

# I. THERMOCHEMICAL PROPERTIES

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## INTRODUCTION

In the present review, thermodynamic data for beryllium, its compounds and alloys, are presented both in individual discussions of experimental measurements on specific substances and in critically compiled tables of selected thermodynamic properties. In preparing these data, reference has been made to various publications containing assessed thermodynamic values, in particular the JANAF Thermochemical Tables [1], Report No.10004 [2] and Technical Note TN 270-6 [3] from the National Bureau of Standards, and Selected Values of Thermodynamic Properties of Metals and Alloys by Hultgren et al. [4]. Since the above-mentioned assessments are generally comprehensive and include some experimental values published as recently as 1971, it has in many cases been possible to accept the tabulated data without change. Indeed, for the sake of consistency, it has frequently been considered undesirable to change values within the error limits quoted in the assessments, and the present effort has therefore largely been concentrated on substances for which new information is available.

Data for beryllium and its inorganic compounds are presented in Sections 1 to 9 and Tables I to VI, and the thermodynamic properties of beryllium alloys are discussed in individual assessments in Section 10.

The more frequently used symbols are listed below.

## NOTATION

<u>Symbol</u>	<u>Meaning</u>	<u>Common units</u>
$C_p$	molar heat capacity	cal/°K · mol
$\Delta G$	free energy of reaction	cal, kcal
$\Delta \bar{G}_i$	partial molar free energy of solution of component i	cal/mol, kcal/mol
$\Delta \bar{G}_i^E$	partial molar excess free energy of solution of component i	cal/mol, kcal/mol
$\Delta H_{298}$	heat of formation at 298°K	cal/mol, kcal/mol
$\Delta H$	heat of reaction	cal, kcal

$\Delta\bar{H}_i$	partial molar heat of solution of component i	cal/mol, kcal/mol
$L_{t, f, s, e}$	molar heats of transformation, fusion, sublimation and evaporation	cal/mol, kcal/mol
$S_{298}^0$	standard entropy at 298°K	cal/°K · mol
$\Delta S$	entropy of reaction	cal/°K · mol
$\Delta\bar{S}_i$	partial molar entropy of solution of component i	cal/°K · mol
$\Delta\bar{S}_i^E$	partial molar excess entropy of solution of component i	cal/°K · mol
ln	$\log_e$	
log	$\log_{10}$	
$N_A$	mole fraction of A	
p	pressure	atm, mmHg (=torr)
T	absolute temperature	°K
< >	solid state	
{ }	liquid state	
( )	gaseous state	
[ ]	dissolved state (subscript denoting solvent)	

## 1. BERYLLIUM

### 1.1. Heat capacity

Published experimental data for the heat capacity of beryllium have been assessed by Hultgren et al. [4].

A number of low-temperature measurements of  $C_p$  have been made [5-10] and these have led to a selected value of  $S_{298}^0 = 2.27 \pm 0.02$  cal/°K · mol.

High-temperature  $C_p$  values are based largely on the measurements by Ginnings, Douglas and Ball [11] (367 - 1169°K) and by Kantor, Krasovitskaya and Kisel [12] (600 - 2200°K), but the data obtained by Kanazawa and Packer [13] (298 - 1368°K), by Walker, Ewing and Miller [14] (303 - 1073°K), by Mit'kina [15] (298 - 748°K) and by Lewis [9] (97 - 463°K) have also been included in the assessment. More recent  $C_p$  measurements have been made by Tye and Brazel [16] using adiabatic and drop calorimetry. In the

temperature range 300 - 1100°K their results are a maximum of 2% higher than those of Ginnings et al. [11].

Selected  $C_p$  values for  $\alpha$ -Be have been fitted by the equation

$$C_p = 5.068 + 1.361 \times 10^{-3} T + 0.23 \times 10^{-6} T^2 - 1.404 \times 10^5 T^{-2} \quad (298-1527^\circ\text{K})$$

The results of Kantor et al. [12] do not include values in the restricted temperature range of stability of  $\beta$ -Be. The heat capacity of  $\beta$ -Be between 1527°K and the melting point of 1560°K has therefore been estimated by Hultgren as 7.7 cal/°K·mol.

The selected  $C_p$  value for liquid beryllium is 7.04 cal/°K·mol and this is assumed to remain constant above 2200°K, the maximum temperature of experimental measurements.

Data for gaseous beryllium have been taken by Hultgren et al. from Hilsenrath, Messina and Evans [17]. The standard entropy at 298°K is given as 32.54 cal/°K·mol, and in the temperature range 298 - 1900°K,  $C_p(\text{Be})$  has a constant value of 4.968. At temperatures between 1900°K and 3000°K the  $C_p$  of the gas has been fitted by the equation:

$$C_p = 4.53 + 0.14 \times 10^{-3} T + 6.51 \times 10^5 T^{-2}$$

## 1.2. Solid transformation and melting characteristics

The temperature of the  $\alpha \rightarrow \beta$  transformation has been determined by Amonenko et al. [18] as  $1527 \pm 5^\circ\text{K}$ . Since the heat content studies of Kantor et al. [12] did not include results in the  $\beta$ -range, a heat of transformation ( $\alpha \rightarrow \beta$ ) was estimated by Hultgren using the suggestion of Dennison, Gschneidner and Daane [19] that  $\Delta S_{\alpha \rightarrow \beta} = 0.2 \times \text{valence}$ , i.e.  $\Delta S_{\alpha \rightarrow \beta} = (0.4)$ . Hence  $L_t(\alpha \rightarrow \beta) = 1527 \times (0.4) = 611$  cal/mol.

The melting point has been reported by Kantor et al. [12] to be  $1560 \pm 5^\circ\text{K}$ . This temperature is in excellent agreement with that given by Martin and Moore [20].

The heat content results of Kantor et al. only allow a combined value of  $L_t(\alpha \rightarrow \beta) + L_f$  to be obtained. This sum is approximately 3500 cal/mol, so that the heat of fusion is obtained by subtraction of the heat of the  $\alpha \rightarrow \beta$  transformation. Hultgren has selected a value of  $L_f$  of 2920 cal/mol.

## 1.3. Vapour pressure

The vapour pressure of beryllium has been determined by Baur and Brunner [21] (1850 - 2331°K, boiling point method), Schuman and Garrett [22] (1174 - 1336°K, Langmuir method), Holden, Speiser and Johnston [23] (1172 - 1552°K, Knudsen and Langmuir methods), Gulbransen and Andrew [24] (1103 - 1229°K, Langmuir method), Kovtun, Kruglykh and Pavlov [25] (1178 - 1373°K, Knudsen and Langmuir methods) and Ansara and Bonnier [26] (1578 - 1665°K, Knudsen method). By applying a Third-Law test to the experimental measurements, Hultgren et al. [4] have obtained standard heats of vaporization at 298°K ranging from 76 210 to 80 620 cal/mol. Their selected value of  $L_e$  (298°K) is  $77\,500 \pm 1500$  cal/mol.

The selected thermodynamic properties of condensed and gaseous beryllium have been used to calculate the following vapour pressure equations for the solid and liquid metal. The additional check that the vapour

pressure is equal to 1 atm at the normal boiling point of 2745°K has also been used.

$$\langle \text{Be} \rangle \log p \text{ (mmHg)} = 11.279 - 0.56 \log T - 17058 T^{-1} \text{ (298 - 1560°K)}$$

$$\{\text{Be}\} \log p \text{ (mmHg)} = 12.483 - 1.04 \log T - 16518 T^{-1} \text{ (1560-2745°K)}$$

## 2. HALIDES

### 2.1. Fluorides

#### 2.1.1. Beryllium monofluoride

In a report presenting a comprehensive assessment of the thermodynamic properties of condensed and gaseous beryllium difluoride, Parker [2] has re-evaluated the data for BeF gas (i.e. (BeF)). The value he selects for  $\Delta H_{298}$  is -41.8 kcal/mol and the standard entropy is given as  $S_{298}^0 = 49.15 \text{ cal/°K} \cdot \text{mol}$ .

The heat capacity of the gas, obtained using molecular constants taken from Herzberg [27], is tabulated in the JANAF Thermochemical Tables [1]. The data may be represented by the equation:

$$C_p = 7.69 + 1.10 \times 10^{-3} T - 0.21 \times 10^{-6} T^2 - 0.85 \times 10^5 T^{-2} \text{ (298 - 3000°K)}$$

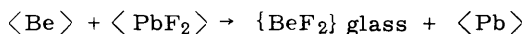
#### 2.1.2. Beryllium difluoride

Experimental results for the heat of formation of  $\langle \text{BeF}_2 \rangle$  ( $\alpha$ -quartz) have been considered in detail by Parker [2]. The methods of investigation used for determining  $\Delta H_{298}$  fall into three main categories:

(a) Measurement of the heat of solution of both the  $\alpha$ -quartz and glassy forms of BeF<sub>2</sub> in acetic acid-sodium acetate solutions. This has been done by Taylor and Gardner [28] who thereby obtained a value for the heat of transformation quartz  $\rightarrow$  glass of 1.12 kcal/mol. This value may be used in conjunction with measured heats of formation of amorphous BeF<sub>2</sub>, obtained by the combustion of  $\langle \text{Be} \rangle$  in (F<sub>2</sub>), to calculate  $\Delta H_{298} \langle \text{BeF}_2 \rangle$  ( $\alpha$ -quartz), assuming the amorphous and glassy states to be equivalent.

(b) Reaction of  $\langle \text{Be} \rangle$  with (F<sub>2</sub>). Measurements have been made by Churney and Armstrong [29] (who also quote in Ref. [30] unpublished work of Simmons), and by Good [31].

(c) Reaction of  $\langle \text{Be} \rangle$  with  $\langle \text{PbF}_2 \rangle$ . Gross [32] has measured the heat of the reaction:



so that from a knowledge of the heat of formation of  $\langle \text{PbF}_2 \rangle$ ,  $\Delta H_{298} \{\text{BeF}_2\} \text{ glass}$  can be obtained.

The above investigations provide values of  $\Delta H_{298} \langle \text{BeF}_2 \rangle$  ( $\alpha$ -quartz) that vary from -244 kcal/mol to -245.7 kcal/mol. Parker has selected a 'best' value for  $\Delta H_{298} \langle \text{BeF}_2 \rangle$  of  $-245.4 \pm 1.0 \text{ kcal/mol}$ . The corresponding value for  $\Delta H_{298} \{\text{BeF}_2\} \text{ glass}$  is  $-244.3 \pm 1.0 \text{ kcal/mol}$ .

The heat capacity of  $\langle \text{BeF}_2 \rangle$  has been measured by Taylor and Gardner [28] using low-temperature adiabatic calorimetry (8 - 300°K) and ice calorimetry (354 - 776°K). Their specimen was composed almost completely of quartz-type crystals and contained about 0.3% oxygen as the major impurity. The value of  $S_{298}^0$  derived from the smoothed  $C_p$  values is  $12.75 \pm 0.05$  cal/°K · mol. From their enthalpy measurements, Taylor and Gardner have selected a transformation temperature for  $\langle \text{BeF}_2 \rangle$  (low quartz  $\rightarrow$  high quartz) of 500°K. This transition has also been studied by Levina [33] by observing the  $C_p$  peak near the transition temperature. The peak was found to begin near 438°K, was complete near 503°K and gave a value of 0.17 kcal/mole for the heat of transition. A value of  $L_t$  of 0.053 kcal/mol obtained in Ref.[1] from a fit of the experimental enthalpy data for the two crystalline forms is preferred. The heat capacity data for  $\langle \text{BeF}_2 \rangle$  have been fitted by the following equations:

$$C_p = 15.56 + 5.15 \times 10^{-3} T - 4.20 \times 10^5 T^{-2} \quad (298 - 500^\circ\text{K})$$

$$C_p = 1.24 + 18.59 \times 10^{-3} T + 13.14 \times 10^5 T^{-2} \quad (500-825^\circ\text{K})$$

The melting temperature of 825°K selected by Taylor and Gardner [28] from their calorimetric studies has been accepted, although  $T_f$  has been variously reported as 815°K [34], 821°K [35], 818°K [36] and  $816 \pm 5^\circ\text{K}$  [37]. A value of 1.135 kcal/mol for the heat of fusion is consistent with the calorimetric data of Taylor and Gardner [28], Melnichak [38] and Gross [39].

The heat capacity of liquid  $\text{BeF}_2$  between 828°K and 1183°K has been determined by Taylor and Gardner [28] from heat content studies. The following equation may be used to represent the heat capacity of  $\{\text{BeF}_2\}$  from the melting temperature to the boiling point of 1448°K and above:

$$C_p = 13.81 + 7.105 \times 10^{-3} T - 4.51 \times 10^5 T^{-2} \quad (825 - 1448^\circ\text{K})$$

The heat of sublimation of  $\text{BeF}_2$  has been determined by a large number of investigators using a variety of vapour pressure methods. In a recent Third-Law analysis of the experimental data [1], a value of  $-55.15 \pm 0.1$  kcal/mol for  $L_s$  (298°K) has been selected. This gives a heat of formation of  $\text{BeF}_2$  gas at 298°K of  $-190.25 \pm 1.0$  kcal/mol. The entropy and heat capacity of  $(\text{BeF}_2)$  given here are also those quoted in Ref.[1].  $S_{298}^0$  has a value of  $54.36 \pm 0.3$  cal/°K · mol and the heat capacity may be represented by the equations:

$$C_p = 12.23 + 2.02 \times 10^{-3} T - 1.59 \times 10^5 T^{-2} \quad (298 - 1000^\circ\text{K})$$

$$C_p = 14.78 + 0.04 \times 10^{-3} T - 7.83 \times 10^5 T^{-2} \quad (1000-3000^\circ\text{K})$$

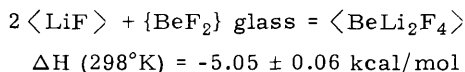
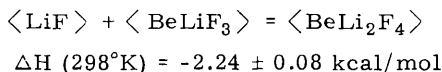
The selected thermodynamic properties of condensed and gaseous  $\text{BeF}_2$  have been used to calculate the following vapour pressure equations:

$$\langle \text{BeF}_2 \rangle \log p \text{ (mmHg)} = 16.950 - 1.69 \log T - 12\,290 T^{-1} \quad (298 - 825^\circ\text{K})$$

$$\{\text{BeF}_2\} \log p \text{ (mmHg)} = 23.599 - 3.75 \log T - 12\,823 T^{-1} \quad (825 - 1448^\circ\text{K})$$

## 2.1.3. Beryllium-lithium fluorides

Heats of formation of  $\langle \text{BeLiF}_3 \rangle$  and  $\langle \text{BeLi}_2\text{F}_4 \rangle$  have been determined from calorimetric measurements made by Gross [40, 41] of the heats of the following two reactions:



Using assessed values for the heats of formation of  $\langle \text{LiF} \rangle$  and  $\{ \text{BeF}_2 \}$  glass (-147.45 kcal/mol [1] and -244.3 kcal/mol, respectively), values of  $\Delta H_{298} \langle \text{BeLiF}_3 \rangle = -394.5 \pm 2.5 \text{ kcal/mol}$  and  $\Delta H_{298} \langle \text{BeLi}_2\text{F}_4 \rangle = -544.2 \pm 2.0 \text{ kcal/mol}$  have been obtained.

Enthalpy data for  $\langle \text{BeLi}_2\text{F}_4 \rangle$  in the temperature range 323 - 723°K have been obtained by Douglas and Payne [42]. The following heat capacity equation for the solid, up to the melting point of 745°K, is based on their experimental data:

$$C_p = 21.99 + 35.36 \times 10^{-3} T - 0.24 \times 10^5 T^{-2} \quad (298 - 745^\circ\text{K})$$

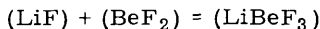
The heat capacity of the liquid between 745°K and 2000°K is assumed to be constant at 55.5 cal/°K·mol, as indicated by Douglas and Payne, and the above results provide a value of 10.61 kcal/mol for the heat of fusion of  $\text{BeLi}_2\text{F}_4$ .

The heat capacity of  $\langle \text{BeLiF}_3 \rangle$  has been estimated [1] from the difference of the  $C_p$  values for  $\langle \text{BeLi}_2\text{F}_4 \rangle$  and  $\langle \text{LiF} \rangle$ . The following equation may be used to represent the data:

$$C_p = 18.43 + 20.29 \times 10^{-3} T - 2.09 \times 10^5 T^{-2} \quad (298 - 633^\circ\text{K})$$

Standard entropy values for  $\langle \text{BeLiF}_3 \rangle$  and  $\langle \text{BeLi}_2\text{F}_4 \rangle$  have been estimated by addition of the  $S_{298}^0$  values for the component fluorides. The values obtained are  $21.3 \pm 2 \text{ cal/}^\circ\text{K} \cdot \text{mol}$  and  $29.8 \pm 2 \text{ cal/}^\circ\text{K} \cdot \text{mol}$ , respectively.

Berkowitz and Chupka [43] have determined a value for the heat of reaction at 900°K of



The value of  $\Delta H_{298} (\text{LiBeF}_3)$  obtained from their reported heat of reaction (53 kcal/mol) using estimated heat capacity data [1] is -212 kcal/mol. The estimated value of  $S_{298}^0$  for  $\text{LiBeF}_3$  gas is 64 cal/°K·mol and the estimated heat capacity between 298°K and 3000°K may be represented by the equations:

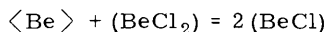
$$C_p = 12.86 + 21.07 \times 10^{-3} T - 9.79 \times 10^{-6} T^2 - 3.26 \times 10^5 T^{-2} \quad (298 - 1000^\circ\text{K})$$

$$C_p = 25.65 + 0.05 \times 10^{-3} T - 18.80 \times 10^5 T^{-2} \quad (1000 - 3000^\circ\text{K})$$

## 2.2. Chlorides

### 2.2.1. Beryllium monochloride

The heat of formation of BeCl gas has been obtained by Greenbaum et al. [44] from molecular flow effusion studies and by Novikov and Tunitskii [45] and Hildenbrand et al. [46] from spectroscopic studies. Second- and Third-Law analyses of the results give values of  $\Delta H_{298}$  varying from about 1 kcal/mol to 15 kcal/mol. A more recent determination of  $\Delta H_{298}$  (BeCl) by Gross and Lewin [47], using the transportation method applied to the reaction:



yields a value of  $2.0 \pm 1.0$  kcal/mol. This figure is in good agreement with the value obtained by Greenbaum et al. [44] and is accepted.

The standard entropy,  $S_{298}^0 = 53.0 \pm 2.5$  cal/°K·mol, is based on the work of Greenbaum et al. [44], and estimated heat capacity data [1] are represented by the equation:

$$C_p = 8.46 + 0.49 \times 10^{-3} T - 0.09 \times 10^{-6} T^2 - 0.97 \times 10^5 T^{-2} \quad (298-3000^\circ\text{K})$$

### 2.2.2. Beryllium dichloride

Beryllium dichloride exists in two crystal forms, denoted  $\alpha$  and  $\beta$ . The heat of formation has been determined by Johnson and Gilliland [48] by direct reaction of beryllium and chlorine. The value they have obtained for  $\Delta H_{298}$  was  $-118.03 \pm 0.56$  kcal/mol, but the crystal form of the product has not been specified. Gross et al. [49] have also obtained the heat of formation by direct combustion of the elements, their value of  $-117.1 \pm 0.4$  kcal/mol relating to the  $\alpha$ -form of  $\langle \text{BeCl}_2 \rangle$ . Thompson et al. [50] have obtained a value of  $\Delta H_{298} \langle \text{BeCl}_2 \rangle = -118.25 \pm 0.5$  kcal/mol from solution calorimetry. In a private communication to JANAF, these authors have quoted their sample as consisting of approximately 50%  $\alpha$ -form and 50%  $\beta$ -form of  $\langle \text{BeCl}_2 \rangle$ . From the above results, values of  $\Delta H_{298} \alpha\text{-}\langle \text{BeCl}_2 \rangle = -117.3 \pm 0.8$  kcal/mol and  $\Delta H_{298} \beta\text{-}\langle \text{BeCl}_2 \rangle = -118.6 \pm 0.8$  kcal/mol have been selected by JANAF.

McDonald and Oetting [51] have measured the heat capacity between 13°K and 304°K and the enthalpy from 676°K to 688°K of  $\alpha\text{-}\langle \text{BeCl}_2 \rangle$ . These authors have also obtained heat capacities between 13°K and 304°K and enthalpies from 298°K to 676°K for  $\beta\text{-}\langle \text{BeCl}_2 \rangle$ . The crystal form of their specimens was confirmed both before and after the experiments. The heat capacity data obtained from their results may be represented by the following equations:

$$\alpha\text{-}\langle \text{BeCl}_2 \rangle: C_p = 18.31 + 2.95 \times 10^{-3} T - 3.29 \times 10^5 T^{-2} \quad (298 - 688^\circ\text{K})$$

$$\beta\text{-}\langle \text{BeCl}_2 \rangle: C_p = 15.69 + 4.99 \times 10^{-3} T - 2.01 \times 10^5 T^{-2} \quad (298 - 676^\circ\text{K})$$

Integration of the heat capacity curves provides  $S_{298}^0$  values for  $\alpha\text{-}\langle \text{BeCl}_2 \rangle$  and  $\beta\text{-}\langle \text{BeCl}_2 \rangle$  of  $19.76 \pm 0.06$  cal/°K·mol and  $18.12 \pm 0.05$  cal/°K·mol, respectively.

The temperature of the  $\beta \rightarrow \alpha$  transition obtained from the results of McDonald and Oetting [51] is 676°K, and the corresponding heat of transition, which depends on the form of the  $C_p$ -curve chosen for  $\alpha$ - $\langle \text{BeCl}_2 \rangle$  between 304°K and 676°K, is  $1.63 \pm 0.15$  kcal/mol.

The heat capacity of liquid  $\text{BeCl}_2$  has again been determined by McDonald and Oetting [51] from enthalpy measurements made in the temperature range 688 - 713°K. Their results indicate that  $C_p$  has a constant value of 29.02 cal/°K·mol and this value is used, up to the normal boiling point of 805°K. The melting point of 688°K and the heat of fusion,  $2.07 \pm 0.06$  kcal/mol, are both based on the results obtained by McDonald and Oetting.

The vapour pressure over  $\beta$ - $\langle \text{BeCl}_2 \rangle$  has been determined by Rahlfs and Fischer [52], Fischer et al. [53], Hildenbrand et al. [54] and Ko et al. [55]. Second- and Third-Law analyses of the results give values for the heat of sublimation at 298°K which vary between 30.9 kcal/mol and 35.6 kcal/mol. The data of Hildenbrand et al. show greatest consistency between Second- and Third-Law values and give a value for the heat of sublimation of  $\text{BeCl}_2$  at 298°K of  $32.5 \pm 1$  kcal/mol. This corresponds to a heat of formation of  $\text{BeCl}_2$  gas at 298°K of  $-86.1 \pm 2.5$  kcal/mol. The heat capacity and standard entropy data for  $(\text{BeCl}_2)$  are those listed by JANAF.  $S_{298}^0$  has a value of  $60 \pm 1$  cal/°K·mol and the heat capacity values have been fitted by the equation:

$$C_p = 13.89 + 0.83 \times 10^{-3} T - 0.18 \times 10^{-6} T^2 - 1.67 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

The selected thermodynamic properties of condensed and gaseous  $\text{BeCl}_2$  have been used to calculate the following vapour pressure equations:

$$\langle \text{BeCl}_2 \rangle: \log p \text{ (mmHg)} = 17.584 - 1.89 \log T - 7365 T^{-1} \quad (298 - 688^\circ\text{K})$$

$$\{ \text{BeCl}_2 \}: \log p \text{ (mmHg)} = 36.605 - 8.07 \log T - 8394 T^{-1} \quad (688 - 805^\circ\text{K})$$

### 2.2.3. Beryllium dichloride (dimeric)

Ko et al. [55] have used the transpiration method to determine the thermodynamic properties and composition of the vapour over  $\langle \text{BeCl}_2 \rangle$  in the temperature range 623 - 683°K. The authors have used an iterative procedure to combine their results with previous torsion-effusion and gravimetric effusion data in the temperature range 440 - 600°K, and thereby obtained a value for the heat of formation of  $\text{Be}_2\text{Cl}_4$  gas at 298°K of -196.3 kcal/mol. In the absence of other experimental information this value is accepted, although the error limit is likely to be large. The value of  $S_{298}^0 = 92.5 \pm 2$  cal/°K·mol [55] is also accepted and is in reasonable agreement with the value of 91.15 cal/°K·mol estimated by JANAF. The estimated heat capacity data [1] for  $(\text{Be}_2\text{Cl}_4)$  have been fitted by the equation:

$$C_p = 31.40 + 0.15 \times 10^{-3} T - 3.58 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$



### 2.3. Bromides and iodides

#### 2.3.1. Beryllium monobromide and monoiodide

Heats of formation, standard entropies and heat capacity data for BeBr and BeI gases have all been estimated by JANAF from the experimental data for (BeF), (BeCl) and the gaseous lithium halides. The values listed by JANAF are as follows:

$$\text{(BeBr): } \Delta H_{298} = 8.8 \pm 5.0 \text{ kcal/mol} \quad S_{298}^0 = (54.84) \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

$$C_p \text{ (fitted)} = 8.80 + 0.14 \times 10^{-3} T - 1.06 \times 10^5 T^{-2} \text{ (298 - 3000}^\circ\text{K)}$$

$$\text{(BeI): } \Delta H_{298} = 24.7 \pm 5.0 \text{ kcal/mol} \quad S_{298}^0 = (56.7) \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

$$C_p \text{ (fitted)} = 8.84 + 0.13 \times 10^{-3} T - 0.93 \times 10^5 T^{-2} \text{ (298 - 3000}^\circ\text{K)}$$

#### 2.3.2. Beryllium dibromide and diiodide

The heats of formation of  $\langle \text{BeBr}_2 \rangle$  and  $\langle \text{BeI}_2 \rangle$  have been estimated by the National Bureau of Standards [56] from results reported by Biltz and Messerknecht [57] and Biltz, Klante and Rahlfs [58], who have measured the heat of solution of BeBr<sub>2</sub> and BeI<sub>2</sub> in [HCl]<sub>aq</sub> to an unknown concentration. Adjusted experimental values were used with data for Be<sup>++</sup> (estimated) and 2Br<sup>-</sup> or 2I<sup>-</sup> to obtain the heats of formation of the crystals. A recent report from NBS by Parker [2] gives recalculated values of  $\Delta H_{298}$  for  $\langle \text{BeBr}_2 \rangle$  and  $\langle \text{BeI}_2 \rangle$ . These are -84.5 kcal/mol and -46.0 kcal/mol, respectively. No error limits are reported. The heat capacity of both dihalides has been estimated graphically by JANAF by comparison with  $\langle \text{BeCl}_2 \rangle$  and  $\langle \text{BeF}_2 \rangle$ , while standard entropy values were obtained using additive entropy values for the halide ions. The selected values are given below:

$$\langle \text{BeBr}_2 \rangle: S_{298}^0 = 25.4 \pm 2.0 \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

$$C_p \text{ (fitted)} = 19.52 + 1.07 \times 10^{-3} T - 2.96 \times 10^5 T^{-2} \text{ (298 - 761}^\circ\text{K)}$$

$$\langle \text{BeI}_2 \rangle: S_{298}^0 = 28.8 \pm 2.0 \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

$$C_p \text{ (fitted)} = 19.91 + 0.86 \times 10^{-3} T - 2.81 \times 10^5 T^{-2} \text{ (298 - 753}^\circ\text{K)}$$

The melting points of BeBr<sub>2</sub> and BeI<sub>2</sub> have been reported by Rahlfs and Fischer [59]. Heats of fusion of 4.5 kcal/mol and 5 kcal/mol, respectively, were estimated by JANAF from the sums of the heats of transition and fusion for BeF<sub>2</sub> and BeCl<sub>2</sub>. Liquid heat capacities were estimated as described for the crystals.

$$\{\text{BeBr}_2\}: C_p = 27.0 \text{ (761 - 794}^\circ\text{K)}$$

$$\{\text{BeI}_2\}: C_p = 27.0 \text{ (753 - 900}^\circ\text{K)}$$

Rahlfs and Fischer [59] have measured the vapour pressure of BeBr<sub>2</sub> in the temperature range 624 - 695°K and of BeI<sub>2</sub> in the temperature range

578 - 703°K. Values for the heats of sublimation at 298°K obtained from their results are 31.1 kcal/mol and 30.3 kcal/mol, respectively. These lead to values of  $\Delta H_{298}(\text{BeBr}_2) = -53.4$  kcal/mol and  $\Delta H_{298}(\text{BeI}_2) = -15.7$  kcal/mol. Heat capacities and standard entropies for the two gases have been estimated by JANAF from data for the gaseous beryllium dihalide series. The values obtained are:

$$\begin{aligned} (\text{BeBr}_2): S_{298}^0 &= 66.4 \pm 2 \text{ cal/}^\circ\text{K} \cdot \text{mol} \\ C_p \text{ (fitted)} &= 14.89 - 2.66 \times 10^5 T^{-2} \text{ (298 - 3000}^\circ\text{K)} \\ (\text{BeI}_2): S_{298}^0 &= 70.4 \pm 2 \text{ cal/}^\circ\text{K} \cdot \text{mol} \\ C_p \text{ (fitted)} &= 14.89 - 2.03 \times 10^5 T^{-2} \text{ (800 - 3000}^\circ\text{K)} \end{aligned}$$

The selected data for condensed and gaseous  $\text{BeBr}_2$  and  $\text{BeI}_2$  have been used to calculate vapour pressure equations:

$$\begin{aligned} \langle \text{BeBr}_2 \rangle: \log p \text{ (mmHg)} &= 19.343 - 2.57 \log T - 7139 T^{-1} \text{ (298 - 761}^\circ\text{K)} \\ \{ \text{BeBr}_2 \}: \log p \text{ (mmHg)} &= 9.457 - 5250 T^{-1} \text{ (761 - 794}^\circ\text{K)} \\ \langle \text{BeI}_2 \rangle: \log p \text{ (mmHg)} &= 19.443 - 2.56 \log T - 6961 T^{-1} \text{ (298 - 753}^\circ\text{K)} \\ \{ \text{BeI}_2 \}: \log p \text{ (mmHg)} &= 32.307 - 6.88 \log T - 7290 T^{-1} \text{ (753 - 900}^\circ\text{K)} \end{aligned}$$

### 3. OXIDES

#### 3.1. Beryllium oxide

Parker, in a fairly recent NBS report [2], has assessed all the experimental values obtained for the heat of formation of  $\langle \text{BeO} \rangle$ . The methods used to obtain  $\Delta H_{298}$  fall into two categories, namely, bomb combustion as performed by Mielenz and von Wartenberg [60], Moose and Parr [61], Neumann, Kröger and Kunz [62], Roth, Börger and Siemonsen [63] and Cosgrove and Snyder [64], and solution of  $\langle \text{Be} \rangle$  or  $\langle \text{BeO} \rangle$  in aqueous HF solution, as carried out by Copaux and Philips [65], Matignon and Marchal [66], Fricke and Wullhorst [67], Neumann, Kröger and Haebler [68], Smirnov and Chukreev [69], Kolesov, Popov and Skuratov [70], Thompson, Sinke and Stull [50], Bear and Turnbull [71], Armstrong and Coyle [72] and Kilday, Prosen and Wagman [73]. The direct, combustion experiments give values of  $\Delta H_{298} \langle \text{BeO} \rangle$  varying between -134.4 kcal/mol and -147.3 kcal/mol, while results from the indirect, solution experiments vary between -141.1 kcal/mol and -146.0 kcal/mol. Parker selects a 'best' value for  $\Delta H_{298} \langle \text{BeO} \rangle$  of  $-145.4 \pm 0.8$  kcal/mol.

The low-temperature heat capacity of  $\langle \text{BeO} \rangle$  between 55.5°K and 292.4°K has been determined by Kelley [74]. On the assumption that  $C_p$  follows the  $T^3$  law below 55.5°K, the value of  $S_{55.5}^0$  has been estimated to be 0.045 cal/°K · mol, and  $S_{298}^0$  has been obtained as  $3.38 \pm 0.05$  cal/°K · mol. High-temperature enthalpy data for  $\langle \text{BeO} \rangle$  have been determined by

Magnus and Danz [75], Kandyba et al. [76], Rodigina and Gorn' skij [77], Walker et al. [78], Victor and Douglas [79] and Greenbaum et al. [80]. The experimental studies cover the temperature range up to 2840°K. Although a high-temperature phase change has been reported at temperatures around 2300°K [81, 82], neither the measurements of Kandyba et al. nor those of Greenbaum et al. were sufficiently accurate to determine a heat of transformation. Heat capacity values obtained from the experimental studies have therefore been fitted by a single equation up to the melting temperature of  $2853 \pm 10^\circ\text{K}$  reported by Greenbaum et al. [80]:

$$C_p = 9.94 + 2.44 \times 10^{-3} T - 0.32 \times 10^{-6} T^2 - 4.15 \times 10^5 T^{-2} \quad (298 - 2853^\circ\text{K})$$

The heat of fusion measurements made by Greenbaum et al. as an integral part of their study provide a value of  $L_f = 19.3 \pm 0.8$  kcal/mol for BeO at 2853°K. The liquid heat capacity, assumed constant up to 4000°K, is estimated to be 15.5 cal/°K·mol.

In the recent Technical Note 270-6 [3], NBS records a value of  $\Delta H_{298}$  BeO gas of 28 kcal/mol. No references are given relating to this value, which is presumably largely based on the work of Chupka et al. [83]. This heat of formation corresponds to a value of 173.4 kcal/mol for  $L_s$  (298°K).

JANAF have used the spectroscopic constants listed by Herzberg [27] to obtain standard entropy and heat capacity data for gaseous beryllium oxide. These are as follows:

$$S_{298}^0 = 47.2 \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

$$C_p(\text{fitted}) = 7.27 + 1.39 \times 10^{-3} T - 0.27 \times 10^{-6} T^2 - 0.64 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

The selected thermodynamic values for condensed and gaseous BeO have been used to derive the following vapour pressure equation:

$$\langle \text{BeO} \rangle: \log p \text{ (mmHg)} = 18.015 - 1.77 \log T - 38247 T^{-1} \quad (298 - 2500^\circ\text{K})$$

It should be noted that at 2300°K the vapour above BeO consists of Be, O, BeO, (BeO)<sub>2</sub>, (BeO)<sub>3</sub>, (BeO)<sub>4</sub>, (BeO)<sub>5</sub>, (BeO)<sub>6</sub>, Be<sub>2</sub>O and other species. Values for the heats of formation of the dimeric, trimeric, tetrameric, pentameric and hexameric forms of gaseous BeO have been tabulated by NBS [3]. The values are presumably again obtained from the work of Chupka et al. [83]. JANAF have estimated corresponding standard entropy and heat capacity data. The results are summarized below:

$$(\text{BeO})_2: \quad \Delta H_{298} = -103 \text{ kcal/mol} \quad S_{298}^0 = 59.2 \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

$$C_p = 15.89 + 3.26 \times 10^{-3} T - 0.69 \times 10^{-6} T^2 - 4.26 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

$$(\text{BeO})_3: \quad \Delta H_{298} = -260 \text{ kcal/mol} \quad S_{298}^0 = 65.3 \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

$$C_p = 20.77 + 9.04 \times 10^{-3} T - 1.90 \times 10^{-6} T^2 - 7.58 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

$$(\text{BeO})_4: \quad \Delta H_{298} = -391 \text{ kcal/mol} \quad S_{298}^0 = 72.3 \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

$$C_p = 32.84 + 9.15 \times 10^{-3} T - 1.95 \times 10^{-6} T^2 - 12.90 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

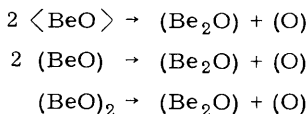
$$\begin{aligned} (\text{BeO})_5: \quad \Delta H_{298} &= -518 \text{ kcal/mol} \quad S_{298}^0 = 77.2 \text{ cal/}^\circ\text{K} \cdot \text{mol} \\ C_p &= 47.73 + 3.64 \times 10^{-3} T - 0.24 \times 10^{-6} T^2 - 20.57 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K}) \end{aligned}$$

$$\begin{aligned} (\text{BeO})_6: \quad \Delta H_{298} &= -651 \text{ kcal/mol} \quad S_{298}^0 = 82 \text{ cal/}^\circ\text{K} \cdot \text{mol} \\ C_p &= 50.94 + 14.02 \times 10^{-3} T - 3.00 \times 10^{-6} T^2 - 21.47 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K}) \end{aligned}$$

The error limits on the above values are very large, e.g. of the order of  $\pm 25$  kcal/mol on  $\Delta H_{298} (\text{BeO})_6$ .

### 3.2. Diberyllium oxide

Hildenbrand, Theard and Ju [84], using a mass spectrometer, have determined equilibrium constants for the reactions:



NBS has presumably used the results of these investigations and its own revised data for BeO [2] to obtain a heat of formation of  $\text{Be}_2\text{O}$  gas of  $\Delta H_{298} = -20$  kcal/mol [3]. The error limit on this value is probably of the order of  $\pm 10$  kcal/mol. The heat capacity and standard entropy have been estimated by JANAF:

$$\begin{aligned} S_{298}^0 &= 52.7 \text{ cal/}^\circ\text{K} \cdot \text{mol} \\ C_p (\text{fitted}) &= 7.74 + 10.61 \times 10^{-3} T - 4.61 \times 10^{-6} T^2 - 0.63 \times 10^5 T^{-2} \quad (298 - 1000^\circ\text{K}) \\ &= 14.73 + 0.05 \times 10^{-3} T - 11.03 \times 10^5 T^{-2} \quad (1000 - 3000^\circ\text{K}) \end{aligned}$$

#### 3.2.1. Diberyllium dilithium oxide

Hayman [85] has reported the value of  $\Delta H_{298} \langle \text{Be}_2\text{Li}_2\text{O}_3 \rangle$  to be  $-437.8 \pm 2.0$  kcal/mol, based on calorimetric measurements made at the Fulmer Research Institute.

### 3.3. Oxyhalides

#### 3.3.1. Beryllium oxyfluoride

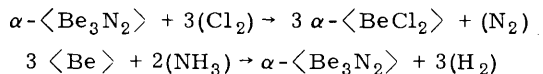
Efimenko [86] has made a mass-spectrometric investigation of the reaction  $\langle \text{BeO} \rangle + (\text{BeF}_2) \rightarrow (\text{Be}_2\text{OF}_2)$  in the temperature range 1570 - 2195°K and has reported two sets of equilibrium constants. Parker [2] has presumably used these values and his own assessed data for BeO and  $\text{BeF}_2$  to calculate a value of  $\Delta H_{298} (\text{Be}_2\text{OF}_2) = -292$  kcal/mol. Estimated heat capacity and standard entropy data are from JANAF

$$\begin{aligned} S_{298}^0 &= 71.4 \text{ cal/}^\circ\text{K} \cdot \text{mol} \\ C_p (\text{fitted}) &= 22.16 + 2.98 \times 10^{-3} T - 0.62 \times 10^{-6} T^2 - 4.52 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K}) \end{aligned}$$

## 4. NITRIDES

4.1. Beryllium nitride

Gross et al. [87] have determined the heat of formation of  $\alpha$ - $\langle \text{Be}_3\text{N}_2 \rangle$  (cubic form) from measurements of the heats of the following two reactions:



The observed heat for the chlorination reaction is  $-210.3 \pm 1.1$  kcal/mol. When combined with the selected heat of formation of  $\alpha$ - $\langle \text{BeCl}_2 \rangle$  ( $-117.3$  kcal/mol), a value of  $\Delta H_{298} \alpha\text{-}\langle \text{Be}_3\text{N}_2 \rangle = -141.6 \pm 1.5$  kcal/mol is obtained. The heat of reaction of beryllium with ammonia has been observed to be  $-214.6 \pm 0.3$  kcal/mol at  $298^\circ\text{K}$ , resulting in a value of  $\Delta H_{298} \alpha\text{-}\langle \text{Be}_3\text{N}_2 \rangle = -140.3 \pm 0.4$  kcal/mol.

Using the torsion-effusion vapour-pressure method, Yates, Greenbaum and Farber [88] have studied the decomposition of  $\langle \text{Be}_3\text{N}_2 \rangle$  to (Be) and ( $\text{N}_2$ ) in the temperature range  $1438 - 1661^\circ\text{K}$  and obtained a Third-Law value of  $\Delta H_{298} \langle \text{Be}_3\text{N}_2 \rangle = -140.3 \pm 1.5$  kcal/mol. The same decomposition has been investigated by Hoenig [89] using the Knudsen method in the temperature range  $1648 - 1946^\circ\text{K}$ . The values of  $\Delta H_{298} \langle \text{Be}_3\text{N}_2 \rangle$  derived from his results are on average about 5 kcal/mol more exothermic than those of Yates et al. [88].

A value of  $\Delta H_{298} \alpha\text{-}\langle \text{Be}_3\text{N}_2 \rangle = -140.9 \pm 0.6$  kcal/mol has been selected from the calorimetric results.

In Ref.[3] a value of  $-136.5$  kcal/mol for the heat of formation of hexagonal  $\langle \text{Be}_3\text{N}_2 \rangle$  is quoted, but no references are given for this value.

The low-temperature heat capacity of  $\alpha$ - $\langle \text{Be}_3\text{N}_2 \rangle$  between  $25^\circ\text{K}$  and  $310^\circ\text{K}$  has been measured by Justice [90]. Integration of these data provides a value of  $S_{298}^0$  of  $8.16$  cal/ $^\circ\text{K} \cdot \text{mol}$ . Furukawa and Reilly [91] also have more recently made low-temperature heat capacity measurements at temperatures between  $20^\circ\text{K}$  and  $315^\circ\text{K}$  and obtained a value of  $8.23 \pm 0.08$  cal/ $^\circ\text{K} \cdot \text{mol}$  for the standard entropy. A value of  $S_{298}^0 \alpha\text{-}\langle \text{Be}_3\text{N}_2 \rangle = 8.20 \pm 0.05$  cal/ $^\circ\text{K} \cdot \text{mol}$  is selected.

The relative enthalpy of  $\alpha$ - $\langle \text{Be}_3\text{N}_2 \rangle$  at temperatures between  $273^\circ\text{K}$  and  $1173^\circ\text{K}$  has been determined by Douglas and Payne [92] using drop calorimetry. Corrections were applied for impurities. Their data have been used to obtain the following heat capacity equations:

$$C_p = 12.89 + 24.75 \times 10^{-3} T - 4.22 \times 10^5 T^{-2} \quad (298 - 430^\circ\text{K})$$

$$C_p = 27.37 + 3.60 \times 10^{-3} T - 14.23 \times 10^5 T^{-2} \quad (430 - 1200^\circ\text{K})$$

## 5. CARBIDES

5.1. Diberyllium monocarbide

The heat of formation of  $\langle \text{Be}_2\text{C} \rangle$  has been determined by Blachnik, Gross and Hayman [93] from acid solution calorimetry measurements at  $110^\circ\text{C}$ . Their experimental value of  $\Delta H_{298} \langle \text{Be}_2\text{C} \rangle$  is  $-27.96 \pm 0.21$  kcal/mol.

The value of  $S_{298}^0$  has been estimated by Krikorian [94] to be  $3.9 \pm 1.0 \text{ cal/}^\circ\text{K} \cdot \text{mol}$ .

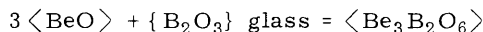
Neely, Teeter and Trice [95] have determined mean heat capacity values in the temperature range 298 - 1200°K. They have quoted the analysis of their powder specimen to be 74 - 80%  $\text{Be}_2\text{C}$  with beryllium oxide and nitride as the main impurities. No corrections have been made for these impurities and the authors have estimated their measured data to be accurate to 15% only. JANAF have extrapolated these heat capacity data from 1200°K to 2400°K so as to approach the value of  $22 \text{ cal/}^\circ\text{K} \cdot \text{mol}$  calculated by Krikorian [94]. The results have been fitted by the following equation:

$$C_p = 9.17 + 10.76 \times 10^{-3} T - 2.29 \times 10^{-6} T^2 - 2.01 \times 10^5 T^{-2} \quad (298 - 2400^\circ\text{K})$$

## 6. BORATES, ALUMINATES AND SILICATES

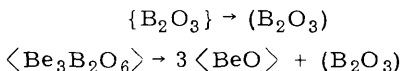
### 6.1. Triberyllium diborate

Gross [96] has carried out calorimetric measurements of the heat of the reaction:

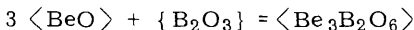


His value of  $-13.38 \pm 0.5 \text{ kcal/mol}$  has been combined with  $\Delta H_{298} \langle \text{BeO} \rangle = -145.4 \pm 0.8 \text{ kcal/mol}$  and  $\Delta H_{298} \{ \text{B}_2\text{O}_3 \} \text{ glass} = -299.3 \pm 0.5 \text{ kcal/mol}$  to obtain a heat of formation for  $\langle \text{Be}_3\text{B}_2\text{O}_6 \rangle$  of  $-748.9 \pm 3.5 \text{ kcal/mol}$ .

Blackburn and Buchler [97] have made vacuum balance and ion intensity investigations of the reactions:



They have reported values of  $K_p$  of  $2.7 \times 10^{-5} \text{ atm}$  and  $9.3 \times 10^{-6} \text{ atm}$  for the two reactions respectively at 1500°K. These values provide Gibbs energies for the two reactions which, when combined, give  $-3.17 \text{ kcal/mol}$  for the reaction



The value obtained by Gross [96] for the heat of this reaction may now be combined with the Gibbs energy value at 1500°K to give an entropy of reaction of  $-6.81 \text{ cal/}^\circ\text{K} \cdot \text{mol}$ . From this latter value and the standard entropies of  $\{ \text{B}_2\text{O}_3 \}$  and  $\langle \text{BeO} \rangle$  a value of  $S_{298}^0 \langle \text{Be}_3\text{B}_2\text{O}_6 \rangle = 22.1 \pm 3 \text{ cal/}^\circ\text{K} \cdot \text{mol}$  is obtained.

The heat capacity of  $\langle \text{Be}_3\text{B}_2\text{O}_6 \rangle$  has been estimated by JANAF from the heat capacities of the component oxides:

$$C_p \text{ (fitted)} = 26.90 + 62.92 \times 10^{-3} T - 21.08 \times 10^{-6} T^2 - 9.51 \times 10^5 T^{-2} \quad (298 - 1768^\circ\text{K})$$

The melting point of  $1768 \pm 5^\circ\text{K}$  is that reported by Blackburn and Buchler [97].

## 6.2. Beryllium aluminates

### 6.2.1. Beryllium monoaluminate

The heat of formation of  $\langle \text{BeAl}_2\text{O}_4 \rangle$ , at about 1000°K, has been determined by Holm and Kleppa [98] using molten oxide solution calorimetry. Their value of -4.0 kcal/mol for formation from the component oxides provides a value of  $\Delta H_{298} \langle \text{BeAl}_2\text{O}_4 \rangle = -549.4$  kcal/mol from the elements. This value is in good agreement with the figure obtained by Young [99] from equilibrium studies.

The low-temperature heat capacity of the compound has been measured by Furukawa et al. [100]. The results give a value of  $S_{298}^0 = 15.84$  cal/°K·mol. High-temperature enthalpy measurements have also been reported by these authors and by Ditmars and Douglas [101], enabling heat capacity data to be obtained at temperatures up to the melting point of 2143°K.

$$C_p = 29.26 + 22.62 \times 10^{-3} T - 9.36 \times 10^{-6} T^2 - 8.93 \times 10^5 T^{-2} \quad (298 - 1200^\circ\text{K})$$

$$= 37.58 + 4.10 \times 10^{-3} T \quad (1200 - 2143^\circ\text{K})$$

### 6.2.2. Beryllium trialuminate

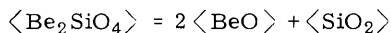
The molten oxide solution calorimetry measurements of Holm and Kleppa [98] provide a value of  $\Delta H_{298} \langle \text{BeAl}_6\text{O}_{10} \rangle = -1342.6$  kcal/mol for formation from the elements. The value of  $S_{298}^0 = 42.0$  cal/°K·mol is reported by NBS [3]. The heat capacity of the compound has been determined by Ditmars and Douglas [102] for temperatures up to 2150°K.

$$C_p = 88.45 + 18.57 \times 10^{-3} T - 2.77 \times 10^{-6} T^2 - 27.75 \times 10^5 T^{-2} \quad (298 - 2150^\circ\text{K})$$

## 6.3. Beryllium silicate

The heat of formation of  $\langle \text{Be}_2\text{SiO}_4 \rangle$  has been determined by Holm and Kleppa [98] using molten oxide solution calorimetry. Their measured value of -4.7 kcal/mol for formation from the oxides at 968°K has been used in conjunction with a room temperature  $C_p$ -value obtained by Kelley [74] from low-temperature heat capacity measurements, and high-temperature heat capacity data based on the  $C_p$ -values for the component oxides, to obtain  $\Delta H_{298} \langle \text{Be}_2\text{SiO}_4 \rangle = -512.8 \pm 2.5$  kcal/mol from the elements. The value of  $S_{298}^0 = 15.37 \pm 0.1$  cal/°K·mol is the figure given by Kelley's data.

At 1833°K,  $\langle \text{Be}_2\text{SiO}_4 \rangle$  dissociates into its component oxides [103] and the resulting requirement that  $\Delta G_{1833} = 0$  for the reaction



was used to refine the estimated heat capacity equation for the compound.

$$C_p = 29.65 + 18.77 \times 10^{-3} T - 8.0 \times 10^{-6} T^2 - 10.84 \times 10^5 T^{-2} \quad (298 - 1833^\circ\text{K})$$

## 7. HYDRIDES AND HYDROXIDES

7.1. Beryllium monohydride

The heat of formation of BeH gas has been selected by JANAF from the tabulations of Gaydon [104]. The value is  $77 \pm 7$  kcal/mol. The heat capacity and entropy have also been calculated by JANAF from the molecular constants listed by Herzberg [27]:  $S_{298}^0 = 42.24$  cal/°K · mol.

$$C_p = 6.44 + 1.98 \times 10^{-3} T - 0.36 \times 10^{-6} T^2 - 0.08 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

7.2. Beryllium dihydride

The heat of formation of  $\langle \text{BeH}_2 \rangle$  has been determined by Akhachinskij et al. [105] and by Ivanov and Karpova [106] using bomb calorimetry. Their results are in good agreement and provide a value of  $\Delta H_{298} = -4.55 \pm 0.5$  kcal/mol.

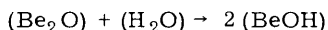
Data for gaseous (BeH<sub>2</sub>) are the estimated values listed by JANAF.

$$\Delta H_{298} = 30 \text{ kcal/mol} \quad S_{298}^0 = 41.4 \text{ cal/°K} \cdot \text{mol}$$

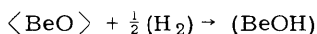
$$C_p = 7.50 + 5.66 \times 10^{-3} T - 1.14 \times 10^{-6} T^2 - 1.95 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

7.3. Beryllium monohydroxide

The heat of formation of BeOH gas has been obtained by Hildenbrand et al. [84] from mass-spectrometric studies of the reaction:



and by Ko et al. [107] from molecular flow effusion studies of the reaction:



The two values of  $\Delta H_{298}$  (BeOH) are not in good agreement, being  $-24.8 \pm 10$  kcal/mol and  $-47.5 \pm 7$  kcal/mol (average of Second- and Third-Law values) respectively. The latter figure is more consistent with values for gaseous (CaOH) and (MgOH) however and has therefore been selected.

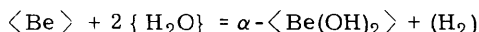
The standard entropy and heat capacity are those estimated by JANAF.

$$S_{298}^0 = 53.28 \text{ cal/°K} \cdot \text{mol}$$

$$C_p = 8.13 + 3.73 \times 10^{-3} T - 0.68 \times 10^{-6} T^2 - 0.98 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

7.4. Beryllium dihydroxide

The heat of formation of  $\alpha$ - $\langle \text{Be}(\text{OH})_2 \rangle$  (tetragonal) has been determined by Bear and Turnbull [71] from calorimetric studies of the heats of solution of pure beryllium metal and of  $\alpha$ - $\langle \text{Be}(\text{OH})_2 \rangle$  in aqueous HF. Values have thereby been obtained for the heat of the reaction:



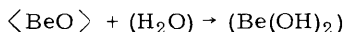


and the value calculated for  $\Delta H_{298} \alpha\text{-}\langle \text{Be}(\text{OH})_2 \rangle = -215.7 \pm 0.5$  kcal/mol.

The heat of formation of  $\beta\text{-}\langle \text{Be}(\text{OH})_2 \rangle$  (orthorhombic) has been determined by Bear and Turnbull [71] in the same manner, while studies made by Fricke and Severin [108] and Baur and Lecocq [109] of the decomposition pressure of water vapour over  $\beta\text{-}\langle \text{Be}(\text{OH})_2 \rangle$  give Third-Law values of  $\Delta H_{298} \beta\text{-}\langle \text{Be}(\text{OH})_2 \rangle$  in very good agreement with the calorimetrically determined value. The selected heat of formation is  $-216.5 \pm 0.5$  kcal/mol. JANAF have estimated a value of  $S_{298}^0$  for  $\beta\text{-}\langle \text{Be}(\text{OH})_2 \rangle = 11.0 \pm 2$  cal/°K·mol, which finds independent confirmation from the data of Baur and Lecocq. The value of  $S_{298}^0 \alpha\text{-}\langle \text{Be}(\text{OH})_2 \rangle = 11.8 \pm 2$  cal/°K·mol has been obtained via the difference in Gibbs energies [110] and heats of formation at 298°K of  $\alpha\text{-}$  and  $\beta\text{-}\langle \text{Be}(\text{OH})_2 \rangle$ . Beryllium dihydroxide has been calculated to decompose into  $\langle \text{BeO} \rangle$  and  $(\text{H}_2\text{O})$  at 407°K in the case of the  $\alpha\text{-}$  form and at 417°K in the case of the  $\beta\text{-}$  form. The heat capacity for both  $\alpha$  and  $\beta$  has been estimated by JANAF and is assumed to be the same for the two crystal structures, namely,

$$C_p = 4.56 + 36.75 \times 10^{-3} T + 0.10 \times 10^5 T^{-2} \quad (298 - 400^\circ\text{K})$$

A number of investigators [99, 111-115] have studied the equilibrium reaction:



Their results have been subjected to Second- and Third-Law analyses by JANAF, who have used their own functions to obtain a best value of  $\Delta H_{298} (\text{Be}(\text{OH})_2) = -156.4 \pm 5$  kcal/mol.

To obtain standard entropy and heat capacity data for  $(\text{Be}(\text{OH})_2)$ , the structure assumed by Altman [116] has been adopted by JANAF. Further estimates have been made to obtain  $S_{298}^0 = (59.2)$  cal/°K·mol and

$$C_p = 15.47 + 6.86 \times 10^{-3} T - 1.27 \times 10^{-6} T^2 - 3.83 \times 10^5 T^{-2} \quad (298 - 3000^\circ\text{K})$$

## 8. SULPHIDE, SULPHATE, SELENATE

### 8.1. Beryllium sulphide

In a recent survey of the thermodynamic properties of sulphides, selenides and tellurides, Mills [117] has selected a value of  $\Delta H_{298} \langle \text{BeS} \rangle = -55.8 \pm 1.0$  kcal/mol. His estimated value for  $S_{298}^0$  is  $8.0 \pm 1.5$  cal/°K·mol and we have estimated the following heat capacity equation:

$$C_p = 9.97 + 1.94 \times 10^{-3} T - 2.30 \times 10^5 T^{-2} \quad (298 - 1800^\circ\text{K})$$

### 8.2. Beryllium sulphate

The heat of formation of  $\alpha\text{-}\langle \text{BeSO}_4 \rangle$  has been determined by Bear and Turnbull [118] from measurements of the heat of solution of  $\langle \text{Be} \rangle$  and  $\alpha\text{-}\langle \text{BeSO}_4 \rangle$  in concentrated  $[\text{HF}]_{\text{aq}}$  and the heat of reaction of

$\text{H}_2\text{SO}_4$  with  $\text{BeSO}_4$  in HF solution. The resulting value is:  $\Delta H_{298} \alpha\text{-}\langle\text{BeSO}_4\rangle = -286.65 \pm 0.5$  kcal/mol. Taylor et al. [119] have measured the heats of solution of  $\langle\text{Be}\rangle$  and  $\alpha\text{-}\langle\text{BeSO}_4\rangle$  in  $\text{H}_2\text{SO}_4$  and obtained a value of  $-287.55 \pm 0.13$  kcal/mol for the heat of formation of  $\alpha\text{-}\langle\text{BeSO}_4\rangle$ . JANAF have selected the average value of these two results to give  $\Delta H_{298} \alpha\text{-}\langle\text{BeSO}_4\rangle = -287.0 \pm 0.8$  kcal/mol.

The standard entropy of  $\alpha\text{-}\langle\text{BeSO}_4\rangle$  has been obtained from the low-temperature heat capacity measurements of Taylor et al. [120], giving  $S_{298}^0 = 18.64$  cal/ $^\circ\text{K} \cdot \text{mol}$ . The same authors have measured the enthalpy of  $\langle\text{BeSO}_4\rangle$  in the temperature range 366 to 864 $^\circ\text{K}$ , while the transformation temperatures of 863 $^\circ\text{K}$  ( $\alpha \rightarrow \beta\text{-}\langle\text{BeSO}_4\rangle$ ) and 908 $^\circ\text{K}$  ( $\beta \rightarrow \gamma\text{-}\langle\text{BeSO}_4\rangle$ ) observed by Bosik et al. [121] have been used by JANAF, together with the single enthalpy value obtained by Taylor et al. at 863.9 $^\circ\text{K}$ , to give a heat of transformation ( $\alpha \rightarrow \beta$ ) of 0.266 kcal/mol at 863 $^\circ\text{K}$ . A value for the heat of the  $\beta \rightarrow \gamma$  transformation has been chosen by JANAF so as to give good agreement with the equilibrium vapour pressure data obtained by Marchal [122] in the temperature range 863 - 1103 $^\circ\text{K}$ . Their selected value for  $L_t \beta \rightarrow \gamma\text{-}\langle\text{BeSO}_4\rangle$  is 4.673 kcal/mol at 908 $^\circ\text{K}$ . The following equations represent the heat capacity of  $\alpha\text{-}$ ,  $\beta\text{-}$  and  $\gamma\text{-}\langle\text{BeSO}_4\rangle$  respectively:

$$\begin{aligned} C_p &= 26.96 - 2.21 \times 10^{-3} T + 18.17 \times 10^{-6} T^2 - 6.62 \times 10^5 T^{-2} \quad (298 - 863^\circ\text{K}) \\ &= 38.73 \quad (863 - 908^\circ\text{K}) \\ &= 69.32 - 12.56 \times 10^{-3} T + 2.03 \times 10^{-6} T^2 - 171.51 \times 10^5 T^{-2} \quad (908 - 1500^\circ\text{K}) \end{aligned}$$

### 8.3. Beryllium selenate

The heat of formation of  $\langle\text{BeSeO}_4\rangle$  has been reported by Selivanova and Shneider [123] to be -213.2 kcal/mol.

## 9. MISCELLANEOUS

Thermodynamic data for a number of substances not discussed previously in this article have been tabulated by the National Bureau of Standards in their recent publication TN 270-6 [3]. No references or error limits have been given with their selected values, which are reproduced in Table I. The references in Table I are obtained from NBS Circular 500 [124] which records the earlier work on most of the substances listed in this table.

## 10. THERMODYNAMIC PROPERTIES OF BERYLLIUM ALLOYS

In this section, published data for beryllium alloys, including inter-metallic compounds, are presented in an assessed form. The tabulations of Hultgren et al. [4] have been frequently used as a reference source and the selected values they quote are sometimes repeated in the following discussions of individual alloy systems. In certain cases, however, values have been adjusted to give better accord with the published phase diagram or with more recent experimental data.

### 10.1. Beryllium-aluminium

Serebryakov et al. [132] have carried out e.m.f. measurements on liquid alloys dilute in beryllium. Their investigations were made in the temperature range 953 - 1073°K for compositions of  $N_{\text{Be}}$  = between 0.00224 and 0.0130. At the experimental temperatures the liquid solutions were found to obey Henry's Law over the entire concentration range investigated. The expression derived by the authors for the temperature variation of the solubility of beryllium in aluminium does not reproduce the liquidus of the phase diagram very closely, and enthalpy and entropy values obtained from the temperature coefficients of the measurements are not considered to be reliable.

Schaub, Potard and Desré [133] have measured the vapour pressure of beryllium and aluminium over liquid alloys of compositions of  $N_{\text{Be}}$  = between 0.389 and 0.956 in the temperature range 1642 - 1760°K. The temperature coefficients of their measurements provide  $\Delta\bar{H}_{\text{Be}}$  and  $\Delta\bar{S}_{\text{Be}}$  values which lead to reasonable agreement between the calculated and experimental liquidus of the phase diagram. The partial enthalpies and entropies of beryllium are therefore considered to be fairly reliable, but some adjustment of the values has been made to give greater consistency with the liquidus.

Bienvenu et al. [134] have determined a value for the activity coefficient of aluminium in liquid beryllium at a temperature of 1600°K from studies of the distribution of aluminium between liquid beryllium and liquid tin.

Data for liquid alloys at 1600°K  
(liquid beryllium and liquid aluminium standard states)

$N_{\text{Be}}$	$\Delta\bar{G}_{\text{Be}}$ (cal/g-atom)	$\Delta\bar{G}_{\text{Al}}$ (cal/g-atom)	$\Delta\bar{H}_{\text{Be}}$ (cal/g-atom)	$\Delta\bar{S}_{\text{Be}}$ (cal/g-atom · °K)	$\Delta G$ (cal/g-atom)
0.001 <sup>a</sup>	-8095				
0.005 <sup>a</sup>	-4900				
0.01 <sup>a</sup>	-3520				
0.4	-1610	-1685	6470	5.05	-1655
0.5	-1143 ± 100	-2152 ± 100	5112 ± 200	3.91 ± 0.3	-1647 ± 100
0.6	-804	-2585	3756	2.85	-1516
0.7	-543	-2977	2450	1.87	-1273
0.8	-322	-3401	1278	1.00	-938
0.9	-164	-4288	380	0.34	-576

<sup>a</sup> The reference temperature for these data is 1000°K (liquid beryllium standard state).

### 10.2. Beryllium-cerium

The vapour pressure of beryllium over the nearly-pure metal ( $N_{\text{Ce}} = 0.0003$ ) and over an alloy of composition  $\text{Be}_{13}\text{Ce}$  ( $N_{\text{Ce}} = 0.0714$ ) has been measured in the temperature range 1193 - 1523°K by Amonenko et al. [135]. Their data are represented by the equations

$\log p$  (mmHg) =  $9.35 - 17000/T$  and  $\log p$  (mmHg) =  $10.473 - 18990/T$  for the two cases respectively. These expressions enable a value of  $\Delta\bar{G}_{\text{Be}}$  of  $-1935$  cal/g-atom to be calculated for the  $\text{Be}_{13}\text{Ce}$  phase at a temperature of  $1400^\circ\text{K}$ .

Data for solid alloys at  $1400^\circ\text{K}$   
(solid  $\alpha$ -Be standard state)

$N_{\text{Be}}$	Phase	$\Delta\bar{G}_{\text{Be}}$ (cal/g-atom)
0.0714	$\text{Be}_{13}\text{Ce}$	-1935

### 10.3. Beryllium-copper

Partial Gibbs energies of beryllium for solid alloys have been obtained from the e.m.f. studies of Anfinogenov et al. [136]. Their measurements were made in the temperature range  $983 - 1108^\circ\text{K}$  for alloys of compositions of  $N_{\text{Cu}}$  = between 0.004 and 0.98. The results are scattered and have been corrected by Hultgren et al. to agree with the solid-phase boundaries given by Jacobson and Hammond [137]. Partial Gibbs energies of copper have been obtained by Gibbs-Duhem integration.

Bienvenu et al. [134] have obtained a value for the activity coefficient of copper ( $\gamma_{\text{Cu}}$ ) at infinite dilution in beryllium from measurements of the distribution coefficient of copper between liquid beryllium and liquid lead. However, the value of  $\Delta\bar{G}_{\text{Cu}}^{\text{L}}$  given below is based on the assessment of Hultgren et al. for  $\gamma_{\text{Cu}}$  at  $N_{\text{Pb}} = 1.0$  in the Cu-Pb system rather than on the value used by the authors.

Values selected by Hultgren et al. for solid and liquid alloys are given below.

Data for solid alloys at  $1073^\circ\text{K}$   
(solid  $\alpha$ -Be and solid copper standard states)

$N_{\text{Cu}}$	Phase	$\Delta\bar{G}_{\text{Cu}}$ (cal/g-atom)	$\Delta\bar{G}_{\text{Be}}$ (cal/g-atom)	$\Delta G$ (cal/g-atom)
0.00	( $\alpha$ -Be)	$-\infty$	0	0
0.057 <sup>a</sup>	( $\alpha$ -Be)	-17 670	-300	-1290
0.191 <sup>a</sup>	$\delta$	-17 670	-300	-3615
0.25		-3630	-3850	-3795
0.324 <sup>a</sup>	$\delta$	-3230	-4000	-3750
0.509 <sup>a</sup>	$\beta^{\dagger}$	-3230	-4000	-3610
0.519 <sup>a</sup>	$\beta^{\dagger}$	$-2665 \pm 800$	$-4600 \pm 800$	$-3595 \pm 800$
0.616 <sup>a</sup>	$\beta$	-2665	-4600	-3405
0.65		-2545	-4810	-3335
0.736 <sup>a</sup>	$\beta$	-1100	-8400	-3030
0.851 <sup>a</sup>	(Cu)	-1100	-8400	-2190
0.90		-820	-10 500	-1790
1.00	(Cu)	0	$-\infty$	0

<sup>a</sup> Phase boundary.

Data for liquid alloys at 1623°K  
(liquid copper standard state)

$N_{\text{Cu}}$	$\Delta \bar{G}_{\text{Cu}}^{\text{E}}$ (cal/g-atom)
0.0	434 ± 600

#### 10.4. Beryllium-iron

Liquid alloys in the concentration range  $N_{\text{Fe}} = 0.0114 - 0.0529$  have been investigated by Daguet et al. [138], who determined the distribution coefficient of iron between liquid tin and liquid beryllium at a temperature of 1645°K. The miscibility gap in the Fe-Sn system was used to calculate the activity coefficient of iron at  $N_{\text{Sn}} = 1.0$ . This value was assumed to be constant over the entire composition range covered, to  $N_{\text{Sn}} = 0.9975$ . Gibbs energy values calculated from the data by Hultgren et al. are given below.

Data for liquid alloys at 1645°K  
(liquid beryllium and liquid iron standard states)

$N_{\text{Fe}}$	$\Delta \bar{G}_{\text{Fe}}$ (cal/g-atom)	$\Delta \bar{G}_{\text{Be}}$ (cal/g-atom)	$\Delta G$ (cal/g-atom)
0.01	-24 140	-35	-276
0.02	-21 410	-75	-502
0.03	-19 545	-123	-706
0.04	-17 785	-186	-890
0.05	-15 210	-310	-1055

#### 10.5. Beryllium-gadolinium

Kruglykh et al. [139] have measured the vapour pressure of beryllium over  $\text{Be}_{13}\text{Gd}$  ( $N_{\text{Gd}} = 0.071$ ) in the temperature range 1328 - 1513°K. From their results they obtained the equation  $\log p$  (mmHg) = 10.0 - 19 180/T. The data have been used to calculate  $\Delta \bar{G}_{\text{Be}}$  for the  $\text{Be}_{13}\text{Gd}$  phase at 1400°K.

Data for solid alloys at 1400°K  
(solid  $\alpha$ -Be standard state)

$N_{\text{Gd}}$	Phase	$\Delta \bar{G}_{\text{Be}}$ (cal/g-atom)
0.071	$\text{Be}_{13}\text{Gd}$	-6850

### 10.6. Beryllium-lanthanum

Amonenko et al. [140] have measured the vapour pressure of beryllium over  $\text{Be}_{13}\text{La}$  ( $N_{\text{La}} = 0.071$ ) in the temperature range 1355 - 1540°K. Their results are represented by the equation  $\log p$  (mmHg) = 8.73 - 16 600/T. From the measurements,  $\Delta\bar{G}_{\text{Be}}$  for the  $\text{Be}_{13}\text{La}$  phase has been calculated at 1400°K.

Data for solid alloys at 1400°K  
(solid  $\alpha$ -Be standard state)

$N_{\text{Be}}$	Phase	$\Delta\bar{G}_{\text{Be}}$ (cal/g-atom)
0.071	$\text{Be}_{13}\text{La}$	-3200

### 10.7. Beryllium-molybdenum

The heat content of a solid alloy of composition  $\text{Be}_{12}\text{Mo}$  ( $N_{\text{Mo}} = 0.0769$ ) has been measured in the temperature range 303 - 1073°K by Walker, Ewing and Miller [14]. Their data have been used to derive the following  $C_p$  equation:

$$C_p = 57.72 + 28.59 \times 10^{-3} T - 12.05 \times 10^5 T^{-2} \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

### 10.8. Beryllium-niobium

Walker, Ewing and Miller [14] have measured the heat content of  $\text{Be}_{12}\text{Nb}$  ( $N_{\text{Nb}} = 0.0769$ ) in the temperature range 303 - 1073°K. Their results have been used to obtain the following equation for the heat capacity of  $\text{Be}_{12}\text{Nb}$ :

$$C_p = 63.70 + 18.81 \times 10^{-3} T - 15.15 \times 10^5 T^{-2} \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

The National Bureau of Standards, in Technical Note TN 270-6 [3], quotes the heats of formation at 298°K of  $\text{NbBe}_2$ ,  $\text{NbBe}_8$  and  $\text{NbBe}_{12}$  as -4.87, -2.22 and -1.55 kcal/g-atom, respectively.

### 10.9. Beryllium-nickel

Kornilov et al. [141] and Ilyushchenko et al. [142] have obtained Gibbs energy values for solid alloys using an e.m.f. method. They have investigated alloys of compositions of  $N_{\text{Ni}}$  = between 0.03 and 0.96 in the temperature range 963 - 1113°K. No attempt has been made to calculate partial enthalpy or entropy values because the temperature coefficients of the data scatter too widely. Values selected by Hultgren et al. are given below.

Data for solid alloys at 1100°K  
(solid  $\alpha$ -Be and solid nickel standard states)

$N_{Ni}$	Phase	$\Delta\bar{G}_{Be}$ (cal/g-atom)	$\Delta\bar{G}_{Ni}$ (cal/g-atom)	$\Delta G$ (cal/g-atom)
0.00	( $\alpha$ -Be)	0	$-\infty$	0
0.04 <sup>a</sup>	( $\alpha$ -Be)	-251	-36 110	-1685
0.16 <sup>a</sup>	$\gamma$	-251	-36 110	-5990
0.20		-4560	-16 715	-6990
0.205 <sup>a</sup>	$\gamma$	-4610	-16 520	-7050
0.46 <sup>a</sup>	$\delta$	-4610	-16 520	-10 090
0.50		$-17\,240 \pm 4000$	$-2403 \pm 500$	$-9820 \pm 2500$
0.51 <sup>a</sup>	$\delta$	-18 160	-1503	-9665
0.92 <sup>a</sup>	(Ni)	-18 160	-1503	-2836
0.95		-32 148	-488	-2071
1.00	(Ni)	$-\infty$	0	0

<sup>a</sup> Phase boundary.

#### 10.10. Beryllium-plutonium

Akhachinskij and Kopytin [143] have determined the heat of formation of  $Be_{13}Pu$  using acid solution calorimetry.

Data for solid alloys at 298°K  
( $\alpha$ -Be and  $\alpha$ -Pu standard states)

$N_{Pu}$	Phase	$\Delta H$ (cal/g-atom)
0.0714	$Be_{13}Pu$	$-2550 \pm 250$

#### 10.11. Beryllium-tantalum

Walker, Ewing and Miller [14] have measured the heat content of  $Be_{12}Ta$  in the temperature range 303 - 1073°K. Their results can be represented by the heat capacity equation:

$$C_p = 58.63 + 25.61 \times 10^{-3} T - 11.83 \times 10^5 T^{-2} \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

Booker, Paine and Stonehouse [144] have measured the vapour pressure of beryllium in equilibrium with the phases  $Be_{12}Ta$  and  $Be_{17}Ta_2$  in the temperature range 1533 - 1728°K. Their results are represented by the

equations  $\log p_{\text{Be}} = 3.277 - 12\,540/T$  and  $\log p_{\text{Be}} = 2.938 - 12\,340/T$ , respectively. From these results  $\Delta\bar{G}_{\text{Be}}$  has been calculated, but integral  $\Delta G$  values cannot be obtained.

Data for solid alloys at 1600°K  
(solid  $\beta$ -Be standard state)

$N_{\text{Ta}}$	Phase	$\Delta\bar{G}_{\text{Be}}$ (cal/g-atom)
0.0769	Be <sub>12</sub> Ta (Ta-rich)	-3726
0.1053	Be <sub>17</sub> Ta <sub>2</sub> (Be-rich)	-3726
0.1053	Be <sub>17</sub> Ta <sub>2</sub> (Ta-rich)	-5293

#### 10.12. Beryllium-titanium

Walker, Ewing and Miller [14] have measured the heat content of Be<sub>12</sub>Ti in the temperature range 303 - 1073°K. Their results can be represented by the equation:

$$C_p = 60.15 + 25.73 \times 10^{-3} T - 13.39 \times 10^5 T^{-2} \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

#### 10.13. Beryllium-uranium

Using acid solution calorimetry, Ivanov and Tumbakov [145] have measured the heat of formation of Be<sub>13</sub>U at 298°K. Pyatkov et al. [146] have determined values of  $\Delta\bar{G}_{\text{U}}$  for solid alloys using an e.m.f. method. They have investigated three alloys of compositions  $N_{\text{U}} = 0.0038, 0.0094$  and  $0.0145$  in the temperature range 973 - 1123°K. From their results a value for the Gibbs energy of formation at 1050°K of Be<sub>13</sub>U of -390 cal/g-atom is obtained ( $\gamma$ -U and  $\alpha$ -Be standard states). By converting the  $\Delta H$  value of Ivanov and Tumbakov to a standard state of  $\gamma$ -U, and assuming  $\Delta C_p = 0$  between 298°K and 1050°K, a value for the entropy of formation of Be<sub>13</sub>U can be calculated from the measured  $\Delta H$  and  $\Delta G$  values.

Data for solid alloys at 298°K  
( $\alpha$ -Be and  $\alpha$ -U standard states)

$N_{\text{U}}$	Phase	$\Delta H$ (cal/g-atom)	$\Delta S$ (cal/g-atom · °K)
0.0714	Be <sub>13</sub> U	-2800 ± (300)	-2.29 ± 1.0



10.14. Beryllium-yttrium

Amonenko et al. [140] have measured the equilibrium vapour pressure of beryllium over  $\text{Be}_{13}\text{Y}$  in the temperature range 1313 - 1563°K. Although the authors state that the phase decomposed into its components at the temperatures of investigation, the phase diagram indicates that this can only be true at temperatures below the eutectic temperature (1343°K). Therefore, the Gibbs energy of formation at 1330°K has been calculated from values obtained below the eutectic temperature.

Data for solid alloys at 1330°K  
(solid  $\alpha$ -Be and solid yttrium standard states)

$N_{\text{Y}}$	Phase	$\Delta G$ (cal/g-atom)
0.071	$\text{Be}_{13}\text{Y}$	-3875 $\pm$ 500

10.15. Beryllium-zirconium

McMullen [147] has measured the equilibrium vapour pressure of beryllium over two-phase alloys of compositions of  $N_{\text{Zr}}$  = between 0.07 and 0.33 in the temperature range 1223 - 1616°K. His results are preferred to the considerably different values obtained by Booker, Paine and Stonehouse [144] ( $N_{\text{Zr}}$  = 0.07, 0.105; 1533 - 1728°K) who obtained vapour pressure values for pure beryllium which differ widely from the selected data. Values of  $\Delta G$  at 1300°K calculated by Hultgren et al. are given below.

Data for solid alloys at 1300°K  
(solid  $\alpha$ -Be and solid zirconium standard states)

$N_{\text{Zr}}$	Phase	$\Delta G$ (cal/g-atom)
0.071	$\gamma$	-4030 $\pm$ 100
0.105	$\delta$	-4320
0.167	$\epsilon$	-4700
0.333	$\zeta$	-4210

The heat content data of Walker, Ewing and Miller [14] for  $\text{Be}_{13}\text{Zr}$  ( $\gamma$ ) in the temperature range 303 - 1073°K have been used to obtain the following  $C_p$  equation:

$$C_p = 60.48 + 32.80 \times 10^{-3} T - 11.98 \times 10^5 T^{-2} \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

## 11. TABULATION

In this section, thermochemical data for beryllium and its inorganic compounds are presented in the form of tabulations of heats of formation and standard entropies (Table II), heats and temperatures of transformation, fusion and vaporization (Table III), heat capacities (Table IV), vapour pressures (Table V), and Gibbs energies of formation (Table VI). The latter table presents values calculated at selected temperatures, thereby avoiding the inaccuracies, although small, which would be caused by representing the data by simple two- or three-term equations. Such equations do not directly reflect the transformations which may occur in the reactants or products. For any temperature, the standard states are the appropriate forms of the pure reactants at that temperature. Uncertain values are enclosed in round brackets.

TABLE I. HEATS OF FORMATION AND STANDARD ENTROPIES  
TABULATED BY NBS [3, 124]

Substance	$\Delta H_{298}$ (kcal/mol)	Reference	$S_{298}^0$ (cal/°K·mol)
$\langle \text{BeBr}_2 \cdot 2\text{H}_2\text{S} \rangle$	-112.1	[125]	
$\langle \text{BeBr}_2 \cdot 4\text{NH}_3 \rangle$	-235.1	[57, 58]	
$\langle \text{BeBr}_2 \cdot 6\text{NH}_3 \rangle$	-274.4	[57, 58]	
$\langle \text{BeBr}_2 \cdot 10\text{NH}_3 \rangle$	-349.2	[57, 58]	
$\langle \text{BeCO}_3 \rangle$	-245		
$\langle \text{BeCl}_2 \cdot 4\text{H}_2\text{O} \rangle$	-432.2	[57]	
$\langle \text{BeCl}_2 \cdot 2\text{NH}_3 \rangle$	-201.7	[57, 58]	
$\langle \text{BeCl}_2 \cdot 4\text{NH}_3 \rangle$	-260.4	[57, 58]	
$\langle \text{BeCl}_2 \cdot 6\text{NH}_3 \rangle$	-298.2	[57, 58]	
$\langle \text{BeCl}_2 \cdot 12\text{NH}_3 \rangle$	-409.9	[57, 58]	
$\langle \text{BeI}_2 \cdot 2\text{H}_2\text{S} \rangle$	-69.8	[125]	
$\langle \text{BeI}_2 \cdot 4\text{NH}_3 \rangle$	-207.6	[57, 58]	
$\langle \text{BeI}_2 \cdot 6\text{NH}_3 \rangle$	-247.2	[57, 58]	
$\langle \text{BeI}_2 \cdot 13\text{NH}_3 \rangle$	-378.4	[57, 58]	
$\langle \text{BeMoO}_4 \rangle$	-328	[126]	
(BeOAl)	-5		
$\langle \text{BeSO}_4 \cdot \text{H}_2\text{O} \rangle$	-364.2	[127-131]	
$\langle \text{BeSO}_4 \cdot 2\text{H}_2\text{O} \rangle$	-435.7	[127-131]	39.01
$\langle \text{BeSO}_4 \cdot 4\text{H}_2\text{O} \rangle$	-579.3	[127-131]	55.68
$\langle \text{BeSeO}_4 \cdot 2\text{H}_2\text{O} \rangle$	-360.3		
$\langle \text{BeSeO}_4 \cdot 4\text{H}_2\text{O} \rangle$	-505.0		

TABLE II. HEATS OF FORMATION AND STANDARD ENTROPIES

Substance	$\Delta H_{298}$ (kcal/mol)	$S_{298}^0$ (cal/°K · mol)
$\langle \text{Be} \rangle$	0	2.27 ± 0.02
(Be)	77.5 ± 1.5	32.54
$\langle \text{BeAl}_2\text{O}_4 \rangle$	-549.4 ± 3	15.84
$\langle \text{BeAl}_6\text{O}_{10} \rangle$	-1342.6 ± 5	42.0
$\langle \text{Be}_3\text{B}_2\text{O}_6 \rangle$	-748.9 ± 3.5	22.1 ± 3
(BeBr)	8.8 ± 5.0	(54.84)
$\langle \text{BeBr}_2 \rangle$	-84.5	25.4 ± 2
(BeBr <sub>2</sub> )	-53.4	66.4 ± 2
$\langle \text{Be}_2\text{C} \rangle$	-27.96 ± 0.5	3.9 ± 1.0
(BeCl)	2.0 ± 1.0	53.0 ± 2.5
$\alpha\text{-}\langle \text{BeCl}_2 \rangle$	-117.3 ± 0.8	19.76 ± 0.06
$\beta\text{-}\langle \text{BeCl}_2 \rangle$	-118.6 ± 0.8	18.12 ± 0.05
(BeCl <sub>2</sub> )	-86.1 ± 2.5	60 ± 1
(Be <sub>2</sub> Cl <sub>4</sub> )	(-196.3)	92.5 ± 2
(BeF)	-41.8 ± 2.5	49.15
$\langle \text{BeF}_2 \rangle$ quartz	-245.4 ± 1.0	12.75 ± 0.05
{BeF <sub>2</sub> } glass	-244.3 ± 1.0	
(BeF <sub>2</sub> )	-190.25 ± 1.0	54.36 ± 0.3
(BeH)	77 ± 7	42.24
$\langle \text{BeH}_2 \rangle$	-4.55 ± 0.5	
(BeH <sub>2</sub> )	(30)	41.4
(BeI)	24.7 ± 5.0	(56.7)
$\langle \text{BeI}_2 \rangle$	-46.0	28.8 ± 2
(BeI <sub>2</sub> )	-15.7	70.4 ± 2
$\langle \text{BeLiF}_3 \rangle$	-394.5 ± 2.5	21.3 ± 2
(BeLiF <sub>3</sub> )	-212	64
$\langle \text{BeLi}_2\text{F}_4 \rangle$	-544.2 ± 2.0	29.8 ± 2
$\langle \text{Be}_2\text{Li}_2\text{O}_3 \rangle$	-437.8 ± 2.0	
$\langle \text{Be}_3\text{N}_2 \rangle$ cubic	-140.9 ± 0.6	8.20 ± 0.05
$\langle \text{Be}_3\text{N}_2 \rangle$ hexag.	-136.5	
$\langle \text{BeO} \rangle$	-145.4 ± 0.8	3.38 ± 0.05
(BeO)	28	47.2
(BeO) <sub>2</sub>	-103	59.2

TABLE II. (cont.)

Substance	$\Delta H_{298}$ (kcal/mol)	$S_{298}^0$ (cal/°K · mol)
(BeO) <sub>3</sub>	-260	65.3
(BeO) <sub>4</sub>	-391	72.3
(BeO) <sub>5</sub>	-518	77.2
(BeO) <sub>6</sub>	-651	82
(Be <sub>2</sub> O)	-20 ± 10	52.7
(Be <sub>2</sub> OF <sub>2</sub> )	-292	71.4
(BeOH)	-47.5 ± 7	(53.28)
$\alpha$ -⟨Be(OH) <sub>2</sub> ⟩	-215.7 ± 0.5	11.8 ± 2
$\beta$ -⟨Be(OH) <sub>2</sub> ⟩	-216.5 ± 0.5	11.0 ± 2
(Be(OH) <sub>2</sub> )	-156.4 ± 5	(59.2)
⟨BeS⟩	-55.8 ± 1.0	8.0 ± 1.5
$\alpha$ -⟨BeSO <sub>4</sub> ⟩	-287.0 ± 0.8	18.64
⟨BeSeO <sub>4</sub> ⟩	-213.2	
⟨Be <sub>2</sub> SiO <sub>4</sub> ⟩	-512.8 ± 2.5	15.37 ± 0.1

TABLE III. HEATS AND TEMPERATURES OF TRANSFORMATION, FUSION AND VAPORIZATION

Substance	$T_t$ (°K)	$I_t$ (cal/mol)	$T_f$ (°K)	$L_f$ (cal/mol)	$T_{b.p.}$ (°K)	$L_e$ at b. p. (cal/mol)	$L_s$ at 298°K (cal/mol)
Be	1527 ± 5	(611)	1560 ± 5	(2919)	2745	69885	77 500 ± 1500
BeBr <sub>2</sub>			761	(4500)	(794)	23 900	31 100 ± 1500
BeCl <sub>2</sub>	676	1630 ± 150	688	2070 ± 60	805	25 000 ± 2000	32 500 ± 1500
BeF <sub>2</sub>	500	53	825	1135	1448	47 650	55 150
BeI <sub>2</sub>			753	(5000)	(755)	(23 000)	30 300 ± 2000
BeLi <sub>2</sub> F <sub>4</sub>			745	10 610			
BeO			2853	19 300 ± 1 000			
BeSO <sub>4</sub>	863; 908	266; 4673					173 400 ± 3000

TABLE IV. HEAT CAPACITIES

$$C_p = a + bT + cT^2 + dT^{-2} \text{ cal/}^\circ\text{K} \cdot \text{mol}$$

Substance	$C_p$ (cal/°K·mol)				Temperature range (°K)
	a	$b \times 10^3$	$c \times 10^6$	$d \times 10^{-5}$	
$\alpha$ -⟨Be⟩	5.068	1.361	0.23	-1.404	298-1527
$\beta$ -⟨Be⟩	7.70				1527-1560
{Be}	7.04				1560-2800
(Be)	4.968				298-1900
	4.53	0.14		6.51	1900-3000
⟨BeAl <sub>2</sub> O <sub>4</sub> ⟩	29.26	22.62	-9.36	-8.93	298-1200
	37.58	4.10			1200-2143
⟨BeAl <sub>6</sub> O <sub>10</sub> ⟩	88.45	18.57	-2.77	-27.75	298-2150
⟨Be <sub>3</sub> B <sub>2</sub> O <sub>6</sub> ⟩	26.90	62.92	-21.08	-9.51	298-1768
(BeBr)	8.80	0.14		-1.06	298-3000
⟨BeBr <sub>2</sub> ⟩	19.52	1.07		-2.96	298-761
{BeBr <sub>2</sub> }	27.0				761-794
(BeBr <sub>2</sub> )	14.88	0.01		-2.66	298-3000
⟨Be <sub>2</sub> C⟩	9.17	10.76	-2.29	-2.01	298-2400
(BeCl)	8.46	0.49	-0.09	-0.97	298-3000
$\alpha$ -⟨BeCl <sub>2</sub> ⟩	18.31	2.95		-3.29	298-688
$\beta$ -⟨BeCl <sub>2</sub> ⟩	15.69	4.99		-2.01	298-676
{BeCl <sub>2</sub> }	29.02				688-805
(BeCl <sub>2</sub> )	13.89	0.83	-0.18	-1.67	298-3000
(Be <sub>2</sub> Cl <sub>4</sub> )	31.40	0.15		-3.58	298-3000
(BeF)	7.69	1.10	-0.21	-0.85	298-3000
⟨BeF <sub>2</sub> ⟩ quartz	15.56	5.15		-4.20	298-500
	1.24	18.59		13.14	500-825
{BeF <sub>2</sub> }	13.81	7.105		-4.51	825-1448
(BeF <sub>2</sub> )	12.23	2.02		-1.59	298-1000
	14.78	0.04		-7.83	1000-3000
(BeH)	6.44	1.98	-0.36	-0.08	298-3000
(BeH <sub>2</sub> )	7.50	5.66	-1.14	-1.95	298-3000
(BeI)	8.84	0.13		-0.93	298-3000
⟨BeI <sub>2</sub> ⟩	19.91	0.86		-2.81	298-753
{BeI <sub>2</sub> }	27.0				753-900

TABLE IV. (cont.)

Substance	$C_p$ (cal/°K·mol)				Temperature range (°K)
	a	$b \times 10^3$	$c \times 10^6$	$d \times 10^{-5}$	
(BeI <sub>2</sub> )	14.89			-2.03	800-3000
⟨BeLiF <sub>3</sub> ⟩	18.43	20.29		-2.09	298-633
(BeLiF <sub>3</sub> )	12.86	21.07	-9.79	-3.26	298-1000
	25.65	0.05		-18.80	1000-3000
⟨BeLi <sub>2</sub> F <sub>4</sub> ⟩	21.99	35.36		-0.24	298-745
{BeLi <sub>2</sub> F <sub>4</sub> }	55.50				745-2000
α-⟨Be <sub>3</sub> N <sub>2</sub> ⟩	12.89	24.75		-4.22	298-430
	27.37	3.60		-14.23	430-1200
⟨BeO⟩	9.94	2.44	-0.32	-4.15	298-2853
{BeO}	15.5				2853-4000
(BeO)	7.27	1.39	-0.27	-0.64	298-3000
(BeO) <sub>2</sub>	15.89	3.26	-0.69	-4.62	298-3000
(BeO) <sub>3</sub>	20.77	9.04	-1.90	-7.58	298-3000
(BeO) <sub>4</sub>	32.84	9.15	-1.95	-12.90	298-3000
(BeO) <sub>5</sub>	47.73	3.64	-0.24	-20.57	298-3000
(BeO) <sub>6</sub>	50.94	14.02	-3.00	-21.47	298-3000
(Be <sub>2</sub> O)	7.74	10.61	-4.61	-0.63	298-1000
	14.73	0.05		-11.03	1000-3000
(Be <sub>2</sub> OF <sub>2</sub> )	22.16	2.98	-0.62	-4.52	298-3000
(BeOH)	8.13	3.73	-0.68	-0.98	298-3000
⟨Be(OH) <sub>2</sub> ⟩	4.56	36.75		0.10	298-400
(Be(OH) <sub>2</sub> )	15.47	6.86	-1.27	-3.83	298-3000
⟨BeS⟩	9.97	1.94		-2.30	298-1800
α-⟨BeSO <sub>4</sub> ⟩	26.96	-2.21	18.17	-6.62	298-863
β-⟨BeSO <sub>4</sub> ⟩	38.73				863-908
γ-⟨BeSO <sub>4</sub> ⟩	69.32	-12.56	2.03	-171.51	908-1500
⟨Be <sub>2</sub> SiO <sub>4</sub> ⟩	29.65	18.77	-8.0	-10.84	298-1833

TABLE V. VAPOUR PRESSURES

$$\log p \text{ (mmHg)} = A + B \log T + CT^{-1}$$

Substance	log p (mmHg)			Temperature range (°K)
	A	B	C	
< Be >	11.279	-0.56	-17 058	298-1560
{ Be }	12.483	-1.04	-16 518	1560-2745
< BeBr <sub>2</sub> >	19.343	-2.57	-7 139	298-761
{ BeBr <sub>2</sub> }	9.457		-5 250	761-794
< BeCl <sub>2</sub> >	17.584	-1.89	-7 365	298-688
{ BeCl <sub>2</sub> }	36.605	-8.07	-8 394	688-805
< BeF <sub>2</sub> >	16.950	-1.69	-12 290	298-825
{ BeF <sub>2</sub> }	23.599	-3.75	-12 823	825-1448
< BeI <sub>2</sub> >	19.443	-2.56	-6 961	298-753
{ BeI <sub>2</sub> }	32.307	-6.88	-7 290	753-900
< BeO >	18.015	-1.77	-38 247	298-2500



TABLE VI. STANDARD GIBBS ENERGIES OF FORMATION FROM THE COMPONENT ELEMENTS  
 Standard states:  $\alpha$ -Be (298-1527°K);  $\beta$ -Be (1527-1560°K); liquid Be (1560-2500°K)

Substance	$\Delta H_{298}$ (kcal/mol)	$\Delta S_{298}$ (cal/°K·mol)	$\Delta G^\circ$ (kcal/mol)							
			298°K	500°K	750°K	1000°K	1250°K	1500°K	2000°K	2500°K
$\langle \text{BeAl}_2\text{O}_4 \rangle$	-549.4	-97.98	-520.2	-500.3	-475.8	-451.3	-425.8	-400.6	-349.6	
$\langle \text{BeAl}_6\text{O}_{10} \rangle$	-1342.6	-245.9	-1269.3	-1219.4	-1158.1	-1096.3	-1031.9	-968.0	-840.7	
$\langle \text{Be}_3\text{B}_2\text{O}_6 \rangle$	-748.9	-134.5	-708.8	-681.5	-648.0	-615.0	-582.8	-551.2		
(BeBr)	8.8	34.4	-1.45	-6.47	-12.09	-17.57	-22.90	-28.10	-37.16	
$\langle \text{BeBr}_2 \rangle$	-84.5	-13.27	-80.6	-74.4	-66.3					
(BeBr <sub>2</sub> )	-53.4	27.74	-61.7	-63.5	-64.8	-66.1	-67.3	-68.4	-69.5	
$\langle \text{Be}_2\text{C} \rangle$	-27.96	-2.01	-27.36	-26.93	-26.28	-25.55	-24.78	-23.98	-20.38	
(BeCl)	2.0	24.09	-5.18	-10.00	-15.83	-21.50	-27.04	-32.44	-41.90	
$\{ \langle \text{BeCl}_2 \rangle \}$	-118.6	-37.44	-107.4	-100.1	-91.7					
(BeCl <sub>2</sub> )	-86.1	4.44	-87.4	-88.3	-89.4	-90.4	-91.4	-92.3	-92.8	
(Be <sub>2</sub> Cl <sub>4</sub> )	-196.3	-18.62	-190.8	-187.2	-183.0	-178.9	-174.8	-170.7	-160.4	
(BeF)	-41.8	22.66	-48.6	-53.1	-58.5	-63.8	-68.9	-73.8	-82.4	
$\{ \langle \text{BeF}_2 \rangle \}$	-245.4	-37.97	-234.1	-226.5	-217.4	-208.9	-200.7			
(BeF <sub>2</sub> )	-190.25	3.64	-191.3	-192.0	-192.8	-193.5	-194.1	-194.6	-194.4	
(BeH)	77	24.37	69.7	64.9	59.0	53.3	47.7	42.2	32.6	
(BeH <sub>2</sub> )	30	7.92	27.6	26.2	24.9	23.7	22.6	21.6	20.9	
(BeI)	24.7	40.48	12.6	5.6	0	-5.5	-10.9	-16.1	-25.2	
$\langle \text{BeI}_2 \rangle$	-46.0	-1.23	-45.6	-43.3	-35.3					
(BeI <sub>2</sub> )	-15.7	40.41	-27.7	-33.5	-35.0	-36.4	-37.7	-39.0	-40.4	

TABLE VI. (cont.)

Substance	$\Delta H_{298}$ (kcal/mol)	$\Delta S_{298}$ (cal/°K · mol)	$\Delta G^\circ$ (kcal/mol)									
			298°K	500°K	750°K	1000°K	1250°K	1500°K	2000°K	2500°K		
$\langle \text{BeLiF}_3 \rangle$	-394.5	-60.59	-376.4	-364.2	-196.8	-190.7	-184.3	-177.9	-163.6			
(BeLiF <sub>3</sub> )	-212	-17.9	-206.7	-202.6	-481.6	-465.3	-450.0	-435.6	-407.7			
$\{ \langle \text{BeLi}_2\text{F}_4 \rangle \}$	-544.2	-83.27	-519.4	-502.5	-107.4	-96.4						
$\langle \text{Be}_3\text{N}_2 \rangle$	-140.9	-44.38	-127.7	-118.6	-127.8	-122.0	-116.3	-110.6	-98.4	-86.3		
$\langle \text{BeO} \rangle$	-145.4	-23.39	-138.4	-133.7	12.9	8.2	3.6	-0.9	-8.4	-15.5		
(BeO)	28	20.43	21.9	17.8	-106.6	-107.3	-107.8	-108.1	-106.1	-103.4		
(BeO) <sub>2</sub>	-103	5.66	-104.7	-105.7	-247.3	-242.1	-236.6	-230.8	-215.6	-199.5		
(BeO) <sub>3</sub>	-260.0	-15.01	-255.5	-252.1	-363.6	-353.6	-343.4	-332.9	-307.3	-280.9		
(BeO) <sub>4</sub>	-391.0	-34.78	-380.6	-373.2	-474.1	-458.6	-442.9	-426.9	-389.0	-350.0		
(BeO) <sub>5</sub>	-518.0	-56.65	-501.1	-489.2	-590.1	-568.8	-547.2	-525.3	-474.8	-423.1		
(BeO) <sub>6</sub>	-651.0	-78.63	-627.6	-611.1	-37.2	-42.4	-47.5	-52.3	-59.3	-65.6		
(Be <sub>2</sub> O)	-20	23.66	-27.1	-31.7	-287.3	-285.5	-283.6	-281.5	-275.1	-268.1		
(Be <sub>2</sub> OF <sub>2</sub> )	-292	-6.09	-290.2	-288.9	-55.0	-56.9	-58.6	-60.1	-61.8	-63.0		
(BeOH)	-47.5	10.91	-50.8	-52.8								
$\langle \text{Be(OH)}_2 \rangle$	-215.7	-70.68	-194.6									
(Be(OH) <sub>2</sub> )	-156.4	-23.28	-149.5	-144.5	-138.1	-131.6	-124.9	-118.2	-103.7	-89.0		
$\langle \text{BeS} \rangle$	-55.8	-1.89	-55.2	-54.6	-55.3	-50.1	-44.9	-39.8				
$\langle \text{BeSO}_4 \rangle$	-287.0	-89.30	-260.4	-242.1	-220.6	-195.5	-171.6	-148.5				
$\langle \text{Be}_2\text{SiO}_4 \rangle$	-512.8	-91.68	-485.5	-466.9	-444.0	-421.4	-398.9	-376.6				

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