Art. II.—*Calorimetry by Combustions with Sodium Peroxide;*

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

Fusion with sodium peroxide is the only way known for finding the heat of oxidation of elements which do not burn in oxygen and which form oxides insoluble in acids. The method is adapted to the determination of the heat of formation of the oxides of a metal and also the heat of combination of metallic oxides with sodium oxide. The writer has used the method the past ten years and can now describe it more completely than was done in any of his papers.

The method is indirect and the heat effect sought is not the observed effect; hence burning in condensed oxygen is preferable where possible. For example, when carbon is burned with sodium peroxide the observed heat (x) is the result of the following reaction

$$2Na_2O_2 + C = Na_2CO_3 + Na_2O = x$$

and x equals the heat of formation of carbon dioxide plus the heat of combination of carbon dioxide with sodium oxide and less the heat required to separate two atoms of oxygen from two molecules of sodium peroxide, thus

$$x = C + 2O + (Na_2O + CO_2) - (2Na_2O + 2O)$$

and

$$C + 2O = x - (Na_2O + CO_2) + (2Na_2O + 2O)$$

Moreover, many substances do not give with sodium peroxide sufficient heat to fuse the mixture and hence some readily combustible substance, such as sulphur or carbon, must be added, which gives in many cases the larger part of the total heat effect.

As yet we have only a few results obtained by fusion with sodium peroxide to compare with those by other methods. They are

	Sodium peroxide method		Other methods
$C + 2O = CO_2 +$	96·4*		94·7*
$Ti + 2O = TiO_2$ (amor.)	215·6†	TiO_2(crys.)	218·4†
$3Fe + 4O$	267.5‡		265·2‡
$2Na + S + 4O$	326·7§		328·6‖
$3Na + P + 4O$	451·4		452·4

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* This Journal, xxix, 130 ; ibid., xix, 434.

† Ibid., xxvii, 343.

‡ Ibid., xxxvi, 55.

§ Ibid., xxvi, 125.

‖ Thomsen.

The values for $C + 2O = CO_2 + 94{\cdot}7$, $Ti + 2O = TiO_2$ crys. $+ 218{\cdot}4$ and $3Fe + 4O = Fe_3O_4$(crys.) $+ 265{\cdot}2$ were obtained by combustion in oxygen. The other values are derived and have the mean error of several experiments. Both values for $C + 2O$ are for acetylene carbon. One reason for the higher value found in the sodium peroxide method is this: The carbon and peroxide were mixed in a mortar, thus allowing the peroxide to absorb a little moisture which added to the heat of the fusion. The amorphous TiO_2 used in the experiments which gave 215·6 was heated to redness for an hour. Apparently it has nearly the same heat of formation as the crystalline form. The value 267·5 for $3Fe + 4O$ is derived from the results of fusions of iron, ferrous oxide, ferric oxide and the mineral magnetite respectively with sodium peroxide, and 265·2 was the result of burning iron in oxygen. The result for $2Na + S + 4O$ is derived from the heat of the reaction of sulphur with sodium peroxide and the heats of formation of SO_3 and Na_2O. The value 451·4 for $3Na + P + 4O$ was derived in a similar way. 452·4, given in the Physikalisch-Chemische Tabellen is derived from Berthelot's data.

Sodium peroxide absorbs water rapidly from the air and hence it should be exposed as little as possible as the hydrated peroxide will give more heat with a combustible than the anhydrous. One of two samples which gives off the less oxygen when fused is the better one. The error from water content is small in good peroxide especially when carbon, for example, is added to make a mixture fuse because the heat effect of the carbon has been found for the carbon and peroxide used. The writer has obtained peroxide in pound packages, containing according to the seller 92 to 95 per cent of Na_2O_2. To ensure uniformity in composition four or five pounds are mixed thoroughly in a large stoppered jar. Then it is rapidly placed in about half pound lots in flasks with necks which are narrowed to half an inch. and the necks are drawn off and hermetically sealed. The flasks containing peroxide should be stored in a metal box as a precaution against fire in case of breakage. For convenience in using, the peroxide is put into an eight ounce bottle having a smooth, unground neck with a smooth red rubber stopper.

Various substances may be added to a peroxide mixture to increase the temperature of the fusion. The writer has used successively acetylene carbon, sulphur and lampblack. Pure rhombohedral sulphur in fine powder would appear to be the best of the three, but it becomes electrified when shaken in the bomb with the other ingredients and sometimes sticks to the bomb and is not completely oxidized. Sulphide is formed and occasionally free sulphur is left. When the bomb is much blackened by a fusion with sulphur the heat result is low. Acetylene carbon is the ideal substance to use, but difficult to obtain. It is constant in composition after heating to expel hygroscopic moisture, and any unburned is not dissolved when the fusion is treated with water or acid and may be collected on a Gooch filter and weighed. Commercial lampblack nearly ash free is prepared as follows: It is heated for two or three hours to 1000° or higher, sifted when cool and shaken in a large bottle to ensure uniformity in composition. A portion for a calorimetric experiment is heated in a crucible, best in an electric furnace, until the top of it is a faint red to expel moisture, then allowed to cool in a desiccator. Finally it is quickly weighed and placed in a bomb. As the lampblack changes in composition with the intensity and time of heating, care should be taken to heat the different portions used uniformly. Lampblack gives a quicker combustion, often of explosive violence, than acetylene carbon or sulphur. Thus far the writer has found no lampblack left in fusion with sodium peroxide.

One part of carbon requires 13 parts of pure sodium peroxide for combustion and it is best to take about 20 parts in determining the heat effect of the carbon or lampblack. For the combustion of sulphur double the calculated amount of peroxide should be used. Oxygen is often evolved in a combustion from the action of an acidic oxide on the sodium peroxide and the heat required to set it free from the peroxide is added to the observed heat. This correction, 1·73 g–cal. for 1^{cc} of oxygen at 0° and 760^{mm}, is derived from Beketoff's $Na_2 + O = 100{\cdot}26$ Cal. and de Forcrand's $Na_2 + 2O = 119{\cdot}8$ Cal. The writer has tested and found no carbon dioxide in the oxygen given off in considerable quantities from fusions of mixtures of sodium peroxide, an acidic oxide and lampblack.

It is best to use large quantities of substances in calorimetric determinations, not only because the errors are less, but because a large fusion remains liquid longer than a small one and hence the combustion is more likely to be complete. A mixture of 20 to 50 grams giving a heat effect of 10 to 20 Cal. answers well.

The bomb, fig. 1, is sterling silver. It is 3/32 in. in thickness. The inside diameter at the top is 1 5/8 in., at the bottom 1 4/8 in., and the length not including the top is 3 1/4 in. It is slightly conical for convenience in fitting the expanded top of the cup *a*, to make a dust-tight joint. A fusion in the cup cools more slowly than when in contact with the cold bomb and hence the reaction is more complete. The cup is fine silver and weighs 15 to 30 grams. The top and fittings are brass. The top is 2 3/4 in. in diameter and 5/8 in. thick

Figs. 1 and 2.

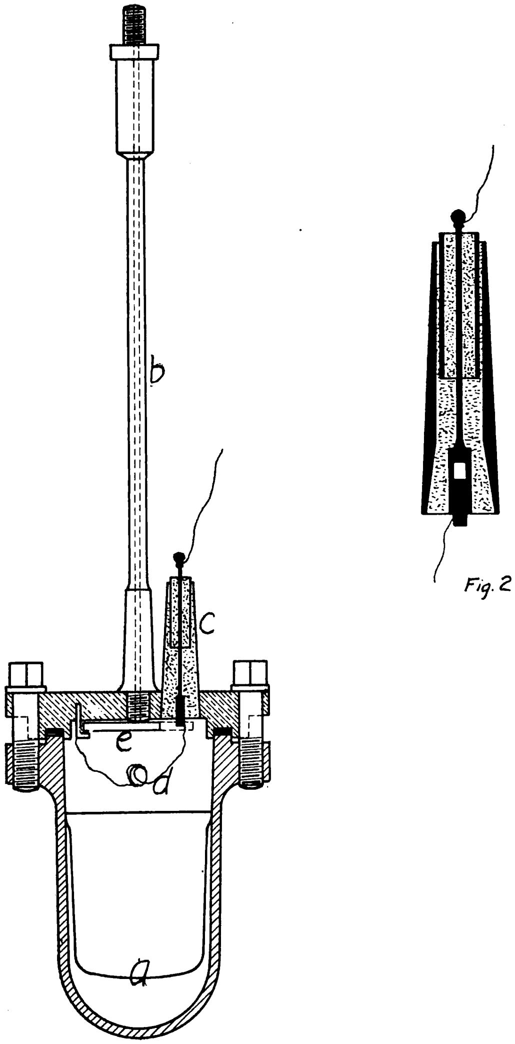


Fig. 2

except the rim which is 1/4 in. The gasket slot in the top is 5/32 in. wide and 1/8 in. deep. It should fit the top of the bomb so that the lead gasket will not flow under pressure. The gasket is easily made by placing a disk of lead 1/25 in. in thickness on the bomb and then pressing the top into place by means of the screws. There are eight screws 5/16 in. in diameter. Four are sufficient except for high pressures. The screws should turn easily with the fingers and are best greased with tallow. A 4 in. solid wrench is a convenient one for tightening them. The tube *b* has a length of 7 1/2 in., including the screw ends. The narrow part of it is 3/16 in. external and 1/20 in. internal diameter. The lower screw joint of *b* is made tight with soft solder, and for the upper one joining the valve shown in the fig. 3 sealing wax answers. The tube *c* is soldered in the tapering hole in the brass top. It is shown full size in fig. 2. The insulated rod in it has a small short tube on the lower end for the plug which fastens the iron wire *d* of fig. 1. The upper end of the tube has a glass tube 1/2 in. in length and is packed with dental phosphate cement. The middle of the tube is filled with a flexible cement of caoutchouc and beeswax, and the rest with phosphate dental cement. To prevent the fusion, in case it is thrown against the top of the bomb, from closing the hole in the tube *b*, it is covered by a thick disk, *e*, of pure silver, which is held in place by three friction lugs. The ignition wire *d* should weigh at least 20 mlg. If less is taken it should be weighted with a bit of silver, otherwise the oxide formed when the iron burns will not drop off into the peroxide mixture.

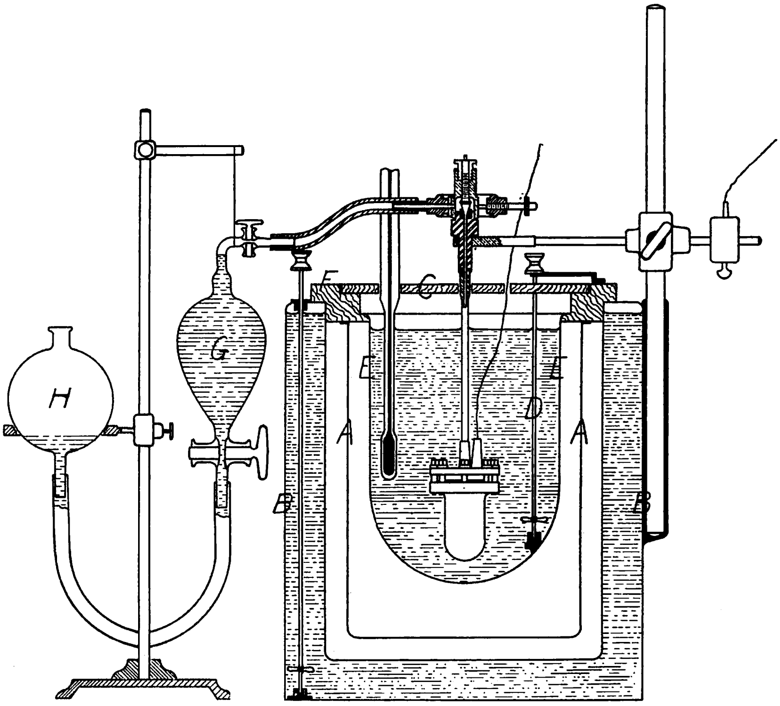
The sterling silver bomb weighed when made 472 grams and after eight years' use 465 grams. The loss is due to corrosion, especially by sulphur, and to polishing. The total weight of the brass work excluding the thick top of the tube *c* is 397 grams. The lead gasket weighs 10 grams. The writer has two nickel-plated German silver cans for holding the water of the calorimeter. The smaller can measures 5 1/2 in. diameter, has a depth 9 1/4 in., and weighs 50·6 grams. The dimensions of the larger one are 6 1/2 in. and 9 1/4 in., and it weighs 51·2 grams.

The water equivalent of a calorimeter and can may be calculated from the specific heats of the metals in it, or may be determined by the method of specific heat. By the latter way 285 and 281·2 grams were obtained for a steel calorimeter and can; calculated 284·7 grams. The specific heat of the metals are quite accurately known, hence a calculated hydro-thermal equivalent of a calorimeter is likely to be more accurate than an experimental one.

* This Journal, xix, 425.

The apparatus shown in fig. 3 is designed for use in a room of varying temperature. A is made of very thin tinned iron (sheet tin) or tin foil, and B is a copper tank, holding in the annular space about 20 liters of water. It is tinned on the surface opposite A, and has one hole in the top for the stirrer, one for a thermometer and another for adding water. The calorimeter can E is supported by the wooden ring F. The cover C is made of two semi-circular pieces of wood. The wooden parts are varnished with shellac. The rod D rests in a cup and is inclined about an inch so that the propeller will give a rotary motion to the water. The bulb G is for collecting gas that may be given off in an experiment. It has a capacity of 500 to 700^{cc} and is connected with the bomb by a small, thick-walled rubber tube and with H by a large rubber tube. Both rubber tubes should be securely fastened by wiring. The lower stop-cock is large so as to allow the water to flow rapidly between the bulbs. If the room and apparatus are colder than desired the latter may be warmed by a lamp flame

FIG. 3.



against B while the water in it is stirred. When the jacket water is rapidly raised 4° or 5° it will be some time before the empty can E is warmed approximately as much. To save time E may be heated by putting into it a closed flask of hot water. If the can E is colder than the water in B when the calorimeter water is cooler than the jacket water, the temperature of the calorimeter may not rise at first and will not rise regularly for some time. And it is better not to let the water in the calorimeter remain long before a combustion on account of loss by evaporation.

Manipulation—The sodium peroxide (weighed in a glass-stopped weighing bottle) and the substance to be burned are placed in the open bomb, which is at once covered with a plate glass cover to keep out moisture from the air. Then the cover is clamped to the bomb by two screws and a wooden piece with a bit of rubber under the middle of it. The ingredients are thoroughly mixed by shaking and then the cover is replaced by the top of the bomb. Before tightening the screws the air is displaced by passing about 200^{cc} of dry oxygen* through the tube *b*, fig. 1. Next the screws are carefully tightened so as not to strain them and the valve is closed. If, however, oxygen from the fusion is to be collected it is left slightly open so that gas may pass slowly. Then the bomb is adjusted as shown in fig. 3, and the required amount of water is poured into the water can. The stirrer is started and the temperature is noted each minute. When it is rising regularly the mixture is ignited by a current passing four 32 candle-power lamps. The temperature usually falls regularly after thirteen minutes and is observed six minutes longer in order to get the rate of fall. Finally the bulb containing the oxygen set free by the fusion is disconnected and the bomb opened and placed in a beaker of water. Rapid evolution of oxygen shows that the mixture contained an excess of peroxide. After the fusion has disintegrated the bomb is removed from the beaker. If an hydroxide insoluble in water is formed it is dissolved by nitric, acetic, or hydrochloric acid as may be best. If some unburned substance remains it is collected on a Gooch filter, washed with water and then ammonia to remove any silver chloride present and its weight is found. If any gas is collected it is brought to atmospheric pressure and known temperature, then the stop-cock of the bulb G, fig. 3, is closed and the rubber tubing removed. The weight of the bulb full of water, less the weight when partly filled with the oxygen collected, equals the number of cubic centimeters of the gas. The weight of the oxygen is found in the usual way.

The silver cup *a*, fig. 1, is usually easily removed from the bomb after an experiment. Sometimes it is necessary to heat

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* Iron wire burned in air does not always ignite the peroxide mixture.

the bomb in order to loosen it. The bomb and cup are cleaned with strong hydrochloric acid, washed and polished. The top is cleaned in the same way but does not require polishing. The silver cup is often partly melted by a sodium-peroxide combustion and a number should be provided. The top of the cup is easily expanded, if desired, by pressing it against the hemispherical bottom of the bomb.

The following experiments* illustrate the use of the sodium-peroxide mixture:

Iron	2·550	1·754	1·754	3·000 grms.
Sulphur	1·500	1·500	1·500	1·500
Sodium peroxide	20·	19·	20·	22·
Water equivalent of system	3080	3078	3188	4108
Temperature interval	4·016	3·573	3·423	3·180°
Heat effect	12369	10998	10912	13063^c
Heat effect of sulphur	− 7905	− 7905	− 7905	− 7860
" " " ignition wire	− 80	− 80	− 60	− 45
	4384	3013	2947	5158
Heat effect of 1 grm. Fe	1719	1718	1680	1719

Ferric oxide	5·403	5·115	5·296 grams
Sulphur	1·500	1·500	1·500
Sodium peroxide	20·	19·	20·
Water equivalent of system	4112	4137	4149
Temperature interval	2·378	2·352	2·353°
Heat effect	9778	9730	9762^c
" " of S	−7860	−7860	−7860
" " " Fe wire	−45	−45	−45
" " " O_2 set free	+80	+31	+82
Heat effect of Fe_2O_3	1953	1856	1939
" " " 1 gram of Fe_2O_3	361	363	366

Pyrite FeS_2	4·011	4·059
Sodium peroxide	24·	24·
Water equiv. of system	4045	4085
Temperature interval	3·301	3·316
Heat effect	13352	13545
" " of iron	−40	−50
" " " FeS_2	13312	13496
" " " 1 grm.	3318	3325

The heats of formation of ferric oxide and pyrite may be derived from the foregoing results. The different heat effects of sulphur given in the tables were found by burning it with the two lots of sodium peroxide used.

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* This Journal, xxxvi, 55, 1913.