

ART. XXXIV.—*The Heat of Formation of Titanium Dioxide, and third paper on the Heat of Combination of Acidic Oxides with Sodium Oxide*; by W. G. MIXTER.

[Contributions from the Sheffield Chemical Laboratory of Yale University]

THE thermochemistry of titanium is limited to that of the reaction  $\text{TiCl}_4 + \text{Aq} = 57,870^\circ$  (Thomsen). As the heat of formation of the tetrachloride is not known, that of the oxide or acid can not be calculated. Good results might be obtained by burning titanium in oxygen if it could be ground to a fine powder. A coarse powder burns well in sodium peroxide, and hence this method was used.\*

The metal used in the investigation was made by Dr. M. A. Hunter in the laboratory of the General Electric Company. The specimen was in irregular nuggets, was malleable when hot and brittle when cold. The density of a bright piece of the metal was found to be 4.51 and that of the pulverized portion 4.49 at 18°. Moissan† states that the density of titanium is 4.87. But the purest he made in the electric furnace contained two per cent of carbon.

For use in the combustions the metal was pulverized in diamond mortar and then ground in an agate one which it did not scratch. It was impossible to grind it to a fine powder, as some particles were flattened and others rounded. It was assumed that the impurities adhering to the nuggets were converted into dust by the grinding and also that the steel from the mortar was dust. Accordingly the dust was floated off in water and only the coarser portion retained. A qualitative analysis revealed no impurities in the metal. For a determination of titanium 0.5662 gram was dissolved in molten potassium pyrosulphate, the fusion was dissolved in cold water and the titanous acid was precipitated by boiling. The titanium dioxide obtained weighed 0.9453 gram, equivalent to 0.5676 gram of titanium or 100.2° per cent. The following are the thermal data:

	1	2
Titanium.....	2.000 grams	2.001 grams
Sulphur.....	1.000 “	1.000 “
Sodium peroxide .....	20 “	20 “
Water equivalent of system..	3,003 “	2,979 “
Temperature interval .....	4.958°	4.958°

\*The details of the sodium-peroxide method are given in the first paper, on the Heat of Combination of Acidic Oxides with Sodium Oxide, in this Journal, xxvi, 125.

†C. R., cxx, 290.

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Heat effect .....	14,889°	14,770°
“ of oxidation of sulphur.	—5,271°	—5,271°
“ “ “ iron .....	6—48°	6—48°
“ “ oxygen absorbed ...	—71°	—70°
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	9,499°	9,381°
For 1 gram of titanium .....	4,749°	4,693°

The mean is 4,721° and for 48.1 grams of titanium it is 227,100°. The temperature of the fusion was above the melting point of silver and no metallic titanium remained. The fusion, when treated with water, left a white residue which dissolved on addition of an excess of hydrochloric acid and the solution had the red color of pertitanic acid.

*Titanic Oxide.*

Titanic oxide was prepared as follows: The hydroxide, purchased for the pure compound, was fused with potassium pyrosulphate, the fusion was dissolved in cold water and the titanic acid was precipitated by boiling. It was washed with hot water, digested with hot ammonia and washed again and finally heated to redness for an hour. It contained no iron, alumina or zirconia. The following are the experimental data:

	3	4	5
Titanic oxide .....	3.302 gr.	4.001 gr.	3.970 gr.
“ “ in residue ...	0.057 “	0.074 “	0.103 “
	<hr/>	<hr/>	<hr/>
“ “ combined ...	3.245 “	3.927 “	3.867 “
Sulphur .....	1.000 “	1.000 “	1.000 “
Sodium peroxide .....	16 “	18 “	19 “
Water equivalent of system	3,081 “	2,956 “	3,022 “
Temperature interval .....	2.417°	2.580°	2.536°
Heat effect .....	7,446°	7,626°	7,664°
“ of oxidation of sulph’r	—5,271°	—5,271°	—5,277°
“ “ “ “ iron ..	—48°	—48°	—48°
“ “ oxygen evolved...	---	+78°	+72°
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	2,127°	2,385°	2,417°
For 1 gram of titanic oxide	655°	607°	625°

The mean is 629° and for 80 grams of titanic oxide it is 50,300°. The solutions of the fusions in hydrochloric acid had the red color of pertitanic acid.

Since a pertitanate is formed when titanium or its dioxide is fused with an excess of sodium peroxide, it is probable that the

same compound results in both cases. Moreover, it makes no difference in the heat effect of  $\text{Ti}+2\text{O}$  derived whether we assume the formation of  $\text{Na}_2\text{O}_2\cdot\text{TiO}_3$  obtained by Mellikoff and Pessarjewsky\* or  $\text{Na}_2\text{O}\cdot\text{TiO}_3$ . Taking the latter compound, the calculations are as follows:

$3\text{Na}_2\text{O}_2 + \text{Ti} = \text{Na}_2\text{O}\cdot\text{TiO}_3 + 2\text{Na}_2\text{O} + \dots\dots$	227,100°
$3\text{Na}_2\text{O} + 3\text{O} = 3\text{Na}_2\text{O}_2 + \dots\dots\dots$	58,200°
	<hr/>
$\text{Na}_2\text{O} + \text{TiO}_2 + \text{O} = \text{Na}_2\text{O}\cdot\text{TiO}_3 \dots\dots\dots$	285,300°
	69,700°
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$\text{Ti} + 2\text{O} = \text{TiO}_2 \text{ (amorphous)} + \dots\dots\dots$	215,600°
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$\text{Na}_2\text{O}_2 + \text{TiO}_2 = \text{Na}_2\text{O}\cdot\text{TiO}_3 + \dots\dots\dots$	50,300°
$\text{Na}_2\text{O} + \text{O} = \text{Na}_2\text{O}_2 + \dots\dots\dots$	19,400°
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$\text{Na}_2\text{O} + \text{TiO}_2 + \text{O} = \text{Na}_2\text{O}\cdot\text{TiO}_3 + \dots\dots\dots$	69,700°

The large heat of formation of titanium dioxide was to be expected because of the difficulty of reducing the oxide to the metal. The heat of combination of  $\text{TiO}_2$  or  $\text{TiO}_3$  with  $\text{Na}_2\text{O}$  cannot be calculated from the experimental results, but it is less than that of silicon dioxide.

### Lead.

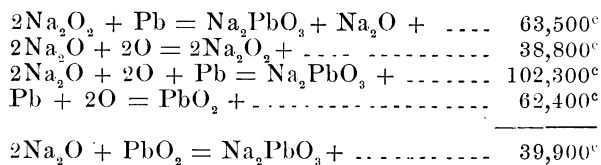
Lead, in a finely divided form for the work, was obtained by scraping a revolving cylinder of the metal with a thin tool. The experimental data were as follows:

Lead .....	20	grams
“ unburned .....	0.94	“
“ burned .....	19.06	“
Sulphur .....	1	“
Sodium peroxide .....	20	“
Water equivalent of system .....	3,982	“
Temperature interval .....	2.822°	
Heat observed .....	11,237°	
“ of oxidation of sulphur .....	—5,271°	
“ “ “ iron .....	—48°	
“ “ oxygen absorbed .....	—62°	
	<hr/>	
	5,856°	
For 1 gram of lead .....	307°	
“ 206.9 grams .....	63,500°	

\* Ber. d. deutsch. chem. Gesell., xxxi, 953.

The fusion was yellow and it yielded to hot water a little sodium plumbate. The insoluble yellowish brown powder left by the water liberated chlorine from hydrochloric acid—a proof of the presence of peroxide.

The heat of  $\text{Pb.O}=50.3$  is Thomsen's. Tscheltzow\* found for  $\text{PbO.O}=12.1$ , hence  $\text{Pb.2O}=62.4$ , which is used in the following calculation :



As the fusion in the foregoing experiment yielded a mixture of lead oxides, it seemed best to use lead dioxide in place of the metal. For this purpose the dioxide was made by acting on lead acetate with a hypochlorite and also by treating red lead with nitric acid, but the products were not pure enough for the purpose. Accordingly dioxide was prepared by electrolyzing a saturated solution of lead nitrate in dilute nitric acid. It was washed, dried, pulverized, and washed again to remove adhering nitrate. Finally the lead dioxide was heated to  $280^\circ$  until the weight was constant, and as it still retained water the temperature was raised until some red lead formed on the bottom of the beaker containing it. The composition of the product was as follows:  $\text{PbO}_2$ , 93.7;  $\text{PbO}$ , 6.0;  $\text{H}_2\text{O}$ , 0.3 per cent. The correction for lead oxide and water would be small and was not made in the following experiments :

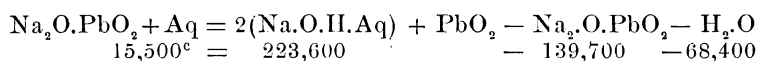
	2		3	
Lead dioxide .....	20.	grams	20.	grams
Sulphur.....	2.	"	1.5	"
Sodium peroxide.....	25	"	15	"
Water equivalent of system.	4,018	"	4,090	"
Temperature interval.....	3.418°		2.658°	
Heat observed .....	13,733°		10,871°	
“ of oxidation of sulphur	—10,542°		—7,906°	
“ “ “ “ iron ...	—48°		—48°	
“ “ oxygen evolved ....	+151°		+260°	
	3,294°		3,177°	
For 1 gram of lead dioxide..	165°		159°	

The mean is  $162^\circ$  for 1 gram of lead dioxide and for 238.9 grams it is  $38,700^\circ$ , which agrees well with the result of experi-

\* C. R., c, 1458.

ment 1. The fusion of 2 when treated with hot water left lead oxide and but little dioxide, while in 3, where less sodium peroxide was used, considerable lead dioxide remained. These facts indicate that the lead dioxide which separates on the hydrolysis of sodium plumbate is reduced to oxide by sodium peroxide in the presence of water. The following results support this view: a mixture of the two oxides was placed in cold water and the whole was heated. The solution contained lead, but gave no chlorine after adding hydrochloric acid and warming. A fusion of equal parts of lead and sodium peroxide left, after exhausting with water, lead dioxide, while when two parts sodium peroxide were taken the insoluble residue was brownish yellow and contained but little lead dioxide.

The heat of hydrolysis of sodium plumbate is derived as follows:



Since the  $\text{PbO}_2$  is in the solid state before and after the hydrolysis of the plumbate, it makes no difference in the thermal result if it first combines with water and is finally dehydrated. The hydrolysis as given above is only complete in a large volume of water, since sodium plumbate is soluble as such in a concentrated solution of sodium hydroxide.

#### Zirconium Dioxide.

Two experiments were made with mixtures of zirconium dioxide, sodium peroxide, and sulphur. The fusions were not good, and the residues remaining after treatment with hot water set free chlorine from hydrochloric acid, indicating the presence of a peroxide. The results were  $251^\circ$  and  $268^\circ$  for 1 gram of zirconium dioxide, mean  $258^\circ$  and for 122.7 grams  $31,700^\circ$ . If the dioxide was all oxidized to trioxide  $19,400^\circ$  are to be added, giving  $51,100^\circ$ . The only interpretation to be given to the result is that the heat of  $\text{ZrO}_2$  or  $\text{ZrO}_3 + \text{Na}_2\text{O}$  is small.

#### Ceric Oxide.

But one experiment was made with ceric oxide with the result of  $94.6^\circ$  for 1 gram and  $16,300^\circ$  for 172 grams. The fusion was placed in cold water and after gas ceased to come off the solution was decanted. When the insoluble residue was treated with hot water much gas was evolved—an indication of the presence of a peroxide of cerium. If  $2\text{CeO}_2$  is oxidized by sodium peroxide to  $\text{Ce}_2\text{O}_6$   $9,700^\circ$  are to be added for the heat of the oxygen taken from sodium peroxide. The thermal result does not indicate combination of sodium oxide with an oxide of cerium.