The Enthalpies of Formation of BeO(c) and BeF₂(c)

Vivian B. Parker

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

Two of the key compounds in the evaluation and synthesis of a consistent set of thermodynamic values for the Be compounds are BeO(c) and BeF₂(c). The available measurements on the enthalpies of formation of these two compounds are presented with a detailed outline of the approach used to select the "best" values, $\Delta H f^{\circ}_{298.15\,K}$ [BeO(c)] $= -145.7 \pm 0.6$ kcal·mol⁻¹ (-609.6 ± 2.5 kJ·mol⁻¹) and $\Delta H f^{\circ}_{298.15\,K}$ [BeF₂(c, quartz)] $= -245.4 \pm 0.8$ kcal·mol⁻¹ (-1026.8 ± 3.3 kJ·mol⁻¹).

Key words: BeF₂(c); BeO(c); beryllium fluoride; beryllium oxide; enthalpies of formation; $\Delta H f^{\circ}_{298.15K}$ [BeF₂(c)]; $\Delta H f^{\circ}_{298.15K}$ [BeO(c)]; thermochemistry.

1. Introduction

Two of the key compounds in the evaluation and synthesis of a consistent set of thermodynamic values for the Be compounds are BeO(c) and BeF₂(c).

One approach used in the preparation of compilations of thermochemical data is to start with a compound for which $\Delta H f^{\circ}$ (or $\Delta G f^{\circ}$) is definitive and independent of $\Delta H f^{\circ}$ of any other compound of that element and preferably involves a minimum of auxiliary $\Delta H f^{\circ}$'s, and to build from the selected value for this compound. An example of this is the direct oxidation of the metal to the oxide, e.g., BeO(c), or the halogenation of the metal to the halide, e.g., BeF₂(amorp), or a set of reactions that can be combined in such a way that only one $\Delta H f^{\circ}$ is unknown, e.g., Be(c)+2HF(aq) → H₂(g)+BeF₂(aq) and BeO(c)+2HF(aq) → BeF₂(aq)+H₂O(liq) so that by difference we can write the possible reaction, Be(c)+H₂O(liq) → BeO(c)+H₂(g); similarly Be₃N₂(c)+3/2O₂(g) → 3BeO(c)+N₂(g) and 3Be(c)+N₂(g) → Be₃N₂(c) giving Be(c)+1/2O₂(g) → BeO(c). We may then relate the $\Delta H f^{\circ}$'s of other compounds of that element to the selected compound by enthalpies of reaction.

If however every subsequent $\Delta H f^{\circ}$ calculated is dependent upon the value selected for one compound, although we have internal consistency, we have no crosscheck as to how good the original value is. We should then have a second compound whose $\Delta H f^{\circ}$ can also be obtained independently and an enthalpy of reaction relating the two to corroborate the choices and to close the cycle.

Until the recent measurements of Kilday, Prosen, and Wagman [1]¹ on the enthalpies of solution of

BeO(c) in aqueous HF solutions and the measurements of Churney and Armstrong [2] on the direct determination of the $\Delta H f^{\circ}$[BeF₂(amorph)], the data available on the direct enthalpies of formation of BeO(c) and BeF₂(c) and the data linking these values were discordant. These new investigations are a significant aid in establishing the values for BeO(c) and BeF₂(c) with more certainty. Our main efforts then, after considering the direct determinations, center upon the use of the solution measurements of BeO(c) in HF(aq) together with the solution measurements of Be(c) in HF(aq) which previously could not be fully utilized to obtain indirectly a definitive value for the $\Delta H F^{\circ}$[BeO(c)] and to relate that value to the determinations on the $\Delta H F^{\circ}$[BeF₂(c)]. Figure 1 schematically presents the reactions and paths discussed in this paper.
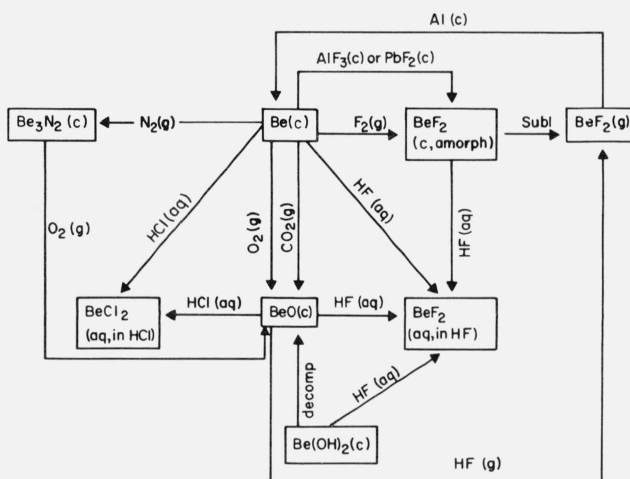

FIGURE 1: *The schematic presentation of the relationships involved in the evaluation of* ΔHf°[BeO(c)] *and* ΔHf°[BeF₂(c)].

---

¹ Figures in brackets indicate the literature references at end of this paper.

491-397 O - 73 - 4

All auxiliary data and constants used in the calculations are given in Wagman et al. [3]. Unless otherwise specified the values quoted are at, or have been corrected to, 298.15 K. Our final selections are reported in both $kJ \cdot mol^{-1}$ and $kcal \cdot mol^{-1}$. However, since this evaluation is included in Parker, Wagman, and Evans [3], where values are expressed in $kcal \cdot mol^{-1}$, we report the individual values and their corrections in the same units in order to preserve the consistency of the relationships.

2. Discussion of Data on BeO(c)

2.1. Bomb Combustion

The following values of $\Delta H(kcal \cdot mol^{-1})$ for the oxidation of Be(c) have been reported: Moose and Parr [4], -134.4; Roth, Börger, and Siemonsen [5], -147.3; Neumann, Kröger, and Kunz [6], -145.3; Mielenz and v. Wartenberg [7], -136.2; and Cosgrove and Snyder [8], -143.1. Neumann, Kröger, and Kunz [6] measured the enthalpy of combustion of Be_3N_2 (crystal form unspecified) to form BeO(c) and $N_2(g)$ as -300.6 kcal·mol^{-1} of $Be_3N_2(c)$. Neumann, Kröger, and Haebler [9] directly determined $\Delta Hf°[Be_3N_2(c)]$ $=-134.1$. By difference we obtain $\Delta Hf°[BeO(c)]$ $=-144.9$. Of these determinations the Cosgrove and Snyder measurement appeared to be the best value and had been generally accepted; however, the measurements of Kolesov, Popov, and Skuratov [10] on the enthalpies of reaction of BeO(c) in aqueous HF and $BeF_2(c)$ in aqueous HF indicate that the value for $\Delta Hf°[BeO(c)]$ should be more negative. This is in line with the fact that Cosgrove and Snyder did not determine the completeness of the reaction; incomplete combustion would cause the value, based on the weight of metal taken, to be too positive. We turn therefore to the indirect determinations of $\Delta Hf°[BeO(c)]$.

2.2. The Enthalpies of Solution of Be(c) and BeO(c) in Aqueous HF Solutions

Matignon and Marchal [11] measured the enthalpies of solution of Be(c) and BeO(c) in 30 percent HF solutions, as have Copaux and Philips [12]. By difference, we obtain for $Be(c) + H_2O(liq) \rightarrow BeO(c) + H_2(g)$, $\Delta H° = -70.9$ and -62.1 kcal, or $\Delta Hf°[BeO(c)] = -139.2$ and -130.4 $kcal \cdot mol^{-1}$, respectively. The individual ΔH's for solution of Be(c) in 30 percent HF are -94.2 from Matignon and Marchal and -82.2 $kcal \cdot mol^{-1}$ from Copaux and Philips. For solution of BeO(c) they are -23.3 and -20.1 $kcal \cdot mol^{-1}$, respectively. More recently, Bear and Turnbull [13] measured the enthalpy of solution of Be(c) in 12, 22.6, 30, and 40 percent HF solutions. The values are -101.5, -101.0, -100.5, and -100.5 kcal. Armstrong and Coyle [14] reported -99.6 kcal for solution in 25 percent HF. For solution of BeO(c) in aqueous HF we also have the results of Kilday et al., e.g., -24.2 kcal in a 30 percent HF solution, the results of Kolesov et al., in a 23 percent HF solution, -24.1 kcal, and Fricke and Wüllhorst [15] -24.3 kcal in

12 percent HF. It appears that the measurements of Matignon and Marchal and Copaux and Philips are not reliable; they give little information as to the experimental details and purity of materials. We cannot rely upon the values for $\Delta Hf°[BeO(c)]$ obtained from the data of either Matignon and Marchal [11] or Copaux and Philips [12], but a judicious combination of the other measurements can yield a more reliable value.

One of the problems associated with combining reactions of Be(c) and BeO(c) in aqueous HF is that in most cases the final solutions are not the same. Not only are there no quantitative data on what Be species are in the final solutions or the percent of each, there are also no direct data on the ΔH_{diln} or ΔH_{mix} of these species in HF solutions. The measurements of Kilday et al., however, provide some insight into the effect of having solutions that do differ in both the amount and concentration of the excess HF(aq).

They have also measured the differential enthalpy of dilution in two of their final solutions,

$$H_2O(liq) + [BeF_2 \text{ in excess HF} \cdot nH_2O] \rightarrow$$
$$[BeF_2 + H_2O \text{ in excess HF} \cdot nH_2O].$$
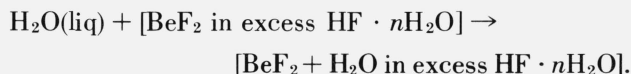
These measurements are important since H_2O(in BeF_2 $+ HF \cdot nH_2O$) is formed in the reaction of BeO(c) with HF(aq), i.e.,

$$BeO(c) + 2HF(aq) \rightarrow [BeF_2 + H_2O] \text{ in excess HF}.$$

We have compared the experimental data with those calculated from the slope $d\varphi_L/dm^{1/2}$ of φ_L HF at n_f H_2O from the values [2] tabulated by Parker [16]. These values are: at $n_f = 2.68$, $\bar{L}_1$ $(cal \cdot mol^{-1}) = -178$ (calc.), and -160 ± 10 (experimental); at $n_f = 3.57$, $\bar{L}_1 = -110$ (calc.) and -85 ± 5 (experimental). Since the agreement is good, we decided to ignore the presence of the BeF_2 in the final solutions and treat the solutions as if they were HF solutions. Since X (the ratio of HF to BeF_2 in the final solution) $\geqq 50$ this is not an unreasonable approach.

We can now set up the equation for the reaction[3] in the form,

$$BeO(c) + (X+2)(HF + n_i H_2O) \rightarrow$$
$$[BeF_2 + H_2O + X(HF + n_f' H_2O)]$$
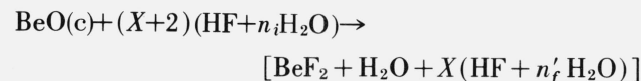
and use the experimental $\bar{L}_1$ values and the φ_L values at the appropriate concentrations from [16] to calculate $\Delta(\Delta Hf°)$ which represents $\Delta Hf°[BeO(c)] - \Delta Hf$ $[BeF_2(aq)]$. Table 1 shows the results as a function of n_f where n_f is the final ratio of H_2O to HF. It includes the mole of H_2O formed. All of their experimental ΔH's

[2] φ_L is the relative apparent molal enthalpy. It is the negative of the integral enthalpy of dilution per mole of solute of a solution at concentration m to an infinitely dilute solution. L_1 is the partial or differential enthalpy of dilution, per mole of solvent, when it is added to a large volume of solution at the given concentration.
[3] $n_f' = n_i(X+2)/X$; it excludes the mole of H_2O formed. n_i is the initial mole ratio of H_2O to HF. X is the mole ratio of HF to BeF_2 in solution.
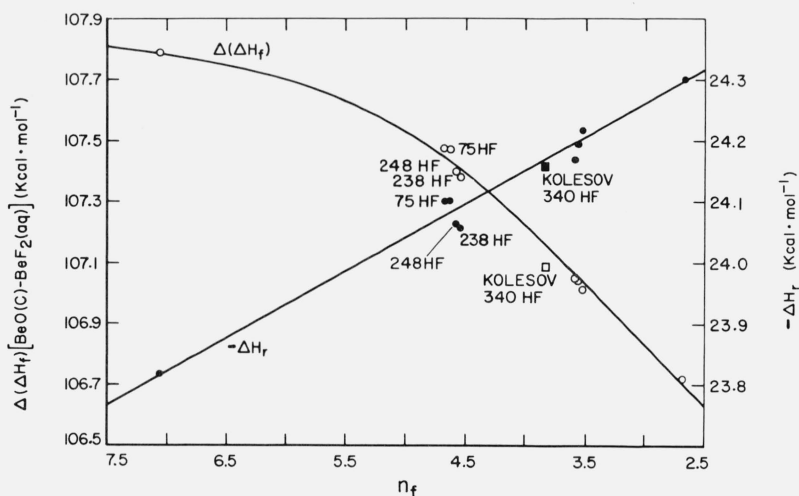
FIGURE 2: *The* $\Delta Hr[BeO(c)]$ *and* $\Delta(\Delta Hf)[BeO(c)-BeF_2(aq)]$ *(uncorrected for the variation in* X*) as a function of the concentration of* HF *in the final solution* $(HF + n_f H_2O)$.

For ΔHr: ● data of Kilday et al.
                   ■ data of Kolesov et al.
For $\Delta(\Delta Hf)$: ○ data of Kilday et al.
                   □ data of Kolesov et al.

are included, corrected to 298.15 K where necessary, using the temperature coefficient given in their work. The number in the first column corresponds to the number of the Kilday et al., experiment.

The values for $\Delta(\Delta Hf)$ within each group are in excellent agreement with one another, within the precision of the experimental data although there are some differences in X and n_f in the final solutions. The values appear to be primarily dependent upon the concentration of HF within the range $50 \leqq \times \leqq 250$. Figure 2 shows a plot of $\Delta(\Delta Hf)$ as a function of n_f. For the $\Delta(\Delta Hf)$ we obtain a smooth curve. The smoothed values are also given in table 1. The variation of ΔH as a function of the concentration of HF without regard to the variation of X may be expressed as $\Delta H = -24.092 - 0.113(4.50 - n_f)$ kcal·mol⁻¹ for $7.1 > n_f > 2.6$.

Kolesov, Popov, and Skuratov [10] also measured the enthalpy of solution of BeO(c) in aqueous HF. Their reaction corresponds to:

$$BeO(c) + 342(HF + 3.801\ H_2O) \rightarrow$$
$$[BeF_2 + H_2O + 340(HF + 3.823\ H_2O)].$$
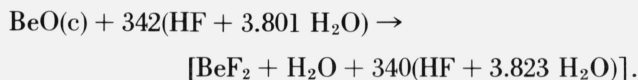
The $\Delta H = -24.158$ kcal·mol⁻¹ of BeO(c) results in $\Delta(\Delta Hf) = 107.085$ kcal·mol⁻¹ (using the same treatment as before). From our straight line plot of ΔH from Kilday et al.'s data, we obtain -24.168 kcal·mol⁻¹ where the final solution contains BeF_2 in $90(HF + 3.826\ H_2O)$. From our plot of $\Delta(\Delta Hf)$ versus n_f we obtain $\Delta(\Delta Hf) = 107.185$ kcal·mol⁻¹. The agreement in ΔH is excellent, fortuitously so; in $\Delta(\Delta Hf°)$ it is not, but still within the experimental uncertainties. In addition X differs by 250 moles HF in the two solutions.

Kilday and Churney, private communication (1971), also made some measurements on the enthalpy of solution of BeF_2(amorph) in HF concentrations of

3.63 H_2O and 5.06 H_2O where X varied from 400 to 2700. From these measurements we obtain the following:

$$\Delta H_{soln} = -8,430 + 0.50\,X\ \text{cal} \cdot \text{mol}^{-1}\ \text{for}\ n = 3.63$$

$$\Delta H_{soln} = -8,680 + 0.60\,X\ \text{cal} \cdot \text{mol}^{-1}\ \text{for}\ n = 5.06.$$

Although the precision of these measurements is not high they do enable us to obtain an approximate correction to $\Delta(\Delta Hf)$ for the variation in X. As a reference solution we have chosen this X to be 100 and have added $-0.55(100 - X)$ cal·mol⁻¹ (an
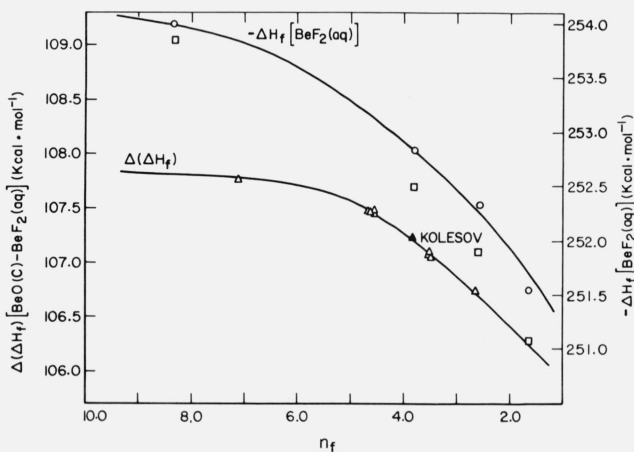

FIGURE 3: *The* $\Delta(\Delta Hf)[BeO(c)-BeF_2(aq)]$ *and the* $\Delta Hf[BeF_2(aq)]$ *as a function of the concentration of* HF *in the final solution* $(HF + n_f H_2O)$.

For $\Delta(\Delta Hf)$: △ Kilday et al. data, corrected to $X = 100$.
                   ▲ Kolesov et al. data, corrected to $X = 100$.
For $\Delta Hf[BeF_2(aq)]$: ○ Bear and Turnbull data, corrected to $X = 100$.
                   □ Bear and Turnbull data, uncorrected for variation in X.

229

TABLE 1. *Data derived from measurements of Kilday et al.*

1	2	3	4	5	6	7	8	9	10	11	12
No.	%HF in initial solution	$-\Delta H^a_{298.15K}$	X	n_f	$\Delta(\Delta Hf)$ [BeO(c)-−BeF$_2$(aq)]	Mean $\Delta(\Delta Hf)$	Mean n_f	$\Delta(\Delta Hf)$ from smooth curve, fig. 2	$\Delta(\Delta Hf)$ corrected to $X=100$	Mean $\Delta(\Delta Hf)$	$\Delta(\Delta Hf)$ from smooth curve, fig. 3
		$kcal \cdot mol^{-1}$			$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$		$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$
20	29.76	24.301	112.58	2.6765	106.710				106.717		
22		24.292	117.42	2.6742	106.707	106.716	2.676	106.70	106.717	106.723	106.71
23		24.315	113.12	2.6762	106.731				106.738		
24		24.299	113.16	2.6762	106.714				106.721		
2	24.33	24.200	94.60	3.5374	107.041				107.038		
4		24.221	96.47	3.5359	107.055	107.051	3.534	107.07	107.053	107.051	107.07
5		24.235	107.53	3.5274	107.057				107.061		
25	24.23	24.221	93.05	3.5581	107.109				107.105		
26		24.197	97.97	3.5538	107.082				107.081		
27		24.176	94.17	3.5571	107.064	107.080	3.555	107.08	107.061	107.078	107.08
28		24.202	91.36	3.5597	107.096				107.091		
29		24.182	114.23	3.5423	107.057				107.065		
30		24.187	92.47	3.5586	107.071				107.067		
1	24.13	24.183	88.82	3.5817	107.113				107.112		
3		24.141	95.48	3.5753	107.070	107.090	3.578	107.09	107.068	107.087	107.09
9		24.163	94.19	3.5765	107.103				107.100		
10		24.183	93.52	3.5771	107.072				107.068		
7	19.80	24.103	75.23	4.6310	107.475	107.475	4.631	107.46	107.461	107.461	107.47
11	19.80	24.055	234.68	4.5407	107.389				107.463		
13		23.955	232.05	4.5412	107.296	107.378	4.540	107.43	107.369	107.454	107.44
18		24.089	247.99	4.5384	107.448				107.529		
6	19.66	24.108	76.47	4.6699	107.473	107.468	4.672	107.47	107.460	107.456	107.48
8		24.091	74.60	4.6731	107.462				107.452		
12	19.66	24.062	237.12	4.5806	107.397				107.472		
17		24.158	256.22	4.5773	107.497	107.404	4.579	107.44	107.583	107.485	107.46
19		23.968	251.47	4.5781	107.318				107.401		
14	14.05	23.787	53.85	7.0644	107.753				107.728		
15		23.862	55.49	7.0563	107.830	107.782	7.061	107.78	107.806	107.758	107.78
16		23.794	54.42	7.0616	107.764				107.739		

^{a} Corrected for BeSO$_4$ impurity.

1	2	3	4	5	6	7	8	9	10	11
% HF	X	n_f	$\Delta Hr°$ Be(c)	ΔHf [BeF$_2$(aq)]	$\Delta Hr°$ of BeO(c) st. line plot, fig. 2	X for (6)	$\bar{L}_1$ H$_2$O	$\Delta(\Delta Hf)$ [BeO – BeF$_2$(aq)] fig. 2	ΔHf [BeF$_2$(aq)] corrected to $X=100$	$\Delta(\Delta Hf)$ [BeO(c)– BeF$_2$(aq)] fig. 3
			$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$		$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$
12	358	8.184	− 101.47	− 253.84	− 23.68	50	0	107.81	− 253.98	107.78
22.6	677	3.811	− 101.02	− 252.51	− 24.17	90	− 0.07	107.18	− 252.83	107.18
30	899	2.597	− 100.52	− 251.89	− 24.31	115	− 0.18	106.68	− 252.33	106.68
40	1079	1.670	− 100.5	a— 251.0	− 24.42	130	− 0.3 (est'd)	106.2	− 251.54	106.2

a This is based on an estimate for $\Delta H_{diln} = -0.9$ kcal·mol⁻¹ for 1079(HF + 1.666H$_2$O) → 1079(HF + 1.670H$_2$O) and φ_L for HF + 1.666H$_2$O = 3.8 kcal·mol⁻¹.

TABLE 3. $\Delta Hf°$[BeO(c)] *in kcal·mol⁻¹ as calculated by various methods from data in table 2*

Method 1 (4, 6, and 8)	Method 2 (5 and 9)	Method 3 (10 and 11)
− 146.11	− 146.03	− 146.20
− 145.24	− 145.33	− 145.65
− 144.70	− 145.21	− 145.65
− 144.7	− 144.8	− 145.3

average value) to the $\Delta(\Delta Hf)$'s (see table 1, columns 10, 11, and 12 and fig. 3). The new $\Delta(\Delta Hf)$'s are in slightly better agreement with one another. For the $\Delta(\Delta Hf°)$ from Kolesov et al., we obtain 107.217 kcal·mol⁻¹ as compared to 107.180 from figure 3, in much better agreement; this lends support to the use of this treatment on the Bear and Turnbull measurements [13] on Be(c) in excess HF solutions, where the final ratio of HF to BeF$_2$ is greater than 340.

Bear and Turnbull used solutions of 12, 22.6, 30, and 40 percent HF. Their results can be treated three ways:

(1) using their ΔH_r with the ΔH_r from our straight line plot of the Kilday et al., data on BeO in HF at the appropriate n_f, with the experimental $\bar{L}_1$, obtaining the reaction, Be(c) + H$_2$O(aq) → BeO(c) + H$_2$(g);
(2) calculating the $\Delta Hf°$[BeF$_2$ in X(HF + n_fH$_2$O)] and using the appropriate $\Delta(\Delta Hf)$ [BeO − BeF$_2$(aq)] at n_f from figure 2;
(3) correcting ΔHf[BeF$_2$(aq)] to $X = 100$ and using the comparable corrected $\Delta(\Delta Hf)$ from figure 3.

The results are summarized in tables 2 and 3. It is obvious that the values for $\Delta Hf°$[BeO(c)] are in better agreement using the third way of calculating. Figure 3 shows a plot of ΔHf[BeF$_2$(aq), in 100(HF+n_fH$_2$O)] and also the uncorrected values derived from the Bear and Turnbull measurements.

For confirmation of the above values we may use the enthalpy of solution of the samples of BeF$_2$(amorph) cited earlier whose $\Delta Hf°$ is known (− 244.3 kcal·mol⁻¹, directly determined by Churney and Armstrong [2]) from which we obtain ΔHf[BeF$_2$(aq) in 100(HF + 3.63H$_2$O)] = −252.68 kcal·mol⁻¹ and ΔHf[BeF$_2$(aq) in 100(HF+5.06 H$_2$O)] = −252.92 kcal·mol⁻¹ (cf − 252.75 and −253.38 kcal·mol⁻¹ from the smoothed curve (fig. 3) of Bear and Turnbull's corrected ΔHf's). Using $\Delta(\Delta Hf) = 107.11$ and $\Delta(\Delta Hf) = 107.57$

kcal·mol⁻¹ from figure 3, we obtain $\Delta Hf°$ BeO(c) = − 145.57 and − 145.35 kcal·mol⁻¹, respectively.

In all the above cases we have used the $\Delta(\Delta Hf)$ [BeO(c)–BeF$_2$(aq)] derived from the Kilday et al. measurements. If we use $\Delta(\Delta Hf) = 107.217$ kcal·mol⁻¹ from the Kolesov et al. measurements and ΔHf BeF$_2$(aq) = − 252.93 kcal·mol⁻¹ from figure 3 we obtain $\Delta Hf°$ BeO(c) = − 145.71 kcal·mol⁻¹.

There is another reaction involving the enthalpy of solution of Be(c) in HF(aq), that by Armstrong and Coyle [14]. They reported that there was an unexplained deficiency of H$_2$ on the order of 0.5 percent. They ascribe an uncertainty of not more than 0.2 percent to the enthalpy of reaction for this contribution. The measurements are on the reaction: Be(c) + 6.470(HF + 3.309 H$_2$O) → [BeF$_2$ + 4.470(HF + 4.789 H$_2$O)] + H$_2$(g) for which $\Delta H = -99.64$ kcal·mol⁻¹ and ΔHf[BeF$_2$(aq) in 4.470(HF + 4.789 H$_2$O)] = − 251.1 kcal·mol⁻¹. Using the same three approaches as for Bear and Turnbull's data we obtain $\Delta Hf°$[BeO(c)] = −143.9 (1); −143.6 (2); and −143.5 kcal·mol⁻¹ (3), where X is corrected to 100. In all cases we assume that the species in the two solutions are the same; in the third case we also assume our correction is applicable to $X = 4.47$, which is probably not justified.

There are two other approaches we can use on their data:

(4) Heretofore we have neglected the effect of the BeF$_2$ on the HF dilution correction. If we assume that the BeF$_2$ present in the solution may be replaced by an equivalent number of moles of HF solution, then we may consider the HF to be in 3.913H$_2$O. This results in ΔHf[BeF$_2$(aq)] = −251.4 kcal·mol⁻¹ and $\Delta Hf°$ [BeO(c)] = −143.9 kcal·mol⁻¹.
(5) We can calculate a ΔH_{mix} for the addition of more of the initial solution, [HF + 3.309 H$_2$O], to their final solution, using the ϕ_L values of HF, and obtain:

[BeF$_2$(aq) + 4.470(HF + 4.789H$_2$O)]
$\qquad$ + 95(HF + 3.309H$_2$O) →
[BeF$_2$(aq) + 99.470(HF + 3.375H$_2$O)]; $\Delta H_{mix} = -0.264$
kcal·mol⁻¹. Combining this with their reported ΔH leads to:
Be(c) + 101.470(HF + 3.309H$_2$O) → [BeF$_2$(aq) + 99.470 (HF + 3.375H$_2$O)] + H$_2$(g); $\Delta H = -99.95$ kcal·mol⁻¹. This value is now in closer agreement with Bear and
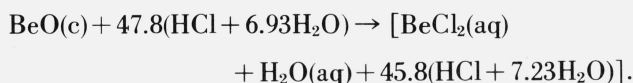
Turnbull's measurements. For the same reaction with BeO(c) we obtain $\Delta H = -24.22$ kcal $\cdot$ mol^{-1}, so that $\Delta Hf°[BeO(c)] = -144.1$ kcal $\cdot$ mol^{-1}. A variation of this would be to use a ΔH_{mix} based on our fourth approach, i.e., to assume the HF is in 3.913 H$_2$O, then $\Delta H = -100.23$ and $\Delta Hf°[BeO(e)] = -144.4$ kcal $\cdot$ mol^{-1}.

2.3. The Enthalpies of Solution of Be(c) and BeO(c) in Aqueous HCl Solutions

The problem of nonidentical final solutions is also present in the Be(c) − BeO(c) − HCl aqueous systems. Kilday et al. [1] have obtained $\Delta H = -12.8$ and -12.7 kcal $\cdot$ mol^{-1} for the solution of BeO(c) in 18 and 22.6 percent HCl, respectively. The complete reactions are:

$$BeO(c) + 40.9(HCl + 9.21H_2O) \rightarrow [BeCl_2(aq)$$
$$+ H_2O(aq) + 38.9(HCl + 9.69H_2O)]$$

and

$$BeO(c) + 47.8(HCl + 6.93H_2O) \rightarrow [BeCl_2(aq)$$
$$+ H_2O(aq) + 45.8(HCl + 7.23H_2O)].$$
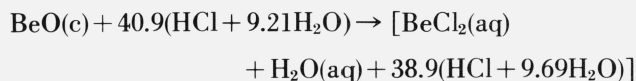
(The experimental $\bar{L}_1$ value = -272 cal $\cdot$ mol^{-1} of H$_2$O (see ref. [1], sec. 5.4) checks well with the $\bar{L}_1$ calculated from the ϕ_L values of HCl [16] at $n = 7.23$H$_2$O).

From these reactions we obtain for BeCl$_2$(aq) in 38.3(HCl + 9.72H$_2$O) $\Delta(\Delta Hf)[BeO(c) - BeCl_2(aq)] =$ 18.6 kcal $\cdot$ mol^{-1} and 16.6 kcal $\cdot$ mol^{-1} for BeCl$_2$(aq) in 45.8(HCl + 7.25H$_2$O).

Thompson, Sinke, and Stull [17] reported $\Delta H = -89.61$ kcal $\cdot$ mol^{-1} for Be(c) + 8.38(HCl + 8.111H$_2$O) $\rightarrow$ [BeCl$_2$(aq) + 6.38(HCl + 10.654H$_2$O)] + H$_2$(g), from which we obtain $\Delta Hf[BeCl_2(aq)] = -163.79$ kcal $\cdot$ mol^{-1}. Blachnik, Gross, and Hayman [18] reported $\Delta H_{383K} = -90.00$ kcal/mol for:

$$Be(c) + 8.86(HCl + 7.991H_2O) \rightarrow H_2(g) + [BeCl_2(aq)$$
$$+ 6.86(HCl + 10.320H_2O)].$$
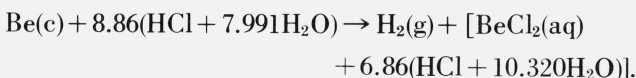
This value, corrected to 298.15 K is in good agreement with the Thompson et al. value.

Using the same approaches as for HF we have:
(1) With ΔH of solution of BeO(c) ≈ -12.8 kcal $\cdot$ mol^{-1} when $n_f = 10.65$, $\Delta Hf°[BeO(c)] = -145.2$ kcal $\cdot$ mol^{-1}.
(2) From an extrapolation of $\Delta(\Delta Hf°)[BeO(c) - BeCl_2(aq)]$ we obtain $\Delta(\Delta Hf°) = 19.4$ kcal $\cdot$ mol^{-1} where the BeCl$_2$ is in 34(HCl + 10.65H$_2$O) and $\Delta Hf°[BeO(c)] = -144.4$ kcal $\cdot$ mol^{-1}.
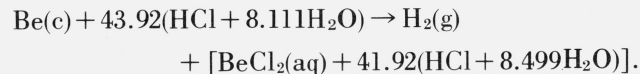(3) Not used since we have no correction for the variation in X.
As in our treatment of the Armstrong and Coyle [14] results we may try the following:
(4) If we assume that the BeCl$_2$ present may be replaced by an equivalent number of moles of HCl solution we may consider the HCl to be in 9.21H$_2$O. Then $\Delta Hf[BeCl_2(aq)] = -165.0$ and $\Delta Hf[BeO(c)] = -145.6$ kcal $\cdot$ mol^{-1}.

(5) We can calculate a ΔH_{mix} by adding more of the initial HCl solution to the final solution. We obtain:

$$[BeCl_2(aq) + 6.38(HCl + 10.654H_2O)] + 35.54(HCl$$
$$+ 8.111H_2O) \rightarrow [BeCl_2(aq) + 41.92(HCl$$
$$+ 8.499H_2O)]; \Delta H = -0.64 \text{ kcal} \cdot \text{mol}^{-1}$$

and $\Delta H = -90.3$ kcal $\cdot$ mol^{-1} for:

$$Be(c) + 43.92(HCl + 8.111H_2O) \rightarrow H_2(g)$$
$$+ [BeCl_2(aq) + 41.92(HCl + 8.499H_2O)].$$
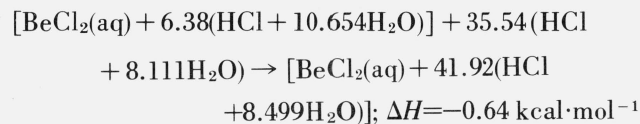
For the reaction with BeO(c) we can say $\Delta H = -12.7$ kcal $\cdot$ mol^{-1} for BeO(c) + 43.92(HCl + 8.111H$_2$O) $\rightarrow$ [BeCl$_2$(aq) + H$_2$O + 41.92(HCl + 8.499H$_2$O)], so that $\Delta H = -77.56$ kcal $\cdot$ mol^{-1} for Be(c) + H$_2$O(aq) $\rightarrow$ BeO(c) + H$_2$(g) and $\Delta Hf°BeO(c) = -146.0$ kcal $\cdot$ mol^{-1}. A variation of this would be to calculate a $\Delta H_{mix} = -1.81$ kcal $\cdot$ mol^{-1} on the basis of (4). Then ΔH for the reaction with Be(c) = -91.4 and $\Delta Hf°[BeO(c)] = -147.2$ kcal $\cdot$ mol^{-1}.

Averaging these five values we obtain -145.7 kcal $\cdot$ mol^{-1} for $\Delta Hf°[BeO(c)]$.

2.4. Other data

From the cell measurements of Smirnov and Chukreev [19] in the temperature range 955 to 1313 K, we obtain a second law $\Delta H° = -94.6$ kcal $\cdot$ mol^{-1} and a third law $\Delta H° = -93.7$ kcal $\cdot$ mol^{-1} for Be(c) + 1/2CO$_2$(g) $\rightarrow$ BeO(c) + 1/2C(graphite), or $\Delta Hf°[BeO(c)] = -141.6$ and -140.8 kcal $\cdot$ mol^{-1}, respectively.

2.5. The Selection of the $\Delta Hf°[BeO(c)]$

It is appropriate at this point to tabulate the values of $\Delta Hf°BeO(c)$, both the direct and indirect determina-

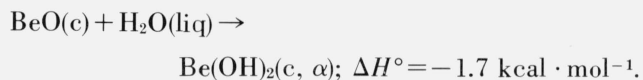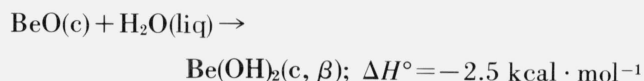TABLE 4. *Summary of values of $\Delta Hf°$ [BeO(c)]*

Investigator	$\Delta Hf°$
	kcal $\cdot$ mol^{-1}
Direct Determinations	
Moose and Parr [4]............................	−134.1
Roth et al. [5].................................	−147.3
Neumann et al. [6]............................	−145.3
Mielenz and v. Wartenberg [7]................	−136.2
Cosgrove and Snyder [8]......................	−143.1
Indirect Determinations	
Neumann et al. [6, 9].........................	−144.9
Smirnov and Chukreev [19]....................	−141.1
Kilday et al. [1] and Bear and Turnbull [13]........	$\begin{cases} -146.20 \\ -145.65 \\ -145.65 \\ -145.3 \end{cases}$
Kilday et al. [1], Kilday and Churney, private communication (1971) and Churney and Armstrong [2]................................	$\begin{cases} -145.6 \\ -145.4 \end{cases}$
Kolesov et al. [10] and Bear and Turnbull [13].......	−145.7
Kilday et al. [1] and Armstrong and Coyle [14].....	−143.9
Kilday et al. [1] and Thompson et al. [17]..........	−145.7

tions (table 4). As is evident, except for the Smirnov and Chukreev value, all the indirect determinations support a more negative value than that of Cosgrove and Snyder. The "best" value now appears to be -145.7 kcal $\cdot$ mol^{-1} in good agreement with the Neumann et al. [6] direct determination. The uncertainties are discussed in section 4.

2.6. The Decomposition of Beryllium Hydroxide as Supporting Evidence

Bear and Turnbull [13] have also measured the enthalpy of solution of $Be(OH)_2$ (β, orthorhombic) and $Be(OH)_2$ (α, tetragonal) in 22.6 percent HF, [679(HF $+3.80H_2O)$]. From these measurements and their measurements on Be(c) we obtain $\Delta H = -79.83$ kcal $\cdot$ mol^{-1} for Be(c)$+2H_2O(liq) \rightarrow Be(OH)_2(\beta)+H_2(g)$ and $\Delta Hf° = -216.5$ kcal $\cdot$ mol^{-1}; similarly for $Be(OH)_2(\alpha)$ we obtain $\Delta H = -79.10$ kcal $\cdot$ mol^{-1} and $\Delta Hf° = -215.7$ kcal $\cdot$ mol^{-1}. Using these values for $\Delta Hf°$ and our tentative "best" value for BeO(c) we obtain:

$$BeO(c)+H_2O(liq) \rightarrow$$
$$Be(OH)_2(c, \beta); \ \Delta H° = -2.5 \text{ kcal} \cdot \text{mol}^{-1}$$

$$BeO(c)+H_2O(liq) \rightarrow$$
$$Be(OH)_2(c, \alpha); \ \Delta H° = -1.7 \text{ kcal} \cdot \text{mol}^{-1}.$$

Fricke and Wüllhorst [15] measured the enthalpies of solution of BeO(c), $Be(OH)_2(c, \beta)$, and $Be(OH)_2(c, \alpha)$ in 11.59 percent HF. From these measurements we obtain $\Delta H° = -2.5$ and -1.8 kcal $\cdot$ mol^{-1}, respectively, in excellent agreement with our $\Delta H°$. Matignon and Marchal [20, 21], from measurements in 30 percent HF, obtained $\Delta H°_{hyd}$ (Be(OH)$_2$, form unspecified)$= -3.2$ kcal $\cdot$ mol^{-1}, in fair agreement. Fricke and Severin [22] measured the equilibrium vapor pressure at 378 K to be 100 mm $H_2O(g)$ over $Be(OH)_2(c, \beta)$. Using a Nernst equation they calculate $\Delta H = 15.5$ kcal $\cdot$ mol^{-1} of $H_2O(g)$, which results in $\Delta H° = -5.0$ kcal $\cdot$ mol^{-1} for the hydration of BeO(c). However they reported that the BeO formed had a distorted lattice which should require a $\Delta Hf°$ more positive than -145.7 kcal $\cdot$ mol^{-1}. Also since the ΔH calculated is based on only one point it can not be considered a definitive value.

It is evident that the related data are supportive of our value for $\Delta Hf°[BeO(c)] = -145.7$ kcal $\cdot$ mol^{-1}.

3. The Enthalpy of Formation of BeF$_2$(c)

3.1. The Enthalpy of Transition of BeF$_2$(gl) and BeF$_2$(amorph) to BeF$_2$ (α, quartz)

There are no published direct determinations of the $\Delta Hf°[BeF_2(c)]$ from combustion of Be(c) in $F_2(g)$; the combustion of Be(c) in $F_2(g)$ results in amorphous material. The indirect reactions, in which BeF$_2$ forms, produce a glassy state.

Taylor and Gardner [23] determined the enthalpy of solution of both the α, quartz form, and the glassy

form in acetic acid-sodium acetate solutions to be -3.64 and -4.76 kcal $\cdot$ mol^{-1}, respectively. This leads to a ΔH_{trans} quartz $\rightarrow$ glass $= 1.12$ kcal $\cdot$ mol^{-1}. If we assume that the amorphous and glassy states are equivalent we can convert both to $\Delta Hf°[BeF_2(\alpha,$ quartz)].

3.2. The Reaction of Be(c) With F$_2$(g)

Churney and Armstrong [2] measured the enthalpy of reaction of Be(c) in $F_2(g)$ to be -244.3 kcal $\cdot$ mol^{-1}. They report BeF$_2$(amorph) to be their product. This results in $\Delta Hf°[BeF_2(c)] = -245.4$ kcal $\cdot$ mol^{-1}. In a preliminary report (1965) they cite the unpublished measurements of Simmons (1961) on the conversion of Be(foil) to partially glassy BeF$_2$, leading to $\Delta Hf°[BeF_2(c)] = -257.0$ kcal $\cdot$ mol^{-1}.

3.3. The Reaction of Be(c) With PbF$_2$(c)

Gross [24] reported $\Delta H° = -84.0$ kcal for the reaction of Be(c) with PbF$_2$(c) to form BeF$_2$(c) and Pb(c). Although no crystallographic identification was made the direction of the results under varying conditions indicates that the value is for the formation of BeF$_2$(c). Since there is some uncertainty in our selection for PbF$_2$(c) we will avoid its use by relating the reaction to the reaction from Gross, Hayman, and Levi [25]:
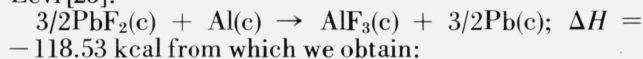
$3/2PbF_2(c) + Al(c) \rightarrow AlF_3(c) + 3/2Pb(c); \Delta H = -118.53$ kcal from which we obtain:

$3/2Be(c) + AlF_3(c) \rightarrow Al(c) + 3/2BeF_2(c); \Delta H = -7.47$ kcal and using $\Delta Hf°[AlF_3(c)] = -359.5$ kcal $\cdot$ mol^{-1}[3], $\Delta Hf°[BeF_2(c)] = -244.6$ kcal $\cdot$ mol^{-1}. However, a more recent direct determination of $\Delta Hf°[AlF_3(c)] = -361.0$ kcal $\cdot$ mol^{-1} by Rudzitis et al. [26] would lead to $\Delta Hf°[BeF_2(c)] = -245.6$ kcal $\cdot$ mol^{-1}.

3.4. Other Data

There is a path to $\Delta(\Delta Hf°)[BeO(c) - BeF_2(c)]$ and another to $\Delta Hf°[BeF_2(c)]$ both of which involve BeF$_2$(g) in high temperature gas phase equilibria. These can be referred to BeF$_2$(c) with the enthalpy of sublimation of BeF$_2$. Table 5 summarizes the second

TABLE 5. *Summary of values for* $\Delta H°_{subl}[BeF_2(c)]$ *at 298 K*

Investigator	Temp. Range of Measurements	Second Law $\Delta H°$	Third Law $\Delta H°$
	K	$kcal \cdot mol^{-1}$	$kcal \cdot mol^{-1}$
Cantor [28]..............	1146–1372	56.03	55.70
Khandamirova et al. [29].....................	846–950	58.7	56.07
Sense and Stone [30]...	1075–1293	55.37	55.65
Sense, Snyder, and Clegg [31]...............	1019–1076	60.8	55.58
	1076–1241	55.9	
Hildenbrand and Theard [32]............	821–942	55.98	55.40
Blauer et al. [33]........	713–795	58.1	53.70
Greenbaum et al. [34].....................	823–1053	56.66	54.86
Novoselova et al. [35].....................	1040–1376	52.3	55.8

and third law $\Delta H°_{subl}$ BeF$_2$ calculated from the vapor pressure measurements on the crystal and liquid. From these data we have chosen $\Delta H°_{subl} = 55.7$ kcal $\cdot$ mol^{-1}. Because the thermal functions of BeF$_2$(g) are based on an estimate for one of the three vibrational frequencies and the thermal functions of the condensed phases at high temperature are only approximate, we estimate an uncertainty of ± 2.0 kcal $\cdot$ mol^{-1}. The gas phase equilibria calculations are summarized in table 6. Because of the many uncertainties inherent in these data, we have not assigned any weight to these measurements. The thermal functions used are given in [27].[4]

TABLE 6. *Gas phase equilibria involving* BeF$_2$(g)

Reference	Reaction	$\Delta(\Delta H f°)$[BeO(c) $-$ BeF$_2$(c)]		$\Delta H f°$[BeF$_2$(c)]	
		2d Law	3d Law	2d Law	3d Law
		kcal $\cdot$ mol^{-1}		*kcal $\cdot$ mol^{-1}*	
[36]........	BeO(c) + 2HF(g) → BeF$_2$(g) + H$_2$O(g)	105	101		
[32]........	BeF$_2$(g) + 2Al(c) → Be(c) + 2AlF(g)			-242	-238

3.5. The Selection of $\Delta H f°$[BeF$_2$(c)] and $\Delta(\Delta H f°)$[BeO(c) $-$ BeF$_2$(c)]

From the values for $\Delta H f°$[BeF$_2$(c)] in 3.2 and 3.3 our "best" value for BeF$_2$(c, quartz) appears to be -245.4 kcal $\cdot$ mol^{-1}. Tentatively, then our $\Delta(\Delta H f°)$ [BeO(c) $-$ BeF$_2$(c)] $= 99.7$ kcal $\cdot$ mol^{-1}.

As cited earlier the data from Kolesov et al. [9] yielded $\Delta(\Delta H f)$ [BeO(c) $-$ BeF$_2$(aq)] $= 107.085$ kcal $\cdot$ mol^{-1}, where the BeF$_2$(aq) is in 340(HF + 3.826H$_2$O). They also measured the enthalpy of solution of BeF$_2$(c, β-cristobalite) to the same final solution, $\Delta H = -8.07$ kcal $\cdot$ mol^{-1}. If we combine these results with our selected value for BeO(c), $\Delta H f° = -145.7$ kcal $\cdot$ mol^{-1} we obtain for BeF$_2$(c, β-cristobalite)-244.7 kcal $\cdot$ mol^{-1}. This indicates an enthalpy of transition of 0.7 kcal $\cdot$ mol^{-1} between the two forms. Reported values for similar transitions in SiO$_2$ [3], CaF$_2$ [37], and BeCl$_2$ [38] are 0.37, 1.14 and 1.32 kcal $\cdot$ mol^{-1}, respectively.

4. Assigned Uncertainties

We have tried to indicate some measure of the uncertainty in the reported values of ΔH and in the derived $\Delta H f°$'s by the number of significant figures given, following the convention that the overall uncertainty lies between 2 and 20 units of the last figure. The uncertainty in the $\Delta H f°$'s depends on the uncertainties of all the determinations in the total chain of reactions used to establish the value. But the values also are given so that the experimental data from which they are derived may be recovered with an accuracy

equal to that of the original experimental quantities.

The overall uncertainties in the ΔH's are based on many factors—the experimental technique used, the details given, the number of measurements, the standard deviation of the reported results, the magnitude and reliability of the corrections to 298.15 K, and the reliability of previous work of the investigators. A strictly mathematical evaluation can therefore not be made. For this reason we shall consider only the discussion of the assignment of uncertainties to our "best" values for $\Delta H f°$[BeO(c)] and $\Delta H f°$[BeF$_2$(c)].

Kilday et al. reported the uncertainty in their measurements of ΔH of solution of BeO(c) in aqueous 24 percent HF to be ± 0.05 kcal $\cdot$ mol^{-1}. Kolesov et al. state their uncertainty to be ± 0.12 kcal $\cdot$ mol^{-1}. Bear and Turnbull state the uncertainties in their measurements to be ± 0.6, ± 0.3, ± 0.6, and ± 0.9 kcal $\cdot$ mol^{-1} for the solution of Be(c) in 12, 22.6, 30, and 40 percent HF solutions, respectively. In calculating the $\Delta(\Delta H f)$ [BeO(c) $-$ BeF$_2$(aq)] and $\Delta H f$[BeF$_2$ aq)] we ir 'roduced errors due to the uncertainties in our values for $\Delta H f°$ F$^-$(aq) and φ_L HF, but these errors essentially cancel in obtaining $\Delta H f°$[BeO(c)]. We introduce a ± 0.05 kcal $\cdot$ mol^{-1} uncertainty by our correction of $\Delta H f$ [BeF$_2$(aq)] to $X = 100$. This is negligible. The overall uncertainty obtained from the combined results of Bear and Turnbull and Kilday et al. is ± 0.6 kcal $\cdot$ mol^{-1}; similarly from the results of Kolesov et al. and Bear and Turnbull. The $\Delta H f°$ [BeO(c)] derived from the combination of the results of Kilday et al., and Churney and Armstrong, is dependent upon $\Delta H f°$[F$^-$(aq)]; hence the overall uncertainty must be ± 1.2 kcal $\cdot$ mol^{-1}.

The uncertainty in the Armstrong and Coyle measurement is ± 0.2 kcal $\cdot$ mol^{-1}. However, the final solution here is not dilute with respect to the BeF$_2$(aq). Even with the estimated mixing correction to the measured ΔH, the uncertainty in the derived $\Delta H f°$ [BeO(c)] must be ± 1.5 kcal $\cdot$ mol^{-1}. Similarly, although the uncertainty in the measurements of Thompson et al., on Be(c) in HCl is ± 0.1 kcal $\cdot$ mol^{-1} (for BeO in HCl from Kilday et al. it is ± 0.5 kcal $\cdot$ mol^{-1}) the overall uncertainty in the derived $\Delta H f°$ [BeO(c)] is $+ 1.5$ kcal $\cdot$ mol^{-1}. For our "best" value for $\Delta H f°$ [BeO(c)] we assign an uncertainty of ± 0.6 kcal $\cdot$ mol^{-1}. Churney and Armstrong assigned ± 0.8 kcal $\cdot$ mol^{-1} to their value for $\Delta H f°$[BeF$_2$(amorph)]. The indirect determination from the measurements of Gross et al. have an overall uncertainty of ± 0.8 kcal $\cdot$ mol^{-1}. We assign an overall uncertainty of ± 0.8 kcal $\cdot$ mol^{-1} to our "best" value for $\Delta H f°$ [BeF$_2$(c)].

5. A Key Assumption

The interpretation of the data and the values given are internally consistent with our value for $\Delta H f°$ [HF(aq, std. state)] [3], and lend support to this value; eg., the values for $\Delta(\Delta H f°)$ [BeO(c)$-$BeF$_2$(quartz)] from our 'selected' values, independent of HF(aq) are in excellent agreement with that derived from the Kolesov et al. difference, HF dependent, if one assumes a ΔH_{trans} of 0.7 kcal $\cdot$ mol^{-1} for the β cristobalite to the quartz form. Also the $\Delta H f$[BeF$_2$(aq, in HF)] from the Bear and Turnbull measurements, dependent upon HF

---

[4] Use of a more recent set of thermal functions [40], also based on an estimate, could change $\Delta H°_{subl}$ of BeF$_2$ by a few tenths of a kcal, well within the assigned uncertainty.

are in excellent agreement with that derived from the ΔH_{soln} (measured by Kilday and Churney) of a BeF_2 (amorph) sample whose $\Delta H f^\circ$ was measured directly by Churney and Armstrong and is thus independent of $\Delta H f^\circ [HF(aq)]$. However there is also evidence [39, 40, 41] that the 'selected' value for HF may be too positive by 0.3 to 0.4 kcal · mol⁻¹. If so, this would involve a reinterpretation of the data.

In summary:

$$\Delta H f^\circ [BeO(c)] = -145.7 \pm 0.6 \text{ kcal} \cdot \text{mol}^{-1}$$

$$(-609.6 \pm 2.5 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta H f^\circ [BeF_2(c, \text{ quartz})] = -245.4 \pm 0.8 \text{ kcal} \cdot \text{mol}^{-1}$$

$$(-1026.8 \pm 3.3 \text{ kJ} \cdot \text{mol}^{-1}).$$

6. References

[1] Kilday, M. V., Prosen, E. J., and Wagman, D. D., J. Res. Nat. Bur. Stand. (U.S.) **77A2** (Phys. and Chem.) No. 2, 217–225 (Mar.–Apr. 1973).

[2] Churney, K. L., and Armstrong, G. T., J. Res. Nat. Bur. Stand. (U.S.) **73A**, (Phys. and Chem.), No. 3, 281–297 (May–June 1969).

[3] Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H., Selected Values of Chemical Thermodynamic Properties, Nat. Bur. Stand. (U.S.), Tech. Note 270–3. 264 pp. (Jan. 1968); Parker, V. B., Wagman, D. D., Evans, W. H., Nat. Bur. Stand. (U.S.), Tech. Note 270–6, 106 pp. (Nov. 1971).

[4] Moose, J. E., and Parr, S. W., J. Am. Chem. Soc. **46**, 2656 (1924).

[5] Roth, W. A., Börger, E., and Siemonsen, H., Z. anorg. u. allgem. Chem. **239**, 321 (1938).

[6] Neumann, B., Kröger, C., and Kunz, H., Z. anorg. u. allgem. Chem. **218**, 379 (1934).

[7] Mielenz, W., and v. Wartenberg, H., Z. anorg. u. allgem. Chem. **116**, 267 (1921).

[8] Cosgrove, L. A., and Snyder, P. E., J. Am. Chem. Soc. **75**, 3102 (1953).

[9] Neumann, B., Kröger, C., and Haebler, H., Z. anorg. u. allgem. Chem. **204**, 81 (1932).

[10] Kolesov, V. P., Popov, M. M., and Skuratov, S. M., Zhur. Neorg. Khim. **4**, 1233 (1959).

[11] Matignon, C., and Marchal, G., Compt. rend. **183**, 927 (1926).

[12] Copaux, H., and Philips, C., Compt. rend. **176**, 579 (1923).

[13] Bear, I. J., and Turnbull, A. G., J. Phys. Chem. **69**, 2828 (1965).

[14] Armstrong, G. T., and Coyle, C. F., U.S. AEC AED–Conf–65–358–1, 35 pp. (1965).

[15] Fricke, R., and Wüllhorst, B., Z. anorg. u. allgem. Chem. **205**, 127 (1932).

[16] Parker, V. B., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 2, 66 pp. (Apr. 1, 1965).

[17] Thompson, C. J., Sinke, G. C., and Stull, D. R., J. Chem. Eng. Data **7**, 380 (1962).

[18] Blachnik, R. O. G., Gross, P., and Hayman, C., Fulmer Research Inst. Scientific Rept. No. 5, Contract AF 61(052)–863 (July 1968).

[19] Smirnov, M. V., and Chukreev, N. Ya., Zhur. Neorg. Khim. **3**, 2445 (1958).

[20] Matignon, C., and Marchal, G., Bull. soc. chim. France [4] **39**, 167 (1926).

[21] Matignon, C., and Marchal, G., Compt. rend. **181**, 859 (1925).

[22] Fricke, R., and Severin, H., Z. anorg. u. allgem. Chem. **205**, 287 (1932).

[23] Taylor, A. R., and Gardner, T. E., U. S. Bur. of Mines Rept. Invest. **6664**, 15 pp. (1965).

[24] Gross, P., Hayman, C., and Bingham, J. T., Fulmer Research Inst. Ltd. Sci. Rept. No. **7**, Contract AF 61(052)–447, 10 pp. (Feb. 1971).

[25] Gross, P., Hayman, C., and Levi, D. L., Met. Soc. Conf. **8**, 903 (1961).

[26] Rudzitis, E., Feder, H. M., and Hubbard, W. N., J. Inorg. Chem. **6**, 1716 (1967).

[27] Dow Chemical Company, JANAF Thermochemical Tables PB 168 370 (Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, August 1965).

[28] Cantor, S., J. Chem. Eng. Data **10**, 237 (1965).

[29] Khandamirova, N. E., Evseev, A. M., Pozharskaya, G., et al., Zhur. Neorg. Khim. **4**, 2192 (1959).

[30] Sense, K. A., and Stone, R. W., J. Phys. Chem. **62**, 453 (1958).

[31] Sense, K. A., Snyder, M. J., and Clegg, J. W., J. Phys. Chem. **58**, 223 (1954).

[32] Hildenbrand, D. L., and Theard, L. P., J. Chem. Phys. **42**, 3230 (1965).

[33] Blauer, J. A., Greenbaum, M. A., and Farber, M., J. Phys. Chem. **69**, 1069 (1965).

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

[35] Novoselova, A. V., Muratov, F. Sh., Reshetnikova, L. P., and Gordeev, I. V., Vestnik Moskov, Univ., Ser. Mat., Mekh., Astron., Fiz. i Khim, No. **6**, 181 (1958).

[36] Greenbaum, M. A., Arin, M. L., and Farber, M., J. Phys. Chem. **67**, 1191 (1963).

[37] Naylor, B. F., J. Am. Chem. Soc. **67**, 150 (1945).

[38] McDonald, R. A., and Oetting, F. L., J. Phys. Chem. **69**, 3839 (1965).

[39] Armstrong, G. T., Hydrogen Fluoride and the Thermochemistry of Fluorine, Nat. Bur. Stand. (U.S.), Tech. Note. 513, 32 pp. (Oct. 1970).

[40] Stull, D. R., and Prophet, H., Eds. JANAF Thermochemical Tables, 2nd ed., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37 (1971).

[41] Domalski, E. S., and Armstrong, G. T., J. Res. Nat. Bur. Stand. (U.S.) **71A**, (Phys. and Chem.) No. 3, 195–202 (1967).