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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

*Technical Report 32-1073*

*The Utilization of Powered Metals as Fuels in  
the Atmospheres of Venus, Earth, and Mars*

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Approved by:

A handwritten signature in black ink, appearing to read "D. F. Dipprey", is written over a horizontal line.

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## **Abstract**

The ignition temperatures of a number of powdered metals have been measured in air, in a simulated Venus atmosphere, and in a simulated Mars atmosphere. Each atmosphere was thought to consist of mixtures of argon, carbon dioxide, and nitrogen. This study was conducted to show that the atmospheres of the planets Mars and Venus might be utilized as sources of oxidizers for chemical energy. The heat liberated from the combustion of lithium, beryllium, and boron in the simulated Venus and Mars atmospheres was calculated from the compositions of the products formed from the combustion of these metals in the simulated Venus and Mars atmospheres. The product compositions were determined by chemical analysis.

# The Utilization of Powdered Metals as Fuels in the Atmospheres of Venus, Earth, and Mars

## I. Results

As part of a program to demonstrate the feasibility of using the atmospheres of the planets as oxidizer sources for chemical energy, the ignition temperatures of various powdered metals<sup>1</sup> in simulated atmospheres of Mars and Venus were measured. The ignition temperatures of these metals heated in air were also measured, in order to determine the relative ease or difficulty of igniting these metals in air, compared to that of the Mars and Venus atmospheres. This effort is an extension of previous work (Ref. 1) wherein the ignition temperatures of these same powdered metals were measured in nitrogen and in carbon dioxide.

The Venus atmosphere was assumed to consist of 5% Ar, 10% N<sub>2</sub>, and 85% CO<sub>2</sub>, and the Mars atmosphere was assumed to consist of 2% Ar, 10% N<sub>2</sub>, and 88% CO<sub>2</sub>. The gas mixtures used here as the simulated planetary atmospheres were supplied by the Matheson Co., Inc., Antioch, California. The actual compositions of these gas mixtures, in volume percent, as determined by

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<sup>1</sup>The metals used, their particle sizes, and the suppliers are listed in Table 1.

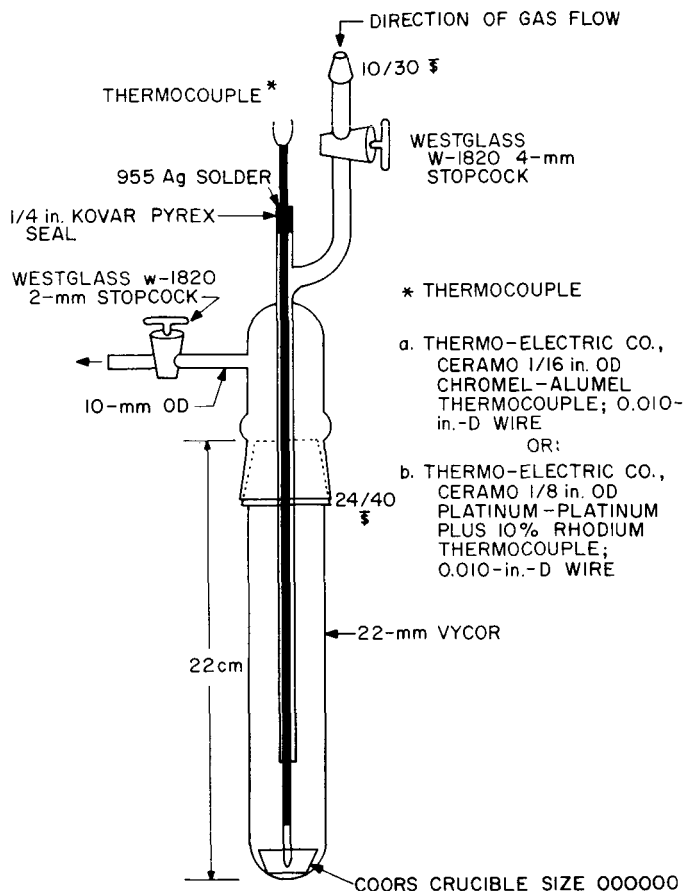
the manufacturer were: Venus atmosphere, 4.10% argon, 9.17% nitrogen, and 86.73% carbon dioxide; Mars atmosphere, 2.16% argon, 11.21% carbon dioxide, and 86.63% nitrogen.

The experimental procedure for measuring the ignition temperatures involved: burying a thermocouple in the powdered metal while immersed in the particular atmosphere, heating the metal, and recording the thermocouple output vs time. The ignition temperature was easily seen as the point where the temperature increased very suddenly with time.

The ignition temperature in air was found by placing a chromel-alumel thermocouple, made of 0.010-in.-diameter wire, into the powdered metal, which filled a size 000000 Coors crucible. This crucible was set into a larger, size 00, Coors crucible; the outside of the size 00 crucible was then heated by a torch. In order to heat the metals in the Venusian and Martian atmospheres, the experiments were conducted in apparatus as shown in Fig. 1. The gas mixture simulating the Mars and Venus atmospheres was passed through the apparatus at a flow rate of 100 ml/min. At the same time, the apparatus was torch-heated very carefully near the bottom so as to

**Table 1. Commercial suppliers of the powdered metals used in this Report**

Metal	Description	Supplier
Lithium	<100 $\mu$ particle size	Foote Mineral Co. New Johnsonville, Tennessee
Beryllium	<0.1 $\mu$ particle size	National Research Co. Cambridge, Massachusetts
Magnesium	-325 mesh, rated 99.9% pure	Reade Manufacturing Co., Inc. Los Angeles, California
Calcium	-325 mesh, rated 99.9% pure	Research Chemical Div. Nuclear Corp. of America Phoenix, Arizona
Boron	<0.1 $\mu$ particle size	Callery Chemical Co. Callery, Pennsylvania
Aluminum	0.02 $\mu$ particle size	National Research Corp. Cambridge, Massachusetts
Cerium	-325 mesh	VARLACOID Chemical Co. New York, New York
Titanium	1-5 $\mu$ particle size	A. D. MacKay Co. New York, New York
Zirconium	3 $\mu$ average particle size, 120-A Grade, 94-95% pure	Charles Hardy, Inc. New York, New York
Thorium	100% 200 mesh, 85% 325 mesh	Rare Earth Div., American Potash and Chemical Corp. Los Angeles, California
Uranium	Depleted uranium, 200 mesh, coated with 2% viton	Great Southern Mfg. and Sales Co. Los Angeles, California

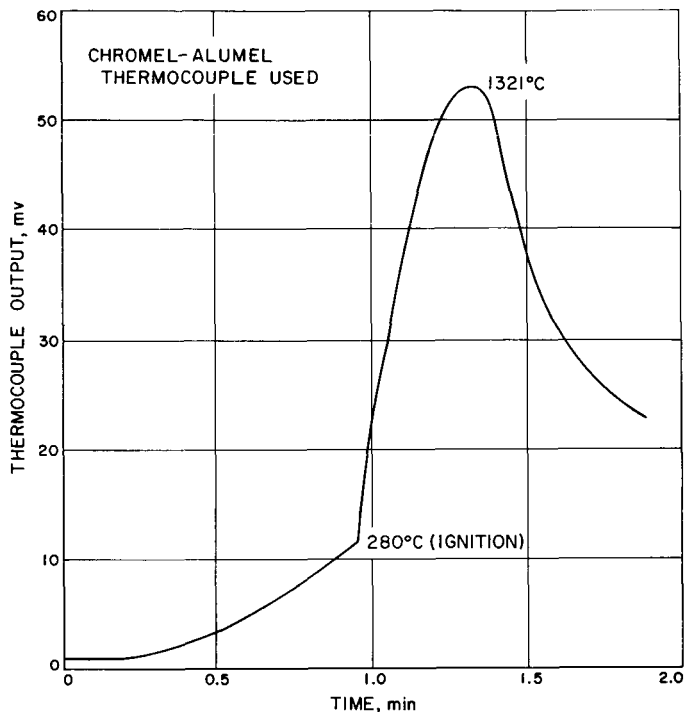


**Fig. 1. Ignition apparatus**

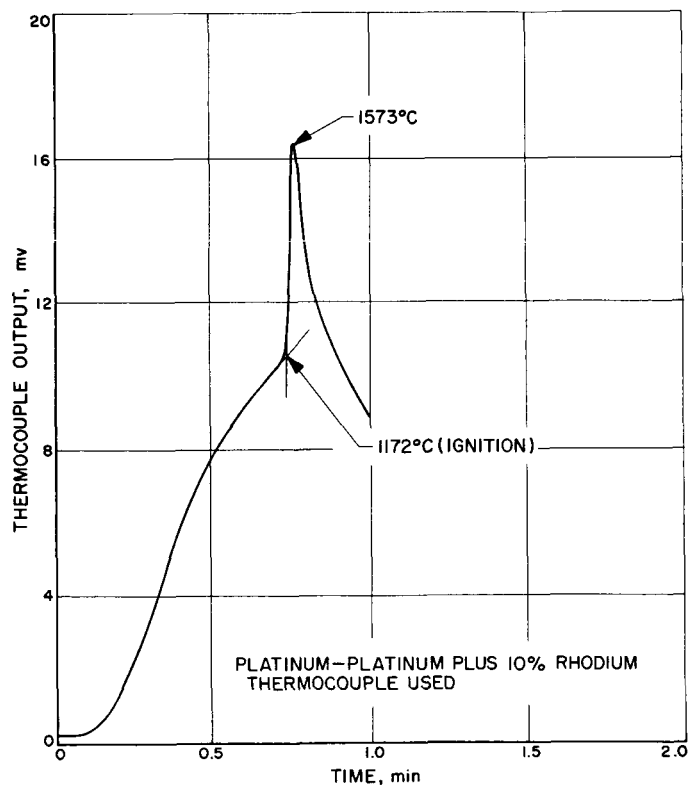
assure even heating of the powdered metal. Heating was continued until the metal ignited. Each experiment was repeated several times. Figures 2 and 3 are typical examples of thermocouple output vs time, with the temperature of ignition indicated. Figure 2 represents the temperature-time relationship obtained when powdered beryllium was heated in a simulated Venus atmosphere; Fig. 3 portrays similar information for powdered boron heated in a simulated Mars atmosphere. The results obtained are summarized in Table 2.

The heat of combustion of Li, Be, and B in Venus and Mars atmosphere was calculated from the composition of the combustion products. In order to get the necessary chemical composition information, a chemical analysis<sup>2</sup>

<sup>2</sup>For the experiment where lithium was burned in the simulated Venus atmosphere, the analysis was performed by Mr. S. P. Vango of the Jet Propulsion Laboratory. The analysis of the combustion products of lithium in the Mars atmosphere, and of the combustion products of beryllium and boron in the Mars and Venus atmospheres were done by Dr. R. F. Muraca of the Stanford Research Institute.



**Fig. 2. Ignition of ultrafine beryllium heated in a simulated Venus atmosphere**



**Fig. 3. Ignition of ultrafine boron heated in a simulated Mars atmosphere**

**Table 2. Ignition temperatures of powdered metals in nitrogen, simulated atmospheres of Mars and Venus, carbon dioxide, and air at 14.7 psia**

Metal <sup>a</sup>	Particle Size	Ignition temperatures, °C					Ref.
		N <sub>2</sub>	Mars Atmosphere 86.63% N <sub>2</sub> 11.21% CO <sub>2</sub> 2.16% Ar	Venus Atmosphere 9.17% N <sub>2</sub> 86.73% CO <sub>2</sub> 4.10% Ar	CO <sub>2</sub>	Air	
Li	<100 μ	388, 410	433, 405, 386		330		1
	<100 μ			367, 414, 310		353, 393	b
Be	<0.1 μ	504, 527			Ambient		1
	<0.1 μ		553, 762, 766	Ambient, 280		Ambient	b
Mg	-325 mesh	No ignition to 1071			749		1
	-325 mesh		No ignition	641, 676		582, 544	b
	100%/100 mesh, 86%/270 mesh }	530			630	490	2
Ca	-325 mesh	327, 360	192, 163	243, 269	293	222, 236	1 b
B	<0.1 μ		1172, 1203, 1231	858, 1000		203, 215	b
	<0.1 μ	1059, 1440			871, 922, 1017		1
Al	<0.1 μ	No ignition to 1080			360, 420		1
	<0.1 μ		No ignition to 1180	671, 705		466, 410	b
Ce	-325 mesh		197, 199	93, 147, 212		115, 108	a
	-325 mesh	216, 230			172, 190		1
	Fine wire	850					5
Ti	1-5 μ		830, 916, 1007	603, 708, 787		648, 602	b
	99%/100 mesh, 62%/270 mesh }	830			670, 680	460	1 2
	10.5 μ	760			550	510	6
	Finely divided	800					7
Zr	3 μ		578, 614, 628	139, 152, 156		193, 197, 240	b
	3 μ	490, 525			363, 366		1
	3.3 μ	790			620	190	6
	-325 mesh	530			560	210	6
Th	85%/-325 mesh, 100%/-200 mesh }		574, 587, 617	544, 552, 627, 685		445, 466	b
	-325 mesh	630			730		1
	7.2 μ	500			450	280	6
U	-200 mesh, viton coated	354, 360			235		1
	-200 mesh, viton coated 10.8 μ	410	152, 168	132, 135		133, 157 100	b 6

<sup>a</sup>Refer to Table 1 for a list of suppliers.

<sup>b</sup>This study.

was performed on a sample of the powdered metals and on a sample of the solid products resulting from the combustion of each of these metals in the Venus atmosphere and in the Mars atmosphere. After igniting as described and allowing the combustion process to continue to extinction, the residue was cooled, the tube was evacuated and sealed, and the products subsequently analyzed. The results of these chemical analyses are presented in Table 3 together with the heats of combustion which were calculated by a procedure given in the Appendix.

As indicated in these data, lithium ignited in all three atmospheres. It was further noted that in each experiment, it first melted and then apparently vaporized so that it was, in fact, the lithium vapor that was burning. The combustion of this metal appeared to be the most intense in air and the least intense in the Mars atmosphere.

The beryllium powder burned very vigorously in each of the three atmospheres. At ambient temperatures it ignited upon contact with both air and, on several occasions, in the Venus atmosphere. The magnesium powder ignited with difficulty and burned sluggishly in the Venus atmosphere and in air; it did not ignite in the Mars atmosphere. However, calcium powder ignited easily and burned vigorously in all three atmospheres.

Boron ignited with difficulty in all three atmospheres. In the Mars atmosphere, boron was especially difficult to ignite, and its combustion was sluggish. Aluminum ignited and burned like boron did in the Venus atmosphere and in air. Aluminum did not ignite in the Mars atmosphere.

Cerium ignited easily and burned vigorously in every experiment.

Titanium, zirconium, and thorium ignited easily and burned vigorously in each of the atmospheres. Although uranium ignited easily in each of the atmospheres, it burned sluggishly. The sluggish combustion was attributed to a viton coating on the uranium particles.

## II. Discussion

These measurements of the ignition temperatures of powdered metals in air and in mixtures of nitrogen and carbon dioxide, simulating the atmospheres of Mars and Venus, are compared in Table 2 with the ignition temperatures of these powdered metals in nitrogen and

in carbon dioxide (Ref. 1). These data illustrate the tendency for higher ignition temperatures in nitrogen than in carbon dioxide, and lower ignition temperatures in air (and therefore including oxygen) and in carbon dioxide. It is suggested that there is a relationship between ignition temperature and bond energy; the bond energies (Pauling, Ref. 9) were given as ( $N \equiv N$ ), 226 kcal/mole; ( $C = O$ ), 174 kcal/mole; and ( $O = O$ ), 96 kcal/mole. Since gas-surface adsorption as well as other phenomena are important in powdered metals combustion (Ref. 2), the ignition temperatures were not always the highest in nitrogen or lowest in air.

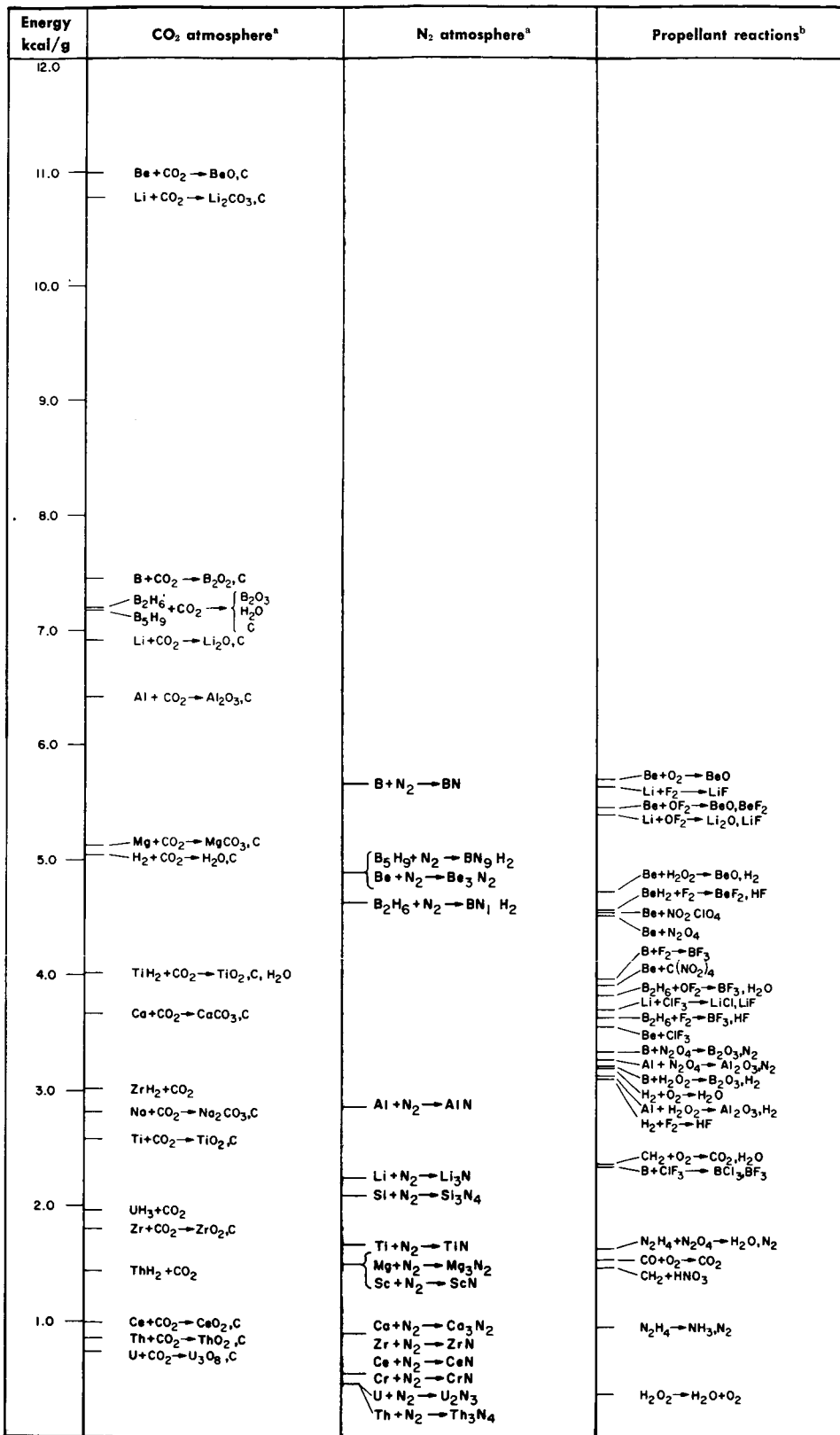
Since a number of the powdered metals did burn in the simulated atmospheres of Mars and Venus, these metals could be considered as possible fuels in these atmospheres. Although the relative merits of the several systems are dependent on a comprehensive analysis for any given application, a figure of merit can be assigned to each fuel if it is assumed proportional to the specific available energy.

The results of some preliminary calculations of the heat of combustion per unit mass for a number of metals which were burned in nitrogen and also in carbon dioxide are shown in Fig. 4 taken from Ref. 1. The results also include a similar number for several conventional fuel-oxidizer combinations. This latter tabulation assumed a stoichiometric mixture. Although this comparison assumes the atmosphere collection and handling to be "free," some tentative conclusions can be drawn. For example, if boron or beryllium were burned in a nitrogen atmosphere, more heat is produced per unit mass than is produced by most space-storable fuel-oxidizer combinations. Likewise, in a carbon dioxide atmosphere, several fuels appear to be promising; the heats of combustion listed in Fig. 4 are based on assumed reaction products. Therefore, the actual heat of combustion may be appreciably different from that shown in Fig. 4, if the combustion products are likewise appreciably different from those assumed in Fig. 4.

From the information in Fig. 4, the most promising fuels for the Venus and Mars atmospheres appear to be beryllium, lithium, and boron in that order. As already mentioned, these metals were burned in the simulated Venus and Mars atmospheres, and the heats of combustion are listed in Table 3.

In summary, it can be seen that beryllium ignited very readily in the simulated Venus atmosphere, burned vigorously, and produced a calculated 7.551 kcal/gram of





<sup>a</sup>The energy evolved is per gram of metal only.

<sup>b</sup>The energy evolved is per gram of total reactant.

Fig. 4. Combustion energies for various reactions

combustion heat. Lithium burned satisfactorily and produced 6.147 kcal/gram, but boron ignited with some difficulty, although its combustion was reasonably vigorous. The heat of combustion of boron in the Venus atmosphere was low (i.e., 2.563 kcal/gram). However, because of the formation of appreciable  $B_4C$ , boron does not appear very promising as a fuel in the simulated Venus atmosphere.

Further, beryllium burned much more vigorously than did lithium in the simulated Mars atmosphere and produced more heat per gram (4.659 and 5.257 kcal/gram for beryllium compared to 3.617 kcal/gram for lithium) and so appears to be a preferred fuel. Boron burned only with difficulty and produced a calculated 2.951 kcal/gram of combustion heat, so boron is not regarded as a promising fuel for the simulated Mars atmosphere.

As shown in Table 3, the following was learned from the chemical analyses of the combustion products:

1. Both  $N_2$  and  $CO_2$  entered into the combustion process, although for Li and Be, the amount of nitride formed was greater when combustion occurred in the Mars atmosphere than for combustion in the Venus atmosphere. This seems reasonable, since the Mars atmosphere contained predominantly  $N_2$ , whereas the Venus atmosphere contained only 9.17%  $N_2$ .
2. In all cases, the metal carbide was formed, along with free carbon. In fact,  $B_4C$  was a major product constituent in the experiments using boron as the fuel; as  $\Delta H_f^{298}(B_4C)$  is relatively small, the formation of appreciable  $B_4C$  produced a rather low heat of combustion of B in  $CO_2$ .
3. The carbonate was formed in the combustion of Li and Be in  $CO_2$ , but only in small amounts.
4. The combustion was more complete, that is, there was more free metal in the combustion products

and in the Venus atmosphere than there was in the Mars atmosphere.

### III. Conclusion

A number of powdered metals have burned in the simulated atmospheres of Venus and Mars. Generally, the powdered metals burned more readily in the simulated Venus atmosphere and in air than in the simulated Mars atmosphere.

The heats of combustion of both lithium and beryllium in the Venus atmosphere, as calculated from a chemical analysis of the combustion products, are high enough to make them attractive as possible fuels. Boron, however, does not appear to be a promising fuel in a  $CO_2$  atmosphere because when it burns, it forms considerable  $B_4C$  and therefore has a rather low heat of combustion.

This work should be extended to include further studies of the combustion of Li and Be in simulated Venus and Mars atmospheres by differential thermal analysis and by thermogravimetric analysis, at pressures representing the surface pressures of those planets. Also, prototype burners should be developed, and engineering studies should be made to optimize the combustion characteristics of Li and Be in the simulated Venus and Mars atmospheres.

The results of the chemical analyses are presented in Table 3 as mole-percentages. Since the chemical analyses were performed on solid materials, the quantities of the vapor of the gaseous species  $N_2$ ,  $CO_2$ ,  $CO$ , and  $B_2O_3$  were calculated from the reaction stoichiometry. Values of  $a_i$  and  $b_i$  were calculated from Table 2. The heats of combustion were then calculated.

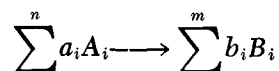
The results of the calculations are given below and in Table 3. The values given refer to the heat of combustion in kcal, per gram of metal consumed in the reaction.

Experiment	Li-V	Li-M	Be-V	Be-M-1	Be-M-2	B-V	B-M
Heat of Combustion $\frac{\text{kcal}}{\text{gram}}$	6.147	3.617	7.551	4.659	5.257	2.563	2.951

## Appendix

### Heat of Combustion Calculations

The heat evolved from the chemical reaction



where  $a_i$ ,  $b_i$  are mole quantities of species  $A_i$  and  $B_i$  can be calculated from the equation

$$H = \sum^n a_i \Delta H_f^{298}(A_i) - \sum^m b_i \Delta H_f^{298}(B_i),$$

where

$\Delta H_f^{298}(A_i)$  and  $\Delta H_f^{298}(B_i)$  are the heats of formation at 298°K of species  $A_i$  and  $B_i$ .

The heats of formation (in kcal/mole) are listed as follows (Ref. A-1):

Compound	CO <sub>2</sub>	Li <sub>2</sub> O	Li <sub>3</sub> N	Li <sub>2</sub> C <sub>2</sub>	BeO	Be <sub>3</sub> N <sub>2</sub>	Be <sub>2</sub> C
$\Delta H_f^{298}$	-94.054	-143.1	-47.5	-13.415	-142.1	-140.6	-21.7
Compound	B <sub>2</sub> O <sub>3</sub>	BN	B <sub>4</sub> C	CO			
$\Delta H_f^{298}$	-305.344	-59.51	-12.62	-26.42			

In addition, for Li<sub>2</sub>CO<sub>3</sub>,  $\Delta H_f^{298} = -290.54$  (Ref. A-2).

To estimate  $\Delta H_f^{298}(\text{BeCO}_3)$  the following assumption was made:

$$\Delta H_f^{298}(\text{BeCO}_3) - \Delta H_f^{298}(\text{BeO}) = \frac{1}{2} \left[ \Delta H_f^{298}(\text{Li}_2\text{CO}_3) - \Delta H_f^{298}(\text{Li}_2\text{O}) + \Delta H_f^{298}(\text{MgCO}_3) - \Delta H_f^{298}(\text{MgO}) \right]$$

From Ref. 3,  $\Delta H_f^{298}(\text{MgCO}_3) = -266$  kcal/mole, and  $\Delta H_f^{298}(\text{MgO}) = -144$  kcal/mole.

This calculation yields  $\Delta H_f^{298}(\text{BeCO}_3) = -291$  kcal/mole. Such a procedure is crude at best, but the amount of BeCO<sub>3</sub> formed is not large, so the error introduced by this calculation would not be large, either.

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