

HEAT OF COMBUSTION OF  
TRIS-(ACETYLACETONATO) GALLIUM III

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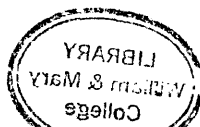
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Of the Requirements for the Degree of  
Master of Arts

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By  
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APPROVAL SHEET

This thesis is submitted in partial fulfillment of  
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## ABSTRACT

The heat of combustion of tris-(acetylacetonato) gallium III as determined by bomb calorimetry has been found to be  $-1896.8 \pm 7.8$  kcal/mole. The energy of the gallium-oxygen bond has been calculated using the appropriate thermochemical cycle, and found to be 51.1 kcal/mole.

In addition, determinations of the heats of combustion of tris-(acetylacetonato) iron III and tris-(acetylacetonato) aluminum III to afford a check of the accuracy of the method by comparison with values of the heats of combustion previously reported in the literature. Calculation of the energies of the metal-oxygen bonds using new experimentally determined values of the heats of sublimation of tris-(acetylacetonato) iron III and tris-(acetylacetonato) aluminum III shows the energy of the iron-oxygen bond to be 57.1 kcal/mole, and the energy of the aluminum-oxygen bond to be 63.7 kcal/mole.

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## INTRODUCTION

The heats of combustion of various metal chelates have been studied recently (6,7). In a continuation of this work, this paper reports the heats of combustion of the tris-2,4-pentanedionato complexes of aluminum III, iron III, and gallium III; of which the heat of combustion of the gallium compound is yet unreported. The aluminum and iron complexes were chosen because the pure compounds were readily available, and because recent work has given values for the heats of combustion of these complexes which affords a comparison for the methods used in this work (6,7). With the heat of combustion and the appropriate thermochemical cycle, an approximation of the metal-oxygen bond energy in each complex may be determined. 2,4-pentanedione (acetylacetone) will be abbreviated as (AAH), and the tris-(acetylacetonato) complexes will be abbreviated as  $\text{Al}(\text{AA})_3$ ,  $\text{Fe}(\text{AA})_3$ , and  $\text{Ga}(\text{AA})_3$ .

## DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

### I. APPARATUS

A Parr series 1200 adiabatic bomb calorimeter with a Parr 2602 temperature controller was used to measure the heat of combustion. The temperatures before and after combustion were measured to the nearest  $0.001^{\circ}\text{C}$  with a Leeds and Northrup platinum resistance thermometer connected to a Honeywell Mueller bridge. Balancing the bridge was accomplished with the help of a Leeds and Northrup D. C. null detector. Identification of the metal oxide after combustion was made using the powder diffraction technique, with a General Electric X-ray spectrophotometer.

### II. EXPERIMENTAL PROCEDURE

#### A. Preparation of Materials

Two grams of 99.99% pure gallium from Fischer Scientific Company were slowly dissolved in warm concentrated nitric acid to yield 20 ml. of solution. Twenty grams of freshly distilled acetylacetone were dissolved in 130 ml. of water by the addition of ammonium hydroxide. The two solutions were mixed and ammonium hydroxide was added drop-wise until the precipitate ceased to form (9). Too rapid addition of ammonium hydroxide produces  $\text{Ga}(\text{OH})_3$  in addition to the  $\text{Ga}(\text{AA})_3$ .

Any  $\text{Ga}(\text{OH})_3$  formed was removed by dissolution of the  $\text{Ga}(\text{AA})_3$  in benzene, and filtration of the solution. The benzene was evaporated and the  $\text{Ga}(\text{AA})_3$  was recrystallized from ethanol in two successive recrystallizations to yield white monoclinic crystals melting at  $194\text{-}195^\circ\text{C}$ . The freshly prepared  $\text{Ga}(\text{AA})_3$  was kept, at room temperature, under a vacuum of  $20\mu$  for 48 hours to remove any traces of ethanol solvent prior to combustion.

$\text{Ga}(\text{AA})_3$  can also form orthorhombic crystals. However, attempts to prepare only orthorhombic crystals in a variety of solvents have not been successful; there is always a large percentage of monoclinic crystals present. Due to the difficulty of separating the orthorhombic from the monoclinic crystals, all of the determinations of the heats of combustion were made on the pure monoclinic crystals.

The tris-(acetylacetonato) aluminum III of 99.99% purity and the tris-(acetylacetonato) iron III of 99.98% purity were obtained from the J. T. Baker Chemical Company.

#### B. Calorimetric Measurements

Calibration of the calorimeter was made at intervals using weighed samples of benzoic acid. The heat capacity of the calorimeter was calculated to be  $2454.54 \text{ cal}/^\circ\text{C}$ .

Due to the high values of the heats of combustion of the acetylacetonates and due to the fact that large powdered samples often left one quarter of their weight scattered

about unburned, pellets of approximately 0.25 grams were used. Simple pelletization, however, was not sufficient to prevent portions of the sample from being thrown out of the volume in which burning was taking place, and thus remaining unburned. Since it was found that merely lowering the oxygen pressure did not slow the combustion process enough, inert gas was added prior to pressurizing with oxygen. After closing the bomb, a stream of argon at 4 psi above atmospheric pressure was passed through for two minutes to flush out the air in order to eliminate the need for any correction for the heat produced during the formation of nitrogen oxides. The outlet was closed, leaving the argon in the bomb, and then the pressure was raised to 15 atm with oxygen. To further slow the combustion process, 15 cm of standard iron fuse wire of 2.3 cal/cm was used instead of the 10 cm which is usually used with the Parr ignition transformer. The extra wire was formed into a short coil with its lower part just touching the pellet. Coiling the wire creates a much larger heated volume through which any particles which might be thrown from the pellet must pass. The extra length, combined with the reduced partial pressure of oxygen, resulted in the wire glowing hotly for approximately two seconds before burning out, rather than the usual flash. Because of the low oxygen pressure, the wire glowed, but did not burn when there was no sample

present. With a sample present, however, once the sample began to burn, the increase in temperature caused the fuse wire to burn out. To determine the amount of resistance heating, the bomb was charged with the usual argon-oxygen mixture, but with no sample for combustion. Current was then passed through the wire for five seconds, and the temperature rise was observed. The amount of heat produced while the wire glowed before combustion took place was experimentally determined to be 14 cal/sec.

Even with these precautions, the samples sometimes burned rapidly enough to be heard as a sharp click outside the calorimeter. As the values of the heats of combustion of these samples were very scattered, and all considerably lower than the values of those which seemed to proceed smoothly, they are not reported here. There was 0.0005 to 0.0006 gm of unburned carbon remaining in the cup after combustion, which is equivalent to 22.04 cal/gm of  $\text{Ga}(\text{AA})_3$ , 21.8 cal/gm of  $\text{Fe}(\text{AA})_3$ , and 21.9 cal/gm of  $\text{Al}(\text{AA})_3$ . All values of the heats of combustion have been corrected for the heat produced by the fuse wire and for the unburned sample, by the appropriate amounts. The combustion products are taken to be  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and the metal oxide. The oxides were identified by X-ray powder diffraction, and found to be  $\alpha\text{Al}_2\text{O}_3$ ,  $\alpha\text{Fe}_2\text{O}_3$ , and  $\beta\text{Ga}_2\text{O}_3$ . The X-ray pattern from the gallium oxide was compared with that of 99.99%  $\text{Ga}_2\text{O}_3$  purchased

from AIAG Metals, Inc., New York, which confirmed that the product of combustion was, in fact,  $\beta\text{Ga}_2\text{O}_3$ .

The calorimetric procedure follows that outlined in the Parr instruction manual. The pressurized bomb was placed in the bucket filled with 2000 gm of water and the electrical connections were made. The calorimeter was closed, the pump started, the temperature of the water jacket was adjusted to the approximate temperature of the bucket, and the automatic controller was turned on. When the controller began cycling smoothly, the time was noted. After four minutes, the resistance of the platinum resistance thermometer inserted in the bucket was noted, and the bomb was fired. Eight minutes after firing, the resistance was noted again, and the bomb was removed from the calorimeter. The pressure in the bomb was released, and the finely divided oxide was collected and mounted on a microscope slide for X-ray analysis.

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It was necessary to remove the needle valve from the bomb head after every run, and to clean the valve and seat, as small amounts of the rather abrasive oxides were carried into this area regardless of how slowly the pressure was released.

## RESULTS AND DISCUSSION

The experimental data are listed in Table 1.

The results are listed in Table 2.

The energy of the metal-oxygen bonds may be determined from the appropriate thermochemical cycle. The cycle used for  $\text{Ga}(\text{AA})_3$  is illustrated in Fig. 1 (5).

$\Delta H_1$  is the heat of sublimation of the metal.  $\Delta H^{\circ}f_1$  is the heat of formation of the keto form of acetylacetone in the liquid phase.  $\Delta H_2$  is the heat of vaporation of the keto form of acetylacetone.  $\Delta H_{\text{trans.}}$  is the heat of transition of acetylacetone from the keto form to the enol form.  $\Delta H_{\text{chel.}}$  is the heat of formation of the metal chelate in the gaseous state from  $\text{Fe}_{(g)}$  and  $(\text{AAH})_{(g)}$ .  $\Delta H_{\text{sub.}}$  is the heat of sublimation of the chelate.  $\Delta H_{\text{c}}$  is the heat of combustion of the chelate; and  $\Delta H_{\text{ox}}$  is the heat of oxidation of the metal going to  $\text{M}_2\text{O}_3$ , graphite to  $\text{CO}_2$ , and  $\text{H}_2$  to  $\text{H}_2\text{O}$ .  $\Delta H^{\circ}f_2$  is the heat of formation of the chelate in its standard state from the elements in their standard states.  $E(\text{O-H})$  is the energy of the oxygen-hydrogen bond, which is taken to be 109.4 kcal/mole (11).  $E(\text{H-H})$  is the energy of the hydrogen-hydrogen bond, and is taken to be 103.2 kcal/mole (11).  $E(\text{M-O})$ , the energy of the metal-oxygen bond is calculated from the

TABLE 1  
EXPERIMENTAL DATA

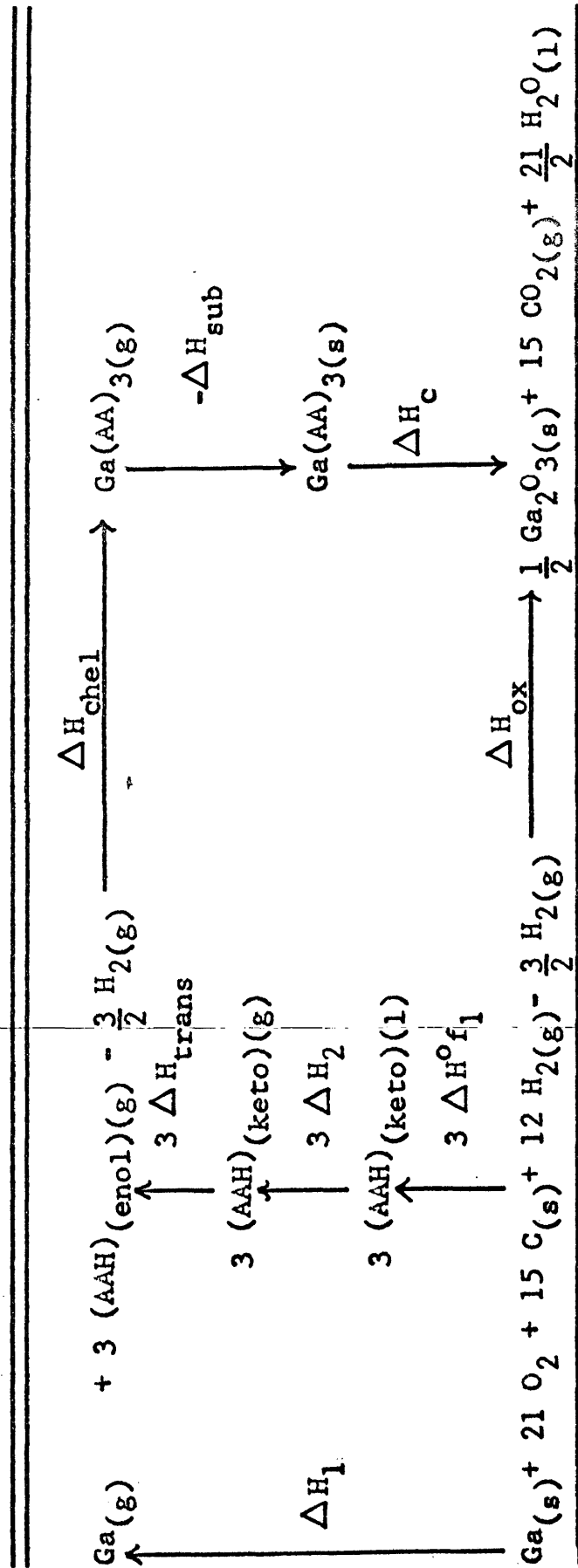
Sample wt gm	cal combustion fuse wire	Total cal	Net cal	cal/gm	$-\Delta E$ combustion kcal/mole
$\text{Ga}(\text{AA})_3$					
0.2887	26	1542.59	1494.59	5173.51	1898.94
0.2678	26	1430.66	1382.66	5163.04	1895.10
0.2936	19	1563.57	1522.57	5185.85	1903.47
0.3290	16	1741.58	1703.58	5178.07	1900.62
0.3265	32	1738.78	1684.78	5160.11	1894.02
0.2500	30	1337.96	1285.96	5143.84	1888.05
0.2527	21	1348.61	1305.61	5166.64	1896.42
0.2358	17	1249.04	1210.04	5131.62	1883.56
$\text{Fe}(\text{AA})_3$					
0.2575	12	1392.98	1358.98	5277.60	1863.94
0.2837	29	1548.81	1497.81	5279.56	1864.64
0.2264	17	1231.70	1192.70	5268.12	1860.59
$\text{Al}(\text{AA})_3$					
0.2974	19	1785.37	1744.37	5865.41	1902.21
0.2973	22	1829.92	1741.92	5859.14	1900.18
0.2960	11	1765.34	1732.34	5852.50	1898.02
0.2860	28	1726.82	1676.82	5863.00	1901.43
0.2509	26	1518.21	1470.21	5859.76	1900.38

TABLE 2  
RESULTS

Ga(AA) <sub>3</sub>		
Average $\Delta E$ of combustion	-1895.02	kcal/mole
3 RT	- 1.78	kcal/mole
Average $\Delta H$ of combustion	-1896.80	kcal/mole
Standard deviation	$\pm 6.56$	kcal/mole
Limits at 99% confidence	$\pm 7.8$	kcal/mole
$\Delta H$ of combustion	-1896.8 $\pm 7.8$	kcal/mole
Fe(AA) <sub>3</sub>		
Average $\Delta E$ of combustion	-1863.06	kcal/mole
3 RT	-1.78	kcal/mole
Average $\Delta H$ of combustion	-1864.84	kcal/mole
Standard deviation	$\pm 2.16$	kcal/mole
Limits at 99% confidence	$\pm 7.3$	kcal/mole
$\Delta H$ of combustion	-1864.8 $\pm 7.3$	kcal/mole
Al(AA) <sub>3</sub>		
Average $\Delta E$ of combustion	-1900.44	kcal/mole
3 RT	-1.78	kcal/mole
Average $\Delta H$ of combustion	-1902.32	kcal/mole
Standard deviation	$\pm 1.58$	kcal/mole
Limits at 99% confidence	$\pm 2.8$	kcal/mole
$\Delta H$ of combustion	-1902.3 $\pm 2.8$	kcal/mole

FIGURE 1

THERMOCHEMICAL CYCLE FOR GALLIUM



$$\Delta H_{\text{chel}} = \Delta H_{\text{ox}} - \Delta H_1 - 3 \Delta H_{\text{f}_1}^{\circ} - 3 \Delta H_2 - 3 \Delta H_{\text{trans}} + \Delta H_{\text{sub}} - \Delta H_{\text{c}}$$

$$\Delta H_{\text{chel}} = 3 E(\text{O-H}) - 6 E(\text{Ga-O}) - \frac{3}{2} E(\text{H-H}) - \frac{3}{2} RT$$

$$\Delta H_{\text{f}_2}^{\circ} = \Delta H_{\text{ox}} - \Delta H_{\text{c}}$$

preceding data. The values of these quantities are given in Table 3.

The energy of the gallium-oxygen bond has been calculated to be 51.1 kcal/mole, that of the iron-oxygen bond to be 57.1 kcal/mole, and that of the aluminum-oxygen bond to be 63.7 kcal/mole. Values for the bond energy of the iron compound of 59.4 kcal/mole (6) and of the aluminum compound of 63 kcal/mole (7) have been reported in the literature.

The energy of each of the six metal-oxygen bonds is assumed to be the same. This is based on an octahedral structure for the complex as shown in Fig. 2. It has been suggested that benzene-type resonance in each of the metal-ligand rings contributes to the stability of these compounds, as shown in Fig. 3 (1).

Raman spectra have indicated that some  $\pi$  bonding plays a part in the stabilization of these complexes, there being donation of electrons from the  $p\pi$  level in oxygen to a  $d\pi$  level in the metal (5). For aluminum and gallium, which have no unfilled inner d-orbitals, it is felt that outer d-orbital hybridization adds to the stability of the complexes (2). It should be mentioned, however, that the contribution of each of the above is small.

Because of the somewhat smaller size of the aluminum ion, the energy of the aluminum-oxygen bond was found to be, as expected, greater than that of both the iron-oxygen and the gallium-oxygen bonds. Iron has an unfilled inner d-orbital,

TABLE 3  
DATA FOR THERMOCHEMICAL CYCLE

	Ga(AA) <sub>3</sub> kcal/mole	Fe(AA) <sub>3</sub> kcal/mole	Al(AA) <sub>3</sub> kcal/mole
$\Delta H_1$	64.62 (7)	96.68 (4)	70.50 (4)
$\Delta H^{\circ}f_1$	-100.95 (9)	-100.95 (9)	-100.95 (9)
$\Delta H_2$	11.5 (6)	11.5 (6)	11.5 (6)
$\Delta H_{trans.}$	2.61 (6)	2.61 (6)	2.61 (6)
$\Delta H_{chel.}$	-133.81	-169.79	-209.34
$\Delta H_{sub.}$	30.60 (9)	27.93 (12)	25.99 (12)
$\Delta H_c$	-1896.8	-1864.8	-1902.3
$\Delta H_{ox}$	-2257.11 (4)	-2226.36 (4)	-2327.65 (4)
$\Delta H^{\circ}f_2$	-360.31	-361.56	-425.35
E(O-H)	109.4 (11)	109.4 (11)	109.4 (11)
E(H-H)	103.2 (11)	103.2 (11)	103.2 (11)
E(M-O)	51.1	57.1	63.7

FIGURE 2  
OCTAHEDRAL CONFIGURATION OF  
TRIS-(ACETYLACETONATO) COMPLEXES

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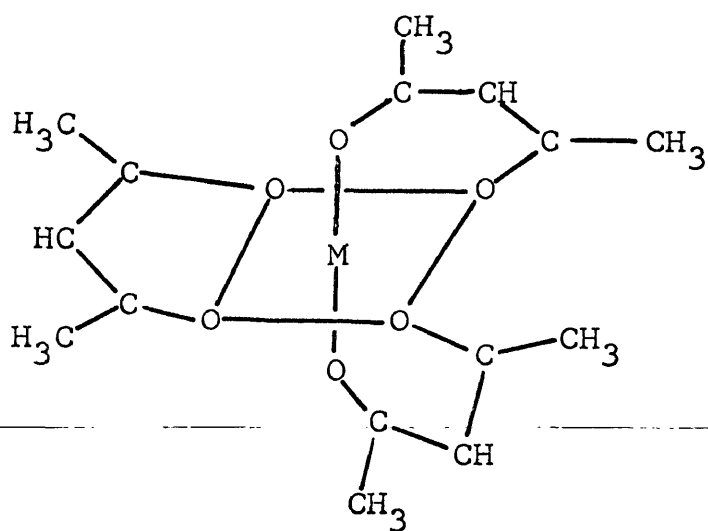
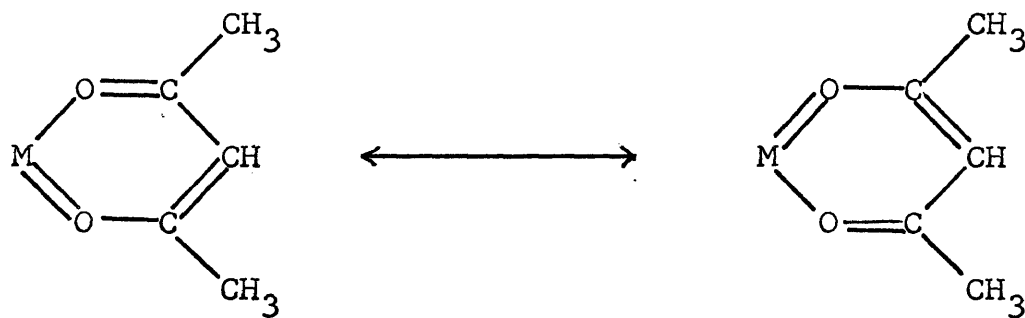


FIGURE 3  
BENZENE-TYPE RESONANCE IN  
METAL-ACETYLACETONATO RINGS

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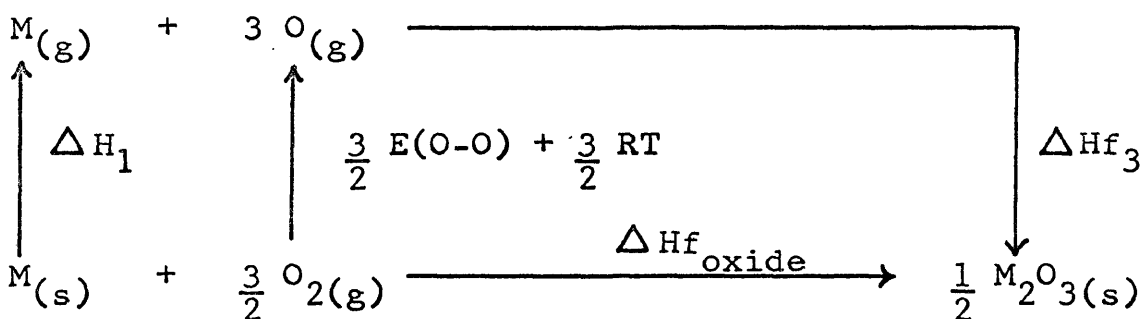
which partially explains why the energy of the iron-oxygen bond is higher than that of the gallium-oxygen bond, a fact that cannot be justified on the basis of size.

The energy of the Ga-O bond seems inexplicably low. The expected result from the consideration of molecular-orbital hybridization would be for the energy of the gallium-oxygen bond to be just slightly lower than that of the iron-oxygen bond. If the heats of formation of the crystalline metal oxides from the metal and oxygen in the gaseous state are compared, it can be seen that this is the result, Fig. 4. To be sure, the heat of formation of the oxide and the energy of the metal-oxygen bond in the chelate are not necessarily directly comparable, particularly when it is recalled that the coordination in  $\alpha\text{Fe}_2\text{O}_3$  is hexagonal, while that in  $\beta\text{Ga}_2\text{O}_3$  is a combination of tetragonal and octahedral (3); nevertheless, it would be expected that the experimental results would more closely parallel the predicted results than they do.

One source of experimental error, for which no correction has been made, is that the temperatures were only read to the nearest  $0.001^\circ$ , thus the value of the difference of the initial and final temperatures could have varied by  $0.001^\circ$  on successive runs even if everything else had been the same. An error of  $0.001^\circ\text{C}$  will produce an error of 2.76 kcal/mole in the heat of combustion. Another error is that a mis-estimation of the length of time the fuse wire glowed before

FIGURE 4

HEAT OF FORMATION OF THE SOLID METAL OXIDE  
FROM OXYGEN AND THE METAL IN THE GASEOUS STATE



	Ga	Fe	Al
$\Delta H_1$	64.62	96.68	70.50
$\frac{1}{2} \Delta H_{oxide}$	-129. (4)	-98.2 (4)	-199.6 (4)
$\frac{3}{2} E(O-O)$	178.35	178.35	178.35
$\Delta H_{f_3}$	-372.86	-374.12	-449.34

$$\Delta H_{f_3} = \Delta H_{oxide} - \Delta H_1 - \frac{3}{2} E(O-O) - \frac{3}{2} RT$$

ignition, by one quarter of a second, will produce an error of 3.92 kcal/mole in the heat of combustion. In view of the above, it is not surprising to find the limits at 99% confidence to be as large as they are. The closer limits for the aluminum compound are apparently fortuitous.

Although the precision of the heats of combustion reported here seems low in comparison with the precision obtainable from the combustion of some other types of organic compounds, it is as precise as most of the other data in the cycle. In any case, it is precise enough to afford some comparison among the energies of the metal-oxygen bonds in these compounds.

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