

A Mass Spectrometric Study of the BeO-BeF₂ System at High Temperatures*

J. Efimenko

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

(August 22, 1967)

Mass spectrometric studies were made at high temperatures of the vapors over BeF₂(s) and BeO(s) individually and of their mixture. The sublimation enthalpy, $\Delta H_0^\circ = 55.56 \pm 0.43$ kcal/mol, where 1 kcal equals 4184 J, was obtained for BeF₂ by the use of a $\log I^+T$ versus $1/T$ plot. A complex molecule appeared in the BeF₂-BeO system at high temperatures which, on the basis of its m/e position, corresponded to Be₂OF₂. For the reaction, $\text{BeO(s)} + \text{BeF}_2\text{(g)} = \text{Be}_2\text{OF}_2\text{(g)}$, a second law treatment of the data gave an enthalpy value, $\Delta H_0^\circ = 41.56 \pm 1.8$ kcal/mol. The data, combined with free energy functions, resulted in a mean reaction enthalpy, $\Delta H_0^\circ = 42.6$ kcal/mol. The heat of formation for Be₂OF₂(g), $\Delta H_0^\circ = -288.3$ kcal/mol, was computed using the reaction enthalpy based on the second law.

Key Words: Beryllium difluoride, beryllium oxide, high temperatures, mass spectrometry, reaction enthalpy, sublimation enthalpy.

1. Introduction

Mass spectrometric studies have been made on the vaporization of BeF₂ [1,2]¹ and BeO [3,4] separately. It was of interest to investigate a more complex system of these elements at high temperatures in order to ascertain whether any unknown product existed under such conditions. Mass spectrometric data on minor species would provide a means to obtain and compute some of its thermodynamic properties.

As no two mass spectrometers have identical operating characteristics, the individual compounds as well as the mixture were examined with the instrument used in this study. The data from the individual compounds aided in distinguishing products of reactions from impurities, background and fragmentation peaks. Almost no studies have been reported on sublimation of solid beryllium difluoride and as part of this study, data on its sublimation enthalpy were obtained.

2. Experimental Procedure

2.1. Mass Spectrometer

The instrument used in this research was based on the design of Chupka and Inghram [5] and was

built by Nuclide Analysis Associates (State College, Pennsylvania). It is classified as a 12-in radius of curvature, 60° sector, directional focusing instrument. This early design has the Knudsen cell source section positioned 30° from the vertical and the generated molecular beam is coaxial with the ion beam produced. A modification was made to the vacuum pumping system with the addition of a 6-in mercury vapor pump to the Knudsen cell chamber.

2.2. Beryllium Difluoride

For the vaporization of beryllium difluoride one effusion cell made from molybdenum and another from nickel were employed. Each was of 1/2-in o.d., 1-in high with a 1/16-in wall thickness and a 1/2 mm diam cylindrical orifice in the cover. Heating was accomplished by radiation from a concentric, cylindrical tungsten helix about the effusion cell. The temperature sensed with a Pt-PtRh (10%) thermocouple (wire diameter 0.25 mm) fastened into a hole in the bottom of the cell was taken to be the vaporization temperature. It was not feasible to determine the temperature gradient along the cell while mounted in the mass spectrometer but no condensation of BeF₂ was visible on the top half of the effusion cells at the conclusion of an experiment.

The beryllium difluoride was provided by the Brush Beryllium Company² (Elmore, Ohio). Their method of preparation was the decomposition of (NH₄)₂BeF₄, and the following is the supplier's analysis in (weight) percent: beryllium as Be, 7.4; equivalent as

*This research was supported by the Advanced Research Projects Agency, Department of Defense, under order number 20 and by the U.S. Air Force Office of Scientific Research, Propulsion Division, ISSA-65-8.

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

(NH₄)₂BeF₄, 99.0; Al, 0.0043; Cr, 0.001; Fe, 0.0017; Mn, 0.0001; Ni, 0.0005. They heated the resulting BeF₂ for 12 hr at 400 °C.

At NBS, an x-ray pattern of the BeF₂ indicated that the degree of crystallinity was low but the crystalline portion was identified as the hexagonal form. Analysis for nitrogen in the sample gave N < 0.01 percent. The large intensities of (HF)⁺ and (H₂O)⁺ mass peaks indicated that the BeF₂ used was not anhydrous at that time. A spectrochemical analysis at NBS of a beryllium difluoride portion detected the following, as elements, in weight percent: Al, 0.01-0.1; Ca, Mg, Mn, Si, Sr, 0.001-0.01; B, Ba, Cr, Cu, Fe, Ni, < 0.001; Pt was uncertain.

2.3. Beryllium Oxide

Beryllium oxide was volatilized from a tungsten effusion cell, 3/4-in o.d., 1 1/4-in long, 1/8-in wall thickness, with a cylindrical orifice in the cover 1 mm in diameter. The cell was heated by a regulated electron bombardment unit (Cambridge Products Corp.) and a Leeds and Northrup optical pyrometer was employed to measure the temperature in a radial hole, with a length to diameter ratio of 5, located near the bottom of the cell.

This beryllium oxide was supplied by the Brush Beryllium Company (Elmore, Ohio) (see footnote 2), in powder form which passed through 20 mesh sieve. The cell was filled three-fourths full with this light powder. At the conclusion of an experiment, visual examination of the BeO remaining in the tungsten cell indicated that the oxide had a gray coating and had shrunk away from the walls of the cell. Also, the tungsten cell was severely eroded and embrittled. A spectrographic analysis at NBS on a sample of the BeO, before use, detected the following contents: 0.001-0.01 percent Al, Fe, Si; 0.0001-0.001 percent Ca, Mg; less than 0.0001 percent Cu.

2.4. Beryllium Oxide + Beryllium Difluoride

Due to the large difference in volatility of these two compounds, a modified reaction cell was devised as shown in figure 1. The low-melting solid BeF₂ was contained in the bottom, B, of a tantalum tube and opposite on the outside wall was spot welded a Pt-PtRh (10%) thermocouple used only to monitor the temperature gradient. The tantalum tube, figure 1, is 79 mm long, 6.3 mm o.d. and 0.375 mm wall thickness. The second tantalum tube employed was 130 mm in length.

The effusion cell was fabricated from molybdenum and contained a cylindrical orifice 0.5 mm diam in the cover. Heating was by electron bombardment, employing two tungsten ribbon loops, concentric with each half of the cell. For temperature measurements, an optical pyrometer was sighted into two blackbody holes, T₁ and T₂. The upper hole, T₁, was 1 mm in diameter, 8 mm deep and served to check the tem-

² Certain commercial products are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards.

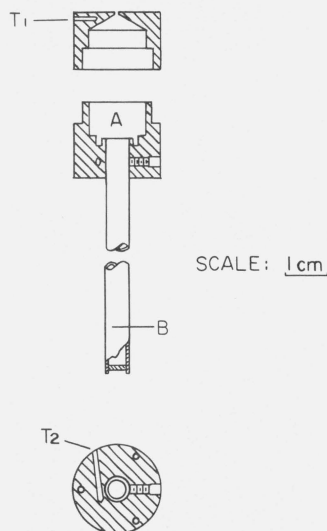


FIGURE 1. Effusion-reaction cell for BeO-BeF₂.

perature gradient in the cover. The lower hole, T₂, 1 mm in diameter, 12 mm deep, was used to obtain the reaction temperature. The bottom view in figure 1 shows the position of this "blackbody" hole and the holes, spaced 120° apart, to take 1.5 mm tungsten rods which supported the reaction cell.

The cell in figure 1 was surrounded by a nest of six cylindrical tantalum radiation shields whose tops allowed unobstructed flow from the effusion cell. A stack of four tantalum disks shielded the bottom of the effusion cell. Three reflectors were placed inside the tantalum tube approximately 1 cm from the end, A, shown in the figure. These reflectors were from tantalum foil 1.27 × 10⁻² mm thick. A small BeO thimble was placed over the tantalum tube at A and the space around and above this thimble was packed with granulated BeO.

The BeO used in this part was a porous solid prepared at NBS. A spectrochemical analysis performed by the NBS Spectrochemical Analysis Section indicated amounts present (weight percent) > 10, Be; 0.01-0.001, Al, Si; < 0.001, Ba, Ca, Cu, Mg, Mn, Pb; questionable trace, Cr, Sn; not found, Ag, As, Au, B, Bi, Cd, Ce, Co, Ni.

3. Results and Discussion

3.1. Beryllium Difluoride

Initial heating of hygroscopic BeF₂ produced copious amounts of ions, *m/e* 18, 19, 20 and some transient species. Those listed in table 1 illustrate the ions produced from an exploratory experiment, with a layer of BeO on top of some BeF₂. In all experiments a large background intensity at *m/e* 28 (CO⁺, N₂⁺) prevented reliable intensity measurements for (BeF)⁺.

A mass spectrometric calibration was not carried out with the effusion cells used for BeF₂ as vapor

pressure data already were available through absolute measurements [2, 8-12].

TABLE 1. Vapor species from $\text{BeF}_2 \cdot \text{XH}_2\text{O} + \text{BeO}$ during initial heating

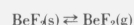
m/e	Probable species	T , °K
18	$(\text{H}_2\text{O})^+$	< 1700
20	$(\text{HF})^+$	
23	$(\text{Na})^+$	
26	$(\text{BeOH})^+$	
27	$(\text{BeOH}_2)^+$	
36	$(\text{HOF})^+$	< 1700
38	$(\text{F}_2)^+$	
44	$(\text{BeOF})^+$	> 1800
47	$(\text{BeF}_2)^+$	
64	$(\text{BeOHF}_2)^+$	< 1600
72	$(\text{Be}_2\text{OF}_2)^+$	> 1850
75	$(\text{BeO})_3$	> 1850

Where no temperature values are given, the intensities were detected only below the optical pyrometer scale, i.e., 700 °C.

Experimental data are presented in table 2 and in the form of a $\log I^+T$ versus $1/T$ plot in figure 2. The curve was fitted by a least squares treatment. From the slope of this curve a sublimation enthalpy,

$\Delta H_{755}^\circ = 54.63 \pm 0.43$ kcal/mol was obtained; 1 kcal = 4184 J. Reduction to the absolute zero reference state was made using the JANAF Tables indicated in table 3; $\Delta H_0^\circ = 55.56 \pm 0.43$ kcal/mol. A tabulation of literature sublimation enthalpies is listed in JANAF Thermochemical Data Tables [6] under beryllium difluoride and the values which were considered acceptable for averaging by the compilers ranged from 54.0 to 57.0 kcal/mol for second law calculations and 54.14 to 55.36 for third law results. Some difference between those results and the work done in this laboratory may exist because the specimen used in this work was mainly of low crystallinity. However, as mentioned in reference 6, the enthalpy difference between glassy and crystalline beryllium difluoride is most likely of the order of one or two kcal per mol.

TABLE 2. Data



Index No.	T , °K	I^+ (1 V scale)	$I^+ T$	$10^3/T$
1	721	1.60	1153	1.3870
2	723	1.60	1157	1.3831
3	724	1.70	1232	1.3812
4	749.1	6.00	4495	1.3349
5	749.7	6.40	4798	1.3339
6	754.4	7.50	5658	1.3256
7	780.3	24.3	18960	1.2816
8	780.1	24.3	18960	1.2819
9	783.2	27.3	21380	1.2768
10	781.1	26.1	20390	1.2802
11	781	24.9	19450	1.2804
12	780	24.3	18950	1.2821
13	795.1	47.0	37370	1.2577
14	796	48.0	38210	1.2563
15	796.5	50.0	39830	1.2555
16	778	23.0	17890	1.2853
17	778	23.3	18130	1.2853
18	777.5	22.8	17730	1.2862
19	776	20.1	15600	1.2887
20	753.5	6.90	5199	1.3271
21	753	6.75	5083	1.3280
22	714	0.95	678	1.4006
23	714	0.90	643	1.4006
24	745.5	4.80	3578	1.3414
25	745.7	4.75	3542	1.3410
26	747.1	5.10	3810	1.3385
27	748.8	6.40	4792	1.3355
28	786.0	29.5	23190	1.2723
29	785.4	29.0	22780	1.2732
30	818.9	111.0	90900	1.2212
31	790.1	38.0	30020	1.2657
32	789.1	38.0	29990	1.2673
33	787.9	38.0	29940	1.2692
34	785.5	34.2	26860	1.2731
35	762.2	12.8	9756	1.3119
36	768	13.5	10370	1.3021
37	768	13.8	10600	1.3021
38	767	13.8	10580	1.3038
39	767	13.5	10350	1.3038
40	777	21.5	16710	1.2870
41	738	3.65	2694	1.3550
42	735	3.45	2536	1.3605
43	705	0.66	465	1.4184
44	710	0.80	568	1.4085
45	746	5.15	3842	1.3405
46	737	3.35	2469	1.3569
47	730	2.75	2008	1.3699
48	776	23.7	18390	1.2887
49	772	19.8	15290	1.2953

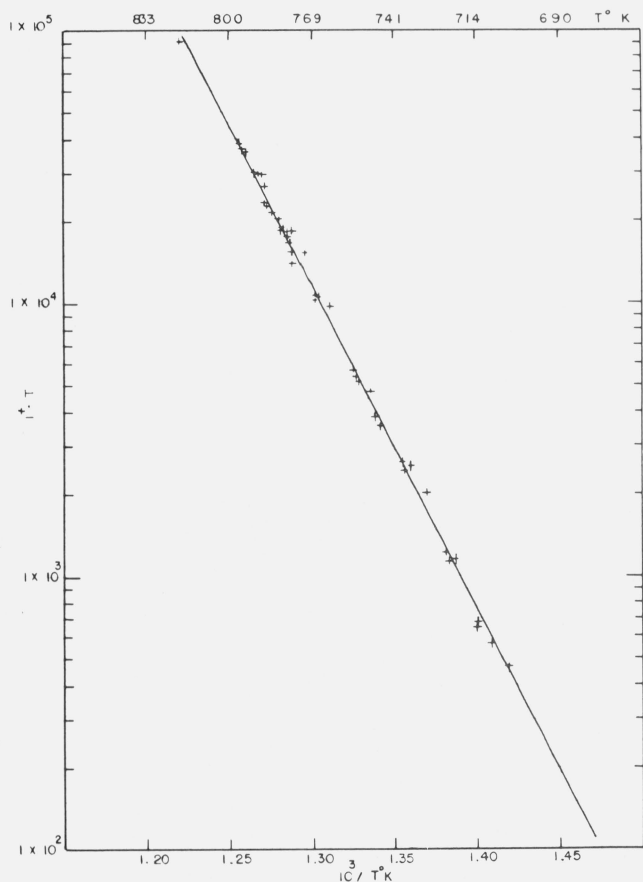


FIGURE 2. The curve is a least squares fit to the data of table 2. The heat of sublimation obtained from this curve is 54.63 ± 0.43 kcal/mol for the arithmetic mean temperature, 755 °K. $\text{BeF}_2(\text{s}) \rightleftharpoons \text{BeF}_2(\text{g})$.

3.2. Beryllium Oxide

The vapor species from the oxide appeared in the following mass positions: $m/e=9, 16, 75, 32, 25, 50$ in decreasing order of intensity at approximately 2100 °C. The positive ions corresponding to these masses are $\text{Be}^+, \text{O}^+, (\text{BeO})_3^+, \text{O}_2^+, (\text{BeO})^+, (\text{BeO})_2^+$, which check with results of previous investigators [3]. A more detailed study of BeO will be presented at a future date.

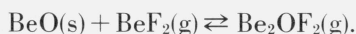
TABLE 3. Auxiliary data for computations

Value	Source
Multiplier efficiency	
$\gamma_{\text{BeF}_2} = 13.0 \times 10^3$	This work
$\gamma_{\text{Be}_2\text{OF}_2} = 12.9 \times 10^3$	This work
$\gamma_{\text{Ag}} = 7.0 \times 10^3$	This work
Sensitivity, $\text{Ag}^{1275} \text{ } ^\circ\text{K} = 4.8 \times 10^{-6} \text{ amp/mmHg}$	This work
Window transmissivity = $5.00 \pm 0.63 \times 10^{-6}$	This work
Relative ionization cross sections, σ	
Be, 6.31	
O, 3.29	J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78 , 546-551 (1956).
F, 1.85	
Ag, 34.8	
Standard heat of formation, ΔH_f° kcal/mol	
BeO(s) , -142.3 ± 0.1	JANAF Tables, Sept. 30, 1963
$\text{BeF}_2(\text{g})$, -187.0 ± 3	JANAF Tables, June 30, 1964

At high temperature, part of the beryllium ion intensity showed a behavior often referred to as "photo-effect" [7] or "anomalous ion effect" with this type of instrument. This effect may be a factor in the discrepancy between mass spectrometric and Knudsen weight loss measurements for the decomposition pressures of BeO . For the type of mass spectrometer used in this work the results are valid only if the ions are formed by electron impact in the ionization source. The routine use of a shutter alone to differentiate the ions issuing from the effusion cell and originating in background gases does not detect the "anomalous" effect.

3.3. Beryllium Oxide-Beryllium Difluoride System

The pressure of Be_2OF_2 in the temperature region above 1600 °K permits examination of the equilibrium:



Data from the first set of experimental conditions, computed equilibrium constants and reaction enthalpies referred to absolute zero are shown in table 4; similar information resulting from higher temperature observations is given in table 5. Auxiliary data and the sources are presented in table 3. Thermodynamic functions for the $\text{Be}_2\text{OF}_2(\text{g})$ molecule were computed from molecular constants (note 1).

NOTE: Dr. D. E. Mann, formerly with NBS Molecular Spectroscopy Section, made the following estimates of molecular parameters using the isoelectronic analog B_2O_3 :

configuration—"V" shaped, similar to B_2O_3 ; symmetry— C_{2v} , apex angle $\text{Be-O-Be} \approx 150^\circ$, symmetry number, $\sigma=2$, O-Be-F

grouping-linear, Be-O distance = 1.40 Å, Be-F distance = 1.36 Å, electronic multiplicity of ground state = 1, vibrational spectrum (with degeneracies) in cm^{-1} , 1500 (1), 1200 (1), 900 (1), 600 (1), 300 (1), 300 (1), 300 (1), 100 (1), 400 (1).

The reaction enthalpy was obtained also by plotting the ratios of ion intensities A , $\text{Be}_2\text{OF}_2/\text{BeF}_2$ as $\log A$ versus $1/T$, illustrated in figures 3 and 4. This treatment is known commonly as the second law or van't Hoff method. Least squares computations determined the slopes for the experimental points and their standard deviations. These slopes were used to give the reaction enthalpies, $\Delta H_{1730}^\circ = 39.25 \pm 3.5$ kcal/mol and $\Delta H_{2035}^\circ = 40.68 \mp 0.86$ kcal/mol. These enthalpies were corrected to absolute zero reference state, giving $\Delta H_0^\circ = 40.50 \mp 3.5$ kcal/mol and 42.62 ± 0.86 kcal/mol from which one has a mean value 41.56 ± 1.8 kcal/mol. The values of the third law reaction enthalpies shown in tables 4 and 5 give a mean value, $\Delta H_0^\circ = 42.6$ kcal/mol. Using the mean enthalpy obtained from the slopes, $\Delta H_0^\circ = 41.56$ kcal/mol and the heats of formation from table 3, the heat of formation of $\text{Be}_2\text{OF}_2(\text{g})$ was computed, $\Delta H_f^\circ = -288.3$ kcal/mol.

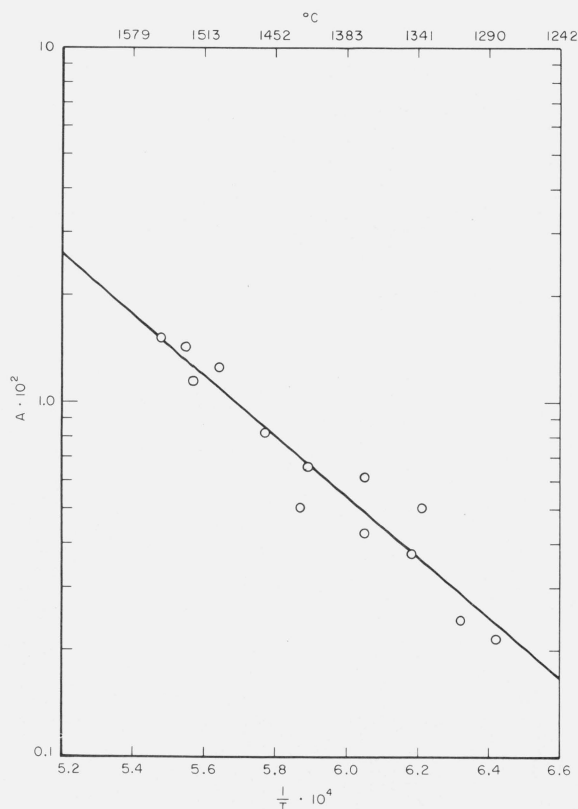


FIGURE 3. Van't Hoff plot of ion intensities ratios for formation of $\text{Be}_2\text{OF}_2(\text{g})$ between 1560 to 1890 °K.

Reaction enthalpy, $\Delta H_{1730}^\circ = 39.25 \pm 3.5$ kcal/mol.

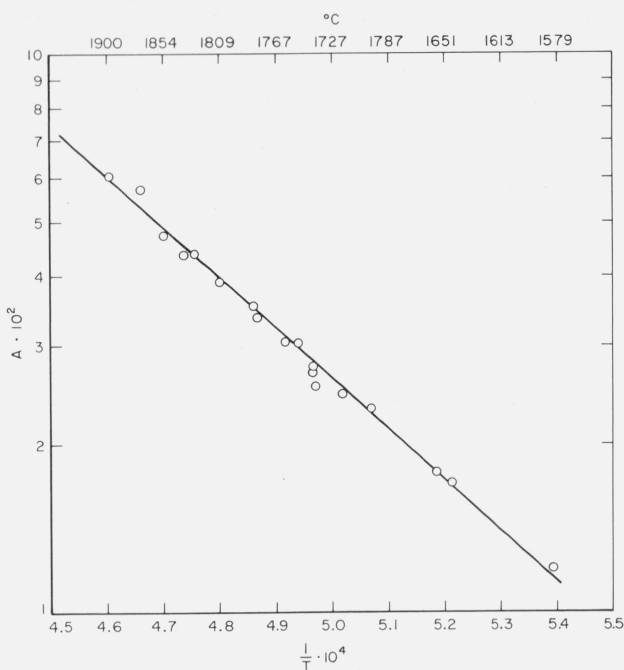


FIGURE 4. Van't plot of ion intensities ratios for the formation of $\text{Be}_2\text{OF}_2(\text{g})$ between 1870 to 2200 °K.

Reaction enthalpy $\Delta H_{2035}^\circ = 40.68 \pm 0.86$ kcal/mol.

TABLE 4. Mass spectrometric temperature-intensity data

Index No.	$T, ^\circ\text{C}$	$T, ^\circ\text{K}_{\text{corr.}}$	$I_{z\text{ volt}}$	$I_{r\text{ volt}}$	$K \times 10^2$	ΔH_0°
4	1285	1570	0.013	7.3	0.908	41.9
5	1307	1592.5	.011	6.6	.852	42.9
1	1337	1623	.025	6.7	1.90	41.1
13	1343	1629	.017	5.7	1.52	42.0
6	1383	1670	.040	8.4	2.43	41.4
3	1425	1713	.081	15.0	3.06	41.7
12	1431	1719	.081	20.4	2.04	43.0
7	1465	1753	.126	19.2	3.35	42.3
2	1500	1789	.530	50.8	5.32	41.5
11	1522	1811	.470	52.0	4.61	42.6
8	1530	1819	.470	42.0	5.72	41.9
10	1548	1838	.700	61.0	5.86	42.2
9	1600	1891	1.200	80.0	7.66	42.4

See footnote at end of table 5.

The chronological sequence of experimental measurements is recorded by the index numbers. Equilibrium constants, K are computed from the data; the ΔH_0° values, heat of reaction at absolute zero, were computed with free energy functions. In table 5, data with index nos. 21-28 and index nos. 31-43 were taken at a day interval. The data in table 5 were taken 6 months after the data of table 4.

The ion intensity ratios were converted to equilibrium constants with the aid of a silver calibration value obtained experimentally and ionization cross

TABLE 5. Mass spectrometric temperature-intensity data

Index No.	$T, ^\circ\text{C}$	$T, ^\circ\text{K}_{\text{corr.}}$	$I_{z\text{ volt}}$	$I_{r\text{ volt}}$	$K \times 10^2$	ΔH_0°
28	1738	2032	0.050	1.98	1.29	43.3
21	1740	2034	.024	0.87	1.40	43.0
22	1740	2034	.020	.74	1.35	43.2
23	1783	2077	.029	.86	1.72	43.0
24	1820	2110	.075	1.41	2.71	41.8
27	1825	2119	.138	3.40	2.07	43.2
25	1855	2150	.108	2.37	2.32	43.2
26	1875	2169	.228	4.00	2.91	42.5
43	1582	1872	.009	0.75	0.61	43.0
42	1640	1937	.019	1.08	.90	42.8
31	1655	1947	.017	0.99	.91	42.9
32	1700	1992	.032	1.38	1.18	42.9
41	1713	2013	.040	1.62	1.26	43.0
33	1750	2045	.051	1.68	1.55	42.8
34	1760	2054	.087	2.85	1.55	43.0
39	1785	2079	.093	2.64	1.80	42.9
35	1810	2105	.110	2.82	2.00	43.0
38	1829	2125	.153	3.50	2.23	42.9
36	1838	2134	.153	3.40	2.30	43.0
37	1857	2153	.273	4.30	3.24	41.9
37	1898	2195	.295	4.90	3.07	42.8

sections shown in table 3. The expressions shown in (1) and (2) relate the ion intensity to partial pressure.

$$p_i = \frac{I_i^+}{S_i(T)} \quad (1)$$

$$S_i = S_s \frac{\sigma_i \gamma_i T_s}{\sigma_s \gamma_s T_i} \quad (2)$$

I_i^+ = positive ion intensity of species i ,

p_i = partial pressure,

S_i = mass spectrometric sensitivity for species i ,

S_s = mass spectrometric sensitivity for calibrating species, Ag^+ ,

σ_i, σ_s = ionization cross sections for i and s ,

γ_i, γ_s = multiplier efficiency for i and s ,

T_i, T_s = absolute temperatures.

Equilibrium constant and reaction enthalpy were computed by the usual thermodynamic functions.

Although Be_2OF_2 may be formed by reaction between BeF_2 and one or more of the polymers of $\text{BeO}(\text{g})$, the reaction postulated is considered to give the greatest contribution because of the low intensities of the beryllium oxide vapor molecules even at the high temperatures of the experiment. The reaction with solid BeO does not occur to a large extent as evidenced by the magnitude of the equilibrium constant. Analysis by x-ray diffraction of the BeO solid before and after reaction with BeF_2 indicated no new phases, only a BeO phase with a slight contamination of molybdenum oxide.

Due to the uncommon design of the Knudsen effusion cell, a check was made for equilibrium conditions by altering the concentration of a reactant. The data in table 4 were obtained using a large concentration of $\text{BeF}_2(\text{g})$ in the reaction zone. Then the concentration was decreased by placing the BeF_2

supply in a lower temperature zone as described in section 2.4 and the data in table 5 were obtained. The straight line plots in figures 3 and 4 imply that either stationary states were present or equilibrium was achieved for the reaction. The two curves overlap up to 1800 °K and the third law ΔH_0° values computed, which depend on the actual partial pressures of the species involved and free energy functions, are constant over the entire experiment range within experimental error. It is improbable that the same stationary state would be established where the reactant concentrations are varied over such a great temperature range.

Spectrochemical analysis indicated three elements that might cause interference with the identification of the product determined, Be_2OF_2 . The BeO contained Si and Al as contaminants in the range 0.01–0.001 weight percent each. Silicon was present probably as the oxide. In a reducing environment a possibility exists that $(\text{Si}_2\text{O})^+$ would have been generated at high temperature. In the presence of an excess of fluoride it is more likely that $(\text{SiOF})^+$ should have appeared at m/e 63. The experimental heating times were lengthy and impurities generally decreased with time but the observed product $(\text{Be}_2\text{OF}_2)^+$, increased with temperature and did not decrease with time. Aluminum in the form of its oxide might react in the presence of water vapor to produce $(\text{Al}_2\text{OH}_2)^+$ under proper high temperature environment. It would be more probable to expect water vapor to react with the BeO, as such a reaction has been observed to occur easily [14, 15]. After extended pumping and low temperature heating the ion intensity of water decreased greatly but this had no effect on the ion intensity of $(\text{Be}_2\text{OF}_2)^+$. One of the isotopic oxides of Mo could appear at mass position 72 as $[\text{MoO}_3]^{++}$. Since the accompanying isotopes of molybdenum were not observed under the operating conditions, this source of $[\text{MoO}_3]^{++}$ was unlikely. Most of the data was obtained at moderate temperatures about 1573 to 2173 °C where the reduction of BeO by Mo is not rapid. Also the efficiency of producing doubly charged ions by electron impact is low at the conditions present.

Ionization of the vapor species with electrons of 70 eV energy must cause some fragmentation. Since the equilibrium constant for this reaction depended on the ratio of product and reactant, each to the same

power, errors due to fragmentation and erroneous ionization cross sections tend to be minimal. However, in a plot of $\log K$ versus $1/T$ any constant parameters included in K shift the line above or below its true position but do not alter the magnitude of the slope of this line. Although there is question that some additive ionization cross sections may be too high [13], no simple advancement has been made over the additivity rule.

In the initial work with beryllium difluoride the assistance of P. Nordine is appreciated. The beryllium difluoride and beryllium oxide were supplied by G. T. Furukawa of the NBS Heat Measurements Section.

4. References

- [1] J. Berkowitz and W. A. Chupka, *Ann. N.Y. Acad. Sci.* **79**, 1073–1078 (1960).
- [2] D. L. Hildenbrand and L. P. Theard, *J. Chem. Phys.* **42**, 3230–3236 (1965).
- [3] W. A. Chupka, J. Berkowitz, and C. F. Giese, *J. Chem. Phys.* **30**, 827–834 (1959).
- [4] L. P. Theard and D. L. Hildenbrand, *J. Chem. Phys.* **41**, 3416–3420 (1964).
- [5] W. A. Chupka and M. G. Inghram, *J. Phys. Chem.* **59**, 100–104 (1955).
- [6] JANAF Thermochemical Tables, Dow Chemical Co., Midland, Mich., August 1965; BeF_2 table, June 30, 1964.
- [7] M. G. Inghram and J. Drowart, *Mass Spectrometry Applied to High Temperature Chemistry*, p. 224, in *Proceedings of an International Symposium on High Temperature Technology*, edited by N. K. Hiester (McGraw-Hill Book Co., New York, N.Y., 1960).
- [8] M. A. Greenbaum, J. N. Foster, M. L. Avin, and M. Farber, *J. Phys. Chem.* **67**, 36–40 (1963).
- [9] K. A. Sense and R. W. Stone, *J. Phys. Chem.* **62**, 453–457 (1958).
- [10] N. E. Khandamirova, A. M. Evseev, G. V. Pozhorskaya, E. A. Borisov, A. N. Nesmeyanov, and Ya. I. Gerasimov, *Zhur. Neorg. Khim.* **4**, 2192–2195 (1959).
- [11] A. V. Novoselova, F. Sh. Muratov, L. P. Reshetnikova, and I. V. Gordeev, *Vestnik. Moskov. Univ., Ser. Mat. Mekh. Astron. Fiz. Khim.* **13**, 181–200 (1958).
- [12] E. P. Ozhigov and A. I. Zatsarin, *Trudy Dol'nevost. Filiala. Akad. Nauk SSSR, Ser. Khim.* **1961**, 24–34 (1961).
- [13] R. F. Pottie, *J. Chem. Phys.* **44**, 916–922 (1966).
- [14] L. I. Grossweiner and R. L. Serfert, *J. Am. Chem. Soc.* **74**, 2701–2704 (1952).
- [15] W. I. Stuart and G. H. Price, *J. Nuclear Mat.* **14**, 417–424 (1964).

(Paper 72A1–482)