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THERMODYNAMIC PROPERTIES
OF BI-METALLIC POWDERS

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ABSTRACT

The heat of combustion of lithium in an oxygen Parr bomb has been determined. The initial difficulties encountered when the combustion occurred in the presence of carbon and/or glass have been eliminated. The release of energy closely corresponds to the heat of formation of lithium oxide, Li_2O .

The heats of solution of aluminum, lithium and aluminum-lithium alloy have been determined in 2 N HCl. From these data the heat of formation of AlLi has been calculated.

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INTRODUCTION

The objectives of this research program are to determine the heats of formation of selected intermetallic compounds. In addition, the heats of formation of the combustion products of the compounds and the constituent elements of these alloys is sought. The calorimetric techniques employed in this work include (1) solution calorimetry, and (2) combustion calorimetry. The solution method is used to determine the heats of formation of those compounds which (along with their constituent elements) exhibit satisfactory dissolution characteristics. The heats of formation of the products of oxidation are determined by the combustion method.

The materials investigated are purchased commercially when possible. Some materials have been prepared in this laboratory, such as the ultra-fine aluminum powder, lithium powder (both of these are discussed in the previous Quarterly Letter Report, dated July 10, 1962) and aluminum-lithium alloy, AlLi. The latter is described in this report.

CALORIMETRY

A. Combustion

1. Lithium

The apparatus employed in determining the heat of formation of the products of combustion of lithium was described in the previous Quarterly Letter Report.

Initially, the lithium used in the combustion runs was sub-micron in size and was analysed to be only 17% active metal.

In addition to this source of error, the gelatin capsule used as an encapsulant for the lithium served as a source of carbon. The thermo-chemical results of the combustion were found to be 20-30 kcal/mole of product higher than the expected value for the formation of Li_2O . Analysis of the product indicated the reason to be (in part, at least) the result of the formation of lithium carbonate. Minimizing the ratio of carbon to lithium did not solve the problem. Substituting the glass capsule for the carbonaceous capsule resulted again in higher values than expected. Analysis by x-ray diffraction showed the presence of lithium silicate in the product. This interaction between the burning metal (and/or the molten oxide) and the material with which it is in contact invalidated the thermodynamic data derived from the combustion. An attempt was then made to burn lithium slivers in the absence of any capsule. These were cut from a lithium rod purchased from the Lithium Corporation of America. The material was 99.9% pure and was cut in a dry CO_2 atmosphere. The alumina crucible upon which the combustion would occur was treated at elevated temperature (red hot) with lithium hydroxide. The intention was to passivate or minimize any reaction during a run between the lithium or lithium oxide and the alumina crucible. The bomb was loaded under dry CO_2 and subsequently flushed and pressurized to 20 atmospheres with dry oxygen. A preliminary loading showed no visible indication of contamination upon subjecting the freshly cut, unprotected lithium slivers into a dry oxygen atmosphere. The results of the combustion are

shown in Table I. The average value of the liberated energy on a molar basis of product formed is seen to be -141.5 ± 4.2 kcal/mole product. This is in close agreement with the value of the heat of formation of Li_2O as listed by the NBS Selected Values, namely -142.5 ± 1.5 kcal/mole. According to Skinner¹ the heat of combustion of lithium has not been measured previously. The NBS value above was obtained by calculation from entropy, heat of solution and vapor pressure data².

B. Solution

1. Method

A detailed description of the solution calorimeter employing a thermistor probe as the temperature sensing element was presented in the previous Quarterly Letter Report.

In addition to this relatively complex calorimeter, a simplified system employing a Beckmann thermometer as the temperature sensing device was assembled (see Figure I). Primarily, this system was set up as a means of rapidly evaluating any modifications to the thermistor calorimeter which were contemplated or which may develop as the program progressed. Secondly, it was intended to serve in preliminary solution studies of the intermetallic compounds of interest, the solvents and conditions of reaction which had yet to be determined.

2. Materials

The source and purity of the materials employed in this study are as listed below.

TABLE I
HEAT OF COMBUSTION OF LITHIUM

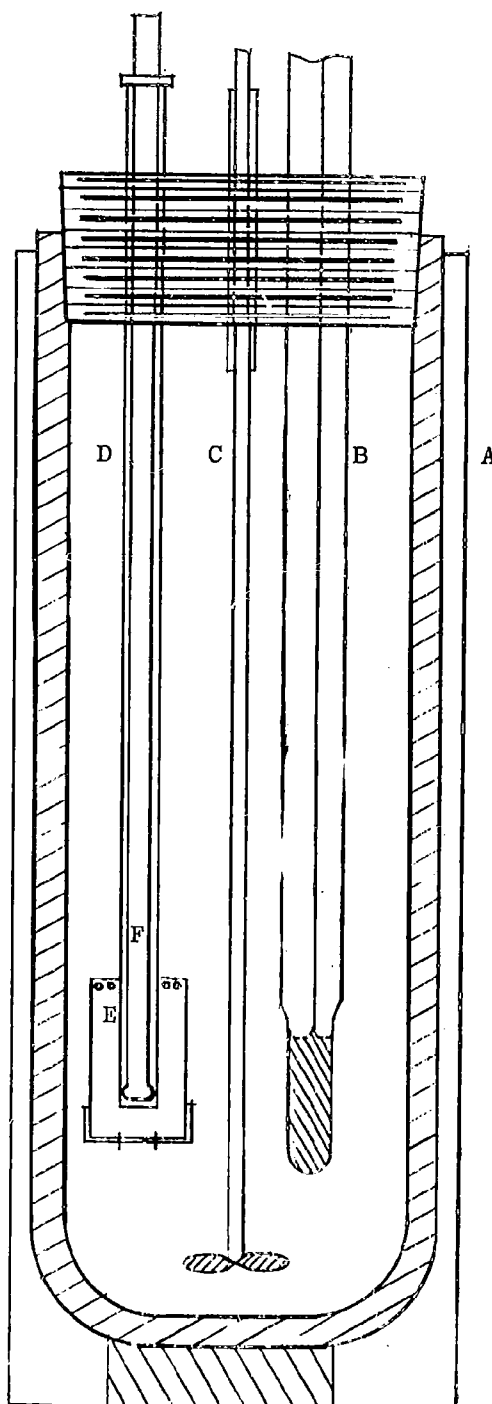
$$\Delta H = E \frac{\Delta t}{m_1 - m_3} \frac{Q_{\text{aid}} - Q_{\text{wire}}}{(6.94) \text{ kcal/mole Li}}$$

Run No.	Date 1962	m_1 (gm)	Δt °C	Ign aid m_2 (gm)	Q_{aid} cals	Q_{wire} cals	Unreacted Li m_3 (gm)	$\frac{\Delta H}{\text{kcal/mole Li}}$	$-\Delta H_{\text{form}}$ kcal/mole Product	Dev.
56	8/7	0.2432	0.973	0.0060	42.9	19.0	0.0093	73.24	146.4	5.4
57	8/9	0.2815	1.119	0.0053	37.9	10.1	0.0078	69.25	138.4	2.6
58	8/9	0.2182	0.840	--	--	16.8	0.0080	67.69	135.2	5.8
60	8/10	0.2722	1.127	--	--	16.3	0.0077	72.18	144.2	3.2
Average								70.59	141.1	4.2

Heat of Combustion $\Delta H = -70.59 \pm 2.1$ kcal/mole Li
Heat of Formation $\Delta H_{\text{Li}_2\text{O}} = -141.1 \pm 4.2$ kcal/mole Li_2O

m_1 = mass of lithium
 m_2 = mass of aluminum ignitor
E = energy equivalent of combustion bomb, 2441 cal/°C

FIGURE I
SOLUTION CALORIMETER #2



- A) Dewar Vessel
- B) Beckmann Thermometer
- C) Stirrer
- D) Sample Admitter Shaft
- E) Polyethylene Basket
- F) Glass Rod Plunger

<u>Material</u>	<u>Source</u>	<u>Purity</u>
Lithium	Lithium Corp. of America	99.9%
Aluminum	Aluminum Corp. of America	99.9%
Magnesium	N. E. Lime Company	99.9%
Zinc	J. T. Baker Company	99.8%

The aluminum-lithium compound was prepared at National Research Corporation by vacuum melting techniques. X-ray diffraction patterns identified aluminum-lithium compound plus free aluminum. The latter was estimated to account for 5% (by weight) of the sample.

3. Preliminary Observations and Modifications

In solution calorimetry the dissolution of a metal in a solvent frequently occurs with the evolution of hydrogen. If the hydrogen is allowed to escape, then a correction must be applied for the heat of evaporation of the water which would be carried away by the hydrogen. In this work a chemical calibration of the system was chosen in place of the electrical method. By so doing, the correction for the evaporation effect was eliminated, since a metal-acid reaction was performed for the calibration (magnesium in hydrochloric acid). The evolved hydrogen was allowed to escape.

The amount of hydrogen evolved may be controlled by properly choosing sample weights. From the accurately known heat of solution of magnesium in the chosen solvent, the energy liberated is quantitatively calculated.

Under such a method of calibration in which the effect of the escaping hydrogen has been canceled out, there is no necessity for using extremely small quantities of material to minimize the evaporative correction. The use of larger quantities of material will, of course, result in a larger temperature rise. A rise of 2°C on a Beckmann thermometer which can be read to a 0.002°C results in an accuracy of 0.1% which is adequate for the determination to be made here. For this particular system then, the simplified calorimeter may be satisfactorily employed, using 2 N HCl as the solvent.

The manner in which hydrogen is evolved by the metals is of importance in regards to retention time within the solvent to allow for sufficient thermal transfer. In the case of aluminum, which remained close to the bottom of the calorimeter, the evolution of hydrogen was in the form of very small bubbles whose retention time was increased by the stirring motion of the solvent. There appeared to be no difficulty in thermal transfer here. The evolution of hydrogen from magnesium was more rapid and the smaller pieces of magnesium tended to be lifted in the solvent by the buoyant effect of the hydrogen. Thus, at least part of the hydrogen was subjected to very short retention time resulting in questionable thermal transfer.

The reaction of lithium with the solvent occurred instantaneously at the surface of the solvent and it was obvious that a method must be developed to admit the sample to the solvent in such a way that the lithium would be confined below the

solvent surface. The device is shown in Figure I. The lithium sample was coated with a thin layer of mineral oil to protect it initially upon contact with the solvent in the admitting shaft. It was plunged rapidly down the shaft and as it left the shaft it rose rapidly to the top of the submerged polyethylene basket. The reaction began moments later and as the hydrogen was generated it collected in the basket and displaced the solvent out through the hole in the bottom of the basket. The holes at the top were small enough to allow this displacement. It was observed that the hydrogen displaced about $3/4$ of the contents of the basket at which time the pressure of the acid forced the hydrogen through the small holes at the top of the basket in the form of fine bubbles. If more lithium remained at this time, the cycle simply repeated itself in this self-pumping method. By this technique then, the retention time was increased to allow for improved heat transfer of the hydrogen prior to its escape. This device was, therefore, incorporated into the calorimeter. It should be noted that the hole at the bottom of the basket was directly below the admitting tube to allow the aluminum to drop through the basket to the vessel bottom where it could be more efficiently dissolved. When magnesium was run the arrangement of the hole was such as to prevent the sample from falling through the basket. All runs were made at 25°C.

4. Dissolution of Magnesium and Zinc

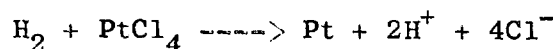
As stated above the calorimeter was calibrated chemically by dissolving magnesium in 300 cc of 2 N HCl. The heat

of formation of Mg^{++} was taken to be -100.376 kcal/mole according to the Selected Values of the National Bureau of Standards. From these runs the heat equivalent of the calorimeter was calculated to be 309.4 calories per $^{\circ}\text{C}$.

One run on commercial grade zinc was made to verify this method. From the solution data, the heat of formation of Zn^{++} was calculated to be -32.42 kcal/mole. The NBS Selected Values assigns the value of -36.4 kcal/mole. (see Table II) whereas Richards³ measured -30.2 kcal/mole.

5. Dissolution of Aluminum

To facilitate the dissolution rate of aluminum in 300 cc of 2 N HCl, eleven drops of platonic chloride was added to the solution. The decomposition of this accelerator:



occurs exothermically as determined by Buck, et al⁴, and the liberated energy was found to be -0.21 ± 0.01 cal/mg of platinum by those investigators. This correction was made by assuming all of the accelerator to be decomposed. (The accelerator gave a yellowish color to the HCl when initially added; upon completion of the metal-acid reaction, the solution was no longer yellow and the precipitated platinum was visible.) The temperature rise, when corrected for exothermicity of the accelerator decomposition is designated at $\Delta t'$ in column 5 of Table II.

The heat of formation of Al^{+++} was found to be -125.246 ± 0.094 kcal/mole. This agrees favorably with the NBS Selected Value of -125.4 kcal/mole.

TABLE II
HEATS OF SOLUTION IN 2 N HCl

(1) Run No.	(2) m mass (grams)	(3) Date 1962	(4) Δt	(5) t -(a) $^{\circ}\text{C}(\text{corr})$	(6) t ' M $\frac{m}{^{\circ}\text{C}/\text{mole}}$	(7) t ' M $\frac{m}{^{\circ}\text{C}/\text{mole}}$	(8) $\frac{m}{M} (\Delta H) (\Delta t)^{-1}$ cal/ $^{\circ}\text{C}$
Al-3	0.1023	9/10	1.533	1.533	404.1	125.008	
Al-4	0.1011	9/10	1.536	1.520	405.4	125.441	
Al-5 (c)	0.1031	9/10	1.563	1.547	404.7	125.194	
Al-7	0.1053	9/11	1.582	1.531	405.2	125.340	
$\Delta H = -125.246 \pm 0.094$ kcal/mole aluminum (b)							
Li-5	.0634	9/6	1.905		208.5 (d)	64.499	
Li-6	.0643	9/6	1.973		212.9	65.861	
Li-7	.0548	9/6	1.618		204.9	63.386	
Li-8	.0331	9/6	1.000		209.7	64.871	
Li-10	.0349	9/7	1.041		207.0	64.035	
Li-11	.0260	9/7	0.787		210.0	64.964	
Li-12	.0237	9/7	0.697		204.1	63.138	
$\Delta H = -64.383 \pm 0.363$ kcal/mole lithium (b)							
Mg-1	.0612	9/5	.0898		356.8	110.376	309.4
Mg-2	.0734	9/5	1.077		356.8	110.376	309.4
$E = 309.4$ calories/ $^{\circ}\text{C}$							
Zn-1	0.3244	9/4	0.520		104.8	32.429	
$\Delta H = -32.420$ kcal/mole zinc (b)							

(a) Corrected for ppt'd Pt

(b) Standard deviation

(c) Li ions in solution prior to run

(d) Δt used in calculations for Li, Mg, and Zn

Run Al-7 was made in an acid solution in which lithium had previously been dissolved. The heat of solution of aluminum in this solution agreed well with the results of the preceding runs and indicated no significant interaction between ions of aluminum and lithium.

6. Dissolution of Lithium

The technique by which the lithium sample was admitted to the solvent was described in the Section II B 1. The data is shown in Table II. The heat of formation of Li^+ was determined to be -64.393 ± 0.363 kcal/mole. This value is approximately 2 kcal/mole lower than that given in the Selected Values. One plausible explanation may be that although the evolved hydrogen has been retarded in its escape from the solution, it may not have allowed for complete thermal transfer.

7. Dissolution and Heat of Formation of AlLi

The platinic chloride solution (10%) was employed as an accelerator for this reaction. The experimental data is shown in Table III.

Column 5 lists the calculated release of energy from a hypothetical physical mixture of the same weight as the compound weight. Column 6 lists the actual value of energy as a result of the dissolution of the compound in 2 N HCl. Using these data, the heat of formation of AlLi was calculated and it is listed in column 7. The heat of formation of AlLi was found to be -15.06 ± 1.44 kcal/mole. Kubaschewski⁵ estimated a value of -12.0 ± 2.5 kcal/mole, and Van Arkel⁶ estimated a value of -15 kcal/mole.

TABLE III

HEAT OF FORMATION OF ALUMINUM-LITHIUM (AlLi)

Run No.	Date	m grams	$\Delta t^{(3)}$	energy ⁽¹⁾ theor. (cals)	energy ⁽²⁾ actual (cals)	$-\Delta H$ kcal/mole
B-AlLi- 9 G	9/27/62	.0671	1.129	356.0	334.1	11.66
" 10 G	9/28/62	.0552	.934	292.9	276.3	10.76
" 11 G	9/28/62	.0339	.554	180.1	163.7	17.31
" 12 G	9/28/62	.0742	1.261	394.1	372.8	10.24
" 13 G	9/28/62	.0639	1.046	339.3	308.7	17.07
" 14 G	10/1/62	.0595	.943	316.1	277.8	22.98
" 15 G	10/1/62	.0678	1.098	360.2	323.9	19.11
" 17 G	10/8/62	.0496	.824	263.2	243.5	13.48
" 18 G	10/8/62	.0915	1.527	486.0	451.0	12.95
						9 135.56
						15.06

$$\Delta H_{\text{AlLi}} = -15.06 \pm 1.44 \text{ kcal/mole}^{(4)}$$

- (1) Calculated heat of solution for the sample weight, assuming constituents to be a physical mixture; includes correction for 5% free aluminum
- (2) Correction for 5% free aluminum
- (3) Corrected for accelerator side reaction (-0.21 cal/mg Pt)
- (4) Standard Deviation

CONCLUSIONS

The heat of combustion of lithium has been determined in a Parr oxygen bomb. On preliminary runs in which carbon was present during the combustions, the energy liberated was greater than expected by 20 kcal/mole product. In addition, and in part the reason for the higher energy value, x-ray diffraction data has shown the products of combustion to be lithium carbonate and lithium oxide (Li_2O). In later experiments (see Table I) the combustion was carried out in the absence of carbon. The energy liberated was -141.5 ± 4.2 kcal/mole product. The heat of formation of Li_2O is listed as -142.5 kcal/mole. The heat of formation of Li_2O has not previously been determined by direct combination. The listed heat of formation of Li_2O has been determined by calculation from heat of solution, entropy and vapor pressure data. The data by direct combustion generated at these laboratories agrees closely with the heat of formation of Li_2O as determined by other methods.

The heat of formation of AlLi has been determined by solution calorimetric techniques, in which the heats of solution of aluminum, lithium, and aluminum-lithium compound (AlLi) have been measured. The calorimeter was calibrated chemically to eliminate the need to correct for solvent evaporation by evolved hydrogen. The heats of solution of the following systems in 2 N HCl were found to be:

Al: -125.246 ± 0.94 kcal/mole

Li: -64.393 ± 0.363 kcal/mole

The heat of solution of AlLi was measured in terms of calories per sample weight. The proper calculations were then made utilizing these solution data in addition to the aluminum and lithium data. From this the heat formation of AlLi was determined and found to be -15.06 ± 1.44 kcal/mole.

BIBLIOGRAPHY

- ¹H. A. Skinner, Experimental Thermochemistry, Vol. II, p. 91, Interscience, New York (1962)
- ²Johnston and Bauer, J. Am. Chem. Soc., 73, 1119 (1951)
- ³Richards, J. Am. Chem. Soc., 32, 431 (1910)
- ⁴Buck, et al, J. Am. Chem. Soc., 74, 136 (1952)
- ⁵Kubaschewski, Metallurgical Thermochemistry, p. 254, Permagon, New York (1958)
- ⁶Van Arkel, Alloys in Solid Rocket Fuels, National Research Corporation Internal Report, October 1960 (External Distribution)