

ART. XV.—*The Heat of Combination of Acidic Oxides with Sodium Oxide, and the Heat of Oxidation of Chromium*; by W. G. MIXTER.

[Contributions from the Sheffield Chemical Laboratory of Yale Univ.]

It is the purpose of the writer to accumulate data on the heat effect of the union of acidic oxides with sodium oxide, and to determine if the position in the Periodic System and the magnitude of the atomic weight of an element have a marked influence on this heat effect. Much has been accomplished by Thomsen, Berthelot and others who have derived the heat of formation of salts from the observed heat of neutralization in solution—a method not applicable in all cases to salts which hydrolyse largely. The reaction with sodium peroxide avoids errors due to hydrolysis and gives fairly accurate results, as shown in a previous paper* in which $2\text{Na}_2\text{O}_2, \text{C}_2 = 133500^\circ$ was the observed heat and 132500° that derived from Thomsen's data. As a test of the method two determinations were made and in each rather more than two grams of rhombic sulphur were burned in a bomb with an excess of sodium peroxide. The heat effect for one gram was 5275° and 5267° respectively; mean 5271° and for 32 grams of sulphur, 168670° . The heat effect of $\text{Na}_2\text{O}, \text{SO}_3$ is derived thus:—

$$\begin{array}{rcl} 3\text{Na}_2\text{O}_2, \text{S} & = & 168700^\circ \\ 3\text{Na}_2\text{O}, 3\text{O} & = & 58200^\circ \\ \hline \text{Na}_2\text{O}, \text{S}, 3\text{O} & = & 226900^\circ \\ \text{S}, 3\text{O} & = & 103200^\circ \dagger \\ \hline \text{Na}_2\text{O}, \text{SO}_3 & = & 123700^\circ \end{array}$$

From Thomsen's data we have

$$\begin{array}{rcl} 2\text{Na}, \text{S}, 4\text{O} & = & 328590^\circ \\ 2\text{Na}, \text{O} & = & 99760^\circ \dagger \\ \text{S}, 3\text{O} & = & 103200^\circ \dagger \\ \hline \text{Na}_2\text{O}, \text{SO}_3 & = & 125630^\circ \end{array}$$

Thomsen used Bekétoff's result for $2\text{Na}, \text{O}$; deForcrand§ considers it too high and that 91000° is probably more accurate. The calculated heat effect of $\text{Na}_2\text{O}, \text{SO}_3$ will not be changed by using this number.

S. W. Parr|| mentioned that oxygen is sometimes liberated in combustion with sodium peroxide and the writer has found

* This Journal, xxiv, 134.

† Thomsen, Thermochemische Untersuchungen, ii, 254.

‡ Ibid., iii, 232.

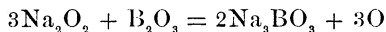
§ C. R., cxxvii, 1449.

|| J. Am. Chem. Soc., xxix, 1606.

that it is necessary to allow for oxygen taken up or set free. The correction of 1.2° for 1 milligram is based on the heat of formation of sodium peroxide from the oxide which according to deForcrand* is 19390° . For oxygen liberated there is a loss of heat which is to be added, and for oxygen absorbed the gain is to be subtracted from the heat observed. The best way to find the change in the oxygen content of the bomb is to connect it after a combustion with a manometer. To avoid excessive detail in the data given of the work only the heat equivalent of the oxygen liberated or taken up is stated. Most of the work was done with a bomb of 500^{cc} capacity and in the work on chromium the oxygen correction was large. To obviate the correction or make it insignificant a sterling silver bomb of 100^{cc} capacity was made. It proved to be admirably adapted for calorimetric work with sodium peroxide. The water equivalent of this bomb and calorimeter can was 109° . The large bomb was used in the experiments in which the water equivalent was over 3200 grams, and the small one in those in which it was less than 3100 grams. When a molten mass is in contact with the cold bomb it solidifies at once and the combustion is not complete. Hence it is better to put the peroxide mixture into a thin silver cup which is in contact with the inner surface of the bomb at only a few points. In order to make ignition certain the bomb was filled with oxygen, as it was found that with air in it the burning iron often failed to start the combustion. The carbon used is the finely divided form made from acetylene and the heat effect of its reaction with sodium peroxide is taken as 11100° † per gram of carbon. The carbon gives the temperature needed to effect the combustion of other substances and also reduces the peroxide to the sodium oxide required in the reaction with an acidic oxide. The initial temperature of the experiments was between 18° and 19° .

Boric Oxide.

The heat effect of the combination of boric oxide with sodium oxide has been determined. The oxide used in the experiments, made by fusing boric acid in a platinum dish, was pulverized and weighed in a stoppered bottle. It was exposed to the air as short a time as possible on account of its hygroscopic character. The reaction of boric oxide on an excess of sodium peroxide yields the orthoborate thus :



No perborate results, as shown by the following experiment :

* C. R., cxxvii, 574.

† This Journal, xix, 434.

A mixture of 1.314 gram of boric oxide and 5 grams of sodium peroxide was heated in an ignition-tube. The loss in oxygen was 0.950 gram; calculated 0.901 gram. Were perborate only formed no oxygen would have been liberated, and if metaborate was the product only one-third as much oxygen would have been set free.

Experiments.

	1	2	3	
Boric oxide	1.269	1.858	1.8862	grams
Carbon	0.661	1.080	1.0384	"
Sodium peroxide	15.	20.	20.	"
Water equivalent of system	3435.	3465.	3431.	"
Temperature interval.	2.679°	4.280°	4.149°	
Heat observed	9202°	14830°	14235°	
Heat of oxidation of carbon	—7337°	—11988°	—11526°	
Heat of oxidation of iron for ignition	—80°	—64°	—80°	
Heat absorbed by oxygen given off	+96°	+60°	+131°	
	<hr/> 1881°	<hr/> 2838°	<hr/> 2760°	
For 1 gram of B_2O_3 uniting with sodium oxide	1482°	1522°	1463°	

The three results are respectively 1482°, 1522°, and 1463°. The average is 1489 for 1 gram and 104200° for a gram molecule of boric oxide reacting with sodium oxide to form sodium orthoborate.

Note on Boron.—The only thermal data on boron are those of Troost and Hautefeuille* and Berthelot,† who determined the heat of formation of boron trichloride and tribromide and the reaction of these halides with water, and from the results they calculated the heat of formation of the trioxide. Since they give no analysis of the boron used, the purity of it is doubtful. Moreover, Moissan‡ has shown that boron prepared by reducing the oxide with sodium or magnesium is not pure. He removed the magnesium which the impure boron contained by fusion with boric oxide, taking precautions to prevent formation of nitride. It may be added that while at work on boron it was learned that another investigator, whose results are not published, considers that none of the methods described in the literature yield pure boron. Some of the observations of the writer in regard to the burning of boron are interesting and

* Ann. Ch. Phys. (5), ix, 74.

† Ann. Ch. Phys. (5), xv, 215.

‡ Ann. Ch. Phys. (7), vi, 296.

may be briefly stated. When a mixture of impure boron and carbon was burned in oxygen under pressure the boric oxide produced volatilized and condensed as a fine white powder, and considerable boron carbide was formed. Impure amorphous boron and also crystalline boron containing aluminum reacted with explosive violence with sodium peroxide. The heat of oxidation of boron may, therefore, be easily found by the peroxide method when pure boron is available.

Aluminium Oxide.

The amorphous oxide used was prepared by igniting a powdery form of hydroxide. For crystalline oxide, crystals of corundum were taken. These were pulverized in a steel mortar, the powder digested with hydrofluoric acid, then sulphuric acid was added and the mixture heated until fumes of the latter acid escaped. Then the oxide was washed. It was white and was found to be free from lime, iron and silica, and to contain a trace of magnesia. Both preparations were floated in water and only the more finely divided portions retained. In order to determine the alumina remaining after a combustion the silver vessel containing the solid product was placed in half a liter or liter of cold water. The fusion dissolved rapidly owing to the presence of sodium peroxide. After solution the silver piece was removed and an excess of nitric acid added and the alumina filtered off. It was washed first with water and then with ammonia to remove any silver chloride present. This residue of alumina was deducted from that taken for an experiment. There is nothing in the literature regarding the solubility of ignited alumina in alkaline solutions other than the statement that the more intensely the oxide is heated the slower it is taken up by alkalis. In order to learn if the residue of alumina mentioned in the experiment is likely to dissolve so as to cause an error, the following tests were made with finely divided alumina which had been heated in a platinum crucible over a large blast lamp. In one test 4 grams of alumina and 20 grams of sodium peroxide were mixed and about 400° of hot water were slowly poured upon the mixture. The violent reaction between the peroxide and water gave at once a boiling concentrated solution of sodium hydroxide. After a few minutes an excess of nitric acid was added and the solution filtered. The alumina found in the filtrate was 2.5 per cent of the quantity taken. In another test about the same quantities of the mixed oxides were added to the surface of warm water. In this case no alumina went into solution. Since the solid residues from the combustions were chiefly sodium carbonate and aluminate, and contained much less sodium peroxide

and alumina than used in the tests mentioned, it is evident that any error due to solubility of alumina is insignificant. Moreover, varying portions of sodium peroxide do not affect thermal results.

Experiments.

	1	2
Aluminium oxide (amorphous)	3.357 grams	4.313 grams
“ “ in residue..	—0.026 “	—0.160 “
“ “ reacting ---	3.331 “	4.153 “
Carbon	1.218 “	1.294 “
Sodium peroxide.....	21. “	25. “
Water equivalent of system..	3528. “	3559. “
Temperature interval.....	4.245°	4.479°
Heat observed.....	14977°	15941°
“ of oxidation of carbon..	—13520°	—14863°
“ “ “ “ iron ----	—60°	—60°
	1397°	1518°
For 1 gram of amorphous alumina		
combining with sodium oxide	419°	365°
	3	4
Aluminium oxide (crystalline)	4.517 grams	4.038 grams
“ “ in residue..	—1.174 “	—0.854 “
“ “ reacting ---	3.343 “	3.184 “
Carbon	0.809 “	0.814 “
Sodium peroxide.....	17. “	17. “
Water equivalent of system..	3087. “	3036. “
Temperature interval.....	3.225°	3.355°
Heat observed.....	9956°	10185°
“ of oxidation of carbon..	—3979°	9035°
“ “ “ “ iron ----	—32°	—64°
	945°	1086°
For 1 gram of crystalline alumina	283°	310°

In experiment 3 the pressure in the bomb was 16^{cm} higher after the combustion than before, and the calculated correction for the oxygen set free was 30°. This is not included in the result above, as changes in pressure were not observed in experiments 1, 2 and 4 with alumina. In experiments 3 and 4 about two-thirds as much carbon was used as in 1 and 2. In order to find if the ratio of the carbon to the alumina influences the result, a calorimetric test was made in which the amounts of carbon and amorphous alumina were nearly the same as in experiments 3 and 4. The result was the same as in 1 and 2, as shown in the following experiment :

Experiment 5.

Aluminium oxide (amorphous)	4.237 grams
“ “ in residue	—0.195 “
“ “ reacting	4.042 “
Carbon	0.778 “
Sodium peroxide	14.
Water equivalent of system	2947.
Temperature interval	3.484°
Heat observed	10267°
“ of oxidation of carbon	—8635°
“ “ “ “ iron	—64°
	<hr/>
	1568°
For 1 gram of amorphous alumina	388°

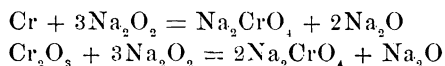
In the reaction, $2\text{Na}_2\text{O}_2 + \text{C} = \text{Na}_2\text{CO}_3 + \text{Na}_2\text{O}$, 1 part of carbon produces 5 parts of sodium oxide. In the formation of sodium metaluminate according to the equation, $\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} = 2\text{NaAlO}_2$, the ratio of the quantities of the oxides is 1 to 0.6, while for the formation of the orthoaluminate three times as much sodium oxide is required. The following table of results, giving the calories evolved for one gram of alumina and the ratio of the alumina to the sodium oxide, shows that sodium orthoaluminate could not have been formed in experiments 3, 4 and 5, as there was not sufficient sodium oxide produced to form it. It should be noted in this connection that too little oxygen was set free in the combustions to indicate any material difference in the quantity of sodium oxide formed.

No. of Exp.	Calories for 1 gram Al_2O_3	C	Al_2O_3	Na_2O formed	Na_2O required to form	
					NaAlO_2	Na_3AlO_3
1	419	1.2	3.3 (amor.)	6.	2.	6.
2	365	1.3	4.2 “	6.5	2.5	7.6
3	283	0.8	3.3 (crys.)	4.	2.	6.
4	310	0.8	3.2 “	4.	2.	6.
5	388	0.8	4. (amor.)	4.	2.4	7.2

It is evident that the chief product in the reactions is sodium metaluminate, but possibly mixed with other aluminates. Assuming that the reaction was essentially the same in all of the combustions, we have for the heat of combination of 1 gram of amorphous alumina with sodium oxide a mean of experiments 1, 2, and 5 of 390°, and for a gram molecule 40,000°. For crystalline alumina it is 30,000°. Hence the transformation of the amorphous alumina into the crystalline form is accompanied with the heat effect of 10,000°.

Chromium.

The thermal constants of chromium are of considerable importance. In Landolt and Bernstein's *Physikalisch-Chemische Tabellen*, p. 439, the statement is made: Die Bildungswärme der Chromverbindungen kann nicht angegeben werden, weil keine Reaction untersucht wurde, an der metallische Chrom theilhaftig ist. Then, too, it is an interesting element to study, forming basic and acidic oxides, both of which yield stable salts. Since chromium and its sesquioxide do not burn in oxygen, it is necessary to resort to indirect methods in determining the thermal constants of chromium compounds. This has been done in solutions by Thomsen, Berthelot, and others. The sodium peroxide method is a better one, and the reactions are



No perchromate is formed as shown by the following result: A mixture of two grams of chromium trioxide and 6 grams of sodium peroxide was placed in an ignition tube closed with a calcium chloride tube to absorb escaping water. On heating gently the mixture glowed. The loss in weight was 0.386 gram; calculated 0.32 gram. If perchromate had been formed, less oxygen would have been given off. Moreover, it is improbable that sodium perchromate can exist in a molten mass containing sodium oxide.

To Dr. C. H. Mathewson I am indebted for a fine specimen of crystalline chromium made at the Goldschmidt factory. The metal was pulverized in a steel mortar and the powder was digested with hydrochloric acid to remove the iron. Analysis proved it to be free from aluminium and silicon and to contain 0.7 per cent of iron. The last may have been from the mortar. Metallic chromium as a very fine powder will undoubtedly burn readily with sodium peroxide, but heat was necessary to effect the reaction with that used, and carbon was therefore added to the mixtures. After a combustion the product was dissolved in water, the solution made acid with nitric acid and the metal remaining was separated and weighed.

Experiments.

	1	2	3
Metal taken	2.000	2.5000	2.500 grams
“ unburned	0.061	0.0043	0.021 “
“ burned	1.939	2.4957	2.479 “
Chromium	1.925	2.4782	2.4615 “
Iron	0.014	0.0175	0.0175 “
Carbon	0.2456	0.3767	0.3800 “
Sodium peroxide	20.	20.	20.5 “
Water equivalent of system	3428.	3514.	3487. “
Temperature interval	2.601°	3.510°	3.520°

	1	2	3
Heat observed.....	8916°	12334°	12274°
“ oxidation of carbon..	—2726°	—4181°	—4218°
“ “ “ iron in			
metal and for ignition	— 94°	— 90°	— 92°
“ due to oxygen absorbed	—288°	—492°	—472°
	<hr/>	<hr/>	<hr/>
	5808°	7571°	7492°
For 1 gram of chromium burn- ing with sodium peroxide..	3012°	3055°	3044°

In the experiments 1, 2, and 3 a bomb of 500^{cc} capacity was used. As the correction for oxygen absorbed was large, a determination was made with the 100^{cc} bomb. The residue insoluble in nitric acid was collected on a Gooch filter, dried and its weight found. Next the carbon was burned off, and finally the weight of unburned chromium was obtained. The pressure in the bomb was 29^{cm} less after the combustion than before.

Experiment 4.

Metal taken	02·0520 grams
“ unburned	·0015 “
“ burned	2·0505, “
Chromium	2·0361 “
Iron	0·0143 “
Carbon taken.....	0·3161 “
“ unburned	0·0017 “
“ burned	0·3144 “
Sodium peroxide.....	15· “
Water equivalent of the system.....	2984· “
Temperature interval.....	3·282°
Heat observed	9793°
“ of oxidation of carbon.....	—3489°
“ “ “ “ iron in metal.....	—23°
“ “ “ “ “ for ignition..	—26°
“ due to oxygen absorbed	—52°
	<hr/>
	6203°
For 1 gram of chromium	3046°

Evidently the correction made for oxygen taken up in the first three experiments was correct. The results are 3012°, 3055°, 3044°, and 3046°. In the first one the correction for oxygen was not made with the care that it was in the others, and hence it is better not to include it in the final value. The mean of the other figures is 3048° for the reaction of 1 gram of crystalline chromium with sodium peroxide, and for 52·1 grams it is 158800°.

Chromium Sesquioxide.

Amorphous chromium sesquioxide was prepared by heating an hydroxide. The crystalline oxide was made according to Ditte's* method of melting together equal parts of pure potassium dichromate and sodium chloride until the evolution of oxygen ceased. After cooling, the soluble portion of the product was dissolved in water and the crystalline powder obtained, washed, digested with hydrochloric acid and washed again. The crystals were so small that some passed through filter paper. Under the microscope they appeared unmixed with any amorphous substance. Tested by the spectroscope the preparation proved to be free from sodium and potassium. The following results show the heat of the reaction between chromium sesquioxide and sodium peroxide :

Experiments.

	1	2	3	4
Chromium sesquioxide.....	4.236	3.831	7.436	6.576 grams
“ “ unburned ..	0.062	0.018	0.805	0.097 “
“ “ burned ..	4.174	3.813	6.631	6.479 “
Carbon	0.516	0.456	0.4015	0.425 “
“ not burned.....	0.007	0.006	0.151	0.012 “
“ burned	0.509	0.450	0.2505	0.413 “
Sodium peroxide	17.	15.	21.	20. “
Water equivalent of system ...	2828.	2902.	2936.	3077. “
Temperature interval	3.047°	2.703°	2.922°	3.038°
Heat observed	8623°	7844°	7579°	9348°
“ of oxidation of carbon	—5650	—4995	—2780	—4584°
“ “ of iron for ignition	—16	—10	—62	—48°
“ due to oxygen absorbed or evolved.....	—69	—70	+14	—30°
	2888	2769	5751	5686°
For one gram of chromium sesquioxide, reacting with sodium peroxide.....	692	726	867	878°

Crystalline sesquioxide was used in experiments 1 and 2. The results are 692° and 726° and a mean of 709° for the heat of the reaction of 1 gram of crystalline chromium sesquioxide with sodium peroxide. For a gram molecule it is 108000°.

The experiments 3 and 4 were with amorphous sesquioxide. The results are 867° and 878° and the mean is 872° for the heat of the reaction of 1 gram of amorphous chromium sesquioxide with sodium peroxide. For a gram molecule it is 132000°.

* C. R., cxxxiv, 336.

In experiment 3 the considerable quantity of unburned substance is due to the fact that the mixture was in contact with the cold bomb and was not in an inner silver cup.

Chromium Trioxide.

The chromium trioxide was free from sulphuric acid and sufficiently pure for the purpose. It was fused, allowed to cool in a desiccator and then coarsely pulverized. A little sesquioxide remained after a combustion. The amount of trioxide equivalent to it was deducted from the trioxide taken. As the heat of oxidation of the sesquioxide to the trioxide is small the error due to reduction is insignificant. The results following show the heat effect of the combination of chromium trioxide with sodium oxide.

Experiments.

	1	2
Chromium trioxide taken	4.000	4.782 grams
“ “ reduced	0.097	0.176 “
“ “ combined	3.903	4.606 “
Carbon	0.515	0.523 “
Sodium peroxide	10.6	16. “
Water equivalent of system	3408.	3504. “
Temperature interval	2.514°	2.595°
Heat observed	8567°	9093°
“ of oxidation of carbon	—5676	—5805°
“ “ “ iron for ignition	—62	—62°
“ absorbed by oxygen given off	+187	+324°
	<hr/>	<hr/>
	3016	3550°
For 1 gram of chromium trioxide ..	773	771°

The mean of the two results is 772° for 1 gram and for a gram molecule of chromium trioxide it is 77000°.

The heat of formation of the oxides of chromium is derived from the above data, thus:

$3\text{Na}_2\text{O}_2 + \text{Cr} = \text{Na}_2\text{CrO}_4 + 2\text{Na}_2\text{O} + \dots\dots\dots$	158800°
$3\text{Na}_2\text{O} + 3\text{O} = 3\text{Na}_2\text{O}_2 + \dots\dots\dots$	58200°
$\text{Na}_2\text{O} + \text{Cr} + 3\text{O} = \text{Na}_2\text{CrO}_4 + \dots\dots\dots$	217000°
$\text{Na}_2\text{O} + \text{CrO}_3 = \text{Na}_2\text{CrO}_4 + \dots\dots\dots$	77000°
$\text{Cr} + 3\text{O} = \text{CrO}_3 + \dots\dots\dots$	140000°

$3\text{Na}_2\text{O}_2 + \text{Cr}_2\text{O}_3(\text{crys.}) = 2\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{O} +$	108000°
$3\text{Na}_2\text{O} + 3\text{O} = 3\text{Na}_2\text{O}_2 +$	58200°
$2\text{Na}_2\text{O} + \text{Cr}_2\text{O}_3 + 3\text{O} = 2\text{Na}_2\text{CrO}_4 +$	166200°
$2(\text{Na}_2\text{O} + \text{CrO}_3) = 2\text{Na}_2\text{CrO}_4 +$	154000°
$\text{Cr}_2\text{O}_3(\text{crystalline}) + 3\text{O} = 2\text{CrO}_3 +$	12200°
$2(\text{Cr} + 3\text{O}) = 2\text{CrO}_3 +$	280000°
$\text{Cr}_2\text{O}_3(\text{crys.}) + 3\text{O} = 2\text{CrO}_3 +$	12200°
$2\text{Cr} + 3\text{O} = \text{Cr}_2\text{O}_3(\text{crystalline}) +$	267800°
$2\text{Cr} + 3\text{O} = \text{Cr}_2\text{O}_3(\text{amorphous}) +$	243800°
Amorphous $\text{Cr}_2\text{O}_3 =$ crystalline $\text{Cr}_2\text{O}_3 +$	24000°

Thomsen* found for $\text{Cr}_2\text{H}_2\text{O}_6$, O_3 , aq = $2\text{CrO}_3 + 18913^\circ$ and Berthelot† gives Cr_2O_3 precip. + $\text{O} + \text{ean.} = 2\text{CrO}_3$ crys. + 16400° . The changes in the oxidation of the hydroxide are different from those in case of the oxide and hence the above results can not be compared with that of the writer. They all, however, show that the heat of formation of chromium trioxide from the sesquioxide is small. Berthelot† derived from reactions in solution the following: $\text{CrO}_3 + \text{K}_2\text{O} = \text{K}_2\text{CrO}_4 + 47800^\circ$. This appears to be too low when considered in connection with the 77000° found for $\text{Na}_2\text{O} + \text{CrO}_3 = \text{Na}_2\text{CrO}_4$, since the heat of formation of potassium salts is commonly greater than that of sodium salts.

Tungsten.

Metallic tungsten used in the work was prepared by reducing the oxide with dry hydrogen at the highest temperature attainable in a gas combustion furnace. Even after ten hours a little water came off, showing that the reduction was not complete. During the first hours occupied in the reduction a little ammonia was formed from the atmospheric nitrogen contained in the hydrogen, but the reduced metal was free from nitrogen. The test was made by heating a mixture of the metallic powder and soda-lime. No ammonia was given off. The tungsten present in the metallic state was determined by finding the increase in weight when a weighed amount of the metal was oxidized by heating in air and finally in oxygen. The tungsten equivalent to the oxygen taken up was 98.14 per cent. Iron was present to the extent of 0.07 per cent, leaving 1.79 per cent by difference of oxide of tungsten as WO_3 . Undoubtedly only the lower oxides were present and there

* Thermochemische Untersuchungen, ii, 464.

† Thermochemie, ii, 272.

‡ Ann. Ch. Phys. (6), i, 195.

was less than 98 per cent of metallic tungsten in the preparation, but the lower oxides give heat when oxidized. Hence we may assume without essential error that the thermal effect is proportional to the amount of tungsten, which is equivalent to the amount of oxygen taken up. After each calorimetric experiment the product in the bomb was dissolved in water and the small residue remaining was separated. It dissolved completely in nitric acid, showing that no metallic tungsten remained. The following experiments give the heat of burning tungsten in sodium per oxide:

Experiment 1.

Tungsten $8.241 \times 0.9814 =$	8.088 grams
Water equivalent of system.....	3596. "
Sodium peroxide.....	21. "
Temperature interval.....	2.859°
Heat observed $3596 \times 2.8593 =$	10281°
" of oxidation of iron in tungsten and used for ignition	-157°
	<hr/>
	10124°
For 1 gram of tungsten.....	1252°

Experiment 2.

Tungsten $8.563 \times 0.9814 =$	8.377 grams
Water equivalent of system.....	3552. "
Sodium peroxide.....	25. "
Temperature interval.....	3.020°
Heat observed $35523 \times 0.2 =$	10727°
" of oxidation of iron in tungsten and used for ignition.....	-125°
	<hr/>
	10602°
For 1 gram of tungsten.....	1267°

The average is 1260° for 1 gram and 231200° for 184 grams.
For the heat effect of $\text{Na}_2\text{O} + \text{WO}_3$ we have

$3\text{Na}_2\text{O}_2 + \text{W} = \text{Na}_2\text{WO}_4 + 2\text{Na}_2\text{O} + \dots$	231800°
$3\text{Na}_2\text{O} + 3\text{O} = 3\text{Na}_2\text{O}_2 + \dots$	58200°
	<hr/>
$\text{Na}_2\text{O} + \text{W} + 3\text{O} = \text{Na}_2\text{WO}_4 + \dots$	291000°
$\text{W} + 3\text{O} = \text{WO}_3 + \dots$	196300°*
	<hr/>
$\text{Na}_2\text{O} + \text{WO}_3 = \text{Na}_2\text{WO}_4 + \dots$	94700°

* Delépine et Hallopeau, C. R., cxxix, 600.

Summary.

$3\text{Na}_2\text{O} + \text{B}_2\text{O}_3 = 2\text{Na}_3\text{BO}_3 + \dots\dots\dots$	104200°
$\text{Na}_2\text{O} + \text{Al}_2\text{O}_3(\text{amorphous}) = 2\text{NaAlO}_2 + \dots\dots\dots$	40000°
$\text{Na}_2\text{O} + \text{Al}_2\text{O}_3(\text{crystalline}) = 2\text{NaAlO}_2 + \dots\dots\dots$	30000°
$\text{Al}_2\text{O}_3(\text{amorphous}) = \text{Al}_2\text{O}_3(\text{crystalline}) + \dots\dots\dots$	10000°
$\text{Na}_2\text{O} + \text{CrO}_3 = \text{Na}_2\text{CrO}_4 + \dots\dots\dots$	77000°
$\text{Cr} + 3\text{O} = \text{CrO}_3 + \dots\dots\dots$	140000°
$2\text{Cr} + 3\text{O} = \text{Cr}_2\text{O}_3(\text{amorphous}) + \dots\dots\dots$	243800°
$2\text{Cr} + 3\text{O} = \text{Cr}_2\text{O}_3(\text{crystalline}) + \dots\dots\dots$	267800°
$\text{Cr}_2\text{O}_3(\text{crystalline}) + 3\text{O} = 2\text{CrO}_3 + \dots\dots\dots$	12200°
$\text{Cr}_2\text{O}_3(\text{amorphous}) + 3\text{O} = 2\text{CrO}_3 + \dots\dots\dots$	36200°
$\text{Na}_2\text{O} + \text{WO}_3 = \text{Na}_2\text{WO}_4 + \dots\dots\dots$	94700°

The results given have been obtained with substances at hand and it is the intention to complete the work as far as possible on the fourth, fifth, and sixth groups.