J·K^{-1} mol^{-1} for 923–1133 K [45REI] and 34.18 J·K^{-1} mol^{-1} at 944.2 K [84SHP/KAG]. However, Shpil'rain *et al.* [84SHP/KAG] showed that the heat capacity of Mg decreases rapidly with temperature to about 27 J·K^{-1} mol^{-1} near 1500 K. It is very probable that the heat capacity of liquid Mg decreases with the temperature; however, the rate of this decrease requires independent confirmation. The data of [84SHP/KAG] are questionable because an error exists in the data for solid Mg.

The following constant values of heat capacity for liquid Mg were recommended in reviews (J·K^{-1} mol^{-1}): 32.6 [73HUL], 34.3 [81GUR], 34.309 [85JAN]. Shpil'rain

et al. [86SHP/KAG] proposed an equation for liquid Mg from 923 to 1600 K in accordance with their measurements [84SHP/KAG]:

$$C_p^\circ / \text{J·K}^{-1}\,\text{mol}^{-1} = 62.134 - 42.380\times10^{-3}T + 13.244\times10^{-6}T^2$$

[86SHP/KAG] recommended a constant heat capacity of 28.23 J·K^{-1} mol^{-1} from 1600 to 2300 K.

In the present evaluation the constant value recommended by McDonald [67MCD] is adopted as the most reliable

$$C_p^\circ / \text{J·K}^{-1}\,\text{mol}^{-1} = 34.30 \qquad (3\text{–}6)$$

The values of $C_p^\circ(T)$, $S^\circ(T)$ and $H^\circ(T) - H^\circ(298.15\ \text{K})$ from 298.15 to 2000 K were calculated using Eqs. 5 and 6. They are listed in the Tables 3–8.

3.4. Phase Equilibrium Data

The melting point of Mg was determined by thermal analysis in several investigations of binary systems to establish the purity of materials and to calibrate the apparatus. The number of studies where the melting point of pure Mg was the principal object of investigation is very limited.

[26HUM]

Hume-Rothery studied the Mg-Sn system and determined the melting point of Mg 99.99% pure as 920 K.

[27HUM/ROW]

Hume-Rothery and Rowell studied the Cd-Mg alloys and obtained a value for the melting point of Mg of 925 K. The sample contained 0.125% metallic impurities. The difference of 5 K between [26HUE] and [27HUE/ROW] shows that these measurements could not have been accurate.

[28CHA]

Chadwick investigated Mg-Zn alloys. The magnesium used contained less than 0.1 wt. % Si; and the value obtained for the melting temperature was 923 K. This work was carefully carried out.

[28ZAL/ZUL]

Zalesinski and Zulinski determined the melting point of Mg, T_{fus}/K = 923, by thermal analysis and the enthalpy of fusion, $\Delta_{fus}H$ = 5600 J·mol^{-1}, by calorimetric measurements.

[31JON]

Jones obtained a melting temperature of 920.5 K during an investigation of the Cu-Mg system. The study cannot be considered accurate.

[34GRU/BOR]

Grube and Bornhak investigated the Mg-Sb system. The specimen was 99.81% pure; the melting point was obtained as 923 K.

[34HAU/PAY]

Haughton and Payne investigated the Mg-Ni system. The magnesium sample had about 0.07% metallic impurities and the melting point was found to be 922 ± 0.5 K.

[35WET]

Wetherill investigated Mg-Co alloys, and obtained a value for the melting point of Mg of 922.5 K with a good accuracy.

[45REI]

Reinartz (quoted from [50KUB]) used 99.6% pure Mg and found a melting point of 922.4 K. The enthalpy of fusion was determined in a mixing calorimeter as 8500 ± 300 J·mol^{-1}. Kubaschewski [50KUB] also mentioned the study of Wittig who obtained the enthalpy of fusion 7650 ± 350 J·mol^{-1}. Kubaschewski recommended from two investigations the enthalpy of fusion, $\Delta_{fus}H$ = 8370 ± 500 J·mol^{-1}, and the melting point, T_{fus}/K = 922.5. It is difficult to estimate the accuracy of [45REI] but judging by the quality of other studies, authored by Kubaschewski, the results of [45REI] should be accurate. Reinartz also measured the heat capacity of liquid Mg from 923 to 1133 K and determined a constant value of 34.18 J·K^{-1} mol^{-1}.

[52NAG/FUJ]

Nagasaki and Fujita quoted a determination of the enthalpy of fusion made by Hirabayashi, $\Delta_{fus}H$ = 8870 J·mol^{-1}; no details are given.

[66CHI/GAR]

Chiotti *et al.* measured the enthalpy of fusion of Mg, $\Delta_{fus}H$ = 8240 J·mol^{-1}, in an adiabatic calorimeter. The magnesium sample was prepared in the Ames Laboratory and was 99.9+% pure: it contained 13 ppm nitrogen and 195 ppm carbon. This measurement is very accurate because a direct method was used and the magnesium sample was pure.

[70GIN/WRI]

Ginsberg and Wrigge measured the enthalpy of fusion of 99.94% pure Mg in an adiabatic calorimeter, $\Delta_{fus}H$ = 9210 ± 200 J·mol^{-1}. Little detail is given in their short communication.

3.5. Discussion of Phase Equilibrium Data

The melting point of Mg was measured accurately in the thirties and the results were confirmed recently [84SHP/KAG], see Table 3–5. The fusion temperature, T_{fus}/K = 923, is established with an accuracy of ± 1 K. The experimentally measured temperatures have been converted to ITS–90.

The experimental data for the enthalpy of fusion are given in Table 3–6. The recommended value is based on a rounded average of the two most accurate determinations by different methods [66CHI/GAR] and [67MCD]. The accuracy of this value is assumed to be ± 200 J·mol^{-1}. The enthalpy value obtained in [45REI] is very

close to the adopted value. Older measurements [26AWB/GRI] and [28ZAL/ZUL] are very inaccurate, and an error was made in [55STU/MCD]. The results of [84SHP/KAG] seem to be less accurate.

3.6. References for Mg

24EAS/WIL Eastman, E. D., Williams, A. M., and Young, T. F., J. Am. Chem. Soc. **46**, 1178–83 (1924); ΔH(293–888 K).

26AWB/GRI Awbery, J. H. and Griffith, E., Proc. Phys. Soc. **38**, 378–98 (1926); ΔH(289–1023 K).

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27HUM/ROW Hume-Rothery, W. and Rowell, S. W., J. Inst. Met. **38**, 137–56 (1927); T_{fus}.

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35WET Wetherill, J. P., Metals and Alloys **6**, 153–155 (1935); T_{fus}.

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54CRA/KRI Craig, R. S., Krier, C. A., Coffee, L. W., Bates, E. A., and Wallace, W. E., J. Am. Chem. Soc. **76**, 238–40 (1954); C_p°(12–320 K).

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61MAR Martin, D. L., Proc. Phys. Soc. Lond. **78**, 1482–8 (1961); C_p°(0.4–1.5 K).

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66MAN/WOL Mannchen, W. and Wolf, G., Z. Naturforsch. A21(8) 1216–20 (1966); C_p°(20–300 K).

67MCD McDonald, R. A., J. Chem. Eng. Data **12**, 131–2 (1967); ΔH(404–1360 K), $\Delta_{fus}H$.

70GIN/WRI Ginsberg, H. and Wrigge, H. Ch., Metall. **24**, 40 (1970); $\Delta_{fus}H$.

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89COX/WAG Cox, J. D., Wagman, D. D., Medvedev, V. A., "CODATA Key Values for Thermodynamics," Hemisphere Publ. Co., NY (1989); Review.

3.7. Adopted Values

Electronic contribution to C_p°: $\gamma = 1.265 \pm 0.01$ mJ·K^{-2} mol^{-1}

Debye temperature at 0 K: $\Theta_D = 403 \pm 4$ K

Heat Capacity Equations

Solid Mg

Temperature range 0–4 K:

$$C_p^\circ = 1.265\times10^{-3}T + 2.97\times10^{-5}T^3 \text{ J·K}^{-1}\text{ mol}^{-1}$$

Temperature range 4–20 K:

$$C_p^\circ = -0.02637 + 0.01052T + 0.06691T^{-2} - 0.001115T^2 + 7.763\times10^{-5}T^3 \text{ J·K}^{-1}\text{ mol}^{-1}.$$

Temperature range 20–100 K.

$$C_p^\circ = -5.153 + 0.1258T + 858.32T^{-2} + 0.00257T^2 - 1.756\times10^{-5}T^3 \text{ J·K}^{-1}\text{ mol}^{-1}.$$

Temperature range 100–298.15 K:

$$C_p^\circ = 12.124 + 0.1106T - 4.5\times10^4T^{-2} - 3.408\times10^{-4}T^2 + 3.953\times10^{-7}T^3 \text{ J·K}^{-1}\text{mol}^{-1}.$$

Temperature range 298.15–923 K

$$C_p^\circ = 28.260 - 6.023\times10^{-3}T - 2.378\times10^5T^{-2} + 11.684\times10^{-6}T^2 \text{ J·K}^{-1}\text{ mol}^{-1}$$

Liquid Mg

Temperature range 923–2000 K.

$$C_p^\circ = 34.30 \text{ J·K}^{-1}\text{ mol}^{-1}$$

Values at the Standard Temperature
$C_p°(298.15\ K) = 24.78 \pm 0.1\ J·K^{-1}\ mol^{-1}$
$S°(298.15\ K) = 32.54 \pm 0.2\ J·K^{-1}\ mol^{-1}$
$H°(298.15\ K) - H°(0) = 4979 \pm 30\ J·mol^{-1}$.

Phase Equilibrium Data
Temperature of fusion: $T_{fus}/K = 923 \pm 1$
Enthalpy of fusion: $\Delta_{fus}H/J·mol^{-1} = 8400 \pm 200$

3.8. Calculated Thermodynamic Functions of Mg

The thermodynamic functions presented in Tables 3–7 and 3–8 are calculated using the equations presented in the previous section. Values in brackets are calculated by using the equation for the next higher adjacent temperature interval.

3.9. Appendix

Experimental Results of Mg

Tables 3–9 to 3–28 present heat capacity or enthalpy data as they are presented in the original article. As a result, the numerical values listed in this Appendix are the actual experimental values, tabular smoothed values, values calculated from equations, or values extracted from a graph. Where necessary, values have been converted to joules (from calories). In all cases, the table heading indicates the type of data listed.

TABLE 3–1. Electronic contribution to the heat capacity and Debye temperature of Mg

Reference	γ, $mJ·K^{-2}\ mol^{-1}$	Θ_D, K	T/K range
Original Studies			
52EST/FRI	1.360	342	2 – 3.7
55SMI	1.318	406 ± 10	1 – 18
57LOG/CLE	1.28	390	3 – 13
58RAY	1.265 ± 0.01	403 ± 4	1.5 – 4.0
61MAR	1.224 ± 0.01	440 ± 50	0.4 – 1.5
65PAN/SAM	1.31	311	2 – 3.7
Review			
73HUL	1.272 ± 0.04		
Adopted			
This study	1.265 ± 0.01	403 ± 4	Based on [58RAY]

TABLE 3–2. Values of [55SMI] and [54CRA/KRI] used to derive the heat capacity equation for Mg

T/K	$C_p°$, $mJ·K^{-1}\ mol^{-1}$	T/K	$C_p°$, $mJ·K^{-1}\ mol^{-1}$
		12	73
4	6.96	13	93
5	10.22	14	112
6	15	15	140
7	20	16	177
8	28	17	217
9	36.5	18	255
10	45.5	19	300
11	60	20	360

TABLE 3–3. Comparison of the heat capacity, enthalpy, and entropy values for Mg at 298.15 K

Reference	C_p°(298.15 K) J·K^{-1} mol^{-1}	S°(298.15 K) J·K^{-1} mol^{-1}	H°(298.15 K) − H°(0) J·mol^{-1}
73HUL	24.895	32.68 ± 0.08	5000
77KEY	–	32.68 ± 0.1	5000 ± 30
81GUR	24.900	32.68 ± 0.1	5000 ± 30
85JAN	24.869	32.671 ± 0.1	4998
87GAR/PAR	24.869 ± 0.02	32.671	4998
89COX/WAG	24.869 ± 0.02	32.71 ± 0.1	4998 ± 30
Adopted	24.78 ± 0.1	32.54 ± 0.2	4979 ± 30

TABLE 3–4. Comparison of heat capacity values obtained from neighboring equations

Node point T/K	Equation	$C_p^\circ(T)$ J·K^{-1} mol^{-1}	Equation	$C_p^\circ(T)$ J·K^{-1} mol^{-1}
4	3–1	0.00696	3–2	0.00700
20	3–2	0.359	3–3	0.396
100	3–3	15.653	3–4	15.671
298.15	3–4	24.775	3–5	24.828

TABLE 3–5. Temperature of Fusion of Mg

Reference	T_{fus}K	Comments
Original Studies		
26HUM	921	Thermal analysis
27HUM/ROW	926	Thermal analysis
28CHA	924	Thermal analysis
28ZAL/ZUL	924	Thermal analysis
31JON	922	Thermal analysis
34GRU/BOR	924	Thermal analysis
34HAU/PAY	923.5 ± 0.5	Thermal analysis
35WET	924	Thermal analysis
45REI	924	Thermal analysis
84SHP/KAG	923 ± 1	Thermal analysis
Reviews		
73HUL	922 ± 0.5	Based on 28CHA, 31JON, 34HAU/PAY
81GUR	923 ± 1	Based on 55STU/MCD
85JAN	923 ± 1	Based on 28CHA, 31JON, 34HAU/PAY
86SHP/KAG	923 ± 1	Based on listed above studies
89COX/WAG	923	
Adopted		
This study	923 ± 1	Based on 81GUR, 85JAN

TABLE 3–6. Enthalpy of fusion of Mg

Reference	$\Delta_{fus}H$, J·mol^{-1}	Comments
Original Studies		
26AWB/GRI	4730	Enthalpy measurements
28ZAL/ZUL	5600	Enthalpy measurements
45REI	8500 ± 300	Enthalpy measurements
52NAG/FUJ	8870	Unknown method
55STU/MCD	8950 ± 200	Enthalpy measurements
66CHI/GAR	8240 ± 300	Adiabatic calorimeter
67MCD	8480 ± 200	Enthalpy measurements
70GIN/WRI	9210 ± 200	Adiabatic calorimeter
84SHP/KAG	9200 ± 120	Pulse-different. calorimeter
Reviews		
73HUL	8950 ± 200	Based on 55STU/MCD
81GUR	8500 ± 200	Based on 67MCD
85JAN	8477 ± 418	Based on 67MCD
86SHP/KAG	8700 ± 400	Based on above studies since 1945
89COX/WAG	8477	
Adopted		
This study	8400 ± 200	Based on 66CHI/GAR, 67MCD

TABLE 3–7. Thermodynamic functions of Mg below 298.15 K

T/K	$C_p^\circ(T)$ J·K^{-1} mol^{-1}	$H^\circ(T)$ $H^\circ(0)$, J·mol^{-1}	$S^\circ(T)$, J·K^{-1} mol^{-1}
5	0.0107	0.020	0.00764
10	0.0456	0.1469	0.02379
15	0.1429	0.5805	0.05766
20	0.3592(0.396)	1.774	0.12485
25	0.697	4.264	0.23473
30	1.414	9.423	0.42083
35	2.346	18.755	0.70671
40	3.404	33.089	1.0880
45	4.536	52.915	1.5537
50	5.710	78.519	2.0921
60	8.092	147.539	3.3439
70	10.398	240.110	4.7663
80	12.502	354.829	6.2950
90	14.291	489.104	7.8745
100	15.653(15.671)	639.223	9.4549
120	18.047	977.932	12.536
140	19.717	1356.455	15.4502
160	20.957	1763.771	18.1678
180	21.907	2192.808	20.6934
200	22.649	2638.661	23.0415
220	23.241	3097.777	25.2290
240	23.721	3567.552	27.2724
260	24.124	4046.110	29.1875
280	24.477	4532.181	30.9884
298.15	24.775(24.828)	4979.161	32.5351

Table 3–8. Thermodynamic functions of Mg above 298.15 K.

T/K	$C_p^\circ(T)$ J·K^{-1} mol^{-1}	$H^\circ(T)$ H°(298.15 K) J·mol^{-1}	$S^\circ(T)$ J·K^{-1} mol^{-1}
298.15	24.83	0	32.54
300.00	24.86	45.96	32.69
400.00	26.23	2607.10	40.05
500.00	27.22	5280.73	46.01
600.00	28.19	8050.62	51.06
700.00	29.28	10923.13	55.49
800.00	30.55	13913.14	59.48
900.00	32.01	17039.308	63.16
923.00(sol)	32.38	17779.71	63.97
923.00(liq)	34.30	26179.71	73.07
1000.00	34.30	28820.80	75.82
1200.00	34.30	35680.80	82.07
1400.00	34.30	42540.80	87.36
1600.00	34.30	49400.80	91.94
1800.00	34.30	56260.80	95.98
2000.00	34.30	63120.80	99.59

TABLE 3–9. SMOOTHED heat capacity values of Mg [24EAS/WIL]

T/K	C_p°, J·K^{-1} mol^{-1}	T/K	C_p°, J·K^{-1} mol^{-1}
373	26.19	673	29.46
473	27.28	773	30.54
573	28.37	873	31.67

TABLE 3–10. EXPERIMENTAL enthalpy values [$H^\circ(T) - H^\circ$(289 K)] of Mg [26AWB/GRI]

T/K	ΔH, J·mol^{-1}	T/K	ΔH, J·mol^{-1}
525	5920	862	15500
525	6270	891	16330
592	7710	922	22110
680	9970	976	23410
739	12220	1023	25830
855	15420		

TABLE 3–11. SMOOTHED heat capacity values of Mg [26AWB/GRI]

T/K	C_p°, J·K^{-1} mol^{-1}	T/K	C_p°, J·K^{-1} mol^{-1}
500	26.36	800	29.30
600	27.34	900	30.28
700	28.32	1000	36.56

TABLE 3–12. EXPERIMENTAL heat capacity values of Mg [30CLU/VAU]

T/K	C_p°, J·K^{-1} mol^{-1}	T/K	C_p°, J·K^{-1} mol^{-1}
11.31	0.054	51.8	6.351
11.43	0.054	55.1	7.213
14.14	0.109	63.7	9.263
14.28	0.117	86.7	13.59
16.94	0.205	93.2	14.84
17.24	0.213	99.2	15.56
19.50	0.314	106.7	16.23
19.64	0.305	115.4	17.572
21.70	0.469	124.2	18.52
24.30	0.707	136.2	19.41
27.10	1.029	145.4	20.21
30.20	1.477	163.4	21.21
34.20	2.230	172.6	21.72
37.60	2.912	182.0	21.88
41.70	3.845	191.2	22.30
45.20	4.694	217.2	22.84
48.70	5.565	228.4	23.10

TABLE 3–13. SMOOTHED heat capacity values of Mg [31SEE]

T/K	C_p J·K^{-1} mol^{-1}	T/K	C_p J·K^{-1} mol^{-1}
291	24.6	573	28.1
373	25.9	673	29.2
473	27.2	773	30.4

TABLE 3–14. SMOOTHED heat capacity values of Mg [52EST/FRI]

T/K	C_p°, mJ·K^{-1} mol^{-1}
2	3.11
3	5.39
4	8.55

TABLE 3–15. SMOOTHED heat capacity values of Mg [54CRA/KRI]

T/K	C_p°, J·K^{-1} mol^{-1}	T/K	C_p°, J·K^{-1} mol^{-1}
12	0.067	150	20.40
14	0.109	160	20.97
16	0.176	170	21.48
18	0.272	180	21.91
20	0.360	190	22.30
25	0.787	200	22.67
30	1.427	210	22.96
35	2.301	220	23.22
40	3.360	230	23.48
45	4.502	240	23.71
50	5.720	250	23.93
60	8.171	260	24.12
70	10.45	270	24.31
80	12.47	280	24.49
90	14.24	290	24.67
100	15.70	298.16	24.81
110	16.95	300	24.84
120	18.02	310	24.98
130	18.94	320	25.10
140	19.74		

TABLE 3–16. SMOOTHED heat capacity values of Mg [55SMI]

T/K	C_p°, mJ·K^{-1} mol^{-1}	T/K	C_p°, mJ·K^{-1} mol^{-1}
1	1.347	11	60
2	2.868	12	78
3	4.738	13	93
4	7.131	14	116
5	10.22	15	140
6	15	16	178
7	20	17	218
8	28	18	255
9	36.5		
10	45.5		

TABLE 3–17. EXPERIMENTAL enthalpy values [$H^\circ(T) - H^\circ$(298.15 K)] of Mg [55STU/MCD]

T/K	$H^\circ(T) - H^\circ$(298 K) J·mol^{-1}	T/K	$H^\circ(T) - H^\circ$(298 K) J·mol^{-1}
716	11300	958	28100
743	12200	978	28800
808	14200	1012	29700
852	15600	1055	31300
894	16900		

TABLE 3–18. SMOOTHED heat capacity values of Mg [55STU/MCD]

T/K	C_p°, J·K^{-1} mol^{-1}	T/K	C_p°, J·K^{-1} mol^{-1}
700.15	29.66	923	Melting point
750	30.17	950	32.43
800	31.05	1000	32.97
850	31.88	1050	33.51
900	32.67	1100	34.06

TABLE 3–19. EXPERIMENTAL heat capacity values of Mg [57LOG/CLE]

T/K	C_p°, mJ·K^{-1}mol^{-1}	
	Sample with Fe	Sample with Mg
3.14	5.4	5.3
4.55	7.9	7.5
5.60	12.9	13.5
6.44	16.5	16.7
7.22	21.2	22.2
7.89	27.5	26.5
8.47	32.5	31.7
9.10	35.8	38.3
9.71	43.2	43.6
10.30	47.9	43.4
10.83	54.7	54.0
11.35	64.0	64.4
11.84	70.4	69.9
12.27	74.9	85.5
12.62	79.6	82.6

TABLE 3–20. SMOOTHED heat capacity values of Mg [57SAB/STE]

T/K	C_p°, J·K^{-1} mol^{-1}	T/K	C_p°, J·K^{-1} mol^{-1}
298.15	24.85	430	26.42
300	24.89	440	26.52
310	25.03	450	26.62
320	25.16	460	26.72
330	25.28	470	26.84
340	25.40	480	26.94
350	25.54	490	27.06
360	25.66	500	27.17
370	25.79	510	27.27
380	25.86	520	27.37
390	26.01	530	27.45
400	26.11	540	27.54
410	26.22	543.16	27.58
420	26.31		

TABLE 3–21. SMOOTHED heat capacity values of Mg [58RAY]

T/K	C_p°, mJ·K^{-1} mol^{-1}
1	1.295
2	2.768
3	4.597
4	6.961
5	10.037

TABLE 3–22. SMOOTHED heat capacity values of Mg [59MAN/BOR]

T/K	C_p°, J·K^{-1} mol^{-1}	T/K	C_p°, J·K^{-1} mol^{-1}
20	0.41	180	22.2
40	3.58	200	23.3
60	9.05	220	23.9
80	12.8	240	24.2
100	16.9	260	24.6
120	18.2	280	24.9
140	20.4	300	25.1
160	21.4		

TABLE 3–23. SMOOTHED heat capacity values of Mg [61MAR]

T/K	C_p°, mJ·K^{-1} mol^{-1}
0.5	0.615
1.0	1.247
1.5	1.913
2.0	2.631

TABLE 3–24. SMOOTHED heat capacity values of Mg [66MAN/WOL]

T/K	C_p°, J·K^{-1} mol^{-1}	T/K	C_p°, J·K^{-1} mol^{-1}
20	0.314	170	21.40
30	1.527	180	21.84
40	3.35	190	22.24
50	5.73	200	22.59
60	8.35	210	22.91
70	10.31	220	23.16
80	12.80	230	23.41
90	14.75	240	23.62
100	16.34	250	23.79
110	17.53	260	23.97
120	18.39	270	24.12
130	19.12	280	24.25
140	19.81	290	24.39
150	20.40	300	24.50
160	20.92		

TABLE 3–25. SMOOTHED Heat Capacity Values of Mg [65PAN/SAM]

T/K	C_p°, mJ·K^{-1} mol^{-1}	T/K	C_p°, mJ·K^{-1}mol^{-1}
1	1.3	5	9.2
2	2.8	10	74
3	4.5	15	216
4	6.6	18	360

TABLE 3–26. EXPERIMENTAL enthalpy values $[H°(T) - H°(298.15\ K)]$ of Mg [67MCD]

T/K	ΔH, J·mol^{-1}	T/K	ΔH, J·mol^{-1}
403.6	2680	954.1	27250
589.3	7740	990.5	28600
683.0	10410	1030.6	29960
777.2	13210	1139.4	33750
874.1	16220	1262.9	37860
914.0	17470		

TABLE 3–27. SMOOTHED heat capacity values of Mg [67MCD]

T/K	$C_p°$, J·K^{-1} mol^{-1}	T/K	$C_p°$, J·K^{-1} mol^{-1}
298.15	24.89	850	31.21
300	24.89	900	32.01
350	25.61	922	32.43
400	26.19	922	34.30
450	26.74	950	34.30
500	27.24	1000	34.30
550	27.74	1050	34.30
600	28.20	1100	34.30
650	28.74	1150	34.30
700	29.29	1200	34.30
750	29.87	1250	34.30
800	30.50	1300	34.30

TABLE 3–28. EXPERIMENTAL heat capacity values of Mg [84SHP/KAG]

T/K	$C_p°$, J·K^{-1} mol^{-1}	T/K	$C_p°$, J·K^{-1} mol^{-1}
347.6	25.67	944.2	34.18
416.9	26.18	992.2	33.87
487.9	26.24	1040.2	32.91
535.2	26.42	1068.2	32.13
599.2	26.89	1117.4	32.43
645.5	26.86	1167.4	30.31
692.0	27.70	1217.4	30.07
738.0	28.30	1268.5	29.78
783.5	28.58	1316.6	28.17
823.2	27.98	1369.3	27.79
869.5	28.45	1423.7	27.36
917.4	29.29	1480.3	27.02
		1525.8	27.31
		1536.9	27.32

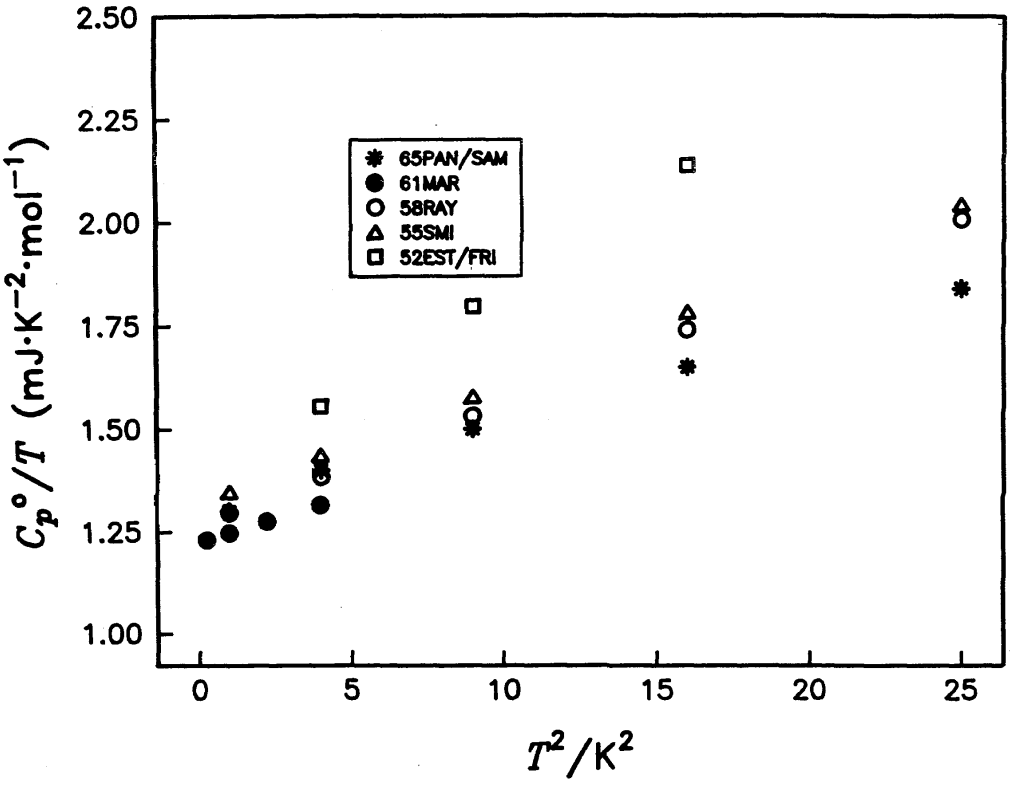

FIG. 3–1. C_p°/T versus T^2 for Mg below 5 K.

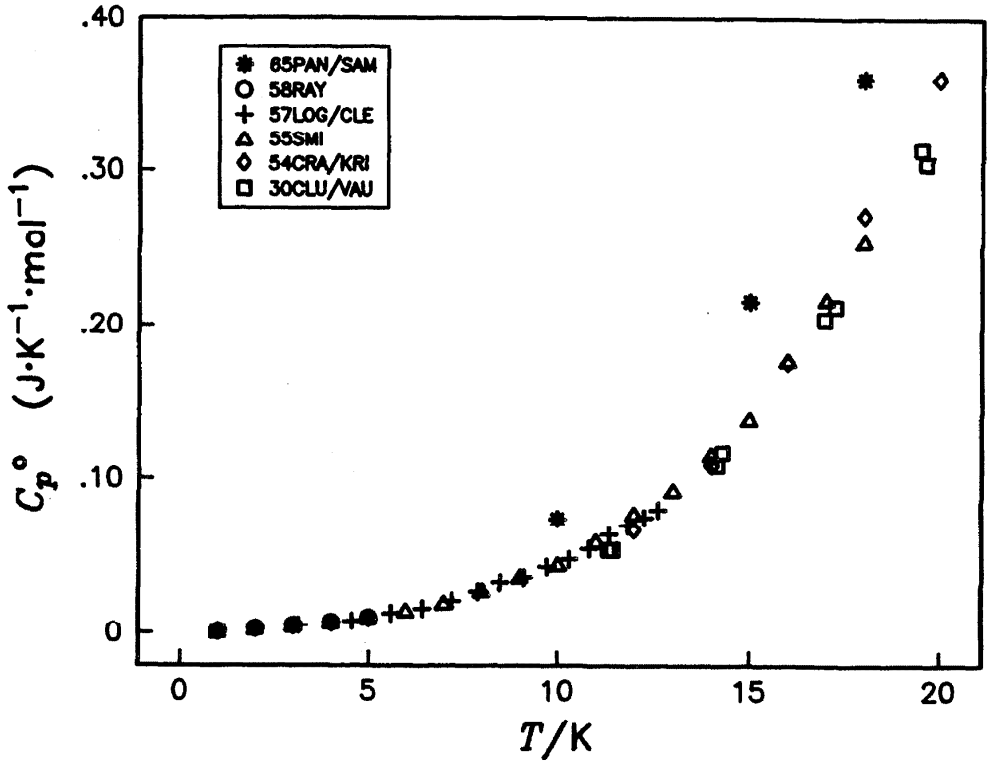

FIG. 3–2. Heat Capacity of Mg below 20 K.

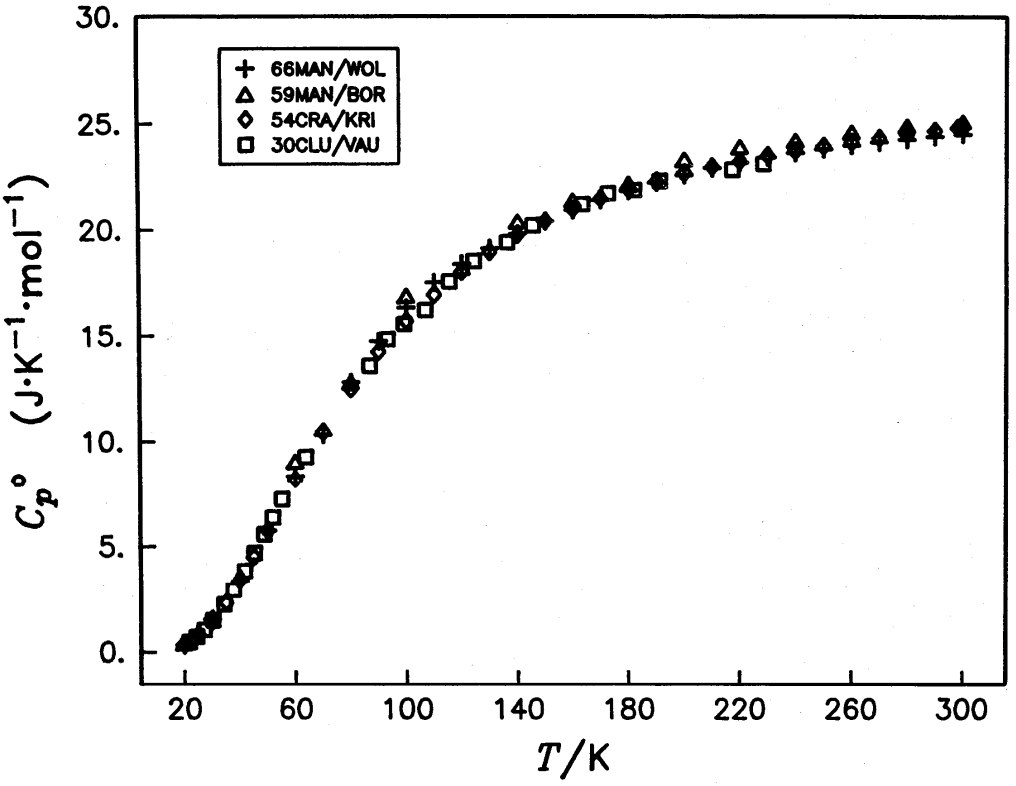

FIG. 3–3. Heat Capacity of Mg at 20–300 K.

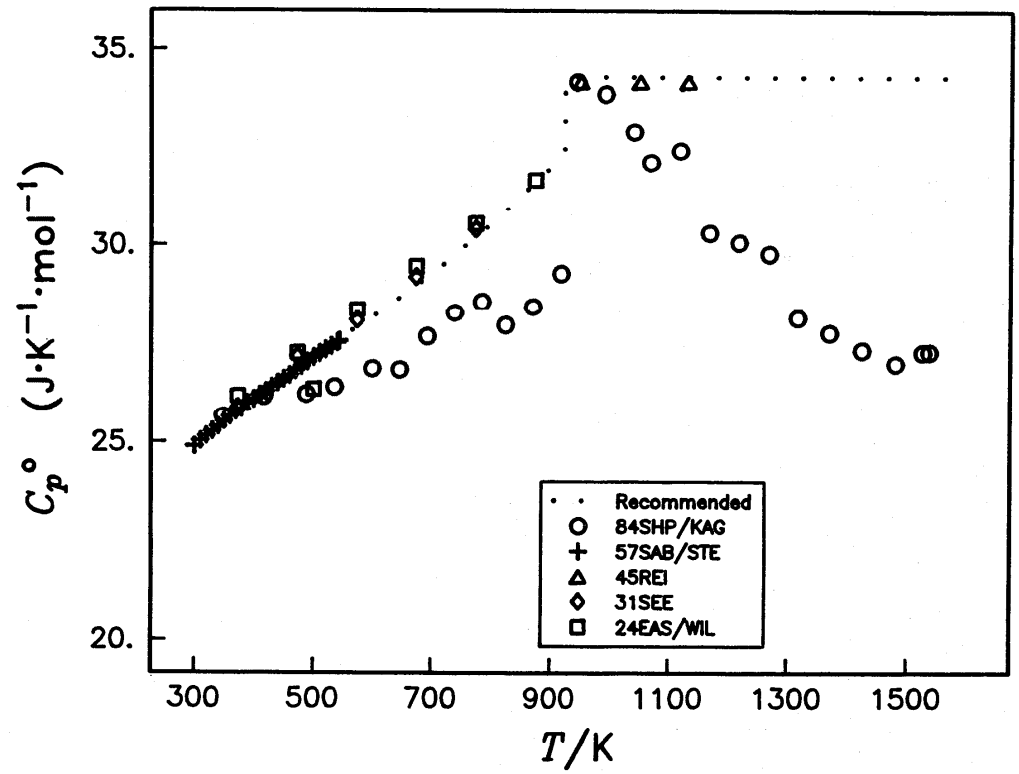

FIG. 3–4. Heat Capacity of Mg at 300–1600 K.

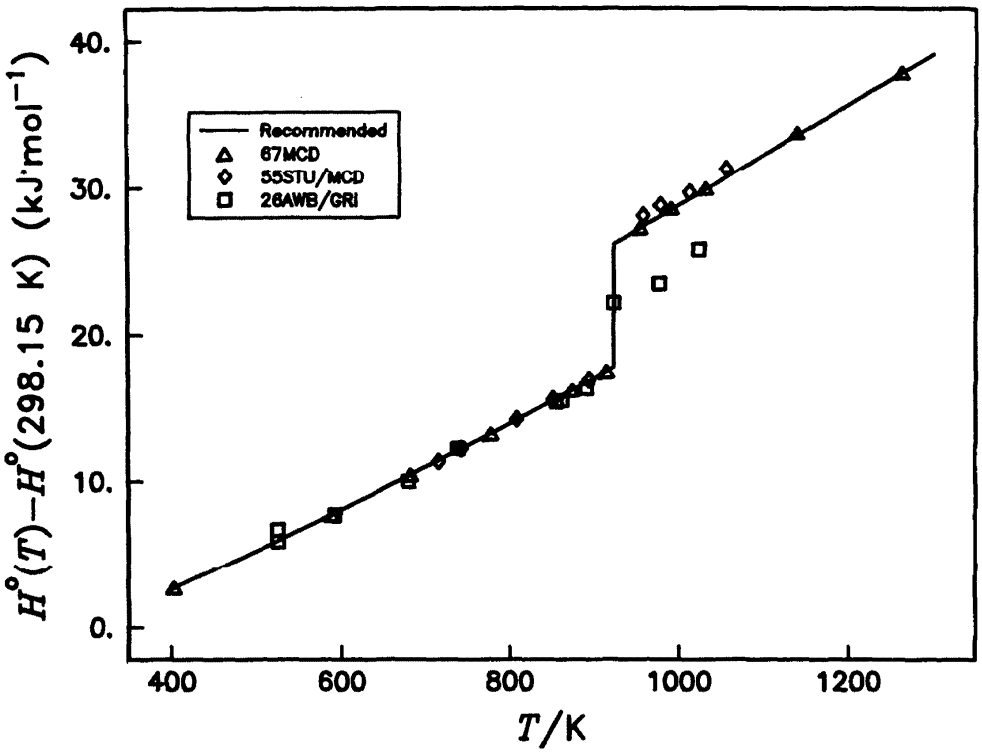

FIG. 3–5. $H°(T) - H°(298.15\ \text{K})$ for solid and liquid Mg.

4. Calcium

4.1. Introduction

At ambient pressure, calcium has two stable crystalline modifications, fcc and bcc (T_{trs}/K = 716). The modifications of Ca were established in the sixties when the role of hydrogen as an impurity was understood. Older thermodynamic information should be considered with caution. Hydrogen has a special significance, as even a small amount converts Ca to different phases of the Ca–H system, the presence of hydrogen makes most available data above 400 K unreliable. The data for liquid Ca are especially poor, and the values are only known with an uncertainty greater than 10%. The recommended thermodynamic values can be considered as only tentative. The data below 298 K are more accurate except for the heat capacity values below 5 K which are scattered.

4.2. Heat Capacity and Enthalpy Measurements

4.2.1. Temperatures below 298.15 K

[30CLU/VAU]

Clusius and Vaughen measured the heat capacity of Ca between 10 and 200 K in an adiabatic vacuum calorimeter. The Ca sample was the purest commercially available. The heat capacity values obtained are shown in Figs. 4-1, 4–2 and 4–3 and are listed in the Table 4-14. The values obtained in [30CLU/VAU] are quite accurate, considering the time of this investigation. For more than fifty years this study was the best available and was quoted in all major reviews.

[57ROB]

Roberts measured the heat capacity of Ca from 1.5 to 20 K in a low-temperature Nernst calorimeter. The material had about 0.5 wt. % metallic impurities. Surface oxides were removed in air; therefore the amount of nonmetallic impurities could be substantial. Roberts presented her results in a graphical form between 1.5 and 4.9 K (27 points). The 18 points between 2.4 and 4.9 K are described by the expression:

$$C_p^\circ/\mathrm{J\ K^{-1}\ mol^{-1}} = \gamma T + 1943(T/\Theta_D)^3,$$

where Θ_D/K = 228.9 ± 1.7 and γ = 2.73 ± 0.06 mJ·K^{-2} mol^{-1}. Roberts tabulated smoothed values of the heat capacity between 1.5 and 20 K. These values are shown in Figs. 4–1 and 4–2 and are listed in the Table 4-18. These measurements are considered to be accurate.

[57GRI/VES]

Griffel *et al*. measured the heat capacity from 1.8 to 4.2 K in an adiabatic calorimeter. The calcium sample was purified by vacuum distillation and had about 0.05 wt. % metallic impurities. The 21 heat capacity values given in a graphic form were fitted to γ = 3.08 ± 0.01 mJ·K^{-2} mol^{-1} and Θ_D = 239 ± 2 K. Using these constants, the heat capacities were calculated and given in the Table 4-17 and Fig. 4–1. These results are close to those of [57ROB] and have about the same accuracy.

[74AGA/BET]

Agarwal and Betterton measured the heat capacity of Ca over the range from 1.1 to 4.2 K. The high purity material (0<50ppm, N<10ppm, metallic impurities 600ppm) was obtained from the Ames Laboratory. The 35 points measured are given as a small graph. They were fitted to γ = 1.99 ± 0.05 mJ·K^{-2} mol^{-1} and Θ_D/K = 250 ± 4. According to the above constants, the heat capacities were calculated and given in the Table 4-19 and Fig. 4–1. The heat capacities obtained are smaller and the Debye temperature is greater than those in the two previous studies [57ROB] and [57GRI/VES]. Judging by the description of experimental technique and material used, these data should be the most reliable.

[85ROB]

Robie measured the heat capacity from 8 to 360 K in an adiabatic calorimeter at the U. S. Geological Survey. The sample was prepared in the Ames Laboratory. The experimental and smoothed results are given in the Tables 4-20 and 4-21 and are shown in Figs. 4-1, 4–2 and 4–3. Below 15 K the heat capacity values are smaller than those of [30CLU/VAU], from 15 to 60 K they are about the same, and between 60 and 160 K they are greater by up to 3%. These heat capacity values are the best available from 10 to 300 K. Robie calculated the thermodynamic values at the standard temperature:

C_p°(298.15 K) = 25.77 ± 0.06 J K^{-1} mol^{-1},
S°(298.15 K) = 42.91 ± 0.1 J K^{-1} mol^{-1},
H°(298.15 K) − H°(0) = 5811 ± 12 J mol^{-1}.

At the low temperature end of this study, there is good agreement with the results of Agarwal and Betterton [74AGA/BET].

4.2.2. Temperatures above 298.15 K

[24EAS/WIL]

Eastman *et al*. [24EAS/WIL] measured the enthalpy by mixing calorimetry between 373 and 873 K. The Ca sample had 97.75 wt. % calcium, 0.85 wt. % chlorine, and 1.08 wt. % iron and aluminum oxides. The enthalpy measurements were made carefully, and the error should not exceed 1%. Eight experimental points for α–Ca and four for β–Ca have not been listed in [24EAS/WIL], and only derived expressions and smoothed calculated data are given:

α–Ca: C_p°/J K^{-1} mol^{-1} = 25.48 + 17.46×10^{-3}(T − 273)
β–Ca: C_p°/J K^{-1} mol^{-1} = 27.66 + 6.37×10^{-3}(T − 273)

The calculated heat capacity values are given in the Table 4-11 and shown in Fig. 4–4. These values are still among the best available despite the poor quality of Ca samples. Some systematic error was probably made. All heat capacity values reported in this study for Mg, Al and Zn are slightly (0.8–1.2%) higher than those adopted in current reference books.

[28ZAL/ZUL]

Zalesinski and Zulinski used a drop method for enthalpy measurements of commercial 99.13% Ca between 580 and 1200 K in the Table 4-12, (Fig. 4–5). The authors found an unusual transformation below the fusion temperature. They also obtained a very high value for the enthalpy of fusion $\Delta_{fus}H$/J·mol^{-1} = 13190. The heat capacity values derived from the enthalpy measurements are listed in the Table 4-13. The accuracy of the study is considered to be low.

[46JAU]

Jauch measured the enthalpy content of Ca in a drop calorimeter from 570 to 1214 K in the Table 4-15, (Fig. 4–5). The Ca sample contained about 0.1 wt. % metallic impurities. Several inconsistencies in calibration, measurements and calculations can be observed in his table of measurements. However, some of the errors probably cancelled each other. The unrevised data obtained for α–Ca seem to be wrong, but those for β–Ca are quite reasonable. The enthalpy and derived heat capacity data of Jauch are listed in the Tables 4–15 and 4-16 (Fig. 4–5). It is interesting to note that the work of Jauch is known through the publications of Kubaschewski [50KUB]. For unknown reasons, Kubaschewski changed some of the original values for liquid Ca. The heat capacity of liquid Ca was reported in [46JAU] as about 43 J K^{-1} mol^{-1}, while [50KUB] gave it as 31 J K^{-1} mol^{-1}. The review by Gurvich *et al.* [81GUR] used the value quoted in [50KUB] and referred to it as [46JAU]. Jauch also obtained reasonable values for the enthalpies of transformation and fusion (see below).

[60KOC/GEL]

Kocherov and Geld measured the enthalpy of distilled Ca with 0.2 wt. % metallic impurities in a high-temperature adiabatic calorimeter from 473 to 1273 K. Ten experimental points (Fig. 4-5) are shown in a small scale graph together with the values, calculated by equations given by Kubaschewski [50KUB]. Despite good agreement between these two sets of values [60KOC/GEL] are considered to be unreliable. It should be added that this work was not mentioned in [81GUR] and [86SHP/KAG].

[82GRI/ROS]

Grimvall and Rosen introduced a new criterion which they called the "entropy Debye temperature", Θ_s, associated with the vibrational entropy and defined through the heat capacity. The value of Θ_s depends weakly on temperature and could be an indicator of the accuracy of the heat capacity measurements. The heat capacity data for twenty metals given in [73HUL] were checked by Grimvall and Rosen [82GRI/ROS]. For α–Ca [73HUL] adopted the data from [46JAU]. These data were all tested, but the temperature dependence of Θ_s, was found to be anomalous. Then the data of [24EAS/WIL] for α–Ca were used, and the behavior of the critical function was normal. Grimvall and Rosen concluded that recommended values for α–Ca should be based on the data of Eastman *et al.* [24EAS/WIL] at least up to 450 K. This recommendation was taken into account in this assessment.

[85ULY]

Ulyanov [85ULY] measured the heat capacity of β–Ca and liquid Ca by a pulse differential technique. The information on this study was taken from [86SHP/KAG]. The measurements (36 points) were made in the temperature range from 782 to 1827 K (see Fig. 4–4 and the Table 4-22). The sample contained about 0.02 wt. % metallic impurities, but the amount of non-metallic impurities was not given. Fifteen experimental points for β–Ca from 780 to 1080 K were fitted to equation:

$$C_p^\circ/\text{J K}^{-1}\text{ mol}^{-1} = 39.81 - 24.58\times10^{-3}T + 22.20\times10^{-6}T^2$$

These values for β–Ca are much higher than those obtained by other investigators.

For liquid Ca (1132–1827 K) 21 experimental points decrease in value from about 33 J K^{-1} mol^{-1} at 1200 K to 31 J K^{-1} mol^{-1} at 1800 K. The data were fitted to equation:

$$C_p^\circ/\text{J K}^{-1}\text{ mol}^{-1} = 40.04 - 8.49\times10^{-3}T + 1.84\times10^{-6}T^2$$

These data should be used with caution. The decrease in the heat capacity of liquid Ca probably shows the correct tendency, but the absolute values of the heat capacity need independent confirmation.

[89DIT]

Ditmars measured the enthalpy increment in a precision ice calorimeter using a Ca sample prepared in the Ames Laboratory. The true heat capacities determined from these measurements were taken from a graph; these data are shown in Fig. 4–4 and are listed in the Table 4-23. Fig. 4–4 shows that the heat capacity of Ca reaches a maximum near 500 K, then decreases, and starts increasing again at about 650 K up to a high value of about 35.5 J K^{-1} mol^{-1} near the transformation temperature. This complex heat capacity dependence indicates certain processes which occurred in the samples during heating. The source of these processes can be impurities in samples inherited from a supplier or acquired from handling or heating procedures. For α–Ca the data are reasonable below 450 K; above this temperature they appear to be in error. For β–Ca the data seem to be more reliable between 716 and 1050 K because they

agree fairly well with the results of other investigators, for example, with [46JAU]. However, above 1050 K the heat capacity determined in [89DIT] increases very rapidly, probably due to some undefined processes which occurred in the samples, and the values become less reliable. These data are accurate probably only within limited temperature ranges.

4.3. Discussion of Heat Capacity and Enthalpy Data

4.3.1. α–Ca below 298.15 K

Below 5 K three studies are available [57ROB], [57GRI/VES], and [74AGA/BET]. These studies are shown in Fig. 4–1. The electronic heat capacities and Debye temperature determined in these studies are listed in Table 4-1. The γ and Θ_D values for [57ROB] were derived only from the data in the region below 4 K.

The data of [74AGA/BET] are selected because the authors used a better sample than [57ROB], [57GRI/VES] obtaining lower heat capacities and a higher Debye temperature. According to [74AGA/BET], the heat capacity between 0 and 5 K is described by equation

$$C_p/\text{J K}^{-1}\text{ mol}^{-1} = 1.99\times10^{-3}T + 1.24\times10^{-4}T^3 \quad (4\text{–}1)$$

Above 5 K three sets of data are available: [57ROB] for the interval 5–20 K, [30CLU/VAU] from 10 to 200 K, and [85ROB] from 8 to 360 K (Figs. 4–2 and 4–3). The recent measurements of Robie *et al.* [85ROB] are more reliable than the data of [30CLU/VAU]. The smoothed values of [85ROB] given in the Table 4-20 are fitted to three equations:

For the range 5–40 K the first value at 5 K is taken from [74AGA/BET] to provide a smooth extention of Equation 4–1:

$$C_p/\text{J K}^{-1}\text{ mol}^{-1} = 1.771 - 0.31\text{T} - 15.93T^{-2} + 1.851\times10^{-2}T^2 - 1.679\times10^{-4}T^3 \quad (4\text{–}2)$$

For the temperature interval 40 – 80 K

$$C_p/\text{J K}^{-1}\text{ mol}^{-1} = 117.816 - 3.804\text{T} - 3.963\times10^{4}T^{-2} + 5.122\times10^{-2}T^2 - 2.287\times10^{-4}T^3 \quad (4\text{–}3)$$

For the temperature interval 80 – 298.15 K

$$C_p/\text{J K}^{-1}\text{ mol}^{-1} = 18.979 + 5.989\times10^{-2}\text{T} - 2.959\times10^{4}T^{-2} - 1.931\times10^{-4}T^2 + 2.408\times10^{-7}T^3 \quad (4\text{–}4)$$

$C_p^\circ(T)$, $H^\circ(T)-H^\circ(0)$ and $S^\circ(T)$ values calculated by Eqs. 4–1 to 4–4 are given in the Table 4–9. At the standard temperature the following values were calculated:

$C_p^\circ(298.15\text{ K}) = 25.719\text{ J K}^{-1}\text{ mol}^{-1}$;
$S^\circ(298.15\text{ K}) = 42.536\text{ J K}^{-1}\text{ mol}^{-1}$;
$H^\circ(298.15\text{ K})-H^\circ(0) = 5782.94\text{ J mol}^{-1}$.

These values can be compared with those given in the major reviews.

The difference in $S^\circ(298.15\text{ K})$ between the present assessment and previous reviews [73HUL], [81GUR], and [85JAN] is mostly due to heat capacities of [85ROB] which are higher than [30CLU/VAU] in the interval from 60 to 160 K. The heat capacity values influence more strongly the choice of standard entropy than the value of $H^\circ(298.15\text{ K})-H^\circ(0)$. The uncertainty in the adopted standard entropy $\pm$ 0.3 J K^{-1} mol^{-1} indicates a necessity for further investigation of the heat capacity of Ca.

4.3.2. α–Ca above 298.15 K

Figures 4–4 and 4–5 show the experimental enthalpies and heat capacities of α–Ca above 300 K [24EAS/WIL], [28ZAL/ZUL], [46JAU], [89DIT]. The data of the two studies [28ZAL/ZUL], [46JAU] are considered to be less reliable.

The review by Gurvich *et al.* [81GUR] combined the data of [24EAS/WIL], [46JAU] and derived an equation which describes the heat capacity of α–Ca from 298 to 716 K:

$$C_p^\circ/\text{J K}^{-1}\text{ mol}^{-1} = 16.314 + 22.209\times10^{-3}T + 2.672\times10^{5}T^{-2}$$

The values recommended by Gurvich *et al.* were adopted in other reviews [86SHP/KAG] and [87GAR/PAR].

The experimental data of Ditmars [89DIT] form a smoothed continuation of the low temperature data of [85ROB] up to 450 K. These values are close to the experimental values of [24EAS/WIL] and to the assessed values of [81GUR] and [82GRI/VES]. Above 450 K the data of [89DIT] are evidently in error. The data of [89DIT] between 300 and 450 K are extrapolated so as to follow a path approximately parallel to the slightly overestimated values of [24EAS/WIL]. The suggested heat capacity values are given in Table 4–3. They are close to those recommended in [81GUR].

The equation which describes the above values for the temperature range from 298 to 716 K is:

$$C_p^\circ/\text{J K}^{-1}\text{ mol}^{-1} = 19.782 + 15.622\times10^{-3}T + 0.952\times10^{5}T^{-2} + 3.036\times10^{-6}T^2. \quad (4\text{–}5)$$

4.3.3. β–Ca

Figures 4–4 shows the data of [24EAS/WIL], [28ZAL/ZUL], [46JAU], and [89DIT] are in reasonably good agreement, while the data of [85ULY] disagree significantly with all other measurements. [73HUL] used the measurements of [46JAU]; [81GUR] adopted a heat capacity equation from Kubaschewski [50KUB] who derived it from the data of [46JAU]:

$$C_p^\circ/\text{J K}^{-1}\text{ mol}^{-1} = 6.276 + 32.384\times10^{-3}T + 10.460\times10^{5}T^{-2}$$

The same heat capacities were recommended in [85JAN] and [87GAR/PAR]. Shpil'rain *et al.* [86SHP/KAG] derived the heat capacity equation for β–Ca using the data of [24EAS/WIL], [46JAU] and their own measurements [85ULY]:

$$C_p^\circ/\text{J K}^{-1}\,\text{mol}^{-1} = 36.090 + 8.977\times10^{-3}T - 5.746\times10^{6}T^{-2}.$$

In this assessment the values of [89DIT] were selected between T_{trs} and 1050 K. Above 1050 K the heat capacity curve was extrapolated graphically to the melting point between the data of [46JAU] and [89DIT]. The suggested heat capacity values for β–Ca are in Fig. 4–4 and are listed in Table 4–4.

An equation which represents these data for the temperature range from 716 to 1115 K is:

$$C_p^\circ/\text{J K}^{-1}\,\text{mol}^{-1} = 47.402 - 48.312\times10^{-3}T + 33.442\times10^{-6}T^2 \quad (4\text{–}6)$$

4.3.4. Liquid Ca

Two sets of measured points are shown in Fig. 4–4. Jauch [46JAU] obtained heat capacity values of liquid Ca which change from 43 to 42 J K^{-1} mol^{-1} between the melting point (1115 K) and 1250 K. Ulyanov [85ULY] obtained heat capacity values which decrease roughly from 33 at 1200 K to 31 J K^{-1} mol^{-1} at about 1800 K. These two studies disagree and have low accuracy. The average of the two studies near the melting point, 38 ± 4 J K^{-1} mol^{-1}, was provisionally adopted, and assigned a constant value between 1115 and 2000 K:

$$C_p^\circ/\text{J K}^{-1}\,\text{mol}^{-1} = 38 \pm 5 \quad (4\text{–}7)$$

Recommendations given in major reviews are no better than the above value. [73HUL] rejected the heat capacity measurements of [46JAU] for liquid Ca and estimated the heat capacity as a constant value 29.3 J K^{-1} mol^{-1}. [81GUR] used the recommendation of Kubaschewski [50KUB], based on converted data of [46JAU], 31 J K^{-1} mol^{-1}. The authors of [85JAN] estimated the heat capacity of liquid Ca, 35 J K^{-1} mol^{-1}, as an intermediate value between the adopted heat capacities for liquid Mg (34.309 J K^{-1} mol^{-1}) and Sr (39.463 J K^{-1} mol^{-1}); the same value for liquid Ca was adopted in [87GAR/PAR]. However, the heat capacity of liquid Sr has not been measured better than that for liquid Ca. Shpil'rain *et al.* [86SHP/KAG] derived an equation for liquid Ca between the melting point and 2300 K using the data of [46JAU] (actually the value 31 J K^{-1} mol^{-1} of [50KUB]) and their own measurements [85ULY]:

$$C_p^\circ/\text{J K}^{-1}\,\text{mol}^{-1} = 36.527 - 3.800\times10^{-3}T + 0.298\times10^{-6}T^2$$

All these data and the recommendations for the heat capacity of liquid Ca are considered unreliable, and so new measurements are necessary.

The values of $C_p^\circ(T)$, and $S^\circ(T)$ and $H^\circ(T) - H^\circ(298.15\text{ K})$ are calculated by Eqs. 4–5 to 4–7 from 298 to 2000 K and are given in Table 4–10.

4.4. Phase Equilibrium Data

4.4.1. α–β Transformation of Ca

An examination of the literature suggests that impurities have a great effect on the number of allotropic modifications which are observed. Current evidence supports the existence of only two allotropic modifications for pure calcium.

[24EAS/WIL]

Eastman *et al.* in their enthalpy measurements found a single α–β transformation in Ca at T_{trs}/K = 673, and estimated the enthalpy of transformation as roughly 420 ± 100 J mol^{-1}.

[31RIN]

Rinck used resistivity measurements and thermal analysis from room temperature to the fusion temperature. Thermal analysis registered a transformation at 722 K on cooling and 725 K on heating. Resistivity measurements confirmed this result. The purity of the Ca sample was not given in [31RIN]. The temperature of fusion of Ca was measured as 1121 K.

[35SCH]

Schulze found two transformations in Ca containing 0.1% metallic impurities. Schulze gave also an enthalpy of transformation 890 J mol^{-1} at 723 K, obtained from measurement in an adiabatic calorimeter.

[46JAU]

Jauch during his enthalpy measurements found the temperature of transformation T_{trs}/K = 713 and the temperature of fusion, T_{fus}/K = 1103. He also determined values for the enthalpy of transformation, 920 J mol^{-1}, and the enthalpy of fusion, 8660 ± 330 J mol^{-1}.

[49SHE]

Sheldon studied Ca by x-ray diffraction at room and high temperatures and by thermal analysis. He found two transformations in Ca at 608 ± 10 K and 883 ± 10 K.

[56SMI/CAR]

Smith *et al.* measured the resistivity and structure of Ca samples of different purity. The samples were obtained by repeated fractional distillation under vacuum at 1173 K. The purest sample contained 0.04 wt. % metallic impurities and had only two modifications, fcc and bcc. A complex hcp phase was found in less pure samples between 573 and 723 K. After the purest sample was held

in an inert atmosphere for many hours, the hcp phase pattern appeared. The temperature of the fcc-bcc transformation was determined as 737 K from a break in the temperature dependence of resistivity.

[58SCH/KIN]

Schottmiller *et al.* confirmed the results of [56SMI/CAR] using pure commercial Ca with 0.2 wt. % metallic impurities and a melting point 1116 ± 1 K. X-ray diffraction analysis showed three phases fcc(α–Ca), hcp(β–Ca) and bcc(γ–Ca). Thermal analysis confirmed the results of Sheldon [49SHE]: fcc – hcp transformation at 617 ± 6 K and hcp – bcc at 883 ± 6 K. The results of [49SHE] and [58SCH/KIN] were rejected in subsequent publications.

[61PET/FAT]

Peterson and Fattore showed that Ca has only two modifications: fcc(α) and bcc(β). The hcp phase observed in [49SHE] and [58SCH/KIN] was a solid solution of hydrogen in Ca. The authors purified a commercial Ca specimen by distillation at 950 °C under vacuum 130 Pa. The hydrogen content of the sample was determined as 120–220 ppm. The melting temperature of pure Ca was then found as 1112 ± 2 K. Only the single fcc(α) – bcc(β) transformation was observed in this sample of Ca. The temperature was determined by thermal analysis on heating as 721 ± 2 K and on cooling as 715 ± 2 K. The former result was recommended in as the transformation temperature. When the amount of hydrogen in the sample was intentionally increased, two transformations were observed. One of them was recorded at about 633 K on heating and at 593 K on cooling. x-ray diffraction of this sample at room temperature showed the existence of CaH_2 in the sample. It was shown in that at about 593 K a eutectoid reaction takes place; a solid solution of hydrogen in Ca with a hexagonal structure (γ phase) decomposes into α-Ca and CaH_2 . The temperature of this reaction is close to that reported in [49 SHE] and [58SHE/KIN] for the fcc--hcp transformation in 'pure' Ca. A transformation at about 883 K, interpreted in [49SHE] and [58SCH/KIN] as an hcp--bcc transformation, was explained as a peritectoid formatiion of the γ-phase from β-Ca and CaH_2 at 873 K. Peterson and Fattore showed the necessity of careful purification of Ca from gases in order to obtain correct thermophysical properties. Later investigations confired their results.

[66CHI/GAR] - Chiotti et al. measured enthalpies of transformation and fusion in a commercial adiabatic calorimeter. The sample was prepared in the Ames Laboratory and contained less than 0.1 wt.% metallic impurity. The enthalpy of transformation was determined as 930 ± 75 J mol^{-1} and the enthalpy of fusion as 8535 ± 500 J mol^{-1}. The temperatures of transformation and fusion were not reported. These results are reliable and they were adopted in [73HUL], [81GUR] and [85JAN].

[67KAY/SOD]

Kayser and Soderquist measured the melting and transformation points and the electrical resistivity of high purity Ca. A commercial Ca specimen was doubly distilled and finally contained only 50 ppm oxygen, 4 ppm nitrogen, and 29 ppm hydrogen. A major metallic impurity was 250 ppm Sr. The sample was sealed in a previously out-gassed Ta container for the DTA measurements. The temperature was cycled several times through the liquid-solid and the α–β transformations at a rate of 1 K/min. No measurable hysteresis was evident in cycling through either transformation; the melting point occurred at 1115 ± 2 K and the transformation at 716 ± 2 K. After the DTA experiments were completed, the sample was removed from the Ta crucible and the ratio of ρ(300 K)/ρ(4.2 K) was measured as 41.3. The magnitude of this ratio shows that the sample remained pure during measurements. These data are very reliable.

[75KAT/NIE]

Katerberg *et al.* measured the electrical resistivity and thermal power from room temperature up to about 973 K. They used a commercial Ca sample of 99.5 wt. % purity from two suppliers. A discontinuity in the thermal power was registered at T_{trs}/K = 701 ± 2. The change in resistivity at this temperature was very small. These data are not considered to be accurate.

[78COO]

Cook measured the electrical resistivity and thermal power of Ca from 300 to 850 K. A high purity Ca sample was prepared by two successive distillations and casting into a sealed Ta container in vacuum. The tested material had a residual resistivity ratio, ρ(273 K)/ρ(4.2 K) = 70. The ρ measurements showed small changes at about 720 K. The changes in thermal power were more pronounced, and a transition was found at 719 K on heating and at 717 K on cooling. This temperature depends on the hydrogen level in the sample, which was not determined.

4.4.2. Fusion of Ca

Some of the important studies of the temperature and enthalpy of fusion have been mentioned above. Two more studies should be added.

[71DWO/BRE]

Dworkin and Bredig studied the Ca–CaF_2 system. They purified Ca by distillation at 1173 K under a dynamic vacuum. The melting point was determined by thermal analysis as 1112 K.

[85ULY]

Ulyanov (quoted from [86SHP/KAG]) obtained values for temperature of fusion by thermal analysis as 1112 K

and the enthalpy of fusion by pulse calorimetry as 8340 ± 250 J mol^{-1}.

4.5. Discussion of Phase Equilibrium Data

4.5.1. α–β Transformation of Ca

The experimental temperatures of transformation are shown in Table 4–5. The adopted value, 716 ± 3 K, was previously selected in [73HUL], [81GUR] and [85JAN]; it corresponds to the best measurements [61PET/FAT], [67KAY/SOD] and [78COO]. The temperatures have been converted to ITS–90. However, corrections from earlier temperature scales to ITS–90 are considerably less than one degree and thus are not meaningful for T_{trs}.

The adopted enthalpy of transformation 930 J mol^{-1} was previously selected in [73HUL], [81GUR], [85JAN], and [86SHP/KAG] from calorimetric measurments of [66CHI/GAR]. It agrees also with the enthalpy measurements of [46JAU] and [35SCH]. The accuracy of this value is about ± 100 J mol^{-1}. Refer to Table 4-6.

4.5.2 Fusion of Ca

The adopted melting point, T_{fus}/K = 1115 ± 2, was previously selected in [81GUR] and [85JAN] according to the best study [67KAY/SOD]. It agrees within the uncertainty limit with most of the recent data quoted above and in Table 4-7. The conversion of temperatures of fusion from earlier temperature scales to ITS–90 results in corrections of the order of 0.3 K [IPTS–68] and 1 K [IPTS–48].

The experimental enthalpy of fusion results are shown in Table 4–8. The adopted enthalpy of fusion, 8540 J mol^{-1}, was previously selected in major reviews from [66CHI/GAR]. This value agrees well with [46JAU] and [85ULY]. The uncertainty is estimated at about ± 200 J mol^{-1}.

4.6. References for Ca

24EAS/WIL Eastman, E. D., Williams, A. M., and Young, T. F., J. Am. Chem. Soc. **46**, 1178–83 (1924); T_{trs}, $\Delta_{fus}H$, C_p°(373–878 K)

28ZAL/ZUL Zalesinski, E. and Zulinski, R., Bull. Intern. Acad. Polon., Part A No. 9–10, 479–505 (1928), ΔH(577–1075 K).

30CLU/VAU Clusius, K., and Vaughen, J., J. Amer. Chem. Soc. **52**, 4684–99 (1930); C_p°(10–201 K).

31RIN Rinck, E., C. R. Acad. Sci. 192, 421–3 (1931); T_{trs}, T_{fus}.

35SCH Schulze, A., Phys. Z. **36**, 595–8 (1935); T_{trs}, $\Delta_{trs}H$.

46JAU Jauch, R., Thesis, Techn. Hochschule, Stuttgart (1946); ΔH(573–1234 K), T_{trs}, $\Delta_{trs}H$, T_{fus}, $\Delta_{fus}H$.

49SHE Sheldon, E. A., Thesis, Syracuse Univ. (1949); T_{fus}.

50KUB Kubaschewski, O., Z. Metallk. **41**, 445–51 (1950); Review.

56SMI/CAR Smith, J. F., Carlson, O. N., and Vest, R. W., J. Electrochem. Soc. **103**, 409–13 (1956); T_{trs}.

57GRI/VES Griffel, M., Vest, R. W., and Smith, J. F., J. Chem. Phys. **27**, 1267–9 (1957); C_p°(1. 8–4. 2 K).

57ROB Roberts, L. M., Proc. Phys. Soc. London B**70**, 738–43 (1957); C_p°(1. 5–20 K).

58SCH/KIN Schottmiller, J. C., King, A. J., Kanda, F. A., J. Phys. Chem. **62**, 1446–9 (1958); T_{fus}.

60KOC/GEL Kocherov, P. V. and Gel'd, P. V., Russ. J. Inorg. Chem. **5**, 861–5 (1960); ΔH(473–1273 K).

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67KAY/SOD Kayser, F. X., and Soderquist, S. D., J. Phys. and Chem. Solids **28**, 2343–6 (1967); T_{trs}, T_{fus}.

71DWO/BRE Dworkin, A. S. and Bredig, M. A., J. Phys. Chem. **75**, 2340–1 (1971); T_{fus}.

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74AGA/BET Agarwal, K. L., and Betterton, J. O., J. Low Temp. Phys. **17**, 509–13 (1974); C_p°(1–4 K).

75KAT/NIE Katerberg, J., Niemeyer, S., Penning, D., and van Zytveld, J. B., J. Phys. F: Met. Phys. **5**, L74–9 (1975); T_{trs}.

77KEY Cox, J. D., "CODATA Recommended Key Values for Thermodynamics, 1976," J. Chem. Thermodyn. **9**, 705–6 (1977); Review.

78COO Cook, J. G., J. Less-Common Met. **57**, 53–67 (1978); T_{trs}.

82GRI/ROS Grimvalle, G., and Rosen, J., Intern. J. Thermophys. **3**, 251–7 (1982); C_p°(100–800 K, theory).

85ROB Robie, R. A., Private Communication to Dr. M. W. Chase, (1985); C_p°(5–350 K).

81GUR Gurvich, L. V., Veits, I. V., Medvedev, V. A., *et al.*, Glushko, V. P., gen. ed., "Thermodynamic Properties of Individual Substances," Nauka, Moscow, vol. **3**, 301–3 (1981); Review.

85JAN Chase, M. W., Jr., Davis, C. A., Downey, J. R., Jr., Frurip, D. J., McDonald, R. A., and Syverud, A. N., "JANAF Thermochemical Tables", J. Phys., Chem. Ref. Data **14**, Suppl 1, 686–8 (1985); Review.

85ULY Ulyanov, S. N., Thesis, Inst. for High Temp., Moscow (1985); T_{fus}, $\Delta_{fus}H$, $\Delta_{trs}H$, C_p°(781–1827 K).

86SHP/KAG Shpil'rain, E. E., Kagan, D. N., and Ulyanov, S. N., Reviews on Thermophysical Properties of Substances, No. **3** (59), Inst. for High Temperatures, Moscow (1986); Review.

87GAR/PAR Editors: Garvin, D., Parker, V. B., and White, H. J., Jr., "CODATA Thermochemical Tables", Hemisphere Publ. Corp., NY (1987); Review.

89COX/WAG Cox, J. D., Wagman, D. D., and Medvedev, V. A., "CODATA Key Values for Thermodynamics," Hemisphere Publ. Corp., New York (1989); Review.

89DIT Ditmars, D. A., Private Communication to V. Itkin (1989); C_p°(300–1100 K).

4.7. Adopted Values

Electronic contribution to C_p°: $\gamma = 1.99 \pm 0.05$ mJ K^{-2}mol^{-1}

Debye temperature at 0 K: $\Theta_D = 250 \pm 5$ K

Heat Capacity Equations

α–Ca

Temperature range: 0 – 5 K

$C_p^\circ = 1.99\times10^{-3}T + 1.24\times10^{-4}T^3$ J K^{-1} mol^{-1}

Temperature range: 5 – 40 K

$C_p^\circ = 1.771 - 0.310T - 15.93T^{-2} + 1.851\times10^{-2}T^2 - 1.679\times10^{-4}T^3$ J K^{-1} mol^{-1}

Temperature range: 40 – 80 K

$C_p^\circ = 117.816 - 3.804T - 3.963\times10^4T^{-2} + 5.122\times10^{-2}T^2 - 2.287\times10^{-4}T^3$ J K^{-1} mol^{-1}

Temperature range: 80 – 298.15 K

$C_p^\circ = 18.979 + 5.989\times10^{-2}T - 2.959\times10^4T^{-2} - 1.931\times10^{-4}T^2 + 2.408\times10^{-7}T^3$ J K^{-1} mol^{-1}.

Temperature range: 298.15 to 716 K

$C_p^\circ = 19.782 + 15.622\times10^{-3}T + 0.952\times10^5T^{-2} + 3.036\times10^{-6}T^2$ J K^{-1} mol^{-1}.

β–Ca

Temperature range: 716–1115 K

$C_p^\circ = 47.402 - 48.312\times10^{-3}T + 33.442\times10^{-6}T^2$ J K^{-1} mol^{-1}.

Liquid Ca

Temperature range: 1115 to 2000 K

$C_p^\circ = 38$ J K^{-1} mol^{-1}.

Values at the standard temperature

$C_p^\circ(298.15\text{ K}) = 25.72 \pm 0.1$ J K^{-1} mol^{-1};

$S^\circ(298.15\text{ K}) = 42.54 \pm 0.3$ J K^{-1} mol^{-1};

$H^\circ(298.15\text{ K}) - H^\circ(0) = 5783 \pm 30$ J mol^{-1}.

Phase Equilibria Data

Temperature of transformation: T_{trs}/K = 716 ± 3

Enthalpy of transformation: $\Delta_{fus}H$/J·mol^{-1} = 930 ± 100

Temperature of fusion: T_{fus}/K = 1115 ± 2

Enthalpy of fusion: $\Delta_{fus}H$/J·mol^{-1} = 8540 ± 200

4.8. Calculated Thermodynamic Functions of Ca

The thermodynamnic functions presented in Tables 4–9 and 4–10 are calculated using the equations presented in the previous section. Values in brackets are calculated by using the equation for the next higher adjacent temperature interval.

4.9. Appendix Experimental Results of Ca

Tables 4–11 to 4–23 present heat capacity or enthalpy data as they were presented in the original article. As a result, the numeric values listed in this Appendix are the actual experimental values, tabular smoothed values, values calculated from equations, or values extracted from a graph. Where necessary, values have been converted to joules (from calories). In all cases, the table heading indicates the type of data listed.

TABLE 4–1. Electronic contribution to the heat capacity and Debye temperature of Ca

Reference	γ, mJ·K^{-2} mol^{-1}	Θ_D, K	T/K range
Original studies			
57ROB	2.73 ± 0.06	228.9 ± 1.7	2.4–4.9
57GRI/VES	3.08 ± 0.01	239.0 ± 2.0	1.8–4.2
74AGA/BET	1.99 ± 0.05	250.0 ± 4.0	1.1–4.2
Reviews			
73HUL	3.00 ± 0.04		Based on 57GRI/VES
Adopted			
This study	1.99 ± 0.05	250 ± 5	Based on 74AGA/BET

TABLE 4–2. Comparison of the heat capacity, enthalpy, and entropy values for α-Ca at 298.15 K

Reference	C_p°(298.15 K) J·K^{-1} mol^{-1}	S°(298.15 K) J·K^{-1} mol^{-1}	$H^\circ(298.15\text{ K}) - H^\circ(0)$ J·mol^{-1}
73HUL	25.313	41.42 ± 0.4	5707
77KEY	–	41.60 ± 0.4	5730 ± 40
81GUR	25.941	41.60 ± 0.4	5730 ± 40
85JAN	25.929	41.588	5736
87GAR/PAR	25.929 ± 0.3	41.588 ± 0.3	5736 ± 40
89COX/WAG	25.929 ± 0.3	41.588 ± 0.4	5736 ± 40
Adopted	25.72 ± 0.1	42.54 ± 0.3	5783 ± 30

TABLE 4–3. Recommended heat capacities of α-Ca at 300–716 K

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
300	25.8	550	29.6
350	26.4	600	30.5
400	27.1	650	31.45
450	27.9	700	32.4
500	28.75	716	32.7

Table 4–4. Recommended heat capacities of β-Ca at 716–1100 K

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
716	30.0	950	31.7
750	30.0	1000	32.65
800	30.15	1050	33.65
850	30.4	1100	34.6
900	30.95		

TABLE 4–5. Temperature of phase transformation of Ca

Reference	T_{trs}, K	Comments
Original Studies		
24EAS/WIL	673	Enthalpy measurements
31RIN	723	Elec. resist., therm. analys.
46JAU	713	Enthalpy measurements
56SMI/CAR	737	Electrical resistivity
61PET/FAT	721 ± 2 (heating)	Thermal analysis
	715 ± 2 (cooling)	Thermal analysis
67KAY/SOD	716 ± 2	Therm. analysis, elec. resist.
75KAT/NIE	701 ± 2	Elec. resist., thermo emf
78COO	718 ± 1	Elec. resist., thermo emf
Reviews		
73HUL	720 ± 3	Based on 61PET/FAT, 66CHI/GAR
81GUR	716 ± 3	Based on 46JAU, 61PET/FAT, 67KAY/SOD
85JAN	716 ± 3	Based on 67KAY/SOD
86SHP/KAG	717 ± 3	Based on 61PET/FAT, 67KAY/SOD, 75KAT/NIE
SOD,KAT/NIE,		78COO
87GAR/PAR	716	
89COX/WAG	716	
Adopted		
This study	716 ± 3	Based on 61PET/FAT, 67KAY/SOD, 78COO

TABLE 4–6. Enthalpy of phase transformation of Ca

Reference	$\Delta_{trs}H$, J mol^{-1}	Comments
Original Studies		
24EAS/WIL	420 ± 00	Enthalpy measurements
35SCH	890	Enthalpy measurements
46JAU	920	Enthalpy measurement
66CHI/GAR	930 ± 75	Adiabatic calorimeter
Reviews		
73HUL	920 ± 200	Based on 46JAU, 66CHI/GAR
81GUR	930 ± 200	Based on 35SCH, 46JAU, 66CHI/GAR
85JAN	930 ± 80	Based on 66CHI/GAR
86SHP/KAG	930 ± 200	Based on 35SCH, 46JAU, 66CHI/GAR
87COX/WAG	930	
Adopted		
This study	930 ± 100	Based on 66CHI/GAR

TABLE 4–7. Temperature of fusion of Ca

Reference	T/K	Comments
Original Studies		
31RIN	1122	Thermal analysis
46JAU	1104	Enthalpy measurements
58SCH/KIN	1117 ± 1	Thermal analysis
61PET/FAT	1113 ± 2	Thermal analysis
67KAY/SOD	1115 ± 2	Thermal analysis
71DWO/BRE	1112 ± 1	Thermal analysis
85ULY	1112	Thermal analysis
Reviews		
73HUL	1112 ± 2	Based on 61PET/FAT, 66CHI/GAR
81GUR	1115 ± 2	Based on 61PET/FAT, 67KAY/SOD
85JAN	1115 ± 2	Based on 67KAY/SOD
86SHP/KAG	1114 ± 3	Misprint in references
89COX/WAG	1115	
Adopted		
This study	1115 ± 2	Based on 67KAY/SOD

TABLE 4–8. Enthalpy of fusion of Ca

Reference	$\Delta_{fus}H$ / J mol^{-1}	Comments
Original Studies		
46JAU	8660 ± 330	Enthalpy measurements
66CHI/GAR	8535 ± 500	Adiabatic calorimeter
85ULY	8340 ± 250	Heat pulse calorimeter
Reviews		
73HUL	8535 ± 400	Based on 66CHI/GAR
81GUR	8540 ± 400	Based on 66CHI/GAR
85JAN	8540 ± 100	Based on 66CHI/GAR
86SHP/KAG	8510 ± 160	Based on 46JAU, 66CHI/GAR, 85ULY
89COX/WAG	8540	
Adopted		
This study	8540 ± 200	Based on 66CHI/GAR

TABLE 4–9. Thermodynamic functions of Ca below 298.15 K

T/K	$C_p^\circ(T)$ J K^{-1} mol^{-1}	$H^\circ(T)-H^\circ(0)$ J mol^{-1}	$S^\circ(T)$ J K^{-1} mol^{-1}
5	0.0256	0.0443	0.0151
10	0.1948	0.6865	0.0989
15	0.6483	2.584	0.2467
20	1.5920	7.994	0.5515
25	2.9408	19.180	1.0451
30	4.5790	37.885	1.7226
35	6.3840	65.248	2.5627
40	8.2314(8.202)	101.796	3.5360
45	9.946	147.471	4.6099
50	11.227	200.503	5.7262
60	13.560	324.392	7.9786
70	15.982	472.125	10.251
80	18.017(18.034)	642.794	12.527
90	19.327	829.909	14.729
100	20.319	1028.344	16.819
120	21.746	1449.970	20.659
140	22.730	1895.284	24.089
160	23.448	2357.417	27.174
180	23.994	2832.077	29.968
200	24.420	3316.378	32.519
220	24.761	3808.305	34.863
240	25.045	4306.449	37.030
260	25.291	4809.862	39.045
280	25.518	5317.973	40.928
298.15	25.719(25.781)	5782.945	42.536

TABLE 4–10. Thermodynamic functions of Ca above 298.15 K

T/K	$C_p^\circ(T)$ J K^{-1} mol^{-1}	$H^\circ(T)-H^\circ(298.15\ \text{K})$ J mol^{-1}	$S^\circ(T)$ J K^{-1} mol^{-1}
298.15	25.78	0.00	42.54
300	25.80	47.71	42.70
400	27.11	2689.46	50.29
500	28.73	5479.98	56.51
600	30.51	8441.22	61.90
700	32.40	11586.04	66.75
716.00 (α)	32.71	12106.90	67.48
716.00 (β)	29.95	13036.90	68.78
800	30.16	15558.22	72.11
900	31.01	18610.87	75.71
1000	32.53	21782.36	79.05
1100	34.72	25139.57	82.25
1115.00 (β)	35.11	25663.30	82.72
1115.00 (l)	38.00	34203.30	90.38
1200	38.00	37433.30	93.17
1400	38.00	45033.30	99.03
1600	38.00	52633.30	104.10
1800	38.00	60233.30	108.58
2000	38.00	67833.30	112.58

TABLE 4–11. SMOOTHED heat capacity values of Ca [24EAS/WIL]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
373	27.24	673	30.21
473	29.00	773	30.63
573	30.71	873	31.46
673	32.47		

TABLE 4–12. EXPERIMENTAL enthalpy values $[H^\circ(T)-H^\circ(293\ \text{K})]$ of Ca [28ZAL/ZUL]

T/K	ΔH, J mol^{-1}	T/K	H, J mol^{-1}
577	7710	953(α)	24310
777	14340	953(β)	22050
793	14760	1075	22550
865	21460	1083	36220
923	23900	1203	41590

TABLE 4–13. CALCULATED heat capacity values of Ca [28ZAL/ZUL]

T/K	C_p°, J K^{-1} mol^{-1}
577	27.00
777	29.60
793	29.64
970	31.65
1028	32.32
1058	32.11
1058	28.93
1075	28.93
1203	44.80

TABLE 4–14. EXPERIMENTAL heat capacity values of Ca [30CLU/VAU]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
10.16	0.184	52.2	11.48
10.66	0.230	59.6	13.35
11.72	0.297	67.7	14.84
11.76	0.301	75.7	16.23
13.02	0.406	83.5	17.26
13.49	0.485	92.7	18.70
15.34	0.678	102.2	19.66
16.58	0.849	111.5	20.56
17.43	0.975	118.4	21.14
18.73	1.21	128.6	21.90
19.36	1.34	138.8	22.37
21.40	1.69	147.2	22.93
24.20	2.43	157.0	23.37
27.6	3.49	168.0	23.65
31.7	4.58	178.0	24.18
34.8	5.77	189.4	24.28
38.8	7.13	200.8	24.81
43.3	8.69		

TABLE 4–15. EXPERIMENTAL enthalpy values $[H°(T) - H°(298.15\ K)]$ of Ca [46JAU]

T/K	ΔH, J mol^{-1}	T/K	ΔH, J mol^{-1}
573	7320	1027	23870
617	8640	1055	25000
632	9000	1057	25050*
687	10900	1072	25560
697	11230		
749	13640	1120	35820
810	15400	1122.5	35600*
829	16500	1136	36230
878	17870	1153	36530
901	18900	1170	37300
922	19690	1213	38530
929	19900	1234	39120
973	21630		
981	21500		

*Average of two measurements

TABLE 4–16. CALCULATED heat capacity values of Ca [46JAU]

T/K	$C_p°$, J K^{-1} mol^{-1}	T/K	$C_p°$, J K^{-1} mol^{-1}
573	26.65	1027	32.64
617	27.03	1055	32.93
631.5	27.45	1057	32.26
687	28.12	1057	32.80
697	28.20	1072	33.05
749	30.33	1122	43.72
810	30.12	1120	43.60
829	30.04	1123	43.30
878	30.75	1136	43.10
901	31.38	1153	42.68
922	31.46	1170	42.76
929	31.63	1213	42.17
973	32.05	1234	41.88
981	31.51		

TABLE 4–17. SMOOTHED heat capacity values of Ca [57GRI/VES]

T/K	$C_p°$, mJ·K^{-1} mol^{-1}
2	7.3
3	13.1
4	21.4

TABLE 4–18. SMOOTHED heat capacity values of Ca [57ROB]

T/K	$C_p°$, J K^{-1} mol^{-1}	T/K	$C_p°$, J K^{-1} mol^{-1}
1.5	0.00464	7	0.081
2.0	0.00676	8	0.118
2.5	0.00935	9	0.158
3.0	0.0126	10	0.205
3.5	0.0165	12	0.348
4.0	0.0213	14	0.550
4.5	0.0270	16	0.833
5.0	0.0344	18	1.19
6.0	0.0540	20	1.63

TABLE 4–19. SMOOTHED heat capacity values of Ca [74AGA/BET]

T/K	$C_p°$, mJ·K^{-1} mol^{-1}
1	2.11
2	4.98
3	9.33
4	15.92

TABLE 4–20. EXPERIMENTAL heat capacity values of Ca [85ROB]

T/K	C_p° J K^{-1} mol^{-1}	T/K	C_p° J K^{-1} mol^{-1}	T/K	C_p° J K^{-1} mol^{-1}
8.343	0.0707	127.535	22.1635	275.214	25.4631
9.388	0.1277	133.085	22.4561	280.484	25.4981
10.242	0.1713	138.601	22.7076	285.733	25.5857
11.271	0.2480	144.096	22.9220	290.971	25.8015
12.555	0.3498	149.570	23.1176	296.194	25.8622
13.958	0.4960	155.022	23.2901	300.682	25.7663
15.515	0.6976	160.451	23.4299	300.865	25.7448
17.256	0.9816	165.861	23.5786	301.419	25.7665
19.173	1.3708			305.735	25.8382
21.302	1.8770			306.013	25.7672
23.690	2.5185	181.835	24.0249	306.559	25.8590
26.364	3.3261	186.917	24.1785	306.626	25.8626
29.361	4.3214	192.015	24.2902	311.014	25.9129
32.724	5.5469	197.211	24.4055	311.496	25.9162
36.495	6.9958	202.397	24.4480	318.096	25.8797
40.746	8.4284	207.570	24.5669	323.188	25.9736
45.475	10.1371	212.741	24.6295	328.170	26.1073
50.722	11.5409	217.904	24.7111	333.155	26.1629
56.618	12.7327	223.064	24.8409	338.272	26.1780
62.874	13.9737	228.232	24.9070	343.398	26.4053
69.159	15.8976	233.419	24.9666	348.536	26.4436
75.389	17.4659	238.622	25.0762	353.663	26.4626
81.478	18.2098	243.842	25.0764	358.783	26.4449
87.444	18.9781	249.076	25.1440	363.893	26.4584
93.337	19.6367	249.783	25.0837		
99.184	20.2350	254.324	25.1888		
104.966	20.7416	254.441	25.2383		
110.686	21.1409	259.528	25.2100		
116.348	21.5169	264.633	25.3102		
121.959	21.8541	269.934	25.4041		

TABLE 4–21. SMOOTHED heat capacity values of Ca [85ROB]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
5	0.038	210	24.60
10	0.191	220	24.77
15	0.651	230	24.93
20	1.592	240	25.05
25	2.941	250	25.14
30	4.555	260	25.25
35	6.400	270	25.38
40	8.219	280	25.53
45	9.897	290	25.70
50	11.30	300	25.79
60	13.53	310	25.87
70	16.02	320	25.95
80	18.04	330	26.11
90	19.31	340	26.28
100	20.30	350	26.43
110	21.10	360	26.47
120	21.75	273.15	25.43
130	22.30	298.15	25.78
140	22.76		
150	23.13		
160	23.43		
170	23.71		
180	23.99		
190	24.24		
200	24.43		

TABLE 4–22. EXPERIMENTAL heat capacity values of Ca [85ULY]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
Solid Ca		Liquid Ca	
781.7	34.09	1134.9	32.57
791.7	34.26	1144.9	32.53
801.7	34.63	1154.9	32.50
834.4	34.46	1201.1	33.15
843.4	34.62	1211.1	33.11
853.4	34.78	1222.1	33.07
896.1	36.51	1257.5	32.50
906.1	36.68	1267.5	32.46
916.1	36.85	1277.5	32.43
968.5	37.04	1336.0	32.47
978.5	37.20	1346.0	32.43
988.5	37.36	1408.3	31.83
1053.6	38.83	1418.3	31.79
1063.6	38.97	1512.9	32.03
1073.6	39.14	1522.9	31.99
1538.8	30.98		
1548.8	30.96		
1621.6	31.00		
1631.6	30.96		
1817.4	30.93		
1827.4	30.89		

TABLE 4–23. CALCULATED heat capacity values of Ca [89DIT]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
α-Ca		β-Ca	
300	25.8	716	30.0
350	26.4	750	30.0
400	27.2	800	30.1
450	28.1	850	30.3
500	30.5	900	31.0
550	28.8	950	31.8
650	28.1	1000	32.7
700	30.8	1100	36.
716	35.5		

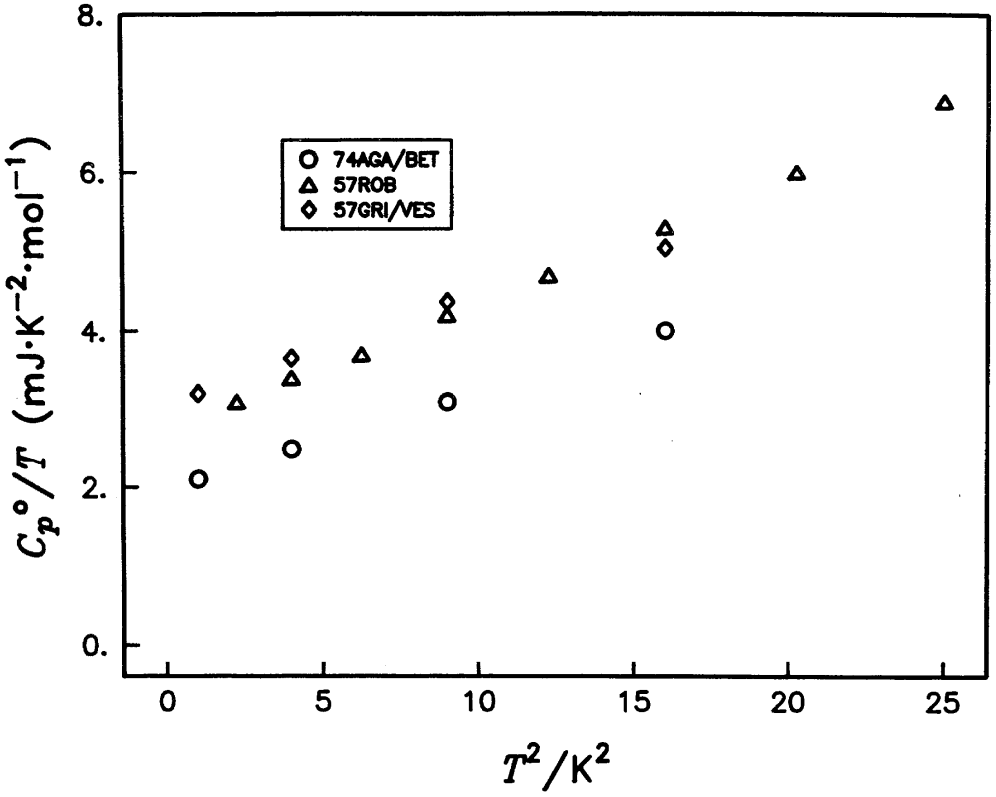

FIG. 4–1. $C_p°/T$ versus T^2 for Ca below 5 K.

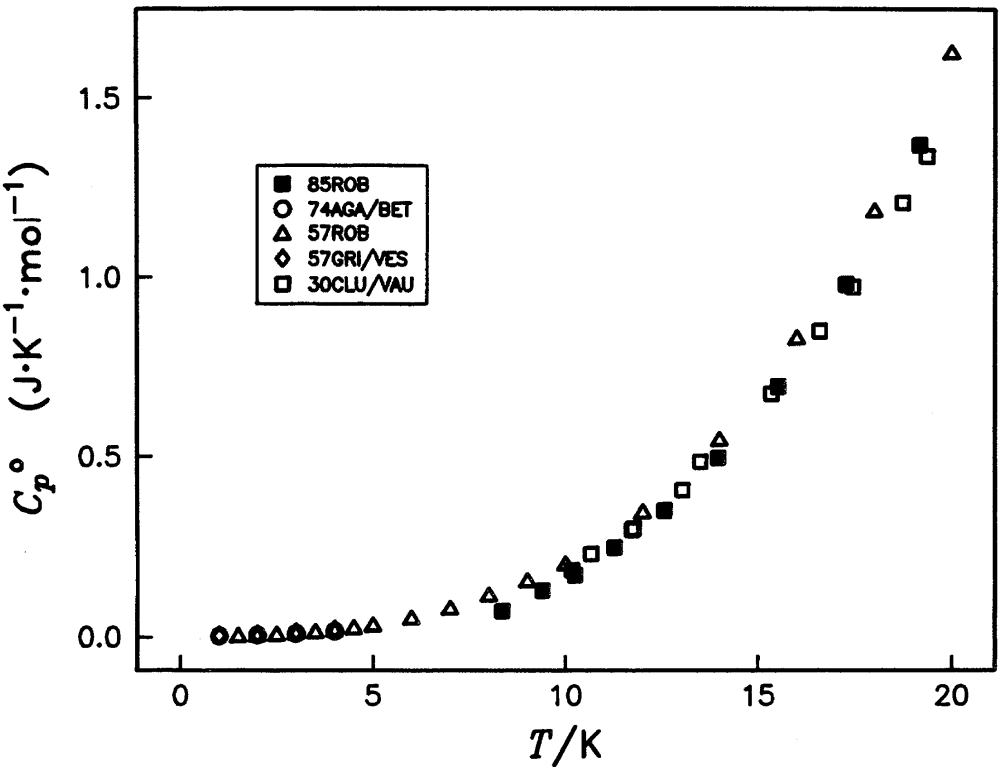

FIG. 4–2. Heat Capacity of Ca below 20 K.

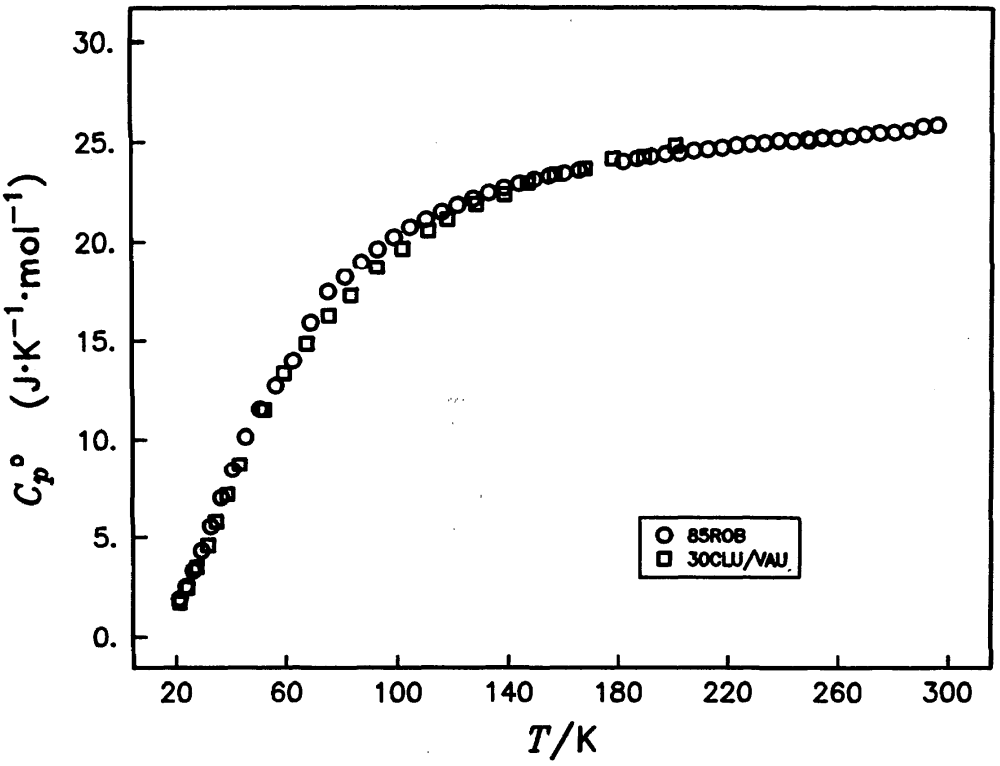

FIG. 4–3. Heat Capacity of Ca at 20–300 K.

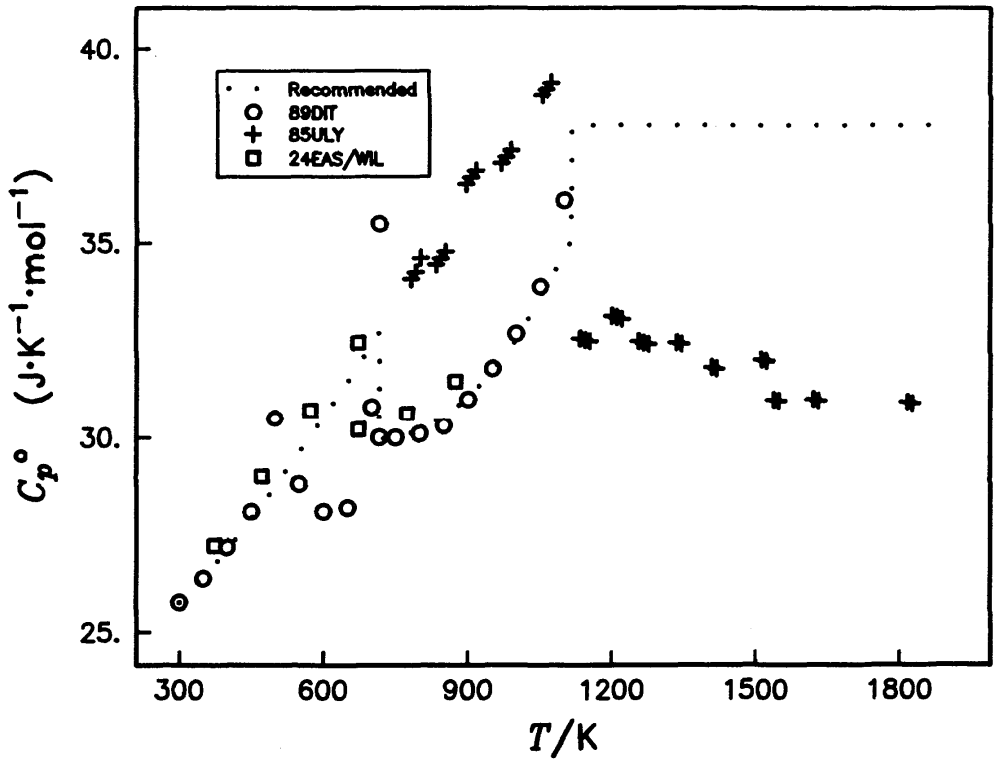

FIG. 4–4. Heat Capacity of Ca at 300–1900 K.

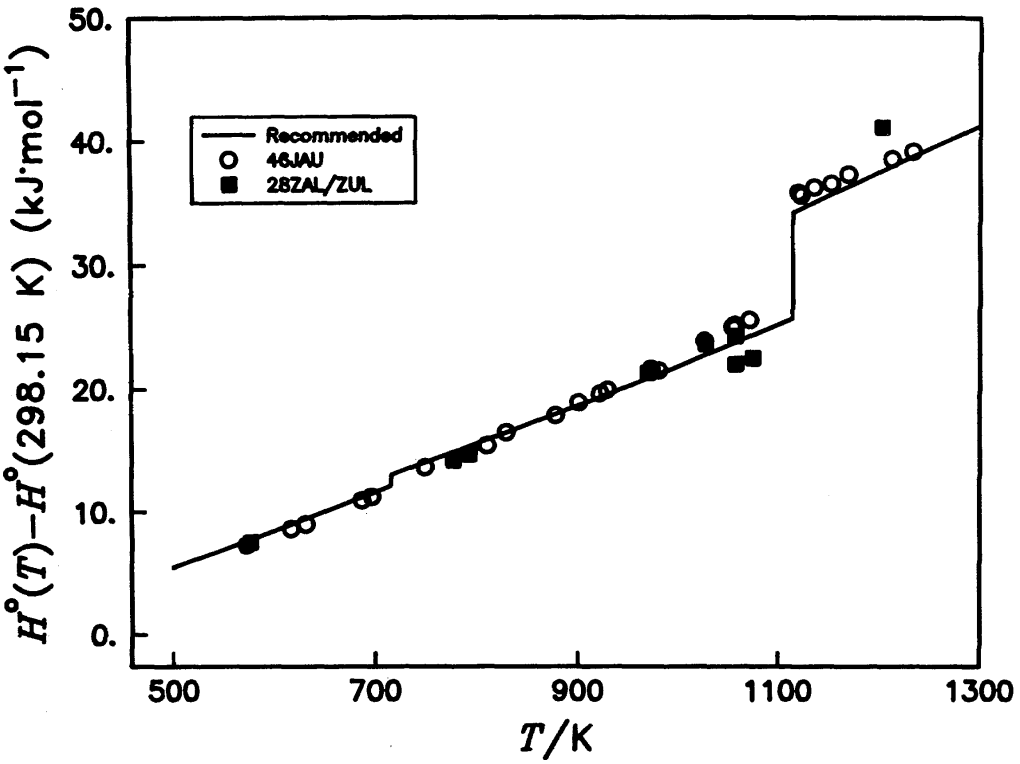

FIG. 4–5. $H°(T) - H°(298.15\ \text{K})$ for solid and liquid Ca.

5. Strontium

5.1. Introduction

Similar to calcium, strontium exists at ambient pressure in two stable crystalline modifications, fcc and bcc (T_{trs} = 820 K), which were established accurately in the sixties. As for Ca the presence of hydrogen in solution affects the measurements for Sr; the data are scattered and have a high uncertainty because of the formation of different phases of the Sr–H system. Above 400 K the heat capacity or enthalpy data are not reliable, and the data for β–Sr and liquid Sr are especially poor. The values are known with an uncertainty of about 10%. The recommended thermodynamic values are therefore only approximate. The low-temperature data are known better than those above 298 K; however, the data are less certain below 10 K, and only one set of heat capacity measurements extends down to 1.5 K [57ROB]. The considerable scatter of points in this source makes the derived Debye temperature and electronic heat capacity coefficient inaccurate.

5.2. Heat Capacity and Enthalpy Measurements

5.2.1. Temperatures below 298.15 K

[57ROB]

Roberts measured heat capacity values from 1.5 to 20 K in a low-temperature Nernst adiabatic calorimeter. The commercial material which was used had about 2 wt. % metallic impurities. Samples were cut from the bulk and most of the surface oxides were removed in the air. Although samples were sealed in the calorimeter under reduced pressure of He, they had probably a significant content of non-metallic impurities. Roberts presented her results in a graphic form from 1.5 to 5.5 K (32 points). The 15 points between 2.4 and 4.3 K are described by the usual expression:

$$C_p / \text{J K}^{-1}\,\text{mol}^{-1} = \gamma T + 1943\,(T/\Theta_D)^3,$$

where Θ_D = 147.0 ± 1.2 K and γ = 3.64 ± 0.18 mJ·K^{-2} mol^{-1}. Above 4.5 K Roberts [57ROB] tabulated twelve smoothed heat capacity values which are shown in Figs. 5–1 and 5–2 and listed in the Table 5–10. Although Roberts used poor samples, the measurements were performed reliably. Her data are better than any other below 20 K.

[76KHR/PAU]

Khriplovich and Paukov measured the heat capacity in an adiabatic vacuum calorimeter from 5 to 300 K (80 points). These authors published only smoothed values. A full description of the study was deposited at the All-Union Institute of Scientific and Technical Information USSR (VINITI, No. 3190–75, Nov. 1975) and is difficult to access. The sample had about 0.7 wt. % metallic impurities (mainly Ba), 0.022 wt. % oxygen and 0.017 wt. % nitrogen. Boerio and Westrum [78BOE/WES] assumed that the actual amount of oxygen in the samples of [76KHR/PAU] was much greater than was reported. The smoothed heat capacity values of [76KHR/PAU] are shown in Figs. 5–1, 5–2 and 5–3 and listed in the Table 5–11.

The authors calculated thermodynamic quantities under standard conditions:

C_p°(298.15 K) = 29.18 ± 0.10 J K^{-1} mol^{-1};
S°(298.15 K) = 55.40 ± 0.17 J K^{-1} mol^{-1};
H°(298.15 K) − H°(0) = 6770 ± 17 J mol^{-1}.

They obtained quite reliable values at low temperatures, but the values above 200 K seem to be high. This might reflect the presence of an oxide phase.

[78BOE/WES]

Boerio and Westrum measured the heat capacity in a calorimeter with an adiabatic shield from 6 to 346 K. The sample was prepared in the Ames Laboratory. The best commercial Sr was fractionally sublimed several times, and after each sublimation the middle portion was extracted. The sublimed product was held in a Ta container under an inert atmosphere for 5 days at 1200 K to remove hydrogen. The sample contained 10–24 ppm H, less than 10 ppm O, 12 ppm N, 40 ppm C, 423 ppm Ca, and 615 ppm Ba. The accuracy of single measurements was estimated as 5% at 10 K, 0.1% at 25 K and 0.06% between 25 and 350 K. Eighty-three experimental points, combined in five series, were reported in [78BOE/WES] and are shown in Figs. 5–2 and 5–3. The results are listed in the Table 5–12; they were fitted with a polynomial expression and the smoothed heat capacity values calculated by this expression are listed in the Table 5–13. The thermodynamic quantities at standard temperature were calculated:

C_p°(298.15 K) = 26.786 J K^{-1} mol^{-1},
S°(298.15 K) = 55.702 ± 0.033 J K^{-1} mol^{-1},
H°(298.15 K) − H°(0) − 6569.7 J mol^{-1}.

These results are entirely based on the measurement of [78BOE/WES]; the previous data of [57ROB] and [75KHR/PAU] were not used. According to the description given in the paper, this study must be the best. However, there are some doubts about the accuracy of the measurements at the lowest temperatures. The values appear to be too high in comparison with [57ROB] and [75KHR/PAU], and at temperatures above 300 K the values appear to be too low in comparison with the high-temperature measurements of [82STE/ROT] and [89DIT]. There also appears to be more scatter than expected at the higher temperatures of this study.

5.2.2. Temperatures above 298.15 K

[82STE/ROT]

Stephens and Roth measured the enthalpy from 350 to 1191 K by drop calorimetry, and the heat capacity by dif-

ferential scanning calorimetry from 398 to 785 K. The sample was identical to that used in [78BOE/WES]. The results are listed in the Tables 5-14 and 5–15 and shown in Figs. 5–4, and 5–5. For α–Sr the heat capacity values of scanning calorimetry are higher than the average heat capacity values calculated from the enthalpy measurements:

$$C_p = H(T) - H(298\ \mathrm{K})/(T - 298)$$

(See Fig. 5–4).

The heat capacity measurements are more accurate than enthalpy measurements. The data of [82STE/ROT] were analyzed in [85JAN]. Fourteen data points of drop and scanning calorimetry were fitted to a polynomial and the derived values are reproduced in Table 5–1.

The above values are close to those obtained by Stephens and Roth by scanning calorimety.

Nine drop-calorimetry points between 820 and 1049 K were used in [85JAN] to derive heat capacity values for β–Sr which increase smoothly from 29.79 J K^{-1} mol^{-1} at 820 K to 30.75 J K^{-1} mol^{-1} at 1050 K. The above increase with temperature is not directly evident from the data of [82STE/ROT] tabulated in the Table 5–14. To obtain such a dependence, certain assumptions and treatment of the experimental data are required. Four enthalpy points, covering almost the entire temperature range of stability of β–Sr from 830 to 990 K, can be roughly considered as lying in one straight line with a slope corresponding to a constant heat capacity value of about 28 J K^{-1} mol^{-1}. This may not be correct because the heat capacity values of β–Sr are expected to increase with temperature similar to other bcc phases: β–Ca and Ba. Indeed, three more data points at 1028, 1035 and 1049 K show a steep increase in the enthalpy and in the heat capacity. Such a sharp increase indicates some processes due to impurities in the samples which may have been acquired during handling and heating of the specimens. This can result in low accuracy of the measurements. An attempt to use all of the enthalpy data points for β–Sr to derive an equation was not successful. Therefore, the result of the treatment made by the authors of [85JAN] was adopted as the best approximation to the experimental data of [82STE/ROT]. For liquid Sr, only three enthalpy points at 1059, 1131 and 1191 K are available [82STE/ROT]. The constant value C_p = 39.33 J K^{-1} mol^{-1} was recommended in [82STE/ROT]. The authors of [85JAN] derived a value C_p = 39.463 J K^{-1} mol^{-1} close to this. However, the data for liquid Sr are the least accurate. If, for example, two points at 1059 and 1131 K are used, the average heat capacity will be much smaller, viz. 34.3 J K^{-1} mol^{-1}. The latter seems to be as reasonable as the value 39.33 J K^{-1} mol^{-1} recommended by Stephens and Roth. The average of the above two values, C_p = 37 ± 3 J K^{-1} mol^{-1}, is probably a better approximation for the heat capacity of liquid Sr. The authors of [82STE/ROT] determined also the temperatures of transformation and melting (see below). Study [82STE/ROT] is not accurate, especially the enthalpy measurements, and the results should be used with caution.

[85ULY]

Ulyanov measured the heat capacity by a pulse-differential technique according to which the heating or cooling rate of the specimen is compared with that of a reference specimen when both are subject to a sudden change in temperature. The original study was not available, and its description was taken from [86SHP/KAG]. The measurements were made in the temperature range 870 to 1780 K, and the sample contained about 0.02 wt. % of metallic impurities. The content of non-metallic impurities was not given in [86SHP/KAG]. The values of [85ULY] are shown in Fig. 5–4 and listed in the Table 5–16. Twenty-eight experimental points for β–Sr measured in a short temperature range (868–983 K) were fitted to the equation

$$C_p\ /\ \mathrm{J\ K^{-1}\ mol^{-1}} = 6.84 + 37.92\times10^{-3}T.$$

The values obtained for β–Sr seem to be unreasonably high, which questions the quality of pulse-differential calorimetric data. It appears that this technique is not sufficiently accurate and reliable, and depends on a precise knowledge of certain coefficients which are usually determined with a large uncertainty.

For liquid Sr (1137–1782 K) Ulyanov obtained the 16 values listed in the Table 5–16 and described by the equation

$$C_p\ /\ \mathrm{J\ K^{-1}\ mol^{-1}} = 56.24 - 18.87\times10^{-3}T + 4.25\times10^{-6}T^2.$$

The measured heat capacity values decrease from 38.3 J K^{-1} mol^{-1} at about 1200 K to 36 J K^{-1} mol^{-1} near 1700 K. The general trend of the heat capacity values of liquid metals of the IIA group to decrease with temperature is probably correct, but the absolute values of the heat capacity and the rates of change with temperature are not reliable and need independent confirmation. The only conclusion which can be derived from Ulyanov's measurement of liquid Sr is that the heat capacity value should be about 37 J K^{-1} mol^{-1}.

[89DIT]

Ditmars measured the enthalpy increment of Sr with a precision Bunsen ice drop calorimeter up to 800 K , using materials prepared in the Ames Laboratory. The results, which were taken from a graph 'true C_p versus temperature' with an accuracy of about 1%, are shown in Fig. 5–4 and listed in the Table 5-17. The data below 500 K appear to be quite reliable. The slow heat capacity increase between 500 and 700 K and the rapid increase above 700 K can be attributed to some processes which occurred in the samples during heating. Such processes probably involve oxygen and water contaminants which are absorbed during the handling procedure.

5.3. Discussion of Heat Capacity and Enthalpy Data

5.3.1. α-Sr below 298.15 K

Between 1.5 and 5 K the only available data are those of [57ROB], as shown in Fig. 5–1. Although the sample was not of high purity, the values were adopted for the temperature range below 5 K. The heat capacity equation for the interval 0–5 K is:

$$C_p \,/\, \mathrm{J\,K^{-1}\,mol^{-1}} = 0.00364T + 6.119\times10^{-4}T^3 \quad (5\text{–}1)$$

where $\gamma = 3.64 \pm 0.18\ \mathrm{mJ\cdot K^{-2}\,mol^{-1}}$ (the same value was adopted in [73HUL]) and $\Theta_D = 147.0 \pm 1.2$ K.

Figure 5–2 shows that between 5 and 20 K, study [57ROB] gives the lowest heat capacity values, [78BOE/WES]—the highest, and [76KHR/PAU]—the medium values, the latter being very close to [57ROB]. The results of [57ROB] were selected as the best for the interval 5–20 K despite the fact that the quality of the Sr specimen was not high.

To support this choice, the analysis and recommended results for other members of Group IIA of the Periodic Table should be discussed. Gmelin [69GME] prepared three Be samples of different purity, containing 100 ppm, 500–800 ppm and 1000–1200 ppm impurities, and the heat capacities were measured from 1 to 80 K. Gmelin found that the Debye temperature decreased and the electronic heat capacity increased when the concentration of impurities increased. This conclusion should be applied to all elements of the second group and was used in the present study to compare the data of [78BOE/WES] and [57ROB]. It was assumed that an assessment could be made in the light of this observation as to which of these studies gave more reliable values at low temperatures.

Boerio and Westrum [78BOE/WES] used materials of a quality much superior to those of Roberts [57ROB]. According to [69GME], it would therefore be expected that the authors of [78BOE/WES] would have obtained a higher Debye temperature and a lower electronic heat capacity and, hence, smaller heat capacity values than those of [57ROB]. However, the heat capacity values of [78BOE/WES] are *higher* than those of [57ROB]. The contradiction between the experimental results for Sr and application of Gmelin's observation for Be probably arises from errors in both studies. It was assumed, first, that the older study [57ROB] was not accurate and reported low, underestimated values. To verify this assumption the results for Ca measured in the same study [57ROB] were compared with other values for Ca. [57GRI/ROS] reported heat capacity values for a sample of Ca of the same purity and obtained results almost coincident with [57ROB]. The authors of [74AGA/BET] worked with a higher purity sample of Ca and obtained values lower than [57ROB] in accordance with [69GME]. Therefore, Roberts appears to have obtained reasonably accurate heat capacity values for the sample of Ca of his degree of purity, and probably his data for Sr have about the same level of accuracy.

The conclusion was made that the data of [57ROB] are more reliable than those of [78BOE/WES], and it seems probable that the technique used by Boerio and Westrum [78BOE/WES] produced high, overestimated heat capacity values at the lowest measured temperatures. Therefore, below 20 K preference was given to Roberts [57ROB], and her heat capacity values between 5 and 20 K (see Table 5–10) were fitted to the equation:

$$C_p \,/\, \mathrm{J\,K^{-1}\,mol^{-1}} = -0.0532 - 8.884\times10^{-2}T + 4.837T^{-2} + 1.658\times10^{-2}T^2. \quad (5\text{–}2)$$

Above 20 K two sets of data are available [76KHR/PAU] and [78BOE/WES]. Below 130 K the heat capacity values of [78BOE/WES] are higher than [76KHR/PAU], and above 130 K they are lower than [76KHR/PAU]. The difference changes with temperature and becomes substantial at 300 K (about 8%). [78BOE/WES] compared their results with those of [76KHR/PAU] and used private information about analyses performed in the USSR. When the authors of [78BOE/WES] assumed that the actual amount of oxygen in the material of [76KHR/PAU] was 6 mol.% and introduced a correction to the data of [76KHR/PAU] for the presence of SrO, they achieved good agreement between two sets of values. Comparison of the two studies showed that the authors of [78BOE/WES] used a better material and a technique of about the same degree of precision; their values near 300 K are more consistent with the high-temperature data of [82STE/ROT] and [89DIT]. Therefore, the data of [78BOE/WES] were selected from 30 to 300 K.

Between 20 and 30 K the following equation:

$$C_p \,/\, \mathrm{J\,K^{-1}\,mol^{-1}} = 16.849 - 2.468T + 0.1278T^2 - 1.728\times10^{-3}T^3 \quad (5\text{–}3)$$

was used to join the data of [57ROB] and [78BOE/WES]. The data of [78BOE/WES] are represented by two equations for the intervals 30–100 K and 100–300 K. The outlying points which deviate from the calculated heat capacity values by greater than 0.5% were dropped according to the treatment made in [78BOE/WES].

The following equations are used for the range 30–100 K:

$$C_p \,/\, \mathrm{J\,K^{-1}\,mol^{-1}} = 1.445 + 0.5939T - 3.12\times10^{3}T^{-2} - 5.65\times10^{-3}T^2 + 1.951\times10^{-5}T^3, \quad (5\text{–}4)$$

and for the range 100–298.15 K:

$$C_p \,/\, \mathrm{J\,K^{-1}\,mol^{-1}} = 17.609 - 8.795\times10^{-2}T - 3.2605\times10^{-4}T^2 + 4.525\times10^{-7}T^3. \quad (5\text{–}5)$$

$C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$ and $S^\circ(T)$ values calculated by Eqs. 5–1 to 5–5 at different temperatures are given in Table 5–8. At standard temperature the following values were obtained:

$C_p°(298.15\ K) = 26.840\ J\ K^{-1}\ mol^{-1}$;
$S°(298.15\ K) = 54.999\ J\ K^{-1}\ mol^{-1}$;
$H°(298.15\ K) - H°(0) = 6558.3\ J\ mol^{-1}$.

These values can be compared with those given in other reviews, as shown in Table 5–2.

A different treatment of the same original data was made in [81GUR], [85JAN] and here. The data of [57ROB] were neglected in [81GUR] and [85JAN]. Although the accuracy of [57ROB] is not very high and the material was not of high purity, the heat capacity values at low temperatures obtained in this study can be considered as the best available. As a result, the calculated and adopted values of $S°(298.15\ K)$ and $H°(298.15\ K) - H°(0)$ are lower than those recommended in [81GUR] or [85JAN]. The accuracy of the adopted standard entropy $\pm 0.3\ J\ K^{-1}\ mol^{-1}$ reflects the necessity for further investigations below 30 K.

5.3.2. α–Sr above 298.15 K

Figure 5–4 shows high-temperature heat capacity data, and Fig. 5–5 shows the enthalpy data above 300 K. Above 300 K, the data of [78BOE/WES], which extend to 350 K, increase with temperature more slowly than below 300 K. This unexpected trend does not have a reasonable explanation except by assumption of a systematic error. The recent enthalpy data of [89DIT] between 300 and 500 K form a smoothed continuation of the low-temperature data of [78BOE/WES]. At 300–500 K they also agree with the results of scanning calorimetry of [82STE/ROT]. Above 500 K the data of [82STE/ROT] obtained by two methods: scanning calorimetry and enthalpy measurements, and the data of [89DIT] disagree. It seems to be most probable that the heat capacity values should form a smooth extension of the data selected between 300 and 500 K, i.e., between Stephens and Roth [82STE/ROT] scanning calorimetry results and Ditmars [89DIT] data. The suggested heat capacity values are listed in Table 5–3.

The above points were fitted to an equation for α–Sr for the interval 298.15–820 K:

$$C_p / J\ K^{-1}\ mol^{-1} = 25.029 + 8.744\times10^{-3}T - 0.569\times10^{5}T^{-2} - 2.032\times10^{-6}T^{2}. \quad (5\text{–}6)$$

[81GUR] estimated heat capacity values of α–Sr using measurements of [78BOE/WES] at 298 and 350 K and assuming that at T_{trs}, $C_p = 33.5\ J\ K^{-1}\ mol^{-1}$. [81GUR] recommended an equation for α–Sr from 298 to 820 K

$$C_p / J\ K^{-1}\ mol^{-1} = 19.795 + 16.196\times10^{-3}T + 1.922\times10^{5}T^{-2}.$$

The same equation was adopted in [86SHP/KAG]. The recommendation of [85JAN] is based on study of [82STE/ROT]. Above 500 K the values recommended in [85JAN] are greater than those adopted here.

5.3.3. β–Sr

Figure 5–4 shows the data of [85ULY] and [82STE/ROT]. The data of [85ULY] for β–Sr are high and appear unlikely, and they were therefore discarded from further consideration. The data of [82STE/ROT] seem to be more reasonable because they give acceptable values for α–Sr, and because they give heat capacity values for β–Sr smaller than those for α–Sr near the transformation temperature. A similar heat capacity relation is observed in Ca. The authors of [85JAN] analyzed the data points of [82STE/ROT] and reported four C_p values 29.79, 30.125, 30.543, and 30.752 $J\ K^{-1}\ mol^{-1}$ at 820, 900, 1000 and 1050 K, respectively; these values can be expressed by equation

$$C_p / J\ K^{-1}\ mol^{-1} = 26.526 + 4.022\times10^{-3}T. \quad (5\text{–}7)$$

Equation 5–7 was adopted here for description of β–Sr. As mentioned above, the accuracy of the data for β–Sr and their representation by Eq. 5–7 is low. [81GUR] derived a heat capacity equation for β–Sr by analogy with the heat capacities of β–Ca:

$$C_p / J\ K^{-1}\ mol^{-1} = 24.234 + 14.435\times10^{-3}T.$$

[86SHP/KAG] based recommendations on their own measurements [85ULY] which were, however, criticized above:

$$C_p / J\ K^{-1}\ mol^{-1} = 6.841 + 37.921\times10^{-3}T.$$

5.3.4. Liquid Sr

Figure 5–4 shows the data of [85ULY] and the value of [82STE/ROT]. Stephens and Roth [82STE/ROT] recommended the constant value $C_p = 39.3\ J\ K^{-1}\ mol^{-1}$ and [85JAN] $39.463\ J\ K^{-1}mol^{-1}$ on the basis of three enthalpy measurements (Fig. 5–5). As was discussed above, the value of $C_p = 37 \pm 3\ J\ K^{-1}mol^{-1}$ appears to be a better approximation to the inaccurate data of [82STE/ROT].

Ulyanov's values for liquid Sr [85ULY] can be interpreted to show a constant C_p of about $37\ J\ K^{-1}\ mol^{-1}$ (see above). The data of [85ULY] for liquid Sr were recommended in [86SHP/KAG] in the form of an equation

$$C_p / J\ K^{-1}\ mol^{-1} = 56.237 - 18.874\times10^{-3}T + 4.253\times10^{-6}T^{2}.$$

It should be also mentioned that [81GUR] estimated very roughly the heat capacity value of liquid Sr as $36 \pm 5\ J\ K^{-1}\ mol^{-1}$ using data for Ba and Ca of doubtful quality. The experimental values of [85ULY] and [82STE/ROT] are not accurate, and none of these studies can be used alone. However, two of them make it possible to select a tentative value, and it is assumed here that the heat capacity of liquid Sr is constant and equal to

$$C_p / J\ K^{-1}\ mol^{-1} = 37. \quad (5\text{–}8)$$

The values of $C_p^\circ(T)$, $S^\circ(T)$ and $H^\circ(T) - H^\circ(298.15\ K)$ were calculated by Eqs. 5–6 to 5–8, with the results being given in Table 5–9.

5.4. Phase Equilibrium Data

5.4.1. α–β Transformation of Sr

Sr has at ambient pressure one fcc-bcc (α–β) transformation. As for calcium, it was not clear until the sixties how many allotropic modifications Sr had.

[52RIN]

Rinck studied the allotropic transformations in Sr using resistivity, thermoelectric and dilatometric measurements, and thermal analysis from room temperature to the melting point. A commercial sample of Sr was purified by double distillation under vacuum, and the measurements were made in an Ar atmosphere. Thermal analysis showed melting between 1041 K and 1043 K and transformation at 813–814 K. Other physical methods registered two transformations in solid Sr at 508 K and at 808–813 K. Rinck concluded that Sr has 3 modifications termed α, β and γ.

[53SHE/KIN]

Sheldon and King studied the structure of Sr by high temperature x-ray diffraction. The specimen was taken from the middle fraction of a commercial material, which was sublimed in a high vacuum. The sample had about 0.5 wt. % metallic impurities and its melting point was 1043 K. The authors confirmed that Sr existed in three modifications fcc(α) below 488 ± 10 K, hcp(β) between 488 and 878 ± 10 K and bcc(γ) above 878 K.

[56HIR/KIN]

Hirst *et al*. studied Sr by x-ray diffraction at room and high temperatures and by thermal analysis. The purest Sr from King Laboratories had a melting point of 1041 K. Three polymorphic forms of Sr were confirmed. The transition temperatures were determined as 488 ± 3 K for the fcc–hcp and 875 K for the hcp–bcc transformations.

[58SCH/KIN]

Schottmiller *et al*. studied transformations in the same material as [56HIR/KIN] with an additional vacuum distillation at 815 °C. The melting point of distilled Sr was 1047 ± 1 K. Thermal analysis showed that the fcc-hcp transformation occurred at 503 ± 6 K, and hcp–bcc at 894 ± 6 K.

Studies [52RIN], [53SHE/KIN], [56HIR/KIN], [58SCH/KIN] stated that Sr has three modifications and two transformation points, but subsequent publications suggested that pure Sr has only two allotropic forms.

[66PET/COL]

Peterson and Colburn found by x-ray and thermal analysis of pure Sr only two modifications: the low-temperature fcc (α) and the high-temperature bcc (β) modification. The hcp phase, found in [53SHE/KIN] and [58SCH/KIN], is actually a solid solution of hydrogen in Sr. Peterson and Colburn purified the best commercial Sr (King Laboratories) by distillation at 825 °C in an Ar atmosphere under a pressure of 1.04 kPa. The distillate was sealed in a Ta container and held for 2 days at 800°C under a vacuum. This treatment reduced the amount of hydrogen from 350 ppm to 95 ppm (0.4 moles per cent of SrH_2). The melting point was determined as 1041 K, and the temperature of transformation was determined as 830 K on heating and 813 K on cooling. After correcting the measured values for residual H, the authors recommended 828 K. When the amount of hydrogen in the sample was increased, the temperature of transformation changed reaching 893 K at 14 mole percent of SrH_2. The above temperature-composition coordinates were interpreted as a peritectoid point of formation of an hcp phase from β–Sr and SrH_2. The temperature of its formation is close to that reported by investigators from Syracuse University [53SHE/KIN],[56HIR/KIN], [58SCH/KIN] for the fcc-hcp transformation in "pure" Sr. The transformation at 483 to 503 K, interpreted in [53SHE/KIN], [56HIR/KIN], and [58SCH/KIN] as an hcp–bcc transformation, was also observed in [66PET/COL] at 513 K in specimens containing a significant amount of hydrogen. This result is explained by an eutectoid decomposition of the hcp phase into α–Sr and SrH_2. As a result, Peterson and Colburn established that Sr at ambient pressure has only two modifications. The following investigations confirmed these results.

[75KAT/NIE]

Katerberg *et al*. measured the electrical resistivity and thermal power from room temperature up to about 700 °C. They used a commercial Sr material of 99.5–99.7 wt. % purity. Breaks in the temperature dependences of the properties were registered at T_{trs} = 815 ± 2 K. No other transformation was observed at high temperatures.

[78COO]

Cook measured the electrical resistivity and thermal power from 300 to 850 K. The Sr sample was prepared by two successive distillations and casting in a sealed Ta container in vacuum. The material had a residual resistivity ratio $\rho(273\ K)/\rho(4.2\ K) = 28$. The resistivity measurements showed that conversion was half completed on heating near 820 ± 1 K, and on cooling at 818 ± 1 K. Cook corrected his results for hydrogen content and assumed that H-free Sr should have a transformation at about $T_{trs} = 804$ K. The latter value seems unlikely.

[82STE/ROT]

According to Stephens and Roth, the transformation occurs at 816 ± 4 K. Most of the heat of transformation (85%) appeared between 812 and 819.6 K, and a small portion, about 15%, between 819.6 and 824.9 K. The transformation temperature was selected as the average of the first interval. The enthalpy of α–β transformation

was estimated from the enthalpy measurements to be 837 ± 170 J mol^{-1}.

5.4.2. Fusion of Sr

In earlier investigations the values obtained for the temperature of melting of Sr varied from 1030 to 1050 K depending on the purity of samples and the accuracy of the measurements. The results obtained in more recent investigations, most of which were mentioned above, are closer to each other. The temperature was determined as 1042 ± 2 K [52RIN], 1041 K [56HIR/KIN], 1047 K [58SCH/KIN], and 1041 ± 2 K [66PET/COL]. Additional information on fusion is given below.

[68DWO/BRO]

Dworkin *et al*. prepared pure Sr by vacuum distillation at 900°C under vacuum. The distilled Sr contained 400 ppm of O_2, 200 ppm of N_2, but the amount of H_2 was not analyzed. The melting point was determined as 1042 ± 1 K.

[82STE/ROT]

Stephens and Roth determined this temperature as 1050 ± 10 K from their enthalpy measurements. This determination is considered to have a low accuracy. The enthalpy of fusion was reported in [82STE/ROT] as 7823 ± 230 J mol^{-1}. The data of [82STE/ROT] were treated differently by the authors of [85JAN] who recommended a smaller value 7431 ± 800 J mol^{-1}.

[85ULY]

According to [86SHP/KAG], Ulyanov [85ULY] determined the melting point by thermal analysis as 1040 K and the enthalpy of fusion by pulse calorimetry as 8100 ± 300 J mol^{-1}.

[81GUR]

Gurvich *et al*. estimated the enthalpy of fusion using the entropy of fusion of Ca for comparison and recommended 8200 ± 2000 J mol^{-1}.

5.5. Discussion of Phase Equilibrium Data

5.5.1. α−β Transformation of Sr

The experimental results are given in Table 5–4. The temperature of 820 ± 3 K is adopted from the average of the DTA hysteresis range of [66PET/COL] and from [78COO]. The values of [75KAT/NIE] and [82STE/ROT] are close to that adopted. All temperatures have been converted to ITS-90.

The enthalpy of a similar transformation in Ca is well established as 930 J mol^{-1}. If it is assumed that the entropies of transformations of Ca and Sr are equal, then the enthalpy of transformation of Sr can be roughly estimated as 1000 ± 300 J mol^{-1}. The value 837 ± 230 J mol^{-1} measured in [83STE/ROT] seems to be probable. This value is rounded and adopted as it is the only available (Table 5–5).

5.5.2. Fusion of Sr

The experimental temperatures of fusion are shown in Table 5–6. The melting point is selected as T_{fus} = 1041 K in [73HUL], [81GUR] and [86SHP/KAG]. This value agrees well with [52RIN], [56HIR/KIN], [66PET/COL], [68DWO/BRO], [85ULY] and is recommended. The temperatures are converted to ITS-90.

For the enthalpy of fusion, the rounded average of two experimental values of [82STE/ROT] and [85ULY] is selected (Table 5–7). Its uncertainty is estimated as about ± 400 J mol^{-1}.

5.6. References for Sr

52RIN Rinck, E., C. R. Acad. Sci. **234**, 845–7 (1952); T_{trs}, T_{fus}.

53SHE/KIN Sheldon, E. A. and King, A. J., Acta Cryst. **6**, 100 (1953); T_{trs}, T_{fus}.

56HIR/KIN Hirst, R. G., King, A. J., and Kanda, F. A., J. Phys. Chem. **60**, 302–4 (1956); T_{trs}, T_{fus}.

57GRI/VES Griffel, M., Vest, R. W., and Smith, J. F., J. Chem. Phys. **27**, 1267–9 (1957); C_p°(of Ca, 1.8–4.2 K).

57ROB Roberts, L. M., Proc. Phys. Soc. (London) **B70**, 738–43 (1957); C_p°(1–20 K).

58SCH/KIN Schottmiller, J. C., King, A. J., and Kanda, F. A., J. Phys. Chem. **62**, 1446–9 (1958); T_{trs}, T_{fus}.

66PET/COL Peterson, D. T. and Colburn, R. P., J. Phys. Chem. **70**, 468–71 (1966); T_{trs}, T_{fus}.

68DWO/BRO Dworkin, A. S., Bronstein, H. R., and Bredig, M. A., J. Phys. Chem. **72**, 1892–4 (1968); T_{fus}.

69GME Gmelin, E., Z. Naturforsch. **24**(1), 291–2 (1969); C_p°(of Be, 1–80 K).

73HUL Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., Kelley, K. K., and Wagman, D. D., "Selected Values of the Elements," Amer. Soc. Metals, Metals Park, OH 44703, pp 487–90 (1973); Review.

74AGA/BET Agarwal, K. L. and Betterton, J. O., J. Low Temp. Phys. **17**, 509–13 (1974); C_p°(of Ca, 1–4 K).

75KAT/NIE Katerberg, J., Niemeyer, S., Penning, D., and van Zytveld, J. B., J. Phys. F: Met. Phys. **5**, L74–9 (1975); T_{trs}.

76KHR/PAU Khriplovich, L. M. and Paukov, I. E., Zh. Fiz. Khim. **50**, 567–8 (1976); Engl. trans., Russ. J. Phys. Chem. **50**, 337 (1976); C_p°(5–300 K).

78BOE/WES Boerio, J. and Westrum, E. F., J. Chem. Thermodyn. **10**, 1–7 (1978); C_p°(6.3–346.4 K).

78COO Cook, J. G., J. Less-Common Met. **57**, 53–67 (1978); T_{trs}.

81GUR Gurvich, L. V., Veits, I. V., Medvedev, V. A., *et al*., Glushko, V. P., gen. ed., "Thermodynamic Properties of Individual Substances," Nauka, Moscow, vol. **3**, 341–4; Review.

82STE/ROT Stephens, H. J. and Roth, E. P., Sandia National Laboratories, Albuquerque, NM, personal communication to Dr. M. W. Chase, May 3, 1982; T_{trs}, $\Delta_{trs}H$, T_{fus}, $\Delta_{fus}H$, ΔH(350–1191 K), and C_p°(398–785 K).

85JAN Chase, M. W., Jr., Davis, C. A., Downey, J. R., Jr., and Syverud, A. N., "JANAF Thermochemical Tables," J. Phys. Chem. Ref. Data **14**, Suppl. 1, 1804–8 (1985); Review.

85ULY Ulyanov, S. N., Thesis, Inst. for High Temp., Moscow (1985); T_{fus}, $\Delta_{fus}H$, C_p°(870–1780 K).

86SHP/KAG Shpil'rain, E. E., Kagan, D. N., and Ulyanov, S. N., Reviews on Thermophysical Properties of Substances, No. 3 (59), Inst. for High Temperatures, Moscow (1986); Review.

89DIT Ditmars, D. A., Private Communication to V. Itkin (1989); C_p°(300–800 K).

5.7. Adopted Values

Electronic Contribution to C_p°: $\gamma = 3.64 \pm 0.18$ m J K^{-2} mol^{-1}

Debye Temperature at 0 K: $\Theta_D = 147 \pm 1.2$ K.

Heat Capacity Equations

α-Sr

Temperature range 0–5 K

$C_p^\circ = 0.00364T + 6.119\times10^{-4}T^3$ J K^{-1} mol^{-1}.

Temperature range 5–20 K:

$C_p^\circ = -0.0532 - 8.884\times10^{-2}T + 4.837T^{-2} + 1.658\times10^{-2}T^2$ J K^{-1} mol^{-1}.

Temperature range 20–30 K:

$C_p^\circ = 16.849 - 2.468T + 0.1278T^2 - 1.728\times10^{-3}T^3$ J K^{-1} mol^{-1}.

Temperature range 30–100 K:

$C_p^\circ = 1.445 + 0.5939T - 3.12\times10^{3}T^{-2} - 5.65\times10^{-3}T^2 + 1.951\times10^{-5}T^3$ J K^{-1} mol^{-1}.

Temperature range 100–298.15 K:

$C_p^\circ = 17.609 + 8.795\times10^{-2}T - 3.2605\times10^{-4}T^2 + 4.525\times10^{-7}T^3$ J K^{-1} mol^{-1}.

Temperature range 298.15 to 820 K

$C_p^\circ = 25.029 + 8.744\times10^{-3}T - 0.569\times10^{5}T^{-2} - 2.032\times10^{-6}T^2$ J K^{-1} mol^{-1}.

β-Sr

Temperature range 820–1041 K

$C_p^\circ = 26.526 + 4.022\times10^{-3}T$ J K^{-1} mol^{-1}

Liquid Sr

Temperature range 1041 to 2000 K.

$C_p^\circ = 37$ J K^{-1} mol^{-1}

Values at the Standard Temperature

C_p°(298.15 K) = 26.84 ± 0.1 J K^{-1} mol^{-1}

S°(298.15 K) = 55.00 ± 0.3 J K^{-1} mol^{-1}

H°(298.15 K) − H°(0) = 6558 ± 30 J mol^{-1}.

Phase Equilibrium Data

Temperature of Transformation: T_{trs}/K = 820 ± 3

Enthalpy of Transformation: $\Delta_{trs}H^\circ$/J mol^{-1} = 850 ± 250

Temperature of Fusion: T_{fus}/K = 1041 ± 2

Enthalpy of Fusion: $\Delta_{fus}H^\circ$/J mol^{-1} = 8000 ± 200

5.8. Calculated Thermodynamic Functions of Sr

The thermodynamic functions presented in Tables 5–8 and 5–9 are calculated using the equations presented in the previous section. Values in brackets were calculated by using the equation for the next higher adjacent temperature interval.

5.9. Appendix – Experimental Results of Sr

Tables 5–10 to 5–17 present heat capacity or enthalpy data as they were presented in the original article. As a result, the numeric values listed in this Appendix are the actual experimental values, tabular smoothed values, values calculated from equations, or values extracted from a graph. Where necessary, values have been converted to joules (from calories). In all cases, the table heading indicates the types of data listed.

TABLE 5–1. Heat capacity values of α-Sr at 300–820 K derived in [85JAN] from [82STE/ROT]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
300	26.809	600	29.814
350	27.298	700	30.864
400	27.777	800	31.935
450	28.278	820	32.151
500	28.785		

TABLE 5–2. Comparison of the heat capacity, enthalpy and entropy values for Sr at 298.15 K

Reference	C_p°(298.15 K) J·K^{-1} mol^{-1}	S°(298.15 K) J·K^{-1} mol^{-1}	H°(298.15 K) − H°(0) J·mol^{-1}
73HUL	–	(52.3 ± 2.0)	–
81GUR	26.786	55.70 ± 0.2	6570 ± 20
85JAN	26.791	55.69 ± 0.1	6568
Adopted	26.84 ± 0.1	55.00 ± 0.3	6558 ± 30

TABLE 5–3. Recommended heat capacities of α-Sr at 300–800 K

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
300	26.85	600	29.40
350	27.35	650	29.70
400	27.85	700	30.00
450	28.25	750	30.35
500	28.70	800	30.65
550	29.05		

TABLE 5–4. Temperature of phase transformation of Sr

Reference	T_{trs}, K	Comments
Original Studies		
66PET/COL	828 (heating)	Thermal analysis
	813 (cooling)	Thermal analysis
75KAT/NIE	815	Elec. resist., thermo emf
78COO	819 ± 1	Elec. resist., thermo emf
82STE/ROT	816 ± 4	Enthalpy measurements
Reviews		
73HUL	830	Based on 66PET/COL
81GUR	828 ± 2	Based on 66PET/COL
85JAN	820 ± 8	Based on 66PET/COL, 82STE/ROT
86SHP/KAG	829 ± 2	Based on 66PET/COL, 75KAT/NIE, 78COO
Adopted		
This study	820 ± 3	Based on 66PET/COL, 78COO

TABLE 5–5. Enthalpy of phase transformation of Sr

Reference	$\Delta_{trs}H$, J mol^{-1}	Comments
Original Studies		
82STE/ROT	837 ± 230	Enthalpy measurements
Reviews		
73HUL	(800)	Estimation
81GUR	(750 ± 200)	Estimation
85JAN	837 ± 170	Based on 82STE/ROT
86SHP/KAG	750 ± 200	Based on 81GUR
Adopted		
This Study	850 ± 250	Based on 82STE/ROT

TABLE 5–6. Temperature of fusion of Sr

Reference	T_{fus}, K	Comments
Original Studies		
52RIN	1043 ± 2	Thermal analysis
53SHE/KIN	1044	Thermal analysis
56HIR/KIN	1042	Thermal analysis
58SCH/KIN	1048	Thermal analysis
66PET/COL	1041	Thermal analysis
68DWO/BRO	1042	Thermal analysis
82STE/ROT	1050 ± 10	Enthalpy measurements
85ULY	1040	Thermal analysis
Reviews		
73HUL	1041	
81GUR	1041 ± 2	Based on 52RIN, 53SHE/KIN, 56HIR/KIN, 66PET/COL
85JAN	1050 ± 10	Based on 82STE/ROT
86SHP/KAG	1041 ± 2	Based on 66PET/COL, 85ULY
Adopted		
This study	1041 ± 2	Based on 66PET/COL, 68DWO/BRO, 85ULY

TABLE 5–7. Enthalpy of fusion of Sr

Reference	$\Delta_{fus}H$, J mol^{-1}	Comments
Original Studies		
82STE/ROT	7828 ± 230	Enthalpy measurements
85ULY	8100 ± 300	Heat pulse
Reviews		
73HUL	(8276)	Estimation
81GUR	(8200 ± 2000)	Estimation from Ca.
85JAN	7431 ± 800	Based on 82 STE/ROT
86SHP/KAG	8100 ± 300	Based on 85ULY
Adopted		
This study	8000 ± 400	Based on 82STE/ROT, 85ULY

TABLE 5–8. Thermodynamic functions of Sr below 298.15 K

T/K	$C_p^\circ(T)$ J K^{-1} mol^{-1}	$H^\circ(T)-H^\circ(0)$ J mol^{-1}	$S^\circ(T)$ J K^{-1} mol^{-1}
5	0.0947(0.1106)	0.1411	0.0437
10	0.7648	1.8631	0.2569
15	2.3662	9.3317	0.8408
20	4.8141(4.785)	26.934	1.8368
25	8.024	58.724	3.2420
30	11.173(11.237)	107.024	4.9945
35	13.600	169.371	6.9120
40	15.460	242.191	8.8540
45	16.966	323.382	10.7648
50	18.206	411.411	12.6186
60	20.086	603.451	16.1147
70	21.388	811.220	19.3149
80	22.299	1029.914	22.2338
90	22.969	1256.393	24.9006
100	23.533(23.596)	1488.935	27.3502
120	24.250	1967.629	31.7121
140	24.773	2458.057	35.4911
160	25.188	2957.826	38.8272
180	25.515	3464.979	41.8136
200	25.777	3977.989	44.5159
220	25.995	4495.768	46.9832
240	26.192	5017.659	49.2536
260	26.388	5543.442	51.3577
280	26.606	6073.329	53.3211
298.15	26.841(26.815)	6558.289	54.9992

TABLE 5–9. Thermodynamic functions of Sr above 298.15 K

T/K	$C_p^\circ(T)$ J K^{-1} mol^{-1}	$H^\circ(T)-H^\circ(298.15\text{K})$ J mol^{-1}	$S^\circ(T)$ J K^{-1} mol^{-1}
298.15	26.82	0.00	55.00
300	26.84	49.63	55.17
400	27.85	2786.09	63.03
500	28.67	5612.70	69.34
600	29.39	8515.92	74.63
700	30.04	11487.61	79.21
800	30.63	14521.68	83.26
820.00 (α)	30.75	15135.51	84.02
820.00 (β)	29.82	15985.51	85.05
900	30.15	18384.30	87.84
1000	30.55	21418.99	91.04
1041.00 (β)	30.71	22674.84	92.27
1041.00 (liq)	37.00	30674.84	99.96
1100	37.00	32857.84	102.00
1200	37.00	36557.84	105.22
1400	37.00	43957.84	110.92
1600	37.00	51357.84	115.86
1800	37.00	58757.84	120.22
2000	37.00	66157.84	124.12

TABLE 5–10. SMOOTHED heat capacity values of Sr [57ROB]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
1.5	0.00752	7	0.253
2.0	0.122	8	0.385
2.5	0.0186	9	0.544
3.0	0.0274	10	0.74
3.5	0.0389	12	1.27
4.0	0.0537	14	1.99
4.5	0.072	16	2.81
5.0	0.096	18	3.76
6.0	0.161	20	4.79

TABLE 5–11. SMOOTHED heat capacity values of Sr [76KHR/PAU]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
5	0.962	100	23.33
6	0.180	110	23.86
8	0.402	120	24.364
10	0.770	130	24.79
12	1.365	140	25.18
14	2.159	150	25.53
16	3.100	160	25.83
18	4.100	170	26.12
20	5.146	180	26.40
25	7.904	190	26.70
30	10.44	200	27.03
35	12.66	220	27.64
40	14.69	240	28.21
50	17.41	260	28.77
60	19.41	273.15	28.96
70	20.80	280	29.05
80	21.84	300	29.19
90	22.67		

TABLE 5-12. EXPERIMENTAL heat capacity values of Sr [78BOE/WES]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
Series I		Series IV	
50.09	18.677*	10.81	1.222
53.20	18.895	12.06	1.602
58.55	18.836	13.38	2.113
64.55	20.761	14.79	2.820
71.77	21.686*	16.38	3.586
79.55	22.246	18.07	4.548
88.47	22.945	19.92	5.636
99.16	23.460	22.01	6.845
110.68	23.916	24.32	8.226
Series II		26.85	9.619
112.25	23.991	29.60	11.046
122.73	24.376	32.66	12.539
132.88	24.644	35.96	13.954
143.18	24.916	39.52	15.297
153.68	25.117	43.64	16.598
164.00	25.271	48.31	17.845
174.35	25.439	52.47	18.753
184.77	25.547	57.20	19.610
Series III		63.61	20.610
182.13	25.799*	70.74	21.397
192.14	25.652	Series V	
202.36	25.740	106.90	23.761
212.48	25.853	117.40	24.142
222.52	26.041	127.77	24.493
232.49	26.137	128.10	24.761
253.01	26.393	148.33	24.999
263.58	26.522	158.50	25.171
274.09	26.627	168.67	25.380
284.68	26.719	178.86	25.460
295.33	26.865*	189.12	25.564
305.75	26.845	199.43	25.648
316.13	26.882	209.61	25.778
326.58	27.096*	219.84	25.966
337.03	27.217*	230.12	26.016
346.42	27.188*	240.43	26.213
Series IV		250.76	26.309
6.28	0.280	261.02	26.435
6.82	0.347	271.22	26.585
7.65	0.460	281.52	26.694
8.61	0.619	291.91	26.761
9.67	0.849	302.28	26.794
		312.61	26.878
		322.91	26.916
		333.19	26.974
		343.42	27.054

* The values excluded from fitting to equations.

TABLE 5-13. SMOOTHED heat capacity values of Sr [78BOE/WES]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
5	0.172	170	25.355
10	0.954	180	25.493
15	2.895	190	25.610
20	5.669	200	25.719
25	8.615	210	25.828
30	11.276	220	25.937
35	13.535	230	26.058
40	15.422	240	26.192
45	16.970	250	26.330
50	18.234	260	26.468
60	20.100	270	26.585
70	21.359	273.15	26.619
80	22.259	280	26.681
90	22.941	290	26.748
100	23.481	298.15	26.786
110	23.916	300	26.794
120	24.275	310	26.845
130	24.573	320	26.907
140	24.815	330	26.978
150	25.025	340	27.024
160	25.200	350	27.033

TABLE 5–14. EXPERIMENTAL enthalpy values $[H°(T)-H°(273\ K)]$ of Sr; measured by drop calorimetry (DC) [82STE/ROT]

T/K	ΔH J mol^{-1}	C_p J K^{-1} mol^{-1}	T/K	ΔH J mol^{-1} J K^{-1}	C_p mol^{-1}
Solid–Sr			801.7	14899	(29.16)
350.1	1360	(25.44)	812.0	14987	(30.78)
350.6	1301	(27.18)	819.6	16058	
449.9	4217	(27.69)	824.9	16343	
451.3	4234	(27.69)	835.6	16828	
500.6	5728	(28.27)	902.4	18811	
550.6	7259	(28.42)	946.3	19748	
551.0	7109	(28.42)	990.5	21167	
600.7	8657	(28.60)	1027.9	23259	
650.4	10096	(28.67)	1035.1	23280	
650.5	10109	(28.67)	1048.8	25016	
697.0	11364	(28.41)	Liquid Sr		
701.6	11435	(28.41)	1059.1	31045	
750.3	13167	(29.11)	1130.5	33493	
			1191.4	36330	

TABLE 5–15. EXPERIMENTAL heat capacity values of Sr; Measured by a differential scanning calorimeter (DSC) [82STE/ROT]

T/K	$C_p°$, J K^{-1} mol^{-1}	T/K	$C_p°$, J K^{-1} mol^{-1}
298.1	26.57	650	30.96
350	27.11	700	31.30
400	28.03	750	31.92
450	28.15	785	33.01
500	29.33	1050	39.3
550	29.58	1130	39.3
600	30.29	1200	39.3

TABLE 5–16. EXPERIMENTAL heat capacity values of Sr [85ULY]

T/K	$C_p°$, J K^{-1} mol^{-1}	T/K	$C_p°$, J K^{-1} mol^{-1}	T/K	$C_p°$, J K^{-1} mol^{-1}
867.5	39.05	961.6	41.70	1361.9	36.80
877.5	39.27	971.6	41.92	1371.9	36.77
887.5	39.48	981.6	42.13	1478.4	36.71
902.7	40.63	1137.4	37.81	1488.4	36.88
912.7	40.85	1147.4	37.78	1537.6	37.13
922.7	41.06	1157.4	37.75	1547.6	37.11
939.2	40.62	1194.8	38.32	1656.3	35.66
949.2	40.83	1204.8	38.29	1666.3	35.64
959.2	41.05	1214.8	38.27	1771.8	36.62
1781.8	36.60				

TABLE 5-17. CALCULATED heat capacity values of Sr [89DIT]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
300	26.8	600	29.1
350	27.5	650	29.2
400	27.9	700	29.5
450	28.4	750	31.3
500	28.6	800	34.3
550	28.9		

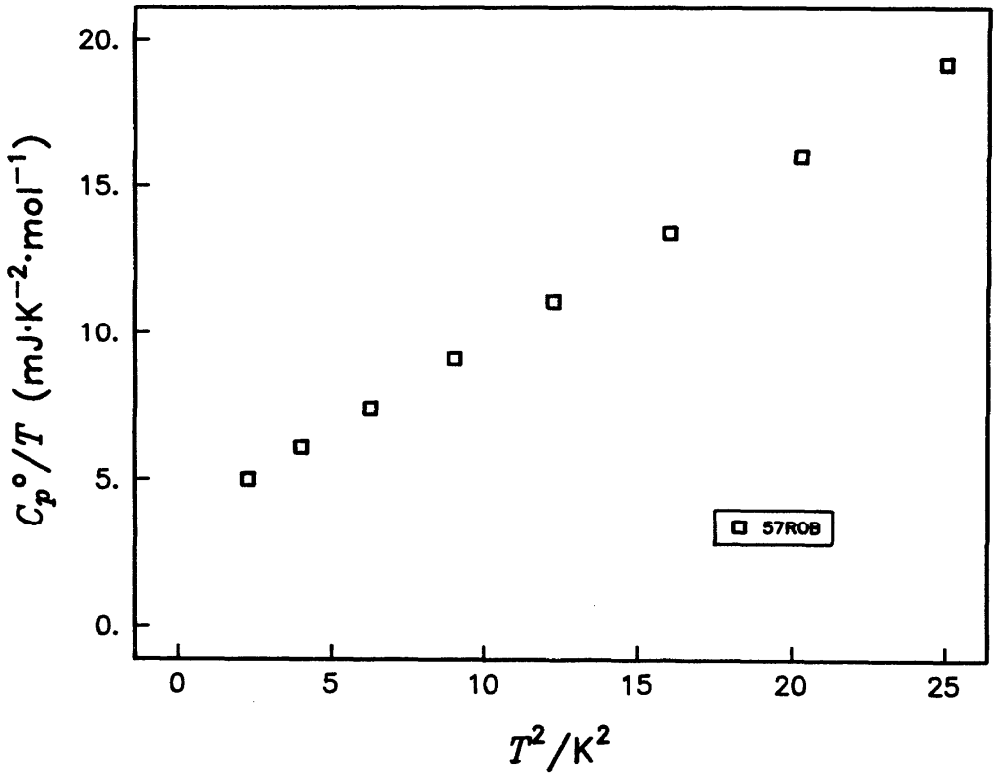

FIG. 5-1. C_p°/T versus T^2 for Sr below 5 K.

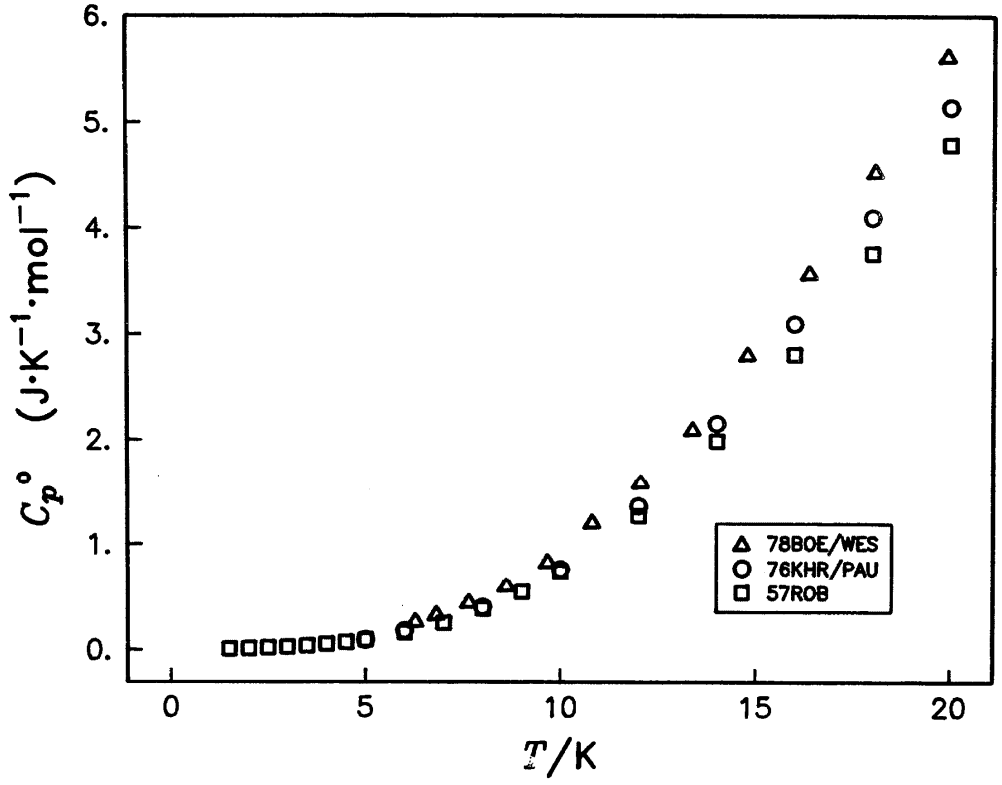

FIG. 5–2. Heat Capacity of Sr below 20 K.

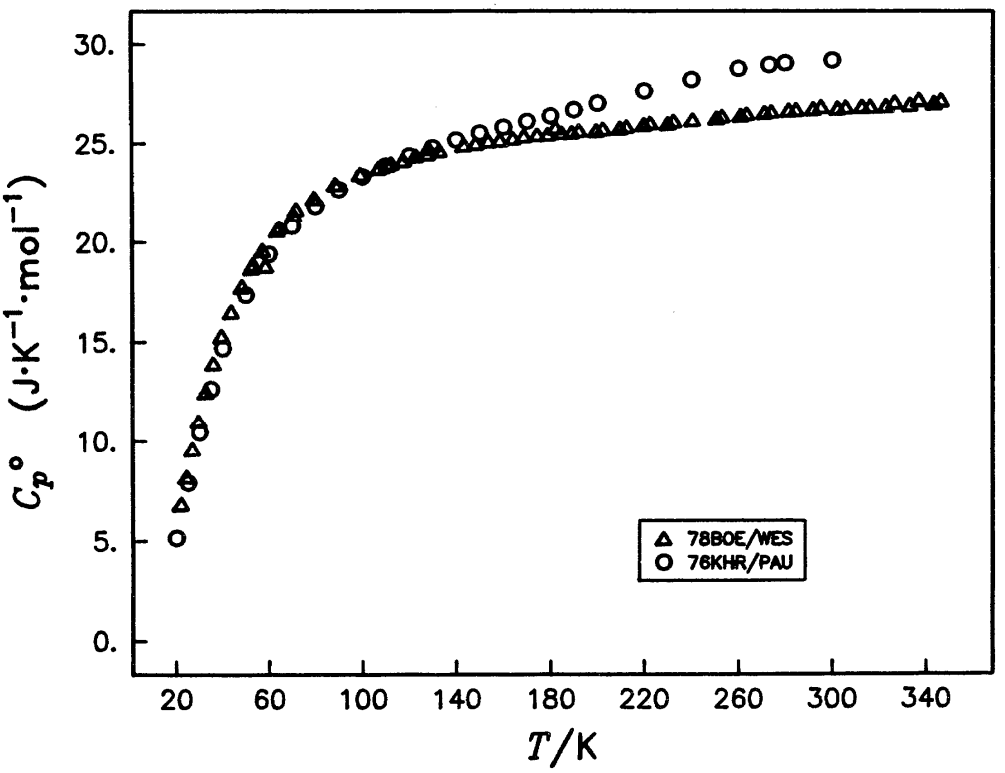

FIG. 5–3. Heat Capacity of Sr at 20–355 K.

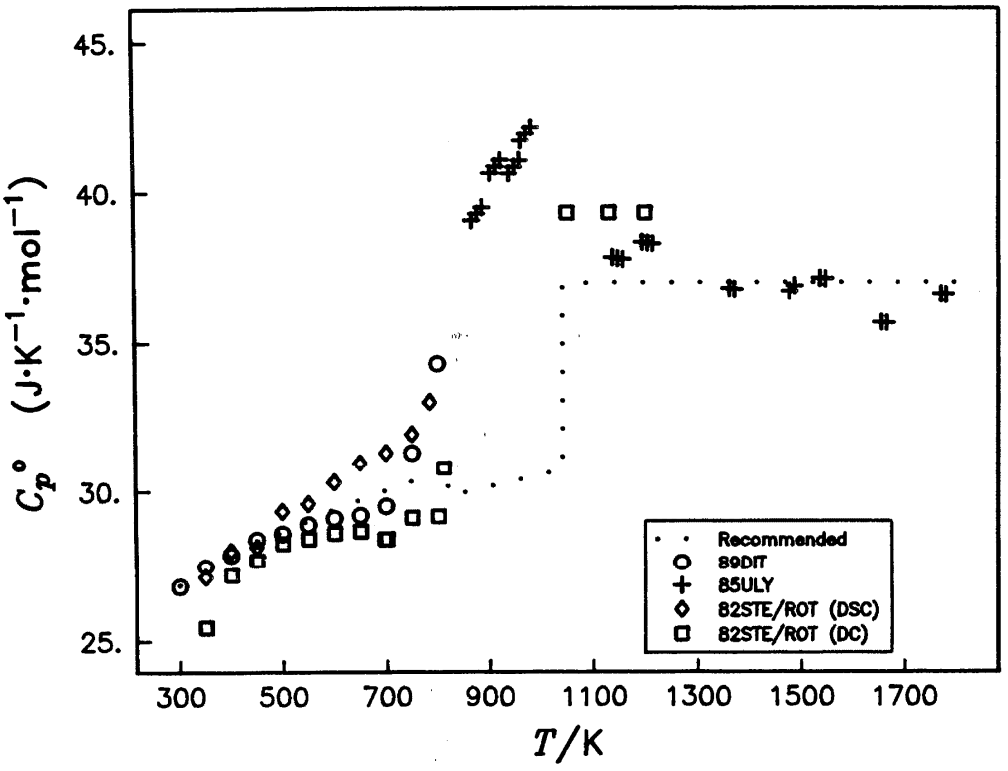

FIG. 5–4. Heat Capacity of Sr at 300–1800 K.

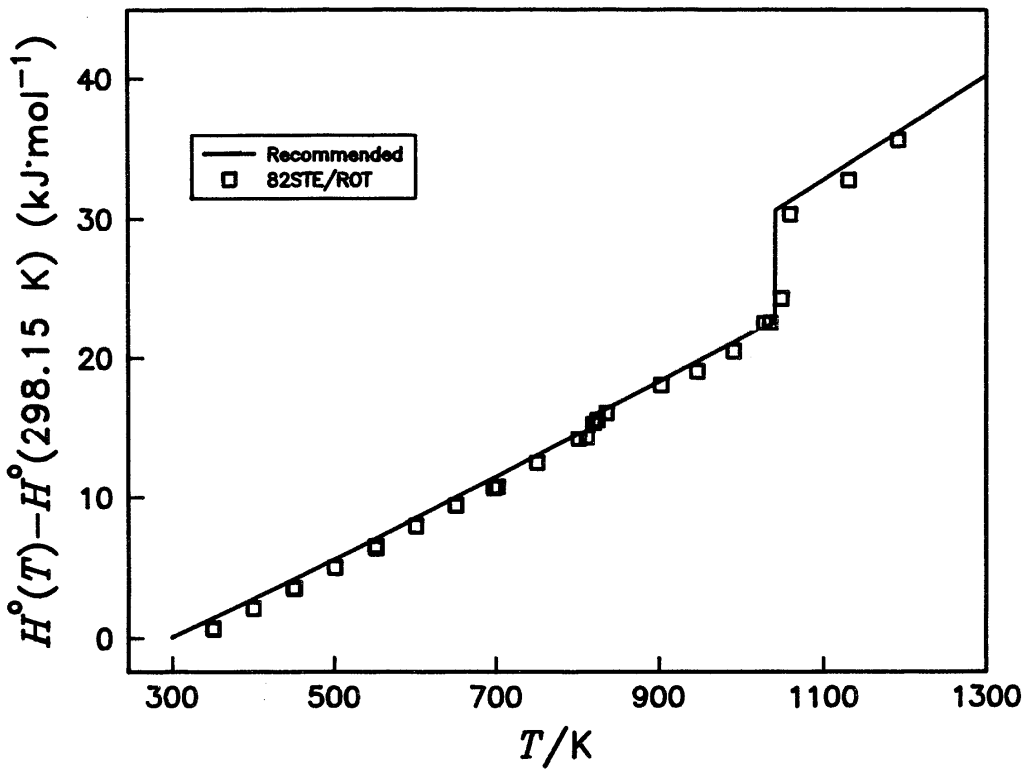

FIG. 5–5. $H°(T)-H°(298.15\ K)$ for solid and liquid Sr.

6. Barium

6.1. Introduction

At ambient pressure, barium has only one stable crystalline modification, bcc, and this was established accurately in the fifties. Nevertheless, the possibility of the existence of other Ba modifications was discussed in the seventies. Oxygen and hydrogen can easily contaminate Ba samples and generate significant thermal effects during enthalpy and heat capacity measurements at elevated temperatures, making all data above room temperature unreliable at the present time. All available sources can be rated as poor, and the uncertainty in the reported values usually exceeds 15%. The recommendations made in this assessment must still be considered as tentative. The melting point and enthalpy of fusion are better known, since several studies yield close results. The heat capacity data below 298 K are satisfactory, except that there is a higher uncertainty below 15 K. Only one study [57ROB] was performed down to 1.5 K, and the derived Θ_D and γ need confirmation.

6.2. Heat Capacity and Enthalpy Measurements

6.2.1. Temperature below 298.15 K

[57ROB]

Roberts measured the heat capacity from 1.5 to 20 K in a low-temperature Nernst adiabatic calorimeter. The commercial sample of Ba had about 0.3 wt. % metallic impurities. The amount of non-metallic impurities was not analyzed by Roberts but this could have been substantial. Roberts presented her results in a graphical form from 1.5 to 4 K (35 points). The 10 points between 2.4 and 3.0 K were described by the equation:

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = \gamma T + 1943(T/\Theta_D)^3,$$

where $\Theta_D = 110.5 \pm 1.8$ K, and $\gamma = 0.0027 \pm 0.0005$ J $K^{-2}mol^{-1}$. Roberts did not report experimental values above 4 K and gave only a table of smoothed heat capacity values from 1.5 to 20 K, shown in Figs. 6–1 and 6–2 and listed in the Table 6-8. Roberts made the only study which extended as low as 1.5 K. However, values of good accuracy for Θ_D and γ can be derived from these heat capacity data.

[70FUR/ISH]

Furukawa and Ishihara measured the heat capacity of Ba in an adiabatic calorimeter from 18 to 370 K. The commercial samples of Ba contained about 0.8 wt. % metallic impurities (mostly Sr) and 0.36 wt. % of oxygen which was assumed to be present in the form of BaO. Corrections were made to the measured values to allow for the presence of BaO. The measured values were energy increments (ΔQ) and the associated thermometer resistances. The 94 experimental points were fitted to a polynomial. The authors reported these smoothed values. However, they did show a graph of deviations of the individual measured points from the calculated values; the deviations did not exceed 0.025%. They combined their values with those of [57ROB] and listed a table of smoothed heat capacities between 0 and 375 K at 5 K steps, as shown partially in Figs. 6-1, 6–2, 6-3 and 6–4 and listed in the Table 6-13. Furukawa and Ishihara noticed an anomaly (i.e., a λ-type transition) in the region 44 to 66 K which corresponds to an absorption of about 4 J mol^{-1}. This anomaly was not confirmed in a subsequent study [76RAK/FRO]. The study by Furukawa and Ishihara is rather accurate except for the anomaly at about 57 K and the deviation upward at temperatures above 300 K. The following values were calculated at 298.15 K:

$C_p^\circ(298.15\text{ K}) = 28.089\text{ J K}^{-1}\text{ mol}^{-1}$
$S^\circ(298.15\text{ K}) = 62.476\text{ J K}^{-1}\text{ mol}^{-1}$
$H^\circ(298.15\text{ K}) - H^\circ(0) = 6912.1\text{ J mol}^{-1}$.

[76RAK/FRO]

Rakhmenkulov *et al.* measured the heat capacity in an adiabatic vacuum calorimeter from 12 to 300 K. The amount of metallic impurities was 0.14 wt. % and oxygen 0.06 wt. %. It is possible that the amount of oxygen was underestimated. The authors did not list their measured values, only smoothed ones. The complete paper was deposited in the All-Union Institute of Scientific and Technical Information, USSR (VINITI, No. 735–76, March 1976) and was not available for this review. Therefore, only smoothed values are reproduced in the Table 6-14 and in Figs. 6-1, 6–2 and 6–3. Below 100 K the heat capacity values of [70FUR/ISH] and [76RAK/FRO] are very close. Above 100 K the values of [76RAK/FRO] are higher than those of [70FUR/ISH]; the difference increases with temperature exceeding 2% at 300 K. Above 100 K the values reported by [76RAK/FRO] are assumed less accurate than those of [70FUR/ISH]. The authors of [76RAK/FRO] calculated the values at 298.15 K:

$C_p^\circ(298.15\text{ K}) = 28.723\text{ J K}^{-1}\text{ mol}^{-1}$
$S^\circ(298.15\text{ K}) = 62.55 \pm 0.2\text{ J K}^{-1}\text{ mol}^{-1}$
$H^\circ(298.15\text{ K}) - H^\circ(0) = 6970 \pm 10\text{ J mol}^{-1}$.

The latter two values are slighly larger than those of [70FUR/ISH].

6.2.2. Temperatures above 298.15 K

[46JAU]

Jauch measured the enthalpy by drop calorimetry from 718 to 1133 K. The Ba sample contained about 0.5 wt. % metallic impurities, while the amount of non-metallic impurities was unknown. Judging by the temperature of fusion determined by Jauch [46JAU], $T_{fus}/K = 950$, the amount of impurities was much greater than 0.5%. Errors were made during the measurements, calibration and calculations; however, some errors probably cancel each other. The same problems existed in his study of calcium.

No attempt to correct the original data of Jauch was made. These data are shown in Figs. 6–5 and 6–6 and are listed in Tables 6–6 and 6–7. The heat capacities of solid Ba are among the highest measured values for this element. The values for the heat capacity of liquid Ba, 53–55 J K^{-1} mol^{-1}, also seem to be too high. However, Jauch obtained a reasonable enthalpy of fusion, 7660 ± 300 J mol^{-1}.

[69SHP/KAG]

Shpil'rain and Kagan measured the enthalpy of Ba with a drop calorimeter based on the evaporation of water (Fig. 6–6 and Table 6–9). The purity of sample was about 99.9 wt. %. The heat capacity derived from these measurements changes monotonically. The authors assumed the existence of two allotropic modifications in Ba with a transformation temperature of 648 K and enthalpy of transformation of 860 J mol^{-1}. They fitted their data to two equations:

"α–Ba" (373–648 K)

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = -4.24 + 78.64\times10^{-3}T,$$

"β–Ba" (648–998 K)

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = 8.86 + 40.16\times10^{-3}T.$$

The heat capacity values calculated by these equations are listed in the Table 6–10. It is established currently that Ba has only one modification. The uneven change of heat capacity values with temperature indicates some chemical reaction processes during measurement. These processes probably originate from impurities in the samples, and distort substantially the temperature dependence of the enthalpy and heat capacity. For liquid Ba (998–1300 K) a constant heat capacity value of C_p° = 40.11 J K^{-1} mol^{-1} was obtained. These data are of poor quality. Shpil'rain *et al.* also determined the enthalpy of fusion of Ba as 7760 ± 170 J mol^{-1}.

[70DIT/DOU]

Ditmars and Douglas measured the enthalpy of Ba in a Bunsen ice calorimeter from 323 to 1173 K. The material used was the same as described in [70FUR/ISH], i.e., it contained a substantial amount of oxygen, 0.36 wt. %. Some processes occurred during measurements which disturbed the monotonic behavior of the enthalpy and heat capacity with increasing temperature. Between room temperature and the fusion temperature, 991 K, three temperature regions were outlined, three modifications of Ba were assumed, and the 21 experimental enthalpy points given in the Table 6–11 and, as shown in Fig. 6–6, were fitted to 3 polynomials:

"α–Ba" (below 582.5 K)

$$C_p^\circ/\text{J K}^{-1}\,\text{mol}^{-1} = -46.26 + 160.44\times10^{-3}T + 2.46\times10^{6}T^{-2},$$

"β–Ba" (582.5–766 K)

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = -16.60 + 84.24\times10^{-3}T,$$

"γ–Ba" (768 991 K)

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = 39.06.$$

The source of such unusual behavior can be due to the presence of oxygen and other non-metallic impurities which might lead to the formation, precipitation and dissolution of various phases at different temperatures. Calculated heat capacity values are shown in Figs. 6–4 and 6–5 and listed in the Table 6–12.

For liquid Ba six data points from 1003 to 1173 K were fitted to the following equation:

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = 55.68 - 12.35\times10^{-3}T.$$

The results of Ditmars and Douglas are of poor quality; however, for solid barium, they succeeded in obtaining an acceptable value for the enthalpy of fusion, 7,975 ± 400 J mol^{-1}, at T_{fus}/K = 991.

[77SHP/FOM], [80SHP/KAG]

Shpil'rain *et al.* measured the heat capacity of solid and liquid Ba by a pulse calorimetric technique. The material used was the same as in [69SHP/KAG]. The results are given in a small graph. Numerical information about this study was given in [86SHP/KAG]. The measurements (90 points) were made from 745 to 1840 K. The results obtained are shown in Figs. 6–4 and 6–5 and listed in the Table 6–15. The experimental heat capacity values were represented by two equations:

solid Ba (745 – 870 K)

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = -22.43 + 77.63\times10^{-3}T,$$

liquid Ba (1012 – 1840 K)

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = 45.14 - 4.31\times10^{-3}\text{T}.$$

The pulse-differential method was used for heat capacity measurements of several elements in the alkaline earth family [86SHP/KAG]. In the case of β–Ca, Mg, β–Sr the results obtained by this method are different from all other investigations (high for β–Sr and β–Ca and low for Mg), and they are assumed to be wrong. This fact discredited the accuracy of pulse-calorimetric measurements, even in those cases when the method may have given reasonable values, for example, for liquid metals and for solid Ba. The results of pulse calorimetry require independent confirmation by other calorimetric methods. The data obtained by this method should be used only with caution.

[89DIT]

Ditmars measured the enthalpy of Ba in the Bunsen ice calorimeter. The sample was prepared in the Ames Laboratory of Iowa State University. The true heat capacities, derived from these measurements, were taken from a graph with an accuracy about 1%. They are reproduced in Fig. 6–4 and listed in the Table 6–16. The maximum in the heat capacity values near 600 K (Fig. 6–4) shows that undesirable processes occurred in the samples due to impurities. Some amount of impurities might have been present in the material sent from the Ames Laboratory, while additional amounts could have been acquired during handling procedure and heating in a container. The

measuring technique appears to be excellent. However, these data cannot be considered as reliable because of impurity effects, which evidently occurred in the samples.

6.3. Discussion of Heat Capacity and Enthalpy Data

6.3.1. Ba below 298.15 K

For temperatures below 4 K the heat capacity data of Roberts [57ROB] are the only source of experimental information available. Using the data between 1.5 and 4 K, heat capacity values are derived from the equation which can be used from 0 to 4 K:

$$C_p^\circ / \text{J K}^{-1}\text{ mol}^{-1} = 2.70\times10^{-3}T + 1.44\times10^{-3}T^3. \quad (6\text{–}1)$$

As given by Roberts [57ROB], this equation corresponds to $\Theta_D = 110.5 \pm 1.8$ K and $\gamma = 0.0027 \pm 0.0005$ J K^{-2} mol^{-1}. Hultgren and co-workers [73HUL] selected $\gamma = 0.0026 \pm 0.0004$ J K^{-2} mol^{-1}.

From 4 to 20 K, Fig. 6–2 shows three sets of data [57ROB], [70FUR/ISH], and [76RAK/FRO]. The data of [70FUR/ISH] and [76RAK/FRO] are close to each other, while the heat capacity values of [57ROB] are essentially smaller. However, above 100 K, the data of [70FUR/ISH] seem to be more reliable, and were therefore also preferred below 100 K. The authors of [70FUR/ISH] combined their data above 20 K with the data of [57ROB] below 10 K. The heat capacities were taken from a smooth curve given in [70FUR/ISH] as 3.08, 4.52, 6.08, 7.70 and 9.25 J K^{-1}mol^{-1} at 12, 14, 16, 18 and 20 K, respectively. These values together with the heat capacities of [57ROB] from 5 to 10 K were fitted to the equation, which is valid for the interval 4 – 20 K:

$$C_p^\circ / \text{J K}^{-1}\text{ mol}^{-1} = 3.018 - 0.909T - 12.212T^{-2} + 0.1004T^2 - 1.96\times10^{-3}T^3. \quad (6\text{–}2)$$

Between 20 and 80 K the data of [70FUR/ISH] were fitted to the equation

$$C_p^\circ / \text{J K}^{-1}\text{ mol}^{-1} = -1.988 + 0.9022T - 1.061\times10^{3}T^{-2} - 0.01142T^2 + 5.171\times10^{-5}T^3. \quad (6\text{–}3)$$

Above 100 K the data of [76RAK/FRO] are higher than those of [70FUR/ISH]. The difference increases with temperature and exceeds 2% at 300 K. The chemical analysis was carefully performed in [70FUR/ISH], and corresponding corrections were made to compensate for the presence of BaO. There is doubt that the authors of [76RAK/FRO] analyzed their Ba sample with similar care. If the amount of oxygen in the sample of [76RAK/FRO] is greater than was reported, then the apparent heat capacity of Ba will be higher than its real value. A similar situation exists in the Sr measurements of [76KHR/PAU]. See Sec. 5.2.1. and 5.3.1. for details. [78BOE/WES] assumed that the amount of oxygen in the Sr sample of [76KHR/PAU] was underestimated. Above 100 K the heat capacities reported in [76RAK/FRO] are greater than those of [70FUR/ISH]; it is very probable that the amount of oxygen in the Ba specimen was also underestimated in [76RAK/FRO]. The difference between [70FUR/ISH] and [76RAK/FRO] is relatively small. However, there is another reason to prefer the data of [70FUR/ISH] solely – they are more consistent with what are considered to be reasonable heat capacity values above 298.15 K. For the temperature range from 80 to 300 K the data of [70FUR/ISH] were used to derive the equation:

$$C_p^\circ / \text{J K}^{-1}\text{ mol}^{-1} = 23.231 + 0.02569T - 9.324\times10^{3}T^{-2} - 7.327\times10^{-5}T^2 + 1.448\times10^{-7}T^3. \quad (6\text{–}4)$$

$C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$ and $S^\circ(T)$ values calculated by Eqs. 6–1 to 6–4 are given in the Table 6–4. The following values were calculated at 298.15 K:

$$C_p^\circ(298.15\text{ K}) = 28.110\text{ J K}^{-1}\text{ mol}^{-1}$$
$$S^\circ(298.15\text{ K}) = 62.352\text{ J K}^{-1}\text{ mol}^{-1}$$
$$H^\circ(298.15\text{ K}) - H^\circ(0) = 6907.0\text{ J mol}^{-1}.$$

These values can be compared with those given in major reviews, as shown in Table 6–1.

The standard entropy and the value $H^\circ(298.15\text{ K}) - H^\circ(0)$ adopted here are very close to those selected in major reviews because they are based mostly on the same heat capacity study [70FUR/ISH]. A small decrease in $S^\circ(298.15\text{ K})$ in this calculation was caused by different equations for the description of data [70FUR/ISH] and by neglecting the erroneous heat effect near 57 K.

6.3.2. Ba above 298.15 K

Figures 6–4, 6–5, and 6–6 show high-temperature enthalpy and heat capacity data measured in [46JAU], [69SHP/KAG], [70DIT/DOU], [80SHP/KAG], [89DIT]. All measured values are of poor quality and very unreliable. Reviews [73HUL] and [85JAN] are based on poor data of [70DIT/DOU]. [81GUR] combined the data of [70DIT/DOU] and [69SHP/KAG] and expressed the heat capacity by the equation

$$C_p^\circ / \text{J K}^{-1}\text{ mol}^{-1} = 42.888 + 3.665\times10^{-3}T - 14.117\times10^{5}T^{-2}.$$

The authors of the review [86SHP/KAG] considered their own (here considered to be unreliable) data [80SHP/KAG] as the best and entered these data with a statistical weight of two, while the other two studies [69SHP/KAG] and [70DIT/DOU] were entered with a weight of one. In addition, a small correction term was introduced to satisfy the condition $H^\circ(1000\text{ K}) - H^\circ(0\text{ K}) = 34470$ J mol^{-1}. This treatment was also described in review [86SHP/KAG]. The heat capacity values were expressed for solid Ba (298–1000 K) as

$$C_p^\circ / \text{J K}^{-1}\text{ mol}^{-1} = 27.863 + 20.239\times10^{-3}T - 0.516\times10^{6}T^{-2}.$$

All of the above suggestions seem to be wrong because a combination of poor data cannot produce a satisfactory estimate. Observing the values shown in Fig. 6–4, it is evident that the points of [46JAU] and [80SHP/KAG] are close at 700–850K while all other data are scattered. A possible solution is to draw a smooth line from the low-temperature measurements of [70FUR/ISH] to the region where the data of [46JAU] and [80SHP/KAG] intersect. However, the heat capacity values of solid Ba will then exceed 45 J K^{-1} mol^{-1} near the melting point. Such high heat capacity values have no reasonable explanation except for errors in the measurements of [46JAU] and [80SHP/KAG]. It should be mentioned that Ditmars [89DIT] recently obtained heat capacity values which are much smaller than any obtained before. It is obvious from the data of Ditmars in Fig. 6–4 that certain processes occurred during measurements which distorted considerably the dependence of heat capacity upon temperature. Nevertheless, the low values of Ditmars could be used as a guide to the magnitude of possible heat capacity values.

A reasonable solution is proposed here. A heat capacity curve for Ba can be drawn in Fig. 6–4 as a straight line from the data of [70FUR/ISH] at 300 K to the value of 40 J K^{-1} mol^{-1} at 1000 K, and that latter value was adopted as the probable heat capacity for liquid Ba (see below). The equation for the range from 298 to 1000 K is

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = 23.059 + 16.941\times10^{-3}\text{T}. \quad (6\text{–}5)$$

6.3.3. Liquid Ba

Several sets of measured points are shown in Figs. 6–5 and 6–6. Jauch [46JAU] measured the enthalpy of liquid Ba between the melting point and 1133 K. The enthalpy values obtained corresponded to a high heat capacity of about 55 J K^{-1} mol^{-1}. Three studies [69SHP/KAG], [70DIT/DOU], [80SHP/KAG] agree rather well and show heat capacity values of about 40 J K^{-1} mol^{-1}. Study [60SHP/KAG] found that the heat capacity is constant while other studies [70DIT/DOU] and [80SHP/KAG] considered the heat capacity to be decreasing with temperature.

A constant heat capacity value for the liquid is provisionally selected.

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = 40 \pm 2. \quad (6\text{–}6)$$

A constant heat capacity for liquid barium was also selected in [73HUL] as 40.58 J K^{-1} mol^{-1} and in [85JAN] as 39.066 J K^{-1} mol^{-1}, while temperature-dependent functions were adopted in [81GUR] for 1000–3000 K

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = 45.105 - 4.309\times10^{-3}T,$$

and in [86SHP/KAG] for 1000–2300K

$$C_p^\circ / \text{J K}^{-1}\,\text{mol}^{-1} = 48.610 - 8.272\times10^{-3}T + 1.122\times10^{-6}T^2.$$

The values of $C_p^\circ(T)$, $S^\circ(T)$ and $H^\circ(T) - H^\circ(298.15\ \text{K})$ were calculated by Eqs. 6–5 and 6–6 and given in the Table 6–5.

6.4. Phase Equilibrium Data

It is currently well established that at ambient pressure, solid Ba has only one allotropic modification. However, this was not always clear. For example, [32RIN] observed two modifications.

The temperature of fusion for Ba was determined by thermal analysis in several studies concerned mostly with binary systems. The melting point was considered as an indicator of the purity of Ba.

[32RIN]

Rinck measured resistivity and thermal power and used thermal analysis up to the melting point. Thermal analysis registered only melting at 983 K. The enthalpy of fusion was roughly estimated from the cooling curves as 3450 J mol^{-1}. A slight change in cooling curves was observed at about 640 K. The resistivity and thermal power measurements showed a distinct break at about 640 to 655 K. Rinck assumed the existence of two modifications in Ba with the transformation point at 648 K.

[49SHE]

Sheldon studied Ba by high-temperature x-ray and thermal analysis. He found that Ba had a single bcc phase from room temperature to the melting point; 997 K on heating and 985 K on cooling. The transformations observed in solid Ba by [32RIN] and other investigators were probably caused by impurities. These transformations have been reported from time to time; for example, Shpil'rain *et al.* [69SHP/KAG] found a transformation during enthalpy measurements at 648 K and Ditmars and Douglas [70DIT/DOU] found two transformations at 582.5 and 768 K. However, in sufficiently pure Ba at ambient pressure no transformation was observed.

[56HIR/KIN]

Hirst *et al.* studied the Ba–Sr system and used commercial barium (King Laboratories) with 99.3 wt. % Ba (major impurity – 0.4 wt. % Sr). The melting point was 987 K.

[58KEL/KAN]

Keller *et al.* studied the Ba–Li system and used commercial Sr-free Ba from King Laboratories which was additionally refined by fractional distillation at 850 °C in vacuum. A major impurity was 0.1 wt. % of Ca; the melting point was 998 ± 1 K.

[59PET/HIN], [60PET/IND]

Peterson and Hinkebein [59PET/HIN] studied the Ba–$BaCl_2$ system and Peterson and Indig [60PET/IND] – the Ba–BaH_2 system. In both studies the authors used Ba of the same quality. Ba was purified by double distillation under pressure of 1.3 kPa Ar. Impurities were 23 ppm Fe,

80 ppm Mn, 73 ppm N and 35 ppm C. The melting point was 1002 K and the thermal arrest was flat.

[60MIL/KOM]

Miller *et al.* used commercially distilled Ba from King Laboratories with 0.4 wt. % of Sr. The sample was held 48 hours in vacuum at 950 °C. The melting point was determined several times until three successive thermal analysis readings agreed within ± 0.5 K. The final value was 999.4 ± 0.5 K.

[65KAN/STE]

Kanda *et al.* studied the Ba–Na system and used the best King Laboratory Ba which contained about 0.1 wt. % metallic impurities. The material was distilled, remelted and cast in vacuum. The melting point 1002 ± 1 K was obtained as an essentially flat plateau on a cooling curve.

[68DWO/BRO]

Dworkin *et al.* studied the Ba–$BaBr_2$ system. Ba was purified by distillation at 900°C under dynamic vacuum for 24 hours. The distilled Ba still contained 600 ppm oxygen, 200 ppm nitrogen and 300 ppm hydrogen. The melting point was determined as 998 ± 1 K.

[71DWO/BRE]

Dworkin and Bredig studied the Ba–BaF_2 system. They purified Ba in a similar manner to [68DWO/BRO] and collected a condensate on a stainless steel cold finger. The melting point was determined as 1004 K.

[84SHP/KAG1]

Shpil'rain *et al.* used a commercial Ba with about 500 ppm each of chlorides and alkali metals, 250 ppm unsoluble residue, 50 ppm each of Fe, Ca, Cr and Si and 10 ppm Cd. A great deal of attention was paid to the method of measurements and the maintenance of a small temperature gradient in the sample during the experiment. The average temperature of fusion was 996.0 ± 0.2 K and crystallization 993.4 ± 0.4 K. The melting point of the sample was selected as 995 ± 1 K. The authors of [84SHP/KAG1] introduced corrections for impurities using phase diagrams and recommended for the melting point of Ba 1000 ± 5 K. The sample of [84SHP/KAG1] contained excessive amounts of impurities and had a low melting point. The corrections cannot be very accurate because the phase diagram boundaries are not known with reasonable certainty.

[85ULY]

Ulyanov (quoted from [86SHP/KAG]) determined the enthalpy of fusion by pulse calorimetry as 8000 ± 400 J mol^{-1}.

6.5. Discussion of Phase Equilibrium Data

Table 6–2 shows the experimental values for the temperature of fusion. The adopted temperature of fusion, T_{fus}/K = 1000 ± 3, was previously selected in reviews [81GUR], [85JAN], and [84SHP/KAG2]. The value is based on average of studies performed since 1958 and listed above. All experimentally reported values for T_{fus} have been converted to ITS–90.

The experimental values of the enthalpy of fusion, shown in Table 6–3, are very close to each other despite the use of different methods and the purities of materials. None of the above studies can be preferred because of the use of either impure materials or an inaccurate technique. Therefore, the rounded average value 7850 ± 400 J mol^{-1} appears a reasonable choice. It differs from the values selected in [81GUR], but is close to [73HUL], [84SHP/KAG2] and [85JAN].

6.6. References for Ba

32RIN Rinck, E., Ann. Chim. (France) **18**, 510–31 (1932); T_{fus}, $\Delta_{fus}H$.

46JAU Jauch, R., Thesis, Techn. Hochsch. Stuttgart (1946); T_{fus}, $\Delta_{fus}H$, ΔH(718–1133 K).

49SHE Sheldon, E. A., Thesis, Syracuse Univ. (1949); T_{fus}.

56HIR/KIN Hirst, R. G., King, A. J., and Kanda, F. A., J. Phys. Chem. **60**, 302–4 (1956); T_{fus}.

57ROB Roberts, L. M., Proc. Phys. Soc. (London) **B70**, 738–43 (1957); C_p^o(1–20 K).

58KEL/KAN Keller, D. V., Jr., Kanda, F. A., and King, A. J., J. Phys. Chem. **62**, 732–3 (1958); T_{fus}.

59PET/HIN Peterson, D. T. and Hinkebein, J. A., J. Phys. Chem. **63**, 1360–3 (1959); T_{fus}.

60MIL/KOM Miller, E., Komarek, K., and Cadoff, I., Trans. Met. Soc. AIME **218**, 978–80 (1960); T_{fus}.

60PET/IND Peterson, D. T. and Indig, M., J. Amer. Chem. Soc. **82**, 5645–6 (1960); T_{fus}.

65KAN/STE Kanda, F. A., Stevens, R. M., and Keller, D. V., J. Phys. Chem. **69**, 3867–72 (1965); T_{fus}.

68DWO/BRO Dworkin, A. S., Bronstein, H. R., and Bredig, M. A., J. Phys. Chem. **72**, 1892–6 (1968); T_{fus}.

69SHP/KAG Shpil'rain, E. E. and Kagan, E. E., Teplofiz, Vys. Temp. **7**, 577–9 (1969); Engl. trans. High Temp. **7**(3), 525–7 (1969); C_p^o(484–1253 K).

70DIT/DOU Ditmars, D. A. and Douglas, T. B., U. S. Nat. Bur. Stand., Rept. No. 10326, Chap. 3 (1970); ΔH(273–873 K).

70FUR/ISH Furukava, G. T. and Ishihara, S., U. S. Nat. Bur. Stand., Rept. No. 10326, Chap. 3, 1970; C_p^o(18–370 K).

71DWO/BRE Dworkin, A. S. and Bredig, M. A., J. Phys. Chem. **75** 2340–1 (1971); T_{fus}.

73HUL Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., Kelley, K. K., and Wagman, D. D., "Selected Values of the Elements," Amer. Soc. Metals, Metals Park, OH 44073, pp 59–64 (1973); Review.

76KHR/PAU Khriplovich, L. M. and Paukov, I. E., Zh. Fiz. Khim. **50**, 567–8 (1976); Engl. trans. Russ. J. Phys. Chem. **50**, 337 (1976); C_p^o(of Sr, 5–300 K).

76RAK/FRO Rakhmenkulov, F. S., Frolov, G. I., and Paukov, I. E., VINITI, Deposited No. 735–76, Moscow (1976) Zh. Fiz. Khim. **50**(6), 1628 (1976); Engl. trans. Russ. J. Phys. Chem. **50**(6), 988 (1976); C_p^o(13–300 K).

77SHP/FOM Shpil'rain, E. E., Fomin, V. A., Kagan, D. N., Sokol, G. F., Kachalov, V. V., and Ul'yanov, S. N., High Temp.-High Press. **9**, 49–55 (1977); C_p^o(1000–1800 K).

78BOE/WES Boerio, J. and Westrum, E. F., J. Chem. Thermodyn. **10**, 1–7 (1978); C_p^o(of Sr, 5–350 K).

80SHP/KAG Shpil'rain, E. E., Kagan, D. N., Fomin, V. A., Kachalov, V. V., Ul'yanov, S. N., and Sokol, G. F., Inzh.-Fiz. Zh. **39**, 972–9 (1980); Engl. transl. J. Eng. Phys. **39**, 1286–91 (1980); C_p^o(1000–1800 K).

81GUR Gurvich, L. V., Veits, I. V., Medvedev, V. A., *et al.*, Glushko, V. P., gen. ed., "Thermodynamic Properties of Individual Substances," Nauka, Moscow, Vol. 3(1), 379–81 (1981); Review.

84SHP/KAG1 Shpil'rain, E. E., Kagan, D. N., and Ul'yanov, S. N., Teplofiz. Vys. Temp. **22**(3), 398–400 (1984); T_{fus}.

84SHP/KAG2 Shpil'rain, E. E., Kagan, D. N., and Ul'yanov, S. N., Teplofiz, Vys. Temp. **22**(3), 485–91 (1984); Engl. trans., High Temp. **22**(3), 391–6 (1984); C_p°(298–2200 K), Review.

85JAN Chase, M. W., Jr., Davis, C. A., Downey, J. R., Jr., Frurip, D. J., McDonald, R. A., and Syverud, A. N., "JANAF Thermochemical Tables," J. Phys. Chem. Ref. Data **14**, Suppl. 1, 316–7 (1985); Review

85ULY Ulyanov, S. N., Thesis, Inst. for High Temp., Moscow (1985); T_{fus}, $\Delta_{fus}H$.

86SHP/KAG Shpil'rain, E. E., Kagan, D. N., and Ulyanov, S. N., Reviews on Thermophysical Properties of Substances, No. 3 (59), Inst. for High Temperatures, Moscow (1986); Review.

89DIT Ditmars, D. A., Private Communication to V. Itkin (1989); C_p°(300–1000 K).

6.7. Adopted Values

Electronic contribution to C_p°: $\gamma = 2.7 \pm 0.5$ mJ K^{-2} mol^{-1}

Debye temperature at 0 K: $\Theta_D = 110.5 \pm 1.8$ K

Heat Capacity Equations

Solid Ba

Temperature range 0–4 K

$C_p^\circ = 2.70\times10^{-3}T + 1.44\times10^{-3}T^3$ J K^{-1} mol^{-1}.

Temperature range 4–20 K:

$C_p^\circ = 3.018 - 0.9097T - 12.212T^{-2} + 0.1004T^2 - 1.96\times10^{-3}T^3$ J K^{-1} mol^{-1}.

Temperature range 20–80 K:

$C_p^\circ = -1.988 + 0.9022T - 1.061\times10^{3}T^{-2} - 0.01142T^2 + 5.171\times10^{-5}T^3$ J K^{-1} mol^{-1}.

Temperature range 80–298.15 K:

$C_p^\circ = 23.231 + 0.02569T - 9.324\times10^{3}T^{-2} - 7.327\times10^{-5}T^2 + 1.448\times10^{-7}T^3$ J K^{-1} mol^{-1}.

Temperature range 298.15 – 1000 K

$C_p^\circ = 23.059 + 16.941\times10^{-3}T$ J K^{-1} mol^{-1}.

Liquid Ba

Temperature range 1000 – 2000 K

C_p° / J K^{-1} mol^{-1} = 40

Values at the Standard Temperature

C_p°(298.15 K) = 28.11 ± 0.1 J K^{-1} mol^{-1}

S°(298.15 K) = 62.35 ± 0.3 J K^{-1} mol^{-1}

H°(298.15 K) – H°(0) = 6907 ± 30 J mol^{-1}

Phase Equilibrium Data

Temperature of fusion: T_{fus} = 1000 ± 3 K

Enthalpy of fusion: $\Delta_{fus}H$ = 7850 ± 400 J mol^{-1}

6.8. Calculated Thermodynamic Functions of Ba

The thermodynamic functions presented in Tables 6–4 and 6–5 are calculated using the equations presented in the previous section. Values in brackets are calculated by using the equation for the next higher adjacent temperature interval.

6.9. Appendix – Experimental Results of Ba

Tables 6–6 to 6–16 present heat capacity or enthalpy data as they were presented in the original article. As a result, the numeric values listed in this Appendix are the actual experimental values, tabular smoothed values, values calculated from equations, or values extracted from a graph. Where necessary, values have been converted to joules (from calories). In all cases, the table heading indicates the type of data listed.

TABLE 6–1. Comparison of the heat capacity, enthalpy, and entropy for Ba at 298.15 K

Reference	C_p°(298.15 K) J·K^{-1} mol^{-1}	S°(298.15 K) J·K^{-1} mol^{-1}	H°(298.15 K) – H°(0) J·mol^{-1}
73HUL	28.087	62.42 ± 0.08	6912
81GUR	28.100	62.50 ± 1.0	6910 ± 100
85JAN	28.096	62.475 ± 0.8	6912
Adopted	28.11 ± 0.1	62.35 ± 0.3	6907 ± 30

TABLE 6–2. Temperature of fusion of Ba

Reference	Temperature, K	Comments
Original Studies		
32RIN	984	Thermal analysis
46JAU	951	Enthalpy measurements
49SHE	998	Thermal analysis
56HIR/KIN	988	Thermal analysis
58KEL/KAN	999 ± 1	Thermal analysis
59PET/HIN	1003	Thermal analysis
60MIL/KOM	1000.2 ± 0.5	Thermal analysis
60PET/IND	1003	Thermal analysis
65KAN/STE	1003 ± 1	Thermal analysis
68DWO/BRO	998	Thermal analysis
71DWO/BRE	1004	Thermal analysis
84SHP/KAG1	995 ± 1	Thermal analysis, impure sample
84SHP/KAG1	1000 ± 5	Estimation for pure Ba
Reviews		
73HUL	1002 ± 2	Based on 59PET/HIN, 60PET/IND
81GUR	1000 ± 5	Based on 58KEL/KAN, 60MIL/KOM,59PET/HIN, 60PET/IND
84SHP/KAG2	1000 ± 5	Based on 58KEL/KAN, 59PET/HIN, 60MIL/KOM, 60PET/IND, 71DWO/BRE, 84SHP/KAG1
85JAN	1000 ± 3	Based on 58KEL/KAN, 59PET/HIN,60PET/IND, 65KAN/STE
Adopted		
This study	1000 ± 3	Based on recent studies

TABLE 6–3. Enthalpy of fusion of Ba

Reference	$\Delta_{fus}H$, J mol^{-1}	Comments
Original Studies		
46JAU	7660 ± 300	Enthalpy measurements
69SHP/KAG	7760 ± 170	Enthalpy measurements
70DIT/DOU	7975 ± 400	Enthalpy measurements
85ULY	8000 ± 400	Heat pulse calorimeter
Reviews		
73HUL	7750 ± 1000	Based on 69SHP/KAG, 70DIT/DOU
81GUR	7120 ± 500	Based on 69SHP/KAG, 70DIT/DOU
84SHP/KAG2	7870 ± 150	Based on 69SHP/KAG, 70DIT/DOU
85JAN	8012 ± 620	Based on 70DIT/DOU
Adopted		
This study	7850 ± 400	Average of above experimental data

TABLE 6–4. Thermodynamic functions of Ba below 298.15 K

T/K	$C_p^\circ(T)$ J K^{-1} mol^{-1}	$H^\circ(T)-H^\circ(0)$ J mol^{-1}	$S^\circ(T)$ J·K^{-1} mol^{-1}
5	0.2460	0.288	0.0798
10	1.8789	4.733	0.6334
15	5.2932	22.137	1.9980
20	9.2735(9.249)	58.614	4.0692
25	12.540	113.517	6.5058
30	15.017	182.677	9.0208
35	16.950	262.789	11.487
40	18.474	351.502	13.854
45	19.674	446.992	16.102
50	20.611	547.802	18.225
60	21.907	760.933	22.108
70	22.728	984.359	25.550
80	23.410(23.435)	1215.028	28.629
90	23.904	1451.817	31.418
100	24.280	1692.799	33.956
120	24.861	2184.503	38.437
140	25.313	2686.403	42.305
160	25.695	3196.565	45.710
180	26.038	3713.934	48.757
200	26.364	4237.965	51.517
220	26.686	4768.453	54.045
240	27.016	5305.449	56.381
260	27.365	5849.216	58.557
280	27.740	6400.204	60.598
298.15	28.110(28.110)	6906.992	62.352

TABLE 6–5. Thermodynamic functions of Ba above 298.15 K

T/K	$C_p^\circ(T)$ J K^{-1} mol^{-1}	$H^\circ(T)-H^\circ$(298.15 K) J·mol^{-1}	$S^\circ(T)$ J K^{-1} mol^{-1}
298.15	28.11	0.00	62.35
300.00	28.14	52.03	62.52
400.00	29.84	2950.87	70.85
500.00	31.53	6019.11	77.69
600.00	33.22	9256.77	83.59
700.00	34.92	12663.83	88.84
800.00	36.61	16240.31	93.61
900.00	38.31	19986.19	98.02
1000.00 (sol)	40.00	23901.49	102.15
1000.00 (liq)	40.00	31751.49	110.00
1100.00	40.00	35751.49	113.81
1200.00	40.00	39751.49	117.29
1400.00	40.00	47751.49	123.46
1600.00	40.00	55751.49	128.80
1800.00	40.00	63751.49	133.51
2000.00	40.00	71751.49	137.72

TABLE 6–6. EXPERIMENTAL enthalpy values $[H^\circ(T)-H^\circ$ (298.15 K)] of Ba [46JAU]

T/K	ΔH, J mol^{-1}	T/K	ΔH, J mol^{-1}
Solid Ba		Liquid Ba	
718	15350	983*	38350
763	17600	989	38500
834	21880	992	38550
865	24270	996	39400
880	24700	1001*	39250
903.5*	26350	1011*	39600
931.5*	28350	1015	40400
936	28500	1034	41300
940.4*	28900	1041	41600
		1073	42500
		1104	43700
		1110	44300
		1133	45400

*average of two measurements.

TABLE 6–7. CALCULATED heat capacity values of Ba [46JAU]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
Solid Ba		Liquid Ba	
718	36.32	982.5	56.07
763	36.90	983	55.94
833.5	40.88	989	55.69
865	43.01	991.5	55.65
880	42.47	996	56.48
903	43.72	1000.5	55.65
904	43.30	1001	55.86
931	45.27	1009.5	55.86
932	43.81	1011.5	55.56
935.5	44.69	1014.5	56.32
940	44.56	1033.5	56.15
940.5	45.40	1041	55.7
940.5	45.48	1072.5	55.02
1104	54.31		
1110	53.85		
1133	54.81		

TABLE 6–8. SMOOTHED heat capacity values of Ba [57ROB]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
1.5	0.0090	7	0.665
2.0	0.0169	8	1.00
2.5	0.0293	9	1.38
3.0	0.0471	10	1.85
3.5	0.0725	12	2.94
4.0	0.107	14	4.11
4.5	0.154	16	5.44
5.0	0.220	18	6.80
6.0	0.408	20	8.16

TABLE 6–9. EXPERIMENTAL enthalpy values [$H°(T) - H°(373.15\ K)$] of Ba [69SHP/KAG]

T/K	ΔH, J mol^{-1}	T/K	ΔH, J mol^{-1}
483.9	3390	861.1	18900
592.3	7240	979.0	24420
634.7	9020	999.6	33040
638.3	9770	1035.2	34760
680.3	11780	1159.6	39130
759.9	14940	1253.3	43550

TABLE 6–10. SMOOTHED heat capacity values of Ba [69SHP/KAG]

T/K	$C_p°$, J K^{-1} mol^{-1}	T/K	$C_p°$, J^{-1} mol^{-1}
400	27.22	900	45.00
500	35.08	998("β")	48.94
600	42.94	998(liq.)	40.11
648("α")	46.72	1000	40.11
648("β")	34.88	1100	40.11
700	36.97	1200	40.11
800	40.99	1300	40.11

TABLE 6–11. SMOOTHED enthalpy values [$H°(T) - H°(273.15\ K)$] of Ba [70DIT/DOU]

T/K	ΔH, J mol^{-1}	T/K	H, J mol^{-1}
323	1459	773	19373
373	2964	823	21291
423	4638	873	23279
473	6511	923	25329
523	8648	973	29095
533	9275	978	31118
543	9709	983	33548
553	10065		Liquid
563	10670	1003	36376
573	11215	1023	37226
583	11709	1048	38316
623	13076	1073	39382
673	14977	1123	41467
723	17086	1173	43558

Note: most data are averages of 2–3 measurements, the data were rounded to nearest 1 K and 1 J mol^{-1}.

TABLE 6–12. CALCULATED heat capacity values of Ba [70DIT/DOU]

T/K	$C_p°$, J K^{-1} mol^{-1}	T/K	$C_p°$, J K^{-1} mol^{-1}
273.15	27.600	582.53("β")	32.468
280.00	27.726	590.00	33.097
290.00	27.919	600.00	33.940
298.15	28.095	620.00	35.625
300.00	28.140	640.00	37.309
310.00	28.405	660.00	38.994
320.00	28.710	680.00	40.679
330.00	29.075	700.00	42.364
340.00	29.470	720.00	44.048
350.00	29.905	740.00	45.733
360.00	30.411	760.00	47.418
370.00	31.005	766.00("β")	48.103
380.00	31.677	766.00("γ")	39.064
390.00	32.420	780.00	39.064
400.00	33.227	800.00	39.064
420.00	35.009	900.00	39.064
440.00	36.981	991.00("γ")	39.064
460.00	39.110	991.00(liq)	43.438
480.00	41.372	1000.00	43.327
500.00	43.745	1020.00	43.080
520.00	46.213	1060.00	42.586
540.00	48.701	1100.00	42.092
560.00	51.379	1120.00	41.845
580.00	54.057	1160.00	41.350
582.53("α")	54.399	1200.00	40.856

TABLE 6–13. SMOOTHED heat capacity values of Ba [70FUR/ISH]

T/K	$C_p°$, J K^{-1} mol^{-1}	T/K	$C_p°$, J K^{-1} mol^{-1}
5.00	0.249	150.00	25.495
10.00	1.930	160.00	25.685
15.00	5.293	170.00	25.866
20.00	9.261	180.00	26.041
25.00	12.512	190.00	26.209
30.00	15.028	200.00	26.369
35.00	16.983	210.00	26.529
40.00	18.488	220.00	26.691
45.00	19.674	230.00	26.858
50.00	20.607	240.00	27.026
55.00	21.333	250.00	27.196
57.00	21.578	260.00	27.368
60.00	21.906	270.00	27.544
65.00	22.377	273.15	27.600
70.00	22.777	280.00	27.726
75.00	23.124	290.00	27.919
80.00	23.427	298.15	28.089
85.00	23.690	300.00	28.129
90.00	23.920	310.00	28.360
95.00	24.121	320.00	28.618
100.00	24.300	330.00	28.904
110.00	24.603	340.00	29.219
120.00	24.858	350.00	29.557
130.00	25.086	360.00	30.910
140.00	25.296	370.00	30.260
375.00	30.427		

TABLE 6–14. SMOOTHED heat capacity values of Ba [76RAK/FRO]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
12	3.356	85	23.66
15	5.510	90	23.92
20	9.071	100	24.35
25	12.221	110	24.67
30	14.719	130	25.23
35	16.631	150	25.74
40	18.179	170	26.18
45	19.443	190	26.60
50	20.468	210	26.98
55	21.284	230	27.31
60	21.912	250	27.65
65	22.393	270	28.08
70	22.761	290	28.53
75	23.087	298.15	28.72
80	23.389	300	28.77

TABLE 6–15. EXPERIMENTAL heat capacity values of Ba [80SHP/KAG] Listed in [86SHP/KAG]

T/K	C_p°, J K^{-1}mol^{-1}	T/K	C_p°, J K^{-1}mol^{-1}	T/K	C_p°, J K^{-1}mol^{-1}
747.8	36.37	1100.3	41.31	1490.2	39.16
757.8	37.15	1101.5	40.03	1494.7	38.22
764.9	36.88	1111.5	39.96	1528.8	37.98
767.8	37.93	1121.5	39.91	1534.3	39.03
774.9	37.65	1135.6	39.57	1538.8	37.90
777.8	38.72	1145.6	39.52	1544.3	38.98
778.0	37.27	1155.6	39.46	1598.8	38.44
782.2	37.80	1183.2	40.51	1643.5	37.97
784.9	38.43	1193.2	40.42	1646.3	37.45
787.8	39.50	1193.8	39.59	1696.3	37.98
788.0	38.03	1196.7	39.56	849.1	43.95
792.2	38.57	1203.2	40.36	856.5	44.34
794.9	39.21	1203.8	39.55	859.1	44.74
798.0	38.79	1206.7	39.50	866.5	45.11
802.2	39.36	1213.8	39.51	1261.6	39.69
804.9	39.98	1216.7	39.44	1266.1	40.28
808.0	39.56	1251.6	39.77	1271.6	39.61
812.2	40.14	1256.1	40.36	1276.1	40.23
818.0	40.35	1319.4	40.02	1711.4	37.28
819.1	41.58	1329.4	39.94	1745.9	37.30
822.2	40.92	1356.7	40.25	1756.6	38.17
826.5	41.36	1366.7	40.13	1840.3	37.51
829.1	42.41	1372.5	38.82		
836.5	42.15	1377.5	39.20		
839.1	43.17	1382.5	38.77		
846.5	43.51	1387.5	39.16		
1012.3	40.88	1409.7	38.54		
1022.3	40.83	1419.7	38.45		
1032.3	40.78	1424.2	39.28		
1078.8	40.29	1426.4	38.34		
1080.3	41.47	1434.2	39.24		
1088.8	40.21	1436.4	38.30		
1090.3	41.39	1480.2	39.19		
1098.8	40.17	1484.7	38.26		

TABLE 6–16. CALCULATED heat capacity values of Ba [89DIT]

T/K	C_p°, J K^{-1} mol^{-1}	T/K	C_p°, J K^{-1} mol^{-1}
300	27.4	700	34.0
350	27.7	750	33.6
400	28.0	800	34.0
450	28.6	850	35.2
500	30.1	900	37.7
550	32.5	950	41.8
600	35.5	1000	46.4
650	35.5		

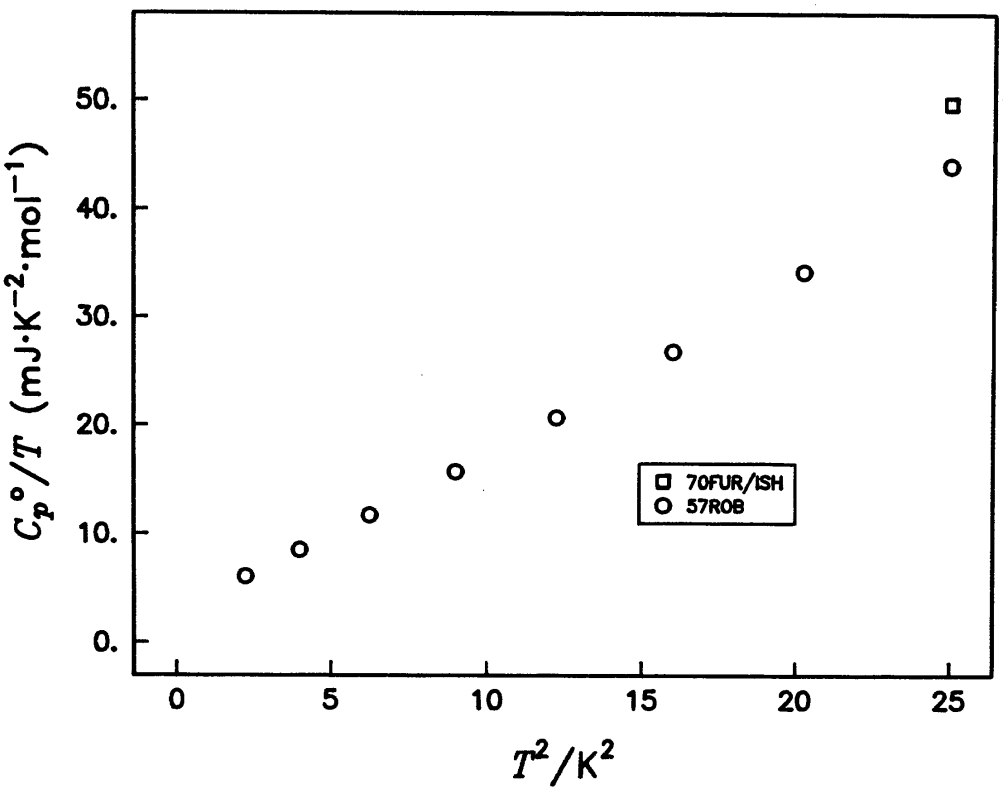

FIG. 6–1. C_p°/T versus T^2 for Ba below 5 K.

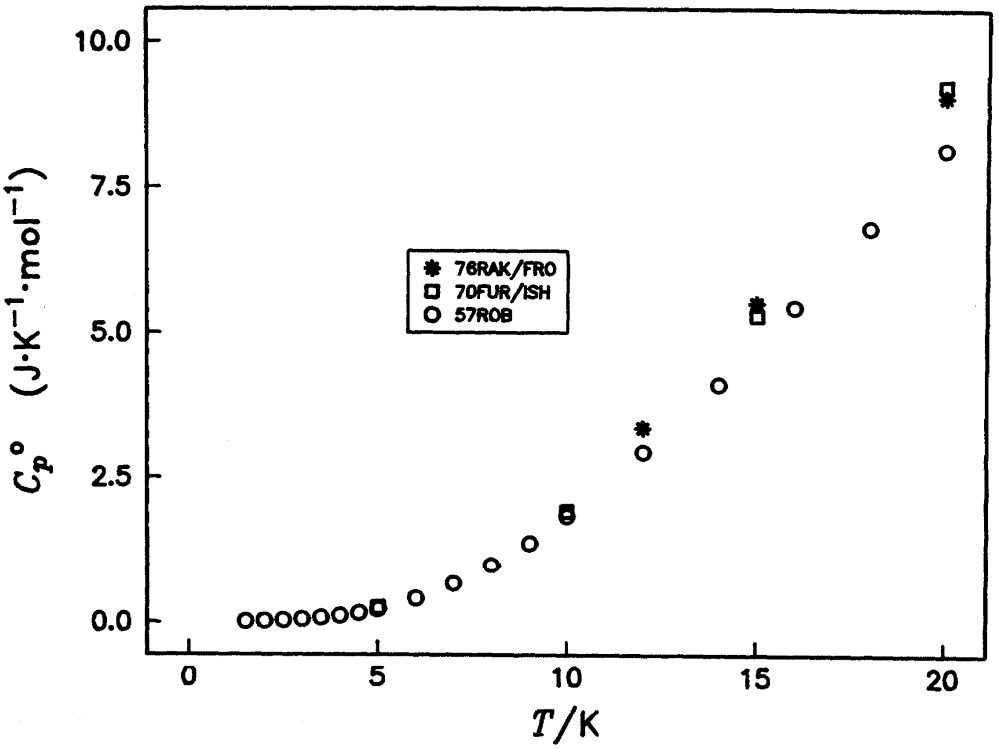

FIG. 6–2. Heat Capacity of Ba below 20 K.

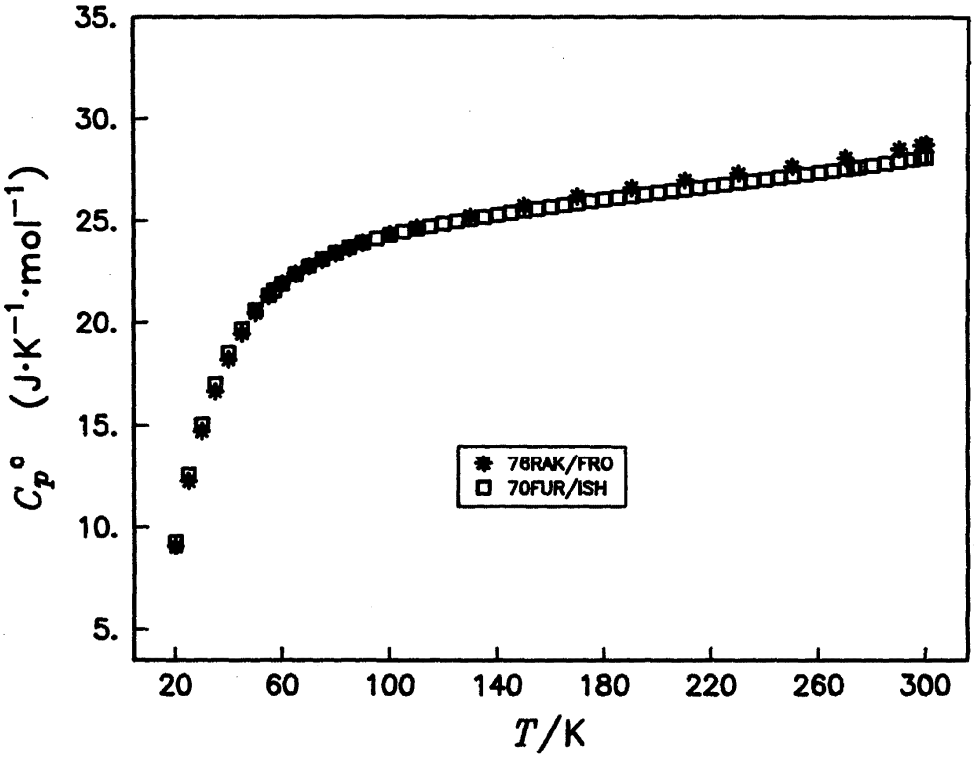

FIG. 6–3. Heat Capacity of Ba at 20–300 K.

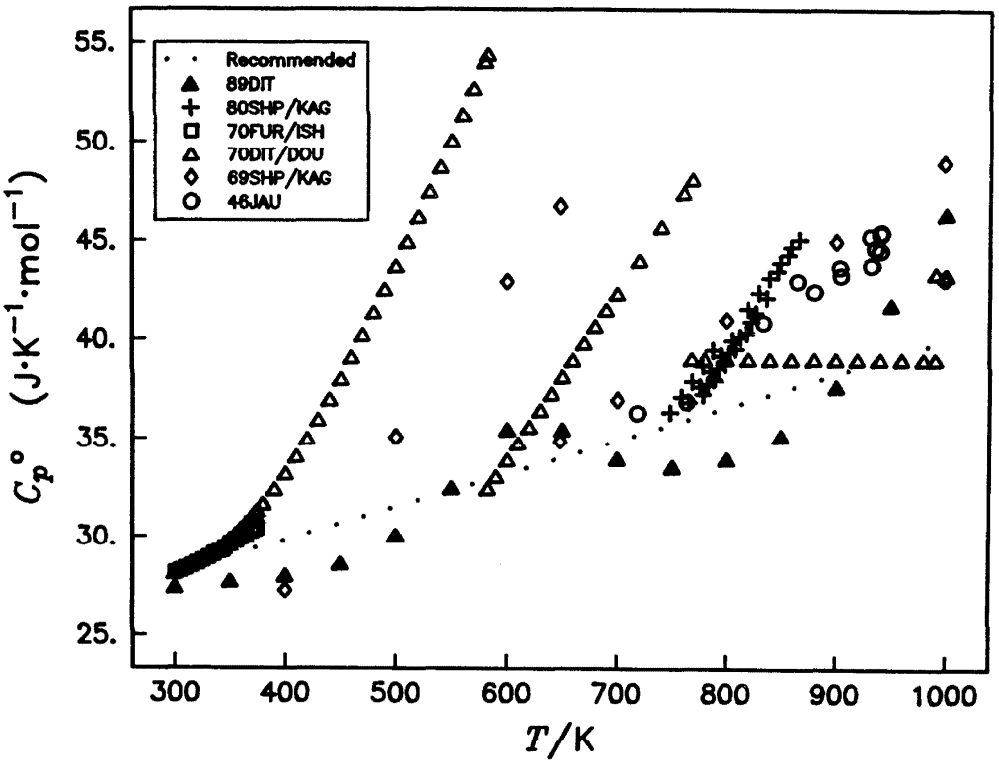

FIG. 6–4. Heat Capacity of Ba at 300–1000 K.

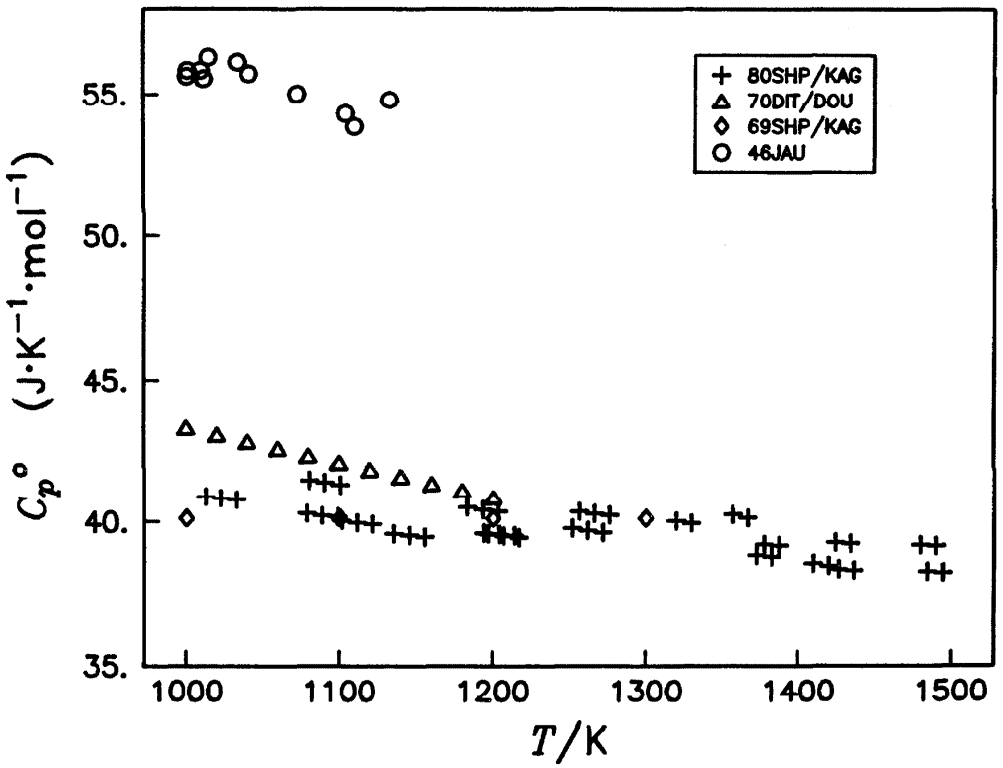

FIG. 6–5. Heat Capacity of solid and liquid Ba at 1000–1500 K.

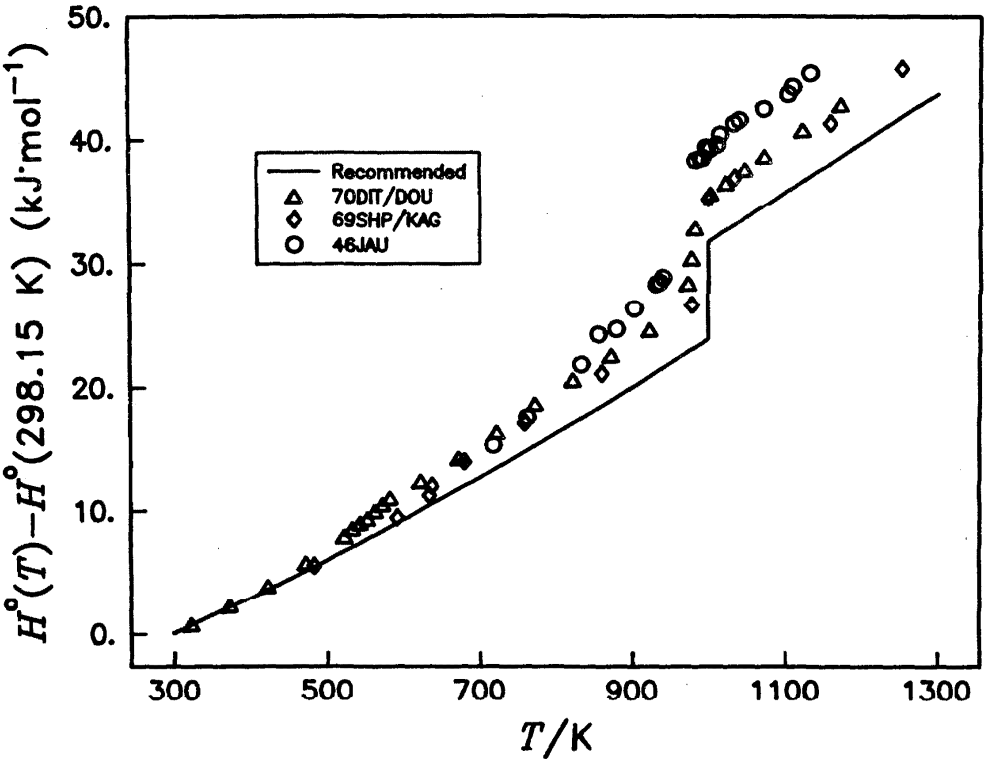

FIG. 6–6. $H°(T)-H°(298.15\ K)$ for solid and liquid Ba.

7. Conclusion

7.1. Comparison of Properties of the IIA Group

Many of the key values for the thermodynamic properties of the elements of the IIA group which have been adopted are given in Tables 7–1 to 7–4 and are shown in Figs. 7–1 and 7–2.

This review has brought to light the difficulties in obtaining reliable data for the Group IIA metals. Investigators, being well aware of the need for pure metals and careful handling procedures, were confronted with final results which revealed unexpected behavior. Thus, even with skilled experimentalists and careful experimentation, we were still faced with questionable data. However, we now have better values for the heat capacity.

The thermodynamic properties of Mg are now quite well known. However, the properties of the other elements of Group IIA (Be, Ca, Sr, and Ba) are not known with high accuracy, especially at high temperatures. The thermodynamic quantities of these elements appear to be the least accurately described when compared with the other groups of the Periodic Table. Currently, there are no experimental data on radium: i.e., no heat capacity or enthalpy data.

Table 7–1 shows the low-temperature properties, the Debye temperature Θ_D and electronic heat capacity coefficient at 0 K. The value of Θ_D decreases and that for γ increases with the atomic number. The only exception is a relatively high value of γ for Sr which gives a hint that the accuracy in the measured heat capacity below 5 K may possibly be low.

Fig. 7–1 shows the heat capacities below 298 K. The results are consistent with the position of the elements in the Periodic Table; light Be has the lowest heat capacity while heavy Ba the highest. Table 7–2 illustrates a similar trend for the heat capacities, entropies and enthalpy differences at the standard temperature.

Fig. 7–2 shows that above 298 K the heat capacity of Be is the smallest of the elements. No specific consistency is apparent for the adopted C_p° values for Mg, Ca and Sr. They intersect several times, probably due to a high inaccuracy in the values for Ca and Sr. The values adopted for Ba are higher than those for Ca and Sr, which is what might be expected. However, it is unreal to place too much emphasis at the present time on a relation between the values for Ba and those for Ca and Sr. No reliable data for Ca and Sr have been found, and this prevents any useful correlation with the values for Ba. The values for Ba shown in Fig. 7–2 can be regarded as high but possible, and they are much lower than those proposed in other reviews [81GUR], [85JAN] and [86SHP/KAG].

The temperature of transformation in Ca and Sr (Table 7–3) is well established. The reported values for the temperature of transformation of Be range from 1525 to 1545 K; none of these measurements can be rated as accurate; a better determination is desirable. The enthalpy of transformation of Be, Ca and Sr listed in Table 7–3 have a considerable uncertainty. The least well known value is for Be which was estimated from a semi-quantitative experiment. The essential difference between the entropies of transformation of Ca and Sr suggests that the adopted enthalpies of transformation of one of these elements or both of them are probably inaccurate. It should be added that the heat capacities of the high-temperature modifications of Ca and Sr are known only approximately and are based on samples which are thought to be of questionable purity; the heat capacity of β–Be has never been measured.

Table 7–4 shows that the temperature of fusion of bcc Be, Ca, Sr and Ba decreases with increase in the atomic number; the absence of a clear dependence of the enthalpy of fusion and heat capacity of the liquid metals suggests a high uncertainty in these data. The precise difference between the entropy of fusion of bcc Be and other bcc metals of the group needs refining and explaining. The heat capacities of the liquid metals are known very approximately.

7.2. Recommendations for Future Measurements

The properties listed below are considered to be inaccurate. They are placed in a sequence depending on their uncertainty. The first property for each element is the least certain.

Beryllium
1) Enthalpy of fusion;
2) Enthalpy of transformation;
3) Heat capacity/enthalpy of β–Be;
4) Temperature of transformation;
5) Temperature of fusion.

Magnesium
1) Enthalpy of fusion;
2) Heat capacity of liquid Mg.

Calcium
1) Heat capacity/enthalpy above room temperature;
2) Enthalpy of transformation;
3) Enthalpy of fusion;
4) Heat capacity below 5 K.

Strontium
1) Heat capacity/enthalpy above room temperature;
2) Heat capacity below 5 K;
3) Enthalpy of transformation;
4) Enthalpy of fusion.

Barium
1) Heat capacity/enthalpy above room temperature;
2) Heat capacity below 5 K;
3) Enthalpy of fusion.

7.3. References for Conclusion

81GUR Gurvich, L. V., Veits, I. V., Medvedev, V. A., *et al.*, Glushko, V. P., gen. ed., "Thermodynamic Properties of Individual Substances," Nauka, Moscow, Vol. 3, (1981); review.

85JAN Chase, M. W., Jr., Davies, C. A., Downey, J. R., Jr., Frurip, D. J., McDonald, R. A., and Syverud, A. N., "JANAF Thermochemical Tables,", J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985); review.

86SHP/KAG Shpil'rain, E. E., Kagan, D. N., and Ulyanov, S. N., Reviews on Thermophysical Properties of Substances, No. 3(59), Inst. for High Temperatures, Moscow (1986); review.

TABLE 7–1. Debye Temperature and Electronic Heat Capacity Coefficient for the Elements of the IIA Group

Element	Θ_D/K	γ/mJ·K^{-2} mol^{-1}
Be	1480 ± 20	0.1714 ± 0.01
Mg	403 ± 4	1.265 ± 0.01
Ca	250 ± 5	1.99 ± 0.05
Sr	147 ± 1.2	3.64 ± 0.18
Ba	110.5 ± 1.8	2.70 ± 0.50

TABLE 7–2. Heat Capacity, Entropy, and Enthalpy Values at 298.15 K for the Elements of the IIA Group

Element	C_p°(298.15 K) J·K^{-1} mol^{-1}	S°(298.15 K) J·K^{-1} mol^{-1}	H°(298.15 K) − H°(0) J·mol^{-1}
Be	16.44 ± 0.08	9.50 ± 0.1	1942 ± 20
Mg	24.78 ± 0.1	32.54 ± 0.2	4979 ± 30
Ca	25.72 ± 0.1	42.54 ± 0.3	5783 ± 30
Sr	26.84 ± 0.1	55.00 ± 0.3	6558 ± 30
Ba	28.11 ± 0.1	62.35 ± 0.3	6907 ± 30

TABLE 7–3. Temperature and Enthalpy of the Phase Transformation for the Elements of the IIA Group

Element	Structure at $T<T_{trs}$	T_{trs}/K	$\Delta_{trs}H$ J·mol^{-1}	$\Delta_{trs}S$ J K^{-1} mol^{-1}	Structure at $T>T_{trs}$
Be	hcp	1543 ± 6	6700 ± 500	4.342	bcc
Ca	fcc	716 ± 3	930 ± 100	1.299	bcc
Sr	fcc	820 ± 3	850 ± 250	1.036	bcc

TABLE 7–4. Temperature and Enthalpy of Fusion for the Elements of the IIA Group

Element	Structure at $T<T_{fus}$	T_{fus}/K	$\Delta_{fus}H$ J·mol^{-1}	$\Delta_{fus}S$ J K^{-1} mol^{-1}	C_p°(liq) J K^{-1} mol^{-1}
Be	bcc	1563 ± 4	8000 ± 500	5.118	30
Mg	hcp	923 ± 1	8400 ± 200	9.101	34.3
Ca	bcc	1115 ± 2	8540 ± 200	7.659	38
Sr	bcc	1041 ± 2	8000 ± 200	7.685	37
Ba	bcc	1000 ± 3	7850 ± 400	7.850	40

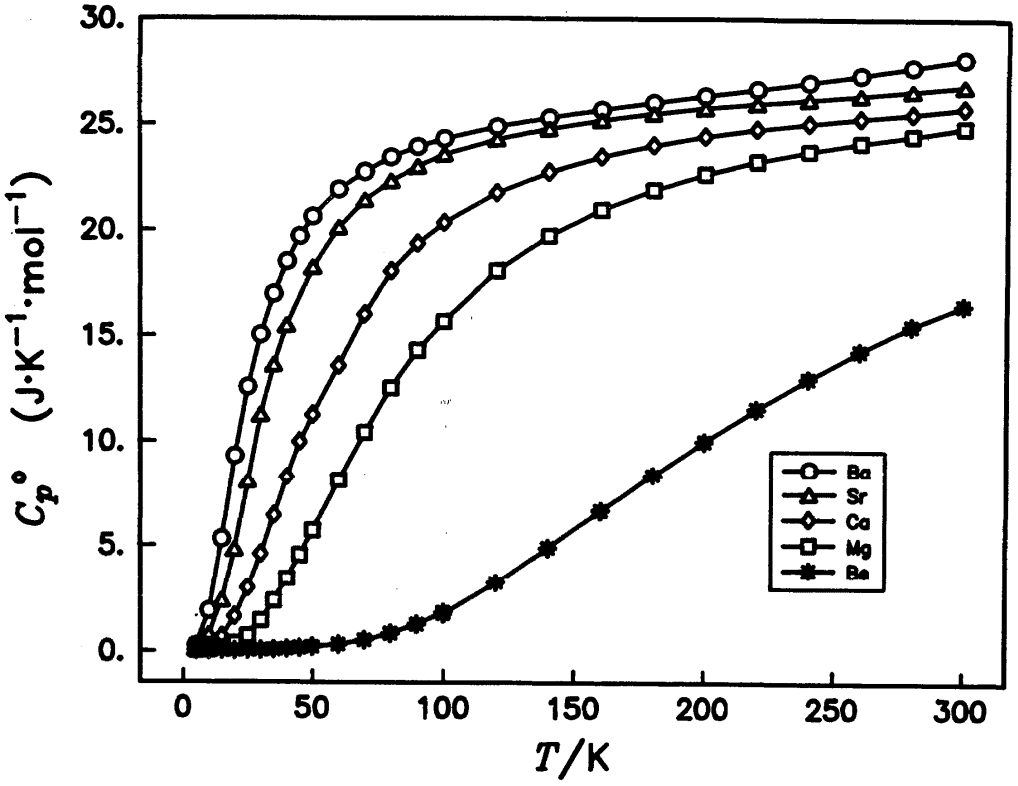

FIG. 7–1. Heat Capacity of the Elements of Group IIA below 300 K.

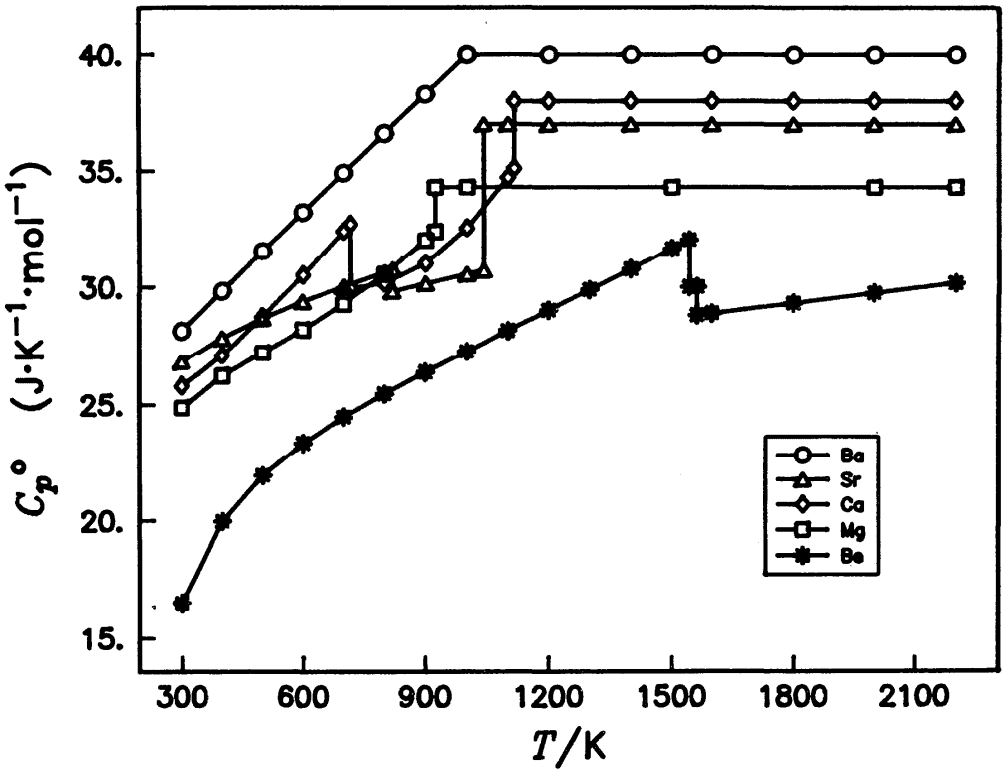

FIG. 7–2. Heat Capacity of the Elements of Group IIA above 300 K.

8. Acknowledgments

This is the first article in a joint effort to re-examine the thermodynamic properties of the elements. The bibliographic and data files of the Chemical Thermodynamics Data Center and the JANAF Thermochemical Tables at NIST were used in conjunction with the available resources at the University of Toronto and the University of Notre Dame. This work was funded by the Standard Reference Data Program (NIST). The authors appreciate the efforts of Linda Riley and Dr. Rajiv Doshi (University of Notre Dame) in providing this manuscript in electronic format.