Thermochemistry of the Beryllia-Water Reaction

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A third-law calculation of the heat of reaction for the beryllia-water reaction with a nonlinear model for Be(OH)₂, shows that a value of about 40 kcal./mole can be derived from the experimental data on this system. Heats of formation of the beryllium aluminates have also been obtained.

AT HIGH TEMPERATURES, beryllia reacts with water vapor to form a volatile compound (*3, 5, 7, 11, 16*). This gaseous species is thought to be beryllium hydroxide, produced in the following manner:

$$BeO(c) + H_2O(g) \rightarrow Be(OH)_2(g) \qquad (1)$$

From water-vapor transpiration experiments around 1700° K., Grossweiner and Seifert (*7*) and Young (*16*) obtained second-law heats for Reaction 1 of the order of 40 kcal./mole. At 298° K., this heat value is about 43 kcal./mole.

If this last value is combined with the heats of formation of crystalline BeO, −143 kcal., and gaseous water, −58 kcal., a heat of formation of about −158 kcal. is obtained for gaseous $Be(OH)_2$.

Hildenbrand and Theard (*10*) have also examined this system with a mass spectrograph. They observed that the presence of water did increase the intensity of the BeOH and $Be(OH)_2$ mass number peaks somewhat above the background. By application of the third law, Hildenbrand and Theard (*10*) obtained lower limits for the heat of formation of BeOH, −21 kcal./mole, and of $Be(OH)_2$, −181 kcal./mole. The seemingly different heats for the formation of $Be(OH)_2$ obtained by the mass spectroscopic and water-vapor transpiration studies (*7, 10, 16*) initiated this reinvestigation of the experimental data bearing on this problem.

METHOD

One of the methods of checking the correctness of the reaction represented by Equation 1 is to obtain similar results by application of the third law:

$$\frac{\Delta H^\circ_{298}}{T} = -\frac{\Delta(F^\circ_T - H^\circ_{298})}{T} - R\ln K$$

$$K = P_{Be(OH)_2}/P_{H_2O}$$

In order to obtain the parameters necessary to calculate the free-energy-function (FEF) for $Be(OH)_2$, a model of this molecule similar to that of hydrogen peroxide (*6*) has been chosen. By analogy with BeF_2 (*1*) the oxygens in the two hydroxy groups are assumed to lie in a straight line with the central Be atom. The hydrogen atoms, like those in H_2O_2, are both assumed to be out of line with the O—Be—O bond and not to lie in the same plane with this bond. The bond angles and lengths given in Table I were used for the *FEF* calculations.

These parameters are for the most part identical with those of H_2O_2. The Be—O bond length is approximately that of gaseous BeO. The Be—O stretching and bending vibrations were obtained by solution of the force-constant equations (*8*) appropriate to a linear O—Be—O group with the Be—O force constant, 7.3×10^5 dyne/cm. The moments of inertia were obtained by the method of Wilson and Badger (*15*).

The thermodynamic properties obtained with this model are given in Table II. The *FEF* is somewhat higher than that obtained from a linear symmetric model for $Be(OH)_2$ (*9*). These data, together with similar BeO(c) and $H_2O(g)$ data (*12*), have been applied to the experimental results of (*3, 4, 5, 7, 11, 16*) to obtain the heats of Reaction 1. The detailed presentation of these calculations is available elsewhere (*2*). A summary of these results is given in Table III.

Young (*16*) has also studied the following reactions:

$$BeO \cdot 3Al_2O_3(s) + H_2O(g) \rightarrow 3Al_2O_3(s) + Be(OH)_2(g) \qquad (2)$$

$$\tfrac{3}{2}BeO \cdot Al_2O_3(s) + H_2O(g) \rightarrow \tfrac{1}{2}BeO \cdot 3Al_2O_3(s) + Be(OH)_2(g) \qquad (3)$$

By analogy with other alkaline earth-alumina mixed oxides (e.g., $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$, $3CaO \cdot Al_2O_3$), we have assumed that the *FEF*'s of $BeO \cdot Al_2O_3$ and $BeO \cdot 3Al_2O_3$ are greater than the sum of the *FEF*'s of the constituent oxides. Therefore, using the sum of the *FEF*'s of BeO and Al_2O_3 for the *FEF* of both aluminates in Reactions 2 and 3

Table I. Molecular Parameters of $Be(OH)_2$[a]

Bond Angles		Vibrations	$Cm.^{-1}$
αBe—O—H	100°	νOH(2)	3610
φH—O—Be—O—H	95°	δOH	1350
Interatomic Distances			
r(Be—O)	1.35A.	δtorsion	520
r(O—H)	0.97A.	δOH	1266
Moments of Inertia			
$I_1 = 107.4 \times 10^{-40}$ (gram-cm.²)		νBeO	855
$I_2 = 4.929 \times 10^{-40}$ (gram-cm.²)		νBeO	1835
$I_3 = 120.9 \times 10^{-40}$ (gram-cm.²)		δBeO(2)	800

[a] Nomenclature taken from (*6*)

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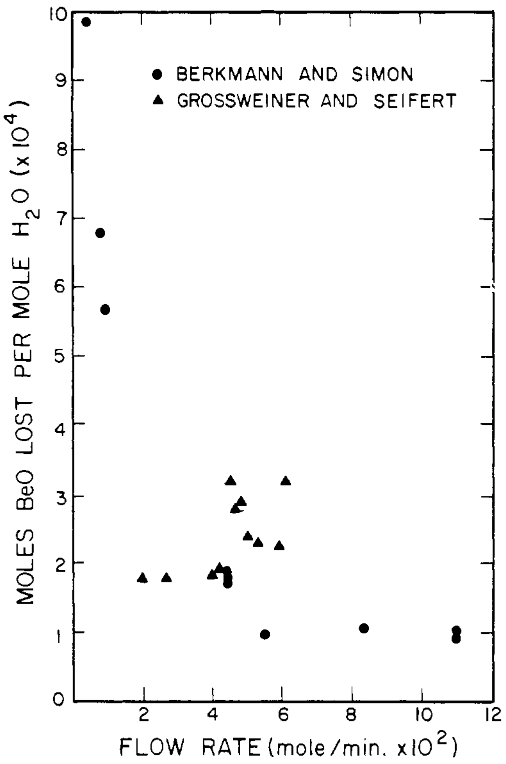

Figure 1. Effect of gas flow rate upon BeO weight loss at 1400° C.

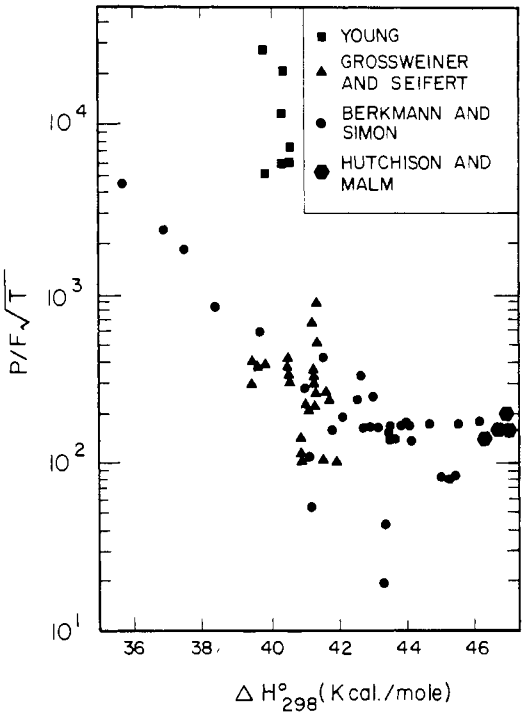

Figure 2. Effect of number of collisions per H_2O molecule on heat of reaction

should give upper limits for the heat of reaction. However, this approach for Reaction 3 yielded 3rd-law heats decreasing with increasing temperature (*2*). This temperature trend can be rectified by arbitrarily increasing the *FEF* for Reaction 3 by 4.5 e.u. A summary of these 3rd-law results is given in Table IV.

DISCUSSION

Both third-law heats calculated from the work of Grossweiner and Seifert (*7*) and Young (*16*) are in good agreement with their second-law results. Most of the experimental data for this system seem to support a heat of the order of 40 kcal./mole. This value gives a ΔH°_{298} of formation for $Be(OH)_2$ of −161 kcal./mole. However, transpiration runs at a given temperature performed at decreasing water-vapor flow rates result in heats lower by several kilocalories (*2*). Grossweiner and Seifert (*7*) carried out such experiments at 1673° K. in order to determine the number of water molecules required to vaporize a mole of BeO. They found that the plot of log $P_{Be(OH)_2}$ *vs.* log P_{H_2O} gave a slope of 0.765 instead of the expected value of unity. Because these data were not obtained at a constant gas-flow rate, it was thought that diffusion-controlled weight loss might be the cause of this discrepancy.

Merten (*13*) has shown that the effects of diffusion upon transpiration weight loss results can be detected by making a plot of the number of moles of material transported *vs.* the gas flow rate. The linear portion of such a plot is relatively free of such diffusion effects. Therefore, a plot of the number of moles of BeO transported per mole of gaseous water *vs.* the total gas flow rate has been made from the original data reported by Berkmann and Simon (*3*) and Grossweiner and Seifert (*7*) at 1400° C. As shown in Figure 1, no useful linear plot can be obtained from these data. Because the data given in (*3*) show that the heat of Reaction 1 increases with increasing water vapor flow rate, the effect of water vapor flow rate upon the reaction between solid BeO and water can be accounted for in the following manner.

If these transpiration experiments are equilibrium measurements, the heat of Reaction 1 should be independent of the number of collisions each water molecule makes with the solid BeO. The number of collisions per second per square centimeter of surface is given by the formula, $PN(2\pi MRT)^{-1/2}$. If this equation is divided by the water vapor flow rate, *F* moles/min., and the H_2O vapor pressure is in mm., the number of collisions each water molecule makes per square centimeter of surface is equal to $5 \times 10^{-7} (P/F\sqrt{T})$.

The value of $P/F\sqrt{T}$ has been calculated for most of the data of (*3, 7, 11, 16*). As shown in Figure 2, the data of

Table II. Thermodynamic Properties of $Be(OH)_2$

Temp., °K.	$(H^\circ_T - H^\circ_0)$ Kcal./Mole	$-(F^\circ_T - H^\circ_0)/T$ E.U.
298	2.655	49.255
500	5.346	54.276
1000	14.274	62.881
1500	24.853	69.133
2000	36.294	74.129
2500	48.219	78.307

Table III. Third-Law Heat of Reaction 1

	ΔH°_{298} (2nd law) Kcal./Mole	ΔH°_{298} (3rd law) Kcal./Mole
Grossweiner and Seifert (*7*)	44.3	41.3 ± 0.3
Young	45.3	40.2 ± 0.3
Hutchison and Malm (*11*)	. . .	46.6 ± 0.2
Elliott (5)	. . .	44.4 ± 1.2
Berkmann and Simon (*3*)	. . .	~42

Table IV. Third-Law Heat of Reactions 2 and 3

	ΔH°_{298} (2nd law) Kcal./Mole	ΔH°_{298} (3rd law) Kcal./Mole
Reaction 2	46	43.9 ± 0.3
Reaction 3	51	50.7 ± 0.3

Young (*16*) were obtained under such conditions that the number of collisions per water molecule was nearly one hundred times that of Grossweiner and Seifert (*7*). Variation in the collision number by a factor of ten gives the same heats within 1 kcal. for all of Young's data. The data of Grossweiner and Seifert obtained over as wide a range of collision numbers gives heats within a range of 3 kcal. However, Berkmann and Simon's data (*3*) exhibit a much greater dependence on collision number, suggesting the presence of nonequilibrium conditions in the course of their experiments. Because the data of Elliott (*5*) and Hutchison and Malm (*11*) lie close to the lower limit of Berkmann and Simon's data, it is thought that same conclusion can be applied to all these data.

Hildenbrand and Theard (*10*) reported that the mass spectroscopic intensity for mass 43 increased from 0.7 to 4.1 units when a P_{H_2O} of 0.1 mm. was added to BeO heated to 1665° C. At the same time, the mass 18 intensity grew from 108 to 3530 units. A lower limit for the heat of Reaction 1 can be obtained by combining these intensities, corrected for the unequal cross sections of both ions (*14*). These data yield a $P_{Be(OH)_2}/P_{H_2O}$ ratio of 3.5×10^{-4} which combined with the appropriate *FEF* values gives a ΔH°_{298} of 44.6 kcal./mole. Similar calculations with the *FEF* values of Hildenbrand (*9*) for $Be(OH)_2$ give heats about 10 kcal./mole less than those obtained with the *FEF* values given in Table II. With similar intensity data for the reaction:

$$BeO(s) + Be(g) + H_2O(g) \rightarrow 2BeOH(g)$$

a ΔH°_{298} of 76.8 kcal./mole has been obtained. This value combined with the heats of formation of BeO(s), Be(g) and $H_2O(g)$ yields a heat of formation for gaseous BeOH of −23 kcal./mole. This is in close agreement with the heat result given by Hildenbrand and Theard (*10*) and shows that gaseous BeOH is of negligible importance in the volatilization of BeO in the presence of water at 1700° K.

The good agreement between Young's heat for Reaction 2 and the third law results suggests that the assumption used to obtain the *FEF* for $BeO\cdot 3Al_2O$ is justified. The absence of significant change in ΔH°_{298} with increasing temperature further supports this conclusion. However, the third-law heat of Reaction 3 decreases with increasing temperature (*2*). The temperature-independent result given in Table IV was obtained by assuming that the *FEF* for $BeO\cdot Al_2O_3$ was less than the sum of the *FEF*'s of BeO and Al_2O_3 by three entropy units. This increased the Δ*FEF* of Reaction 3 by 4.5 e.u. The heat value for reaction of 50.7 ± 0.3 kcal./mole is, hence, of lesser reliability than the other third-law enthalpies.

From these third-law results, the following enthalpies of formation of the beryllium aluminates from the constituent oxides can be derived.

$$BeO(s) + Al_2O_3(s) \rightarrow BeO\cdot Al_2O_3(s)\ -8.1\ \text{kcal./mole}$$

$$BeO(s) + 3Al_2O_3(s) \rightarrow BeO\cdot 3Al_2O_3(s)\ -3.6\ \text{kcal./mole}$$

These heat results together with the assumed *FEF*'s show that $BeO\cdot 3Al_2O_3$ converts to $BeO\cdot Al_2O_3$ and alumina at temperatures below 1500° K. This last result agrees with that of Young (*16*) who reports that $BeO\cdot 3Al_2O_3$ is unstable at 1425° K. Because of their method of calculation, it is thought that these values represent lower limits.

Hildenbrand *et al.* (*10*), in a later publication, Rep. U-2231 (July 31, 1963), report mass spectroscopic intensity data obtained at 2054° C. These data yield a $P_{Be(OH)_2}/P_{H_2O}$ ratio of 6.1×10^{-3} which combined with the appropriate *FEF* values gives a ΔH°_{298} of 39.7 kcal./mole.

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