

**Bis(pyrrolealdethylimino)palladium(II) (IIIc, M = Pd).**—The procedure was the same as that used for the methyl compound above except that pyrrolealdethylimine was used. Recrystallization from chloroform gave 0.40 g (46%) of yellow needles, dec pt 241°.

**Bis(pyrrolealdisopropylimino)palladium(II) (III d, M = Pd).**—The pyrrolealdehyde (0.49 g, 5 mmoles) was dissolved in 10 ml of neat isopropylamine with stirring until a clear yellow solution was obtained. A solution of 0.45 g (2.5 mmoles) of palladium(II) chloride in 80 ml of water was added and stirring was continued for an additional 6 hr. After collection of the yellow-green precipitate, drying at 80°, and recrystallization from chloroform, 0.80 g (82% yield) of yellow needles was obtained, dec pt 215°.

**Bis(pyrroleald-*t*-butylimino)palladium(II) (IIIe, M = Pd).**—The same procedure was used as for the isopropyl compound above except that the isopropylamine was replaced by *t*-butylamine. The resulting fine yellow crystals were obtained in 65% yield, mp 170°. Unlike the other palladium(II) complexes in this series, this product was highly soluble in chloroform and could never be obtained in a state of purity sufficient for satisfactory elemental analysis. Its nmr spectrum showed two different kinds of methyl groups present.

**Bis(pyrrolealdphenylimino)palladium(II) (III f, M = Pd).**—The procedure was the same as used for the methyl and ethyl compounds in this series. The product exhibited very limited solubility in common organic solvents and was recrystallized from hot chloroform only with great difficulty to yield 0.20 g (20%) of yellow-green needles, dec pt 280°.

**Interaction of Platinum(II) with Pyrrolealdimines.**—A 0.24-g (2.4-mmole) portion of pyrrolealdmethylimine was dissolved in 20 ml of *n*-propyl alcohol and 15 ml of a solution containing 0.50 g (1.2 mmoles) of K<sub>2</sub>PtCl<sub>4</sub> (prepared according to the method of Keller<sup>9</sup>) added dropwise with stirring. After 3 hr of stirring at room temperature, the light blue crystals were collected, washed with water and ethanol, dried at 80°, and washed again with boiling chloroform. This produced 0.27 g of solid which was insoluble in common organic solvents but very slightly soluble in hot water, dec pt 205°.

*Anal.* Calcd for C<sub>6</sub>H<sub>14</sub>N<sub>4</sub>Pt: C, 35.20; H, 3.44; N, 13.70. Calcd for C<sub>4</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>4</sub>Pt<sub>2</sub>: C, 7.00; H, 2.90; N, 7.80. Found: C, 7.29; H, 3.03; N, 8.53. With pyrrolealdethylimine 0.28 g of light pink crystals was obtained, dec pt 190°.

*Anal.* Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>Pt: C, 38.04; H, 4.14; N, 12.81. Calcd for C<sub>8</sub>H<sub>28</sub>N<sub>4</sub>Cl<sub>4</sub>Pt<sub>2</sub>: C, 13.58; H, 3.92; N, 7.82. Found: C, 13.48; H, 3.93; N, 7.87.

**Interaction of Platinum(II) with Amines in the Presence of Pyrrolealdehyde.**—A 0.23-g (2.4-mmole) portion of pyrrolealdehyde was dissolved in 10 ml of isopropylamine and stirred constantly at 50° until the solution turned yellow. An aqueous solution containing 0.50 g (1.2 mmoles) of K<sub>2</sub>PtCl<sub>4</sub> in 15 ml was added with stirring, and stirring was continued for 3 hr. After collection, washing with water and ethanol, drying at 80°, and washing again with boiling chloroform, 0.35 g of light gray crystals was obtained, dec pt 225°.

*Anal.* Calcd for C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>Pt: C, 41.27; H, 4.77; N, 12.04. Calcd for C<sub>12</sub>H<sub>38</sub>N<sub>4</sub>Pt<sub>2</sub>Cl<sub>4</sub>: C, 19.14; H, 4.84; N, 7.28. Found: C, 18.75; H, 4.84; N, 7.28.

Use of *t*-butylamine produced 0.30 g of light green crystals, dec pt 260°.

*Anal.* Calcd for C<sub>18</sub>H<sub>26</sub>N<sub>4</sub>Pt: C, 43.78; H, 5.32; N, 11.34. Calcd for C<sub>16</sub>H<sub>44</sub>N<sub>4</sub>Cl<sub>4</sub>Pt<sub>2</sub>: C, 23.50; H, 5.39; N, 6.78. Found: C, 23.31; H, 5.32; N, 6.79.

Use of methylamine or ethylamine produced compounds which were identical in solubilities, decomposition points, and infrared spectra with those obtained previously from the pyrrolealdimines. The infrared spectra of all of the platinum(II) complexes exhibited one or more absorption bands in the 3100–3350-cm<sup>-1</sup> region. All were insoluble in common organic solvents but slightly soluble in hot water.

**Acknowledgment.**—The authors are grateful to Mr. G. J. Boudreaux of the Southern Regional Research Laboratory, Agricultural Research Service, U. S. Department of Agriculture, for the nmr spectra and to the American Cancer Society for partial support of this work.

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## Tentative Phase Diagram of Beryllia-Lithia System

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Received October 14, 1966

In connection with some work done on materials for storing solar thermal energy, BeO was considered because it has the highest heat of fusion and thermal conductivity of the low-atomic-weight oxides. Other low-atomic-weight oxides of interest are Al<sub>2</sub>O<sub>3</sub>, CaO, Li<sub>2</sub>O, and MgO. A search of the literature yielded information on the binary systems BeO–Al<sub>2</sub>O<sub>3</sub>, BeO–CaO, and BeO–MgO. Nothing was found on the BeO–Li<sub>2</sub>O system nor on ternaries or quaternaries containing these two oxides; therefore, an examination of the high BeO side of the binary system was undertaken.

Melting point, total heat content, chemical analysis, and X-ray diffraction data were believed to be sufficient for an initial evaluation of this system. This note is, therefore, confined to these results and the tentative phase diagram derived from them.

### Experimental Section

**Specimen Preparation and Testing.**—The raw materials used in this work were Brush Beryllium Co. UOX-grade BeO (800 to 1500 ppm total impurities) and analytical reagent grade Li<sub>2</sub>CO<sub>3</sub> (Mallinckrodt Chemical Co.). Various proportions of these materials were mixed for 15 min in a Mix-R-Mill (Spex Industries) and then heated in argon in a tungsten resistance furnace in a platinum or rhenium crucible to the fusion point shown. A rhenium crucible was used for compositions fusing at temperatures above the melting point of platinum. All samples were furnace-cooled in approximately 2.5 hr. Melting temperatures were measured optically. Although the true heat of fusion was not measured, the amount of heat required to achieve complete melting from ambient was determined by the drop calorimeter technique.

**Chemical Analysis.**—Reaction products were leached in a hot 1:4 HNO<sub>3</sub> solution to dissolve any unreacted Li<sub>2</sub>CO<sub>3</sub> and rhenium metal contamination resulting from reaction with the crucible. The compositions shown in Figure 1 were determined by wet chemical analysis of the leached residues. After dissolution in H<sub>2</sub>SO<sub>4</sub>–HNO<sub>3</sub>, beryllium was precipitated with NH<sub>4</sub>OH as Be(OH)<sub>2</sub>. The hydroxide was filtered off and converted to BeO by ignition at 1000°. Lithium was recovered from the filtrate by addition of H<sub>2</sub>SO<sub>4</sub> and evaporation to dryness. The Li<sub>2</sub>O content was obtained by igniting the sulfate at about 500° and weighing as Li<sub>2</sub>SO<sub>4</sub>.

**X-Ray Methods.**—Powder diffraction photographs of the

(9) R. N. Keller, *Inorg. Syn.*, **2**, 247 (1946).

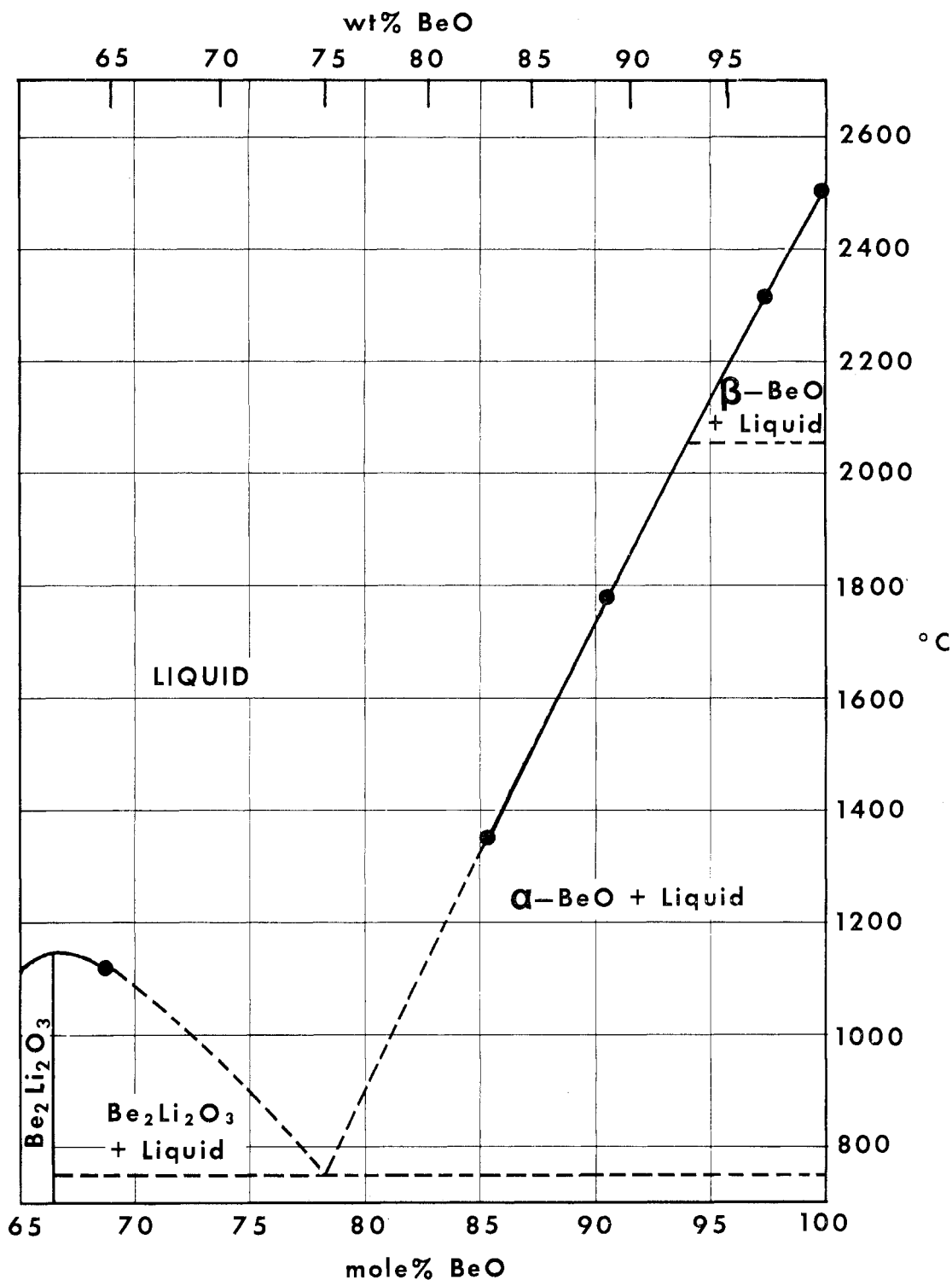


Figure 1.—Tentative phase diagram for BeO-Li<sub>2</sub>O.

leached samples were taken with a 114.59-mm Debye-Scherrer camera. Finely pulverized powder in 0.2-mm glass capillary tubes was exposed to Mn-filtered Fe K $\alpha$  radiation for periods of up to 18 hr. Relative line intensities were estimated visually. Diffractometer patterns were made with Ni-filtered Cu K $\alpha$  radiation using a scanning rate of  $\frac{1}{2}$  or  $1^\circ$ /min at a chart speed of 30 in./hr. For quantitative X-ray analysis, total counts were accumulated over the  $2\theta$  range from  $32$  to  $54^\circ$ . Integrated intensities of the strong (100), (002), and (101) lines of BeO were measured. After applying corrections for background, the ratio

of BeO counts to total counts was calculated. This method was used in conjunction with chemical analysis for determining the composition of the Be-Li-O compound.

To determine the symmetry and lattice constants of this compound, single-crystal photographs were taken with a Weissenberg camera using Ni-filtered Cu K $\alpha$  radiation and a precession camera using Zr-filtered Mo K $\alpha$  radiation. Specimens used were small transparent platelike crystals. The calculated density was checked by pycnometric measurements using toluene as the displacement liquid.

## Results and Discussion

For BeO-Li<sub>2</sub>O compositions containing 85 and 90 mole % BeO, the melting points were approximately 1350 and 1780°, respectively; the heat necessary to achieve complete melting from ambient to 1350° and ambient to 1780° was about 350 cal/g for the former and 600 cal/g for the latter. The heat content for the 97.5 mole % BeO-Li<sub>2</sub>O composition was not measured because melting occurred above the BeO transition temperature and out of the temperature range of interest. When X-ray data of the fused materials revealed the presence of a new phase, the range of compositions studied was extended down to about 65 mole % BeO in order to characterize this compound.

The tentative phase diagram for the beryllia-lithia system from 65 to 100 mole % BeO is presented in Figure 1. The liquidus line is based on the observed melting temperatures for several mixtures which were chemically analyzed after melting. The solid-state transformation line shown at 2050° is based on the value reported by Smith, *et al.*<sup>1</sup> The eutectic point at 78.5 mole % BeO on the diagram (Figure 1) was extrapolated from the experimental data as shown by the dotted line. A compound exists at the composition 2BeO-1Li<sub>2</sub>O, melting congruently at 1150 ± 40°.

method of analysis was attempted in which the ratio of BeO counts to total counts is plotted against the BeO content as determined chemically. This method was inconclusive, however, because the thin flakes of the compound produced orientation effects which strongly affected the X-ray intensity measurements. Fortunately, one of the samples was found to contain mostly the unidentified compound with only a trace of free BeO being detected in the X-ray diffraction pattern. Chemical analysis gave 64.78 wt % BeO; the calculated value for Be<sub>2</sub>Li<sub>2</sub>O<sub>3</sub> is 62.5 wt % BeO.

Rotation, Weissenberg, and precession photographs showed that Be<sub>2</sub>Li<sub>2</sub>O<sub>3</sub> is monoclinic with an A-centered lattice and parameters of  $a_0 = 14.89 \pm 0.01$  A,  $b_0 = 5.020 \pm 0.005$  A,  $c_0 = 8.547 \pm 0.007$  A, and  $\beta = 101.6 \pm 0.2^\circ$ ; however, it has a pseudo-rhombohedral lattice with hexagonal cell parameters of  $a_0 \approx b_0 = 4.98 \pm 0.05$  A and  $c_0 = 43.72 \pm 0.05$  A. The hexagonal  $c$  axis and monoclinic  $a$  axis are coincident. The indexed X-ray powder pattern shown in Table I gives a comparison of observed interplanar spacings with values calculated from the monoclinic parameters given above.

The measured pycnometric density was 2.52 g/cc, in excellent agreement with the calculated X-ray value

TABLE I  
X-RAY POWDER DIFFRACTION DATA FOR Be<sub>2</sub>Li<sub>2</sub>O<sub>3</sub>

$I/I_0$	$hkl$	$d_{\text{obsd.}}$ , A	$d_{\text{calcd.}}$ , A	$I/I_0$	$hkl$	$d_{\text{obsd.}}$ , A	$d_{\text{calcd.}}$ , A
45	200	7.3	7.29	5	004, 122	2.098	2.093, 2.099
5	011	4.31	4.31	5	420	2.070	2.068
10	111	4.02	4.02	5	611, 313	2.037	2.029, 2.041
10	211	3.90	3.89	2	222	2.002	2.009
20	400	3.64	3.65	2	520, 613	1.902	1.903, 1.897
2	211	3.55	3.55	20	800	1.820	1.824
2	202	3.35	3.35	2	604, 422	1.774	1.772, 1.775
10	402, 311	3.08	3.07, 3.07	15	620, 811, 713	1.746	1.746, 1.745, 1.743
5	411	2.940	2.937	15	513	1.722	1.728
5	411	2.646	2.651	2	231	1.614	1.614
10	020	2.515	2.510	5	720, 324, 315	1.602	1.604, 1.602, 1.603
15	120, 113	2.481	2.474, 2.478	5	231, 722	1.587	1.588, 1.581
100	600	2.429	2.432	2	802	1.560	1.561
5	220	2.377	2.373	5	10,0,2; 911, 431	1.474	1.473, 1.468, 1.475
5	113	2.340	2.340	2	10,0,0; 324, 531	1.459	1.459, 1.461, 1.455
15	320	2.231	2.230	25	133, 233, 624	1.443	1.443, 1.437, 1.443
2	611, 413	2.219	2.218, 2.216	10	722, 206	1.425	1.426, 1.424
15	213	2.192	2.200	10	10,1,3; 920	1.361	1.362, 1.362
2	122	2.170	2.162	10	813, 533	1.348	1.351, 1.344

Heating this compound in air at this temperature results in the loss of Li<sub>2</sub>O so that this is not strictly an equilibrium diagram under atmospheric conditions. Any further investigation should be carried out in sealed pressure capsules to minimize Li<sub>2</sub>O volatilization.

The Be-Li mixed oxide was usually found with varying amounts of unreacted BeO. In order to determine the composition of this compound, a quantitative X-ray

of 2.54 g/cc for twelve formula units of Be<sub>2</sub>Li<sub>2</sub>O<sub>3</sub> in the monoclinic cell (the pseudo-rhombohedral cell contains six units). Single crystal photographs of three different crystals of Be<sub>2</sub>Li<sub>2</sub>O<sub>3</sub> showed twinning about the monoclinic  $a$  axis. There was also evidence that grinding of this material produced twinning as well as disorder in the crystal structure.

**Acknowledgment.**—The authors wish to thank Mr. R. A. Hein for the calorimetric data and Mr. E. A. Schaefer for the chemical analyses.

(1) D. K. Smith, C. F. Cline, and S. B. Austerman, *Acta Cryst.*, **18**, 393 (1965).