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THE HEATS OF SOLUTION OF BERYLLIUM IN
CHEMICAL MILLING SOLUTIONS

James D. Navratil

Franklin L. Oetting

DOW CHEMICAL U.S.A. ✓
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

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James D. Navratil and Franklin L. Oetting

Abstract. The enthalpies of solution of beryllium in chemical milling solutions were measured in an LKB reaction calorimeter. The enthalpy of $-107.3 \pm 1.3 \text{ kcal}\cdot\text{mol}^{-1}$ for a used chemical milling solution containing $\sim 5 \text{ g/l}$ beryllium was measured at 25°C and is compared to an enthalpy of $-119.8 \pm 6.8 \text{ kcal}\cdot\text{mol}^{-1}$ for the dissolution of beryllium in fresh milling solution.

INTRODUCTION

A chemical milling solution is presently used to mill beryllium to predetermined dimensions.¹ During the exothermic chemical milling operation local temperature control of the solution is maintained by cooling coils ($\sim 70^\circ\text{C}$). Since the milling rate is a function of the temperature, temperature control of the milling solution is very important. Subsequently, accurate enthalpy values for beryllium in fresh and used chemical milling solutions are necessary for proper design and operation of the cooling coils. Therefore, the enthalpy values of the dissolution of beryllium in fresh and used chemical milling solutions were measured in an LKB reaction calorimeter.

SUMMARY AND CONCLUSIONS

The enthalpy of solution of beryllium ($0.11 - 0.16 \text{ g/l}$) in a chemical milling solution (an aqueous solution of 750 ml/l H_3PO_4 , 31 ml/l H_2SO_4 , and 71 g/l CrO_3) was measured in an LKB reaction calorimeter. An enthalpy value of $-119.8 \pm 6.8 \text{ kcal}\cdot\text{mol}^{-1}$ was determined at 25.0°C . Concentration dependence of the heat of solution was found insignificant in the 0.11 to 0.16 g/l concentration range. The calculated enthalpy of solution of beryllium at 70°C is also not significantly different from the above value measured at 25.0°C . The enthalpy of $-107.3 \pm 1.3 \text{ kcal}\cdot\text{mol}^{-1}$ for the used chemical milling solution containing $\sim 5 \text{ g/l}$ beryllium was measured at 25°C and is compared to an enthalpy of $-119.8 \pm 6.8 \text{ kcal}\cdot\text{mol}^{-1}$ for the dissolution of beryllium in fresh milling solution.

EXPERIMENTAL

Reagents

Two batches of 0.01 -inch-diameter beryllium wire (0.80 mg beryllium per centimeter of beryllium wire) were used with

the fresh chemical milling solution, and a third batch of beryllium wire was used for measurements with the used solution. The first and third batches of beryllium were obtained from Alfa Products, Division of Ventron Corporation; and the second batch was obtained from K&K Laboratories, Inc. The respective analyses are shown in Table 1.

Table 1. Summary of Beryllium Analytical Data.

	Beryllium No. 1 (ppm)	Beryllium No. 2 (ppm)	Beryllium No. 3 (ppm)
Al	900	850	820
C	285	220	120
Cl	250	112	112
Cr	30	50	70
Cu	50	50	50
Fe	800	1300	725
Mg	170	210	30
Mn	190	110	90
N	22	55	25
Ni	130	70	180
O	828	665	170
Si	750	900	550
Ti	160	200	190
All Others	<310	<300	<140
Difference (Mass %)	99.436	99.430	99.650
Chemical Assay (Mass %)	99.40	99.18	99.65

The beryllium assay was determined in duplicate by ammonium fluoride titration after hydrochloric acid dissolution. The percent beryllium does not include beryllium as refractory BeO . The impurities were determined in duplicate by spark source mass spectroscopy and emission spectroscopy. The average major impurities are shown in Table 1. The percent beryllium taken by difference of the total impurities, where C, N, and O were assumed to be chemically combined with beryllium, is in excellent agreement with the chemical assay results except for the second batch. The percent beryllium obtained by difference was the more accurate and was used to correct the beryllium weights for impurities. Heat contributions from the reactive metallic impurities ($\sim 15 \text{ cal}\cdot\text{mol}^{-1}$) were neglected since they would not significantly change the beryllium enthalpy results.

The fresh chemical milling solution (designated A) had the following composition: $750 \pm 1 \text{ ml/l}$, Precision Chemical

Corporation, reagent ACS, ortho phosphoric acid (85-87%); 71 ± 0.5 g/l Baker reagent chromium trioxide (99.7%); 31 ± 0.5 ml/l Baker "Ultrex" sulfuric acid (99.3%); and the balance (to 1.0 ± 0.002) distilled water. The used chemical milling solution (designated B) was composed of ~ 4 g/l Be; 750 ± 15 ml/l H_3PO_4 (85-87%); 71 ± 2 g/l CrO_3 (99% technical flake); 30 ml/l H_2SO_4 (95-98%); and 200 ± 5 ml/l de-ionized water. A solution (designated C) identical to B, except containing no beryllium, was also used.

Calorimeter

A modified LKB reaction calorimeter of the isoperibol type was used for the measurements. Details of the description and operation of the calorimeter may be found elsewhere.² The precision and accuracy of the calorimeter was determined by one standard fast reaction and a known slow reaction. The enthalpy of the calorimetric standard reaction, the neutralization of TRIS [tris-(hydroxymethyl)amino-methane] SRM 724 in excess 0.1*N* hydrochloric acid, was determined under conditions recommended by the National Bureau of Standards.³ Our value of -7109 ± 4 cal·mol⁻¹ is in excellent agreement with values reported by Fitzgibbon and Holley (7111 ± 5 cal·mol⁻¹),⁴ Gunn (7107 ± 1 cal·mol⁻¹),⁵ and Sunner, et al. (7110 ± 1 cal·mol⁻¹).⁶

A slower known reaction ($\Delta t \approx 24$ minutes) was also measured because it had a comparable reaction time to the beryllium-chemical milling solution reaction time. The enthalpy of dissolution of beryllium (0.12 g/l) in 1.0-1.2*M* sulfuric acid was determined at 25.0°C as -91.814 ± 0.085 kcal·mol⁻¹. This value is in fair agreement with the reported value of -92.83 ± 0.11 kcal·mol⁻¹,⁷ however, the calculated heats of formation for beryllium sulfate and its hydrates resulting from our enthalpy of dissolution results were found to be in better agreement with other studies.² This indicated that the calorimeter was performing properly under these conditions.

Procedure

A typical run consisted of breaking a one milliliter glass ampoule containing the beryllium wire into 99.8 ± 0.1 ml of chemical milling solution at $25.000 \pm 0.001^\circ\text{C}$. Calibration runs followed the experimental runs and consisted of supplying to the heater a known amount of power to match the temperature rise of the reaction. The corrected temperature rise was determined via a computer program by the Regnault-Pfaundler calculation method.²

RESULTS AND DISCUSSION

All results are expressed in defined calories (1 calorie = 4.184 abs joules). All sample weights were corrected to true mass (using 1.848 for the density of beryllium), and the formula weight of 9.01218 for beryllium was used. Uncertainties stated are twice the standard deviation of the mean, $2 \{ \sum d^2 / n(n-1) \}^{1/2}$.

Table 2 contains the experimental enthalpy data using the three batches of beryllium. Experiments number one and six were not included because of instrument problems during the calibration run.

Table 2. Enthalpy of Solution Data for Beryllium in 99.8 ml of Chemical Milling Solutions.

Experiment No. and Solution Designation ^a	Mass of Beryllium ^b (mg)	ϵ^c (cal·K ⁻¹)	ΔT^d (K ⁻¹)	Δt^e (min.)	$-\Delta H$ (298.15°K) (kcal·mol ⁻¹)
2A	11.077	79.115	1.7926	63.1	115.4
3A	11.196	79.516	1.9046	69.0	122.3
4A	11.226	79.427	1.6848	74.3	107.4
14A	11.759	79.265	1.8655	56.7	113.3
15A	11.700	79.466	1.8027	60.2	110.3
5A	15.936	78.859	2.4478	65.0	109.2
7A	15.697	79.586	2.4498	68.1	111.9
8A	15.727	79.819	2.4265	62.8	111.0
9A	15.817	79.977	2.8456	55.7	129.7
10A	16.333	79.185	2.6378	59.7	115.1
11A	16.323	79.060	2.6476	60.1	115.6
12A	16.512	79.064	2.5503	61.0	110.0
13A	15.627	79.402	3.2997	44.4	151.1
20C	11.893	83.348	2.2906	50.6	144.7
21C	11.913	82.559	2.1977	55.7	137.2
22C	11.883	83.641	1.7864	63.9	113.3
16B	12.033	82.871	1.7469	69.8	108.4
17B	11.973	84.231	1.6977	72.4	107.6
18B	11.784	84.118	1.6738	70.0	107.7
19B	11.764	84.182	1.6350	76.0	105.4

^a Fresh (A, C) and used (B) solutions.

^b Corrected to true mass and for impurities. Experiments 2 through 9, 14, and 15 used Beryllium Batch No. 1; Experiments 10 through 13 used Beryllium Batch No. 2; and Experiments 16 through 19 used Beryllium Batch No. 3.

^c ϵ is the electrical energy equivalent.

^d ΔT is the corrected reaction temperature change.

^e Δt is the corrected reaction time.

The enthalpy values were not corrected for the heat absorbed (0.4 kcal·mol⁻¹) when the water was vaporized by the escaping hydrogen because the noncorrected value is more representative of the heat generated during the chemical milling operation. The heat of ampoule breaking, heat

of vaporization, etc., ($\sim 1 \text{ cal}\cdot\text{mol}^{-1}$) were found insignificant for the magnitude of the enthalpy values reported here.²

The average enthalpy value ($-119.8 \pm 6.8 \text{ kcal}\cdot\text{mol}^{-1}$) for fresh chemical milling solutions is independent of the batch of beryllium (No. 1, 2, 3), the batch of chemical milling solution (A, C), and the weight of the beryllium (0.11 to 0.16 g/l) used. However, erratic results were obtained with the fresh chemical milling solutions and account for the comparatively high error limit. Since relatively normal, electrical-energy equivalents and heat-leakage constants were observed, the erratic results could not be attributed to significant experimental measurement errors but are attributed to unknown side reactions.

Because the actual chemical milling operation is performed at 70°C , the $\Delta H(280.15^\circ\text{K})$ of $-120.0 \pm 6.8 \text{ kcal}\cdot\text{mol}^{-1}$ for the fresh solution was estimated using a ΔC_p of $3.93 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{mol}^{-1}$.⁸

The average enthalpy of solution ($-107.3 \pm 1.3 \text{ kcal}\cdot\text{mol}^{-1}$) for the used solution is apparently different than the heat of solution for the fresh solutions. However, since the batch of beryllium wire was different as well as the grade of materials comprising the used chemical milling solution, several runs (20-22) were made duplicating these conditions. Since these latter results are characteristic of data from runs 1-12, it was concluded that the heats of solution between the fresh and used chemical solutions are significantly different.

The difference between the fresh and used chemical milling solution is also evident in the reaction times. The reaction times per gram of beryllium ($\Delta t/\text{g}$), comparing the runs using 12 mg of beryllium, were significantly different for the fresh chemical milling solution ($5.34 \pm 0.56 \text{ min./g}$)

opposed to the used chemical milling solution ($6.06 \pm 0.28 \text{ min./g}$).

Different reaction(s) occurring in the fresh chemical milling solution opposed to the used solution could account for the different enthalpies obtained. A similar explanation is also attributed to the erratic enthalpy results obtained with the fresh solution. The chemistry of these systems is very complex. Results of the chemical analyses of Cr^{3+} , Cr^{6+} , and H^+ did not differ significantly between the fresh and used solutions. Therefore, no further attempts were made to elucidate the reactions involved. However, the enthalpies obtained are a valuable aid in the design of cooling coils.

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