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HEATS OF COMBUSTION OF RUBBER AND OF RUBBER-SULPHUR COMPOUNDS

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ABSTRACT

Measurements with a bomb calorimeter have been made of the heats of combustion of samples of rubber purified by various methods, and of compounds of rubber and sulphur containing up to 32 percent sulphur. In the calorimetric combustion experiments on rubber-sulphur compounds, an amount of aqueous Na_2CO_3 or NaOH more than sufficient to react with the products of combustion containing sulphur was placed in the bomb before each experiment in order to obtain a definite final state for the system.

The average value obtained for the heat of combustion of ether-soluble rubber in gaseous oxygen to form gaseous carbon dioxide and liquid water at a temperature of 30°C and a constant pressure of one atmosphere is 45,207 international joules per gram (weight in vacuo). The estimated uncertainty of this value is 0.2 percent. The average values obtained for ether-insoluble and total rubber are lower by 0.9 and 0.4 percent, respectively, than the value for ether-soluble rubber. The samples of ether-insoluble and total rubber contained considerably more ash than those of ether-soluble rubber, and there is some evidence which indicates that the ash does not represent the total inert impurity in the samples. It is possible that if the inert impurity could be determined with greater accuracy the values for the heats of combustion of the different kinds of rubber would be very nearly the same.

The values obtained for the heats of combustion of compounds of rubber and sulphur in gaseous oxygen to form gaseous carbon dioxide, gaseous sulphur dioxide, and liquid water at a temperature of 30°C and a constant pressure of one atmosphere may be represented by the empirical equation:

$$Q_c = 45,200 - 37,823 m$$

where Q_c is the heat of combustion in international joules per gram (weight in vacuo) of compound and m is the mass of sulphur per gram of compound. The average difference between observed values of heat of combustion and values calculated from this equation is 0.1 percent, and the maximum difference is 0.4 percent.

From these data on the heats of combustion of rubber and of rubber-sulphur compounds, and the data of Eckman and Rossini on the heat of combustion of sulphur, the heat of combination of rubber with rhombic sulphur at a temperature of 30°C and a constant pressure of one atmosphere, has been calculated to be 1,881 international joules per gram of sulphur, or 60.3 international kilojoules per mole of sulphur, independent of the percentage of sulphur in the compound. The estimated uncertainty of these values is 15 percent.

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I. INTRODUCTION

The work described in this paper is part of a series of investigations at the National Bureau of Standards to determine the properties of purified rubber and of compounds of purified rubber and sulphur.

Values of the heat of combustion of rubber have been reported by a number of observers, and values of the heat of combination of rubber and sulphur, determined as the difference in the heats of combustion of vulcanized and unvulcanized rubber-sulphur mixtures, have been reported by several observers. The results obtained by the various investigators are not in satisfactory agreement. The values reported in the literature for the heat of combustion of rubber vary over a range of about 4.5 percent, and the two recent sets of data on the heat of combination of rubber and sulphur differ radically, as may be seen from figure 2.

It was thought that these differences might be due, in part at least, to differences in the composition of the rubber, and that more consistent results might be obtained by using purified rubber. The data presented in this paper were obtained on samples of purified rubber and on compounds of purified rubber and sulphur prepared in connection with an investigation of the electrical properties of rubber and rubber-sulphur compounds by Scott, McPherson, and Curtis.¹

II. PREPARATION OF SAMPLES

Two of the samples of purified rubber, designated as samples E₃₉ and E₄₀, were prepared by the method described by McPherson.² Briefly, this consists in digestion of latex with water at a temperature of 190° C, and extraction with water and ethyl alcohol. This process gives a material which is completely and readily soluble in ether. This method of preparation of rubber is designated as "steam purification" in this paper.

The remaining samples of purified rubber were prepared by the method described by Smith, Saylor, and Wing.³ This method involves the use of trypsin for the removal of protein, and is designated as "trypsin purification." It was developed with the aim of preserving the structure of the rubber hydrocarbon as it exists in the latex. Rubber prepared by this method consists of about 75 percent ether-soluble and 25 percent ether-insoluble rubber, and is designated in this paper as "total" rubber. Samples of ether-soluble and ether-insoluble rubber were obtained from trypsin purified rubber by ether extraction. When the two fractions are separated by this method, the insoluble impurities are concentrated in the ether-insoluble fraction.

All of the rubber-sulphur compounds were prepared from steam purified rubber. The specimens used in heat of combustion measurements were vulcanized between aluminum plates for 40 hours at a temperature of 141° C in an autoclave containing carbon dioxide under a pressure of about 3 atmospheres. Details of compounding the rubber and sulphur have been reported by Scott, McPherson,

¹ BS J. Research 11, 173(1933); RP585.

² BS J. Research 8, 751(1932); RP449.

³ BS J. Research 10, 479(1933); RP544.

and Curtis.⁴ The residual uncombined sulphur was less than 0.1 percent of the total compound, except when the total sulphur amounted to 32 percent. In this case uncombined sulphur was present in varying amounts up to 0.8 percent. The effect on the measured heat of combustion of 0.8 percent uncombined sulphur is about 0.05 percent.

III. HEATS OF COMBUSTION

1. APPARATUS AND METHODS

The calorimetric apparatus and methods employed in this work were essentially the same as those used by Jessup and Green,⁵ and are described in the reference cited. The "Illum" bomb used is of the type devised by Parr, and has a capacity of 377 cm³.

Temperatures were measured by means of a platinum resistance thermometer of the calorimetric type described by Sligh,⁶ used in conjunction with the Wheatstone bridge described by Waidner, Dickinson, Mueller, and Harper.⁷

The heat capacity of the calorimeter was determined by several combustions of benzoic acid (National Bureau of Standards Standard Sample No. 39e). The value used for the heat of combustion of the benzoic acid is that recently determined in this laboratory,⁵ namely, 26,419 international joules per gram (weight in vacuo), when the reaction is referred to 25° C, the initial oxygen pressure is 30 atmospheres absolute, and the masses of benzoic acid and water placed in the bomb are each 3 grams per liter of bomb volume. The precision of the heat capacity determinations was about 0.03 percent. Details of the procedure followed in heat of combustion measurements are given in the reference cited.

2. PURIFIED RUBBER

The samples of rubber were contained in a platinum crucible, and burned at constant volume in oxygen under an initial pressure of 30 atmospheres. One cm³ of water was placed in the bomb before each experiment. The oxygen, before being admitted to the bomb, was passed through a tube containing copper oxide heated to about 750° C in order to remove combustible impurities.

The results obtained on samples of purified rubber are summarized in table 1. The value given for each sample is the mean of at least two determinations. The average deviation of the results of individual experiments on any one sample from the mean for that sample is 0.04 percent, and the maximum deviation is 0.14 percent.

⁴ BS J. Research 11, 173(1933); RP585.

⁵ Heat of combustion of benzoic acid, J. Research NBS 13 (October 1934).

⁶ BS Sci. Pap. 17, 49(1921); S407.

⁷ Bul. BS 11, 571(1914); S241.

TABLE 1.—Summary of results on purified rubber

A. STEAM PURIFIED RUBBER

Sample	Heat of combustion at 30° C and a constant pressure of 1 atmosphere	Deviation from mean	Ash	Remarks
E ₄₀	Int. j/g 45, 255	Int. j/g +16	Percent 0.02	Ether-soluble. Do.
E ₃₉	45, 223	-16	.03	
Mean.....	45, 239	-----	-----	

B. TRYPSIN PURIFIED RUBBER

1. Ether-soluble

E _{34B}	45, 225	+39	0.01	Benzol-soluble.
S ₃	45, 239	+53	.14	
E _{41(sol.)}	45, 095	-91	.11	
Mean.....	45, 186	-----	-----	

2. Ether-insoluble

S ₂	44, 942	+154	0.73	Benzol-insoluble.
E _{34D}	44, 457	-331	1.85	
E _{41(insol.)}	44, 965	+177	.64	
Mean.....	44, 788	-----	-----	

3. Total

E ₃₄	45, 039	+4	0.42	E ₃₄ exhausted at 100° C with mercury pump to constant weight. Loss 0.25 percent.
F _{34A}	45, 019	-16	.42	
S ₁	44, 890	-145	.50	9 months after preparation, acetone extracted, kept between aluminum plates.
E ₃₃	45, 030	-5	.16	
E ₄₁	45, 197	+162	.17	
Mean.....	45, 035	-----	-----	

NOTE.—E_{34B} and E_{34D} were prepared from trypsin-purified latex-rubber which had soaked for about 3 months in C₆H₆ in the dark at room temperature.

E_{41(sol.)} and E_{41(insol.)} were prepared directly from E₄₁ by ether extraction without any other solvent treatment.

All trypsin-purified samples were acetone extracted (acetone removed several days in vacuum dessicator) just before final drying previous to making combustion experiments.

Samples S₁, S₂, and S₃ were prepared by W. H. Smith.

The method of calculating the results is illustrated in table 2. The observed heat of combustion at 30° C ($-\Delta U_B$) was reduced by the method described by Washburn⁸ to the difference ($-\Delta U_R$) in the internal energies of the initial and final systems when the rubber and pure gaseous oxygen of the initial system, and the pure gaseous carbon dioxide and pure liquid water of the final system are each under a pressure of 1 atmosphere at 30° C. The heat of combustion at a constant pressure of 1 atmosphere was then calculated by adding to the value of $-\Delta U_R$ the value of $-\Delta(pv)$ for the reaction at a pressure of 1 atmosphere (75 joules per gram of rubber).

⁸ BS J. Research 10, 525(1933); RP546.

TABLE 2.—Calculation of heat of combustion of purified rubber from observed data

Experiment 8

Sample.....	E ₄₀
Method of purification.....	Steam
Initial oxygen pressure.....	30.0 atm
Mass of sample (wt in vacuo).....	1.0072 g
Mass of ash.....	.0002 g
Mass of rubber.....	1.0070 g
Heat evolved.....	45,604. int. joules
Correction for:	
Firing energy.....	-23. int. joules
Formation of HNO ₃	-77. int. joules
Unburned carbon.....	0. int. joules
Heat produced by combustion of rubber.....	45,504. int. joules
Observed heat of combustion (-ΔU _B).....	45,187. int. joules/g
Reduction to <i>p</i> =1 atm.....	-15. int. joules/g
Energy change for reaction at 1 atmosphere (-ΔU _A).....	45,172. int. joules/g
Heat of combustion of ash-free rubber at const. <i>p</i> =1 atm.....	45,247. int. joules/g

After some of the experiments, there remained in the crucible a small quantity (as much as 0.3 mg in some cases) of unburned carbon, the amount of which was determined by weighing. Correction for this unburned carbon was made, using the approximate value 33,000 joules per gram for the heat of combustion of carbon.

The gaseous products of combustion of several samples were examined for carbon monoxide using the method described by Eiseman, Weaver, and Smith.⁹ No carbon monoxide was found even when unburned carbon was left in the crucible.¹⁰

The thermal effect of solution of oxygen in the rubber samples prior to ignition in the combustion experiments was determined as follows: The empty bomb was placed in the calorimeter, the temperature of which was very nearly the same as that of the jacket. Oxygen was then slowly admitted to the bomb through a coil of tubing immersed in the jacket water, and the temperature rise of the calorimeter was measured. The experiment was then repeated with seven 1-gram samples of steam-purified rubber in the bomb. The final oxygen pressure in the bomb was 30 atmospheres in each experiment. The valve which controlled the flow of oxygen was located between the oxygen supply tank and the coil of tubing which was immersed in the jacket water, so that practically all of the throttling of the oxygen took place before it entered this coil. Corrections were applied for heat interchange between calorimeter and jacket and for heat of stirring of the water in the calorimeter. The results obtained with rubber in the bomb were corrected to take account of the smaller volume available for the oxygen, and for the increased heat capacity of the system due to the presence of the rubber. The finally corrected temperature rise of the calorimeter in the experiments with the empty bomb was the same, within the limits of the precision of the measurements, as the corrected temperature rise in the experiments in which rubber was placed in the bomb. This indicates that there is no appreciable thermal effect arising from solution of oxygen in the rubber. The precision of the measurements, as indicated by the reproducibility of the results, was sufficiently high to detect an effect which would have caused an error of 0.01 percent in the measured heat of combustion of the rubber.

⁹ BS J. Research 8,669(1932); RP446.¹⁰ The tests for carbon monoxide were made by C. Creitz.

Table 1 shows that the data on ether-soluble rubber are fairly concordant, although the result for sample E₄₁(sol.), is about 0.3 percent lower than the average for the other four samples. For the total and the ether-insoluble rubbers the agreement is not so good, the spread of the results being 0.7 percent and 1.1 percent, respectively.

Although the data given in table 1 are corrected for the observed ash contents of the various samples, there is some indication that the ash does not represent the total inert impurity in the rubber, and that the differences in the observed heats of combustion of the different samples of rubber are due to this fact. If the observed heats of combustion of the various samples are plotted against the observed ash contents, the points lie approximately on a straight line as shown in figure 1. The curve indicates that the heat of combustion of a

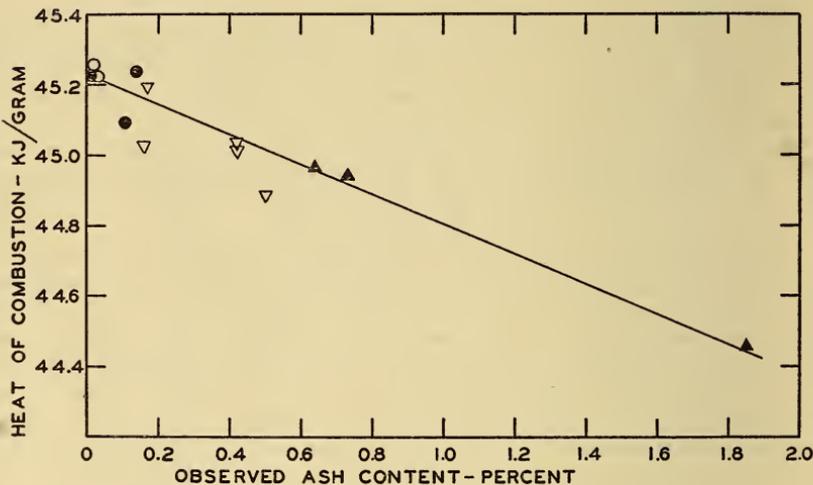


FIGURE 1.—Observed heat of combustion of purified rubber plotted against observed ash content.

- Steam-purified, ether-soluble.
- Trypsin-purified, ether-soluble.
- ▽ Trypsin-purified, total.
- ▲ Trypsin-purified, ether-insoluble.

sample containing p percent ash is lower by about p percent than that of a sample containing no ash. This might be explained by assuming that the inert impurity consists of approximately equal parts by weight of volatile and nonvolatile materials. The observed ash content would then be only half of the total inert impurity in the sample of rubber.

Two or three determinations of benzol-insoluble matter in several samples of rubber were in satisfactory agreement with the ash determinations. This fact does not necessarily prove that the above assumption in regard to volatile inert impurity is incorrect, since such impurity might be both volatile and soluble in benzol. It is possible that if the inert impurity could be determined with greater accuracy, the values obtained for the heats of combustion of the different kinds of rubber would be very nearly the same.

The differences between the results for the various samples may also be partly due to chemical combination of ash or of oxygen with

the rubber. It would be very desirable to investigate these various possibilities further, but it has not yet been possible to carry out this work.

The consistency of the results for samples of ether-soluble rubber prepared in different ways indicates that the average value for the heat of combustion of this material, 45,207 international joules per gram (weight in vacuo) at a temperature of 30° C and a constant pressure of 1 atmosphere, is not in error by more than 0.2 percent.

If the atomic weights of carbon and hydrogen are taken as 12.00 and 1.0078, and if it is assumed that rubber is the compound $(C_5H_8)_x$, the value obtained for the heat of combustion of ether-soluble rubber at a temperature of 30° C and a constant pressure of 1 atmosphere is $(3,077 \pm 6)x$ international kilojoules per mole.¹¹ The temperature coefficient of the heat of combustion is so small that this figure is practically unchanged by reduction to 25° C.

Using this value for the heat of combustion of rubber, and the values given in table 4 for the heats of formation of CO₂ and water, the heat of formation of ether-soluble rubber, at a temperature of 25° C and a constant pressure of 1 atmosphere, from gaseous hydrogen and carbon in the form of diamond is found to be $(42 \pm 6)x$ international kilojoules per mole of $(C_5H_8)_x$.

3. RUBBER-SULPHUR COMPOUNDS

The first two experiments on rubber-sulphur compounds were performed in the same way as the experiments on purified rubber, except that 10 cm³ of water were placed in the bomb to absorb the products of combustion containing sulphur. Examination of the products of combustion showed that part of the sulphur had been oxidized to SO₂ and part to SO₃, and that about half of the SO₃ was in the liquid and half in the gas phase. As it was not known how much water was associated with the SO₃ in the gas phase, it was not possible to calculate from the observed results, the heat of combustion of the sample corresponding to any definite final state.

In each of the next three experiments, slightly more than enough normal solution of NaOH was placed in the bomb to combine with the products of combustion containing sulphur. In the remaining experiments, pure sodium carbonate was placed in the bomb, the amount being 5 to 10 percent in excess of that required to combine with the products of combustion containing sulphur. The sodium carbonate was dissolved in distilled water, the amount of water varying from 2 to 20 cm³ in the various experiments. The combustion was carried out in the same manner as for purified rubber. The time required to reach a steady state after the combustion was from 40 to 60 minutes in the experiments on rubber-sulphur compounds, as compared with 4 or 5 minutes when purified rubber was burned.

Tests showed that when a solution of NaOH or Na₂CO₃ was placed in the bomb before an experiment, the washings from the bomb after combustion contained only Na₂SO₄, NaNO₃, and a little NaHCO₃ formed by reaction of CO₂ and water with the excess NaOH or Na₂CO₃. No Na₂SO₃ was found in the bomb washings, although when no NaOH or Na₂CO₃ was placed in the bomb, some SO₂ was

¹¹ Values given for the uncertainty of data obtained in this investigation are based partly on the consistency of the data and partly on estimates of the probable effect of systematic errors.

found. A possible explanation of this is that minute traces of copper may have acted as a catalyst in increasing the velocity of oxidation of Na_2SO_3 to Na_2SO_4 . It has been shown by Titoff¹² and by Mack, Osterhof, and Kramer¹³ that the velocity of this reaction is greatly increased by very small amounts of copper.

The amounts of Na_2SO_4 , NaNO_3 , and NaHCO_3 in the bomb washings were determined for each experiment as follows: The washings were filtered, evaporated to dryness on the steam bath, dried 2 hours at 150°C , and the residue weighed. The residue was then dissolved in distilled water to make 100 ml of solution. Ten ml of this solution were evaporated to dryness and used to determine the nitrate by the phenoldisulphonic acid method used in water analysis. The remaining solution, containing in addition to the substances mentioned above a little Na_2CO_3 formed by decomposition of the NaHCO_3 in drying, was titrated with $N/100$ acid and the phenolphthalein and methyl orange end-points recorded. From the data obtained, the amounts of Na_2CO_3 , NaHCO_3 , and NaNO_3 were calculated, and the amount of Na_2SO_4 found by difference. The amount of NaHCO_3 reported was the amount found plus the NaHCO_3 equivalent of the Na_2CO_3 found.

TABLE 3.—*Calculation of the heat of combustion of a rubber sulphur compound*

Experiment 10	
Sample.....	$E_{25}-26$
Initial oxygen pressure.....	30.1 atm
Mass of water in bomb.....	20.0 g
Mass of Na_2CO_3	1.066 g
Mass of Na_2SO_4	1.1514 g
Mass of NaHCO_3	0.3116 g
Mass of NaNO_3	0.0023 g
Mass of sample.....	1.0020 g
Mass of ash.....	.0005 g
Mass of compound, m	1.0015 g
Mass of sulphur.....	.2599 g
Mass of C_8H_87416 g
Percent sulphur.....	25.95
$-m \Delta U_B$	38, 140. int. joules
q_1	23. int. joules
$-\Delta U_D$	38. int. joules
$-\Delta U_{O_{25}}$	7. int. joules
$-\Delta U_{\text{Na}_2\text{SO}_4}$	2, 689. int. joules
$-\Delta U_{\text{NaHCO}_3}$	57. int. joules
$-\Delta U_{\text{NaNO}_3}$	2. int. joules
$-m \Delta U_B$	35, 324. int. joules
$-\Delta U_B$	35, 271. int. joules/g
$-\Delta(pv)$	57. int. joules/g
Q_c	35, 328. int. joules/g

Table 3 illustrates the method used in calculating the heats of combustion of the rubber-sulphur compounds when Na_2CO_3 was used to react with the products of combustion of the sulphur. The item, $-m\Delta U_B$, in this table is the heat evolved in the actual bomb process when m grams of rubber-sulphur compound are burned, the initial system consisting of the solid compound, gaseous oxygen containing a small amount of nitrogen, and a liquid aqueous solution of Na_2CO_3 and oxygen, all at 30°C and under a pressure of 30 atmospheres; and the final system consisting of a gaseous mixture of oxygen and carbon dioxide, and a liquid solution of O_2 , CO_2 , Na_2SO_4 , NaHCO_3 , and NaNO_3 , all at 30°C and under the pressure existing in the bomb

¹² Z. Physik. Chem. 45, 641 (1903).¹³ J. Am. Chem. Soc. 45, 617 (1923).

at the end of the experiment. The quantity, $-m\Delta U_R$, is the internal energy of the initial system minus that of the final system when the initial system consists of the solid rubber-sulphur compound and gaseous oxygen, both at 30° C and under a pressure of one atmosphere; and the final system consists of liquid water, gaseous CO₂, and gaseous SO₂, each at 30° C and under a pressure of 1 atmosphere. The heat of combustion of the compound at constant pressure of 1 atmosphere (Q_C) is obtained by adding to $-\Delta U_R$ the value of $-\Delta(pv)$, the difference in the product of pressure and volume of the initial and final systems at 30° C and a pressure of 1 atmosphere.

The value of $m\Delta U_R$ is obtained from that of $m\Delta U_B$ by means of the relation

$$m\Delta U_R = m\Delta U_B - (-q_1 + \Delta U_D + \Delta U_{Gas} + \Delta U_{Na_2SO_4} + \Delta U_{NaHCO_3} + \Delta U_{NaNO_3}) \quad (1)$$

where the first 3 terms in parentheses are defined as follows:

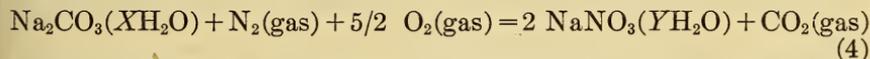
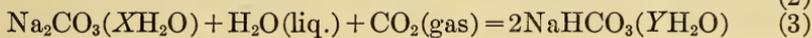
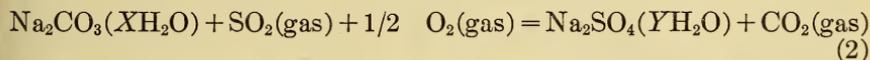
q_1 = the energy used in firing the charge.

ΔU_D = the increase in internal energy of the system due to solution of CO₂ in the aqueous solution in the bomb at the end of the experiment.

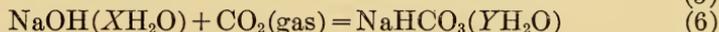
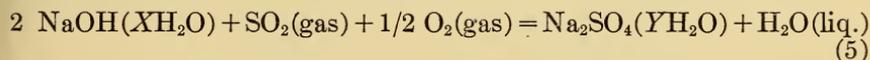
ΔU_{Gas} = the increase in internal energy for the reaction which takes place in the bomb minus the increase in internal energy for a reaction identical with that which takes place in the bomb except that the gaseous oxygen of the initial system and the gaseous oxygen and carbon dioxide of the final system are each at 30° C and under a pressure of 1 atmosphere.

The values of ΔU_D and ΔU_{Gas} were calculated by the methods given by Washburn,¹⁴ with such modifications as were necessary on account of the fact that the material burned contained sulphur in addition to carbon and hydrogen.

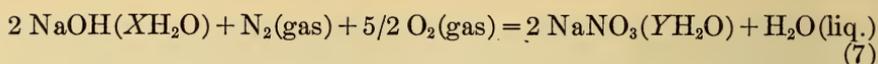
The items $\Delta U_{Na_2SO_4}$, ΔU_{NaHCO_3} , and ΔU_{NaNO_3} are defined differently depending on whether Na₂CO₃ or NaOH was placed in the bomb to react with the products of combustion of the sulphur. If Na₂CO₃ was placed in the bomb, these items are the internal energies of the final systems minus those of the initial systems in the following reactions, respectively:



If NaOH was placed in the bomb, the items $\Delta U_{Na_2SO_4}$, ΔU_{NaHCO_3} , and ΔU_{NaNO_3} are respectively, the internal energies of the final systems minus those of the initial systems in the following reactions:



¹⁴ BS J. Research 10, 525(1933); RP546.



In all the reactions 2 to 7 inclusive, each of the reactants and products is under a pressure of 1 atmosphere at 30° C, and the masses are those actually involved in the reactions which took place in the bomb.

The difference in the energies of the initial and final systems at 30° C in the reactions represented by equations 2 to 7 were calculated from the heats of formation at 18° C of each of the compounds involved, data on the specific heats of all of the substances involved, and data on the densities of the gases at 30° C and atmospheric pressure. The values used for the heats of formation of the compounds are given in table 4.

TABLE 4.—Values used for the heats of formation of various compounds at 18° C

Compound	Heat of formation ¹	Compound	Heat of formation ¹
	<i>Int. kilo-joules/mole</i>		<i>Int. kilo-joules/mole</i>
CO ₂ (gas)	² 395.12	NaOH (100 H ₂ O)	468.95
SO ₂ (gas)	296.71	NaOH (50 H ₂ O)	469.30
H ₂ O (liq.)	286.01	Na ₂ SO ₄ (400 H ₂ O)	1,333.57
Na ₂ CO ₃ (400 H ₂ O)	² 1,152.59	Na ₂ SO ₄ (200 H ₂ O)	1,334.62
Na ₂ CO ₃ (200 H ₂ O)	² 1,152.64	Na ₂ SO ₄ (100 H ₂ O)	1,336.56
Na ₂ CO ₃ (100 H ₂ O)	² 1,155.39	Na ₂ SO ₄ (50 H ₂ O)	1,339.35
Na ₂ CO ₃ (50 H ₂ O)	² 1,158.07	NaNO ₃ (400 H ₂ O)	449.22
Na ₂ CO ₃ (25 H ₂ O)	² 1,161.25	NaHCO ₃ (200 H ₂ O)	² 930.0

¹ The data in this table were supplied by F. D. Rossini, who has been critically reviewing the literature on thermochemistry.

² Heat of formation from diamond, gaseous oxygen, etc.

The heats of combustion of the purified ether-soluble rubber and of the rubber-sulphur compounds in gaseous oxygen to form gaseous CO₂, gaseous SO₂, and liquid water, at a temperature of 30° C and a constant pressure of 1 atmosphere can be represented within the limits of experimental error by the empirical equation:

$$Q_c = 45,200 - 37,823m \quad (8)$$

where Q_c is the heat of combustion in international joules per gram mass (weight in vacuo) of compound, and m is mass of sulphur per gram of compound. The average difference between observed values of the heats of combustion of rubber-sulphur compounds, and values calculated from this equation is 0.1 percent, and the maximum difference is 0.4 percent.

IV. HEAT OF COMBINATION OF RUBBER WITH SULPHUR

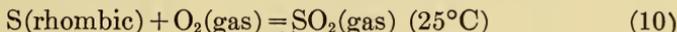
The heat of combination of rubber with sulphur at 30° C and atmospheric pressure can be calculated from the heats of combustion of the rubber-sulphur compounds and of unvulcanized rubber-sulphur mixtures. The heats of combustion of unvulcanized mixtures can

be calculated from the heats of combustion of rubber and rhombic sulphur by means of the relation:

$$Q_M = mQ_s + (1 - m) Q_R \quad (9)$$

where Q_R , Q_s , and Q_M are respectively, the heats of combustion per gram of rubber, sulphur, and the unvulcanized mixture of rubber and sulphur, and m is the mass of sulphur in a one-gram sample of the mixture.

The heat of combustion of sulphur has been determined by Eckman and Rossini,¹⁵ who give for the heat of the reaction:



the value 296.79 ± 0.20 international kilojoules per mole (32.065g) of sulphur, and for the temperature coefficient of the heat of reaction the value 12 joules per degree per mole. These data yield the value 9258 ± 6 international joules per gram of sulphur for the heat of combination of rhombic sulphur and gaseous oxygen to form gaseous SO_2 at 30°C .

Using this value for Q_s and 45,200 international joules per gram for Q_R , equation (9) becomes

$$Q_M = 45,200 - 35,942m \text{ int. joules per gram} \quad (11)$$

The calculated heat of combination of rubber and sulphur at 30°C is then given by the difference between equations 8 and 11, or

$$Q_v = Q_M - Q_c = (1881 \pm 300)m \text{ int. joules} \quad (12)$$

where Q_v is the heat evolved when m gram of rhombic sulphur and $(1 - m)$ gram of rubber combine at 30°C and under a constant pressure of 1 atmosphere, to form 1 gram of vulcanized rubber.

According to equation 12 the heat of combination of sulphur with rubber is independent of the amount of rubber (provided the sulphur does not exceed 32 percent of the total) and is equal to 1881 ± 300 international joules per gram of sulphur, or 60.3 ± 9.6 international kilojoules per mole of sulphur.

In table 5 are given the observed heats of combustion of rubber and of the rubber-sulphur compounds, together with values calculated from equation 8; and derived values of the heat of combination of rubber and sulphur, together with values calculated from equation 12. The derived values of heat of combination of rubber and sulphur are obtained from the relation:

$$Q_v(\text{der}) = Q_M(\text{calc}) - Q_c(\text{obs}) \quad (13)$$

¹⁵ BS J. Research 3,597(1929);RP111.

TABLE 5.—*Observed and calculated values of heats of combustion of purified sol rubber and rubber-sulphur compounds, and heats of vulcanization of the compounds, at a constant pressure of one atmosphere at 30° C.*

Sample	Ash	Sulphur in ash-free material	Q _c				Q _v			
			Observed	Calculated (equation 8)	Obs-calc	100 $\frac{\text{Obs-calc}}{\text{calc}}$	Derived (equations 11, 13)	Calculated (equation 12)	Der-calc	100 $\frac{\text{Der-calc}}{\text{calc}}$
	Percent	Percent	Int.j/g	Int.j/g	Int.j/g	Percent	Int.j/g	Int.j/g	Int.j/g	Percent
E ₄₀ -----	0.02	0.00	45255	45200	+55	+0.12				
E ₃₉ -----	.03	.00	45223	45200	+23	+0.05				
E _{31B} -----	.01	.00	45225	45200	+25	+0.06				
S ₃ -----	.14	.00	45239	45200	+39	+0.09				
E ₄₁ (sol.)	.11	.00	45095	45200	-105	-0.23				
E ₂₉₋₂ -----	.15	2.06	44381	44421	-40	-0.09	79	39	+40	+102
Do-----	.15	2.09	44412	44409	+3	+0.01	37	39	-2	-5
E ₃₁₋₆ -----	.10	6.05	42914	42912	+2	.00	112	114	-2	-2
Do-----	.10	6.14	42928	42878	+50	+0.12	65	116	-51	-43
E ₂₉₋₁₀ -----	.13	10.06	41318	41395	-77	-0.19	266	189	+77	+41
Do-----	.13	10.10	41311	41380	-69	-0.17	259	190	+69	+36
E ₁₄₋₁₆ -----	.08	16.03	39163	39137	+26	+0.07	275	301	-26	-9
Do-----	.08	16.07	39148	39122	+26	+0.07	276	302	-26	-9
E ₂₈₋₂₀ -----	.03	20.03	37612	37624	-12	-0.03	389	377	+12	+3
Do-----	.03	20.20	37554	37560	-6	-0.02	386	380	+6	+2
E ₂₈₋₂₆ -----	.05	25.90	35433	35405	+28	+0.08	458	487	-29	-6
Do-----	.05	25.95	35328	35385	-57	-0.16	545	488	+57	+12
E ₂₈₋₃₂ -----	.07	31.33	33262	33350	-88	-0.26	677	589	+89	+15
Do-----	.07	31.71	33203	33206	-3	-0.01	600	597	+3	+1
Do-----	.07	31.88	33103	33142	-39	-0.12	639	600	+39	+7
Do ¹ -----	.07	32.00	33058	33097	-39	-0.12	641	602	+39	+6
Do ¹ -----	.07	32.09	33187	33059	+128	+0.39	476	604	-128	-21
Do ¹ -----	.07	32.17	33116	33032	+84	+0.25	521	605	-84	-14

¹ NaOH was placed in the bomb to react with the products of combustion containing sulphur in these experiments. Na₂CO₃ was used for this purpose in all other experiments on rubber-sulphur compounds.

V. PREVIOUS WORK

Measurements of the heat of combustion of rubber have been made by Weber,¹⁶ Kirchoff and Matulke,¹⁷ Blake,¹⁸ Messenger,¹⁹ and Hada, Fukaya, and Nakajima.²⁰ The results reported by these investigators are given in the second column of table 6. Conversion to joules per gram was made by means of the relation

$$1 \text{ calorie} = 4.183_3 \text{ international joules,}$$

and the values of heat of combustion at constant pressure were obtained by adding 75 joules per gram to the values of heat of combustion at constant volume. The results are not reduced to standard initial and final states, as recommended by Washburn,²¹ since this reduction would change the figures given by only a negligible amount.

TABLE 6.—*Values of the heat of combustion of rubber reported by various observers*

Observer	Constant volume	Constant pressure
	Cal/g	Int. joules/g
Weber-----	10,669	44,710
Kirchoff and Matulke-----	10,700	44,840
Blake-----	10,547	44,200
Messenger-----	10,970	45,970
Hada, Fukaya, and Nakajima-----	10,495	43,980
Present work (total rubber)-----		45,040

¹⁶ The Chemistry of India Rubber, p. 107, J. B. Lippincott and Co., Philadelphia (1903).

¹⁷ Ber. Deut. Chem. Ges. **57B**, 1266 (1924).

¹⁸ Ind. Eng. Chem. **22**, 737 (1930).

¹⁹ Rubber Chem. Tech. **3**, 24 (1930).

²⁰ Rubber Chem. Tech. **4**, 507 (1931).

²¹ BS J. Research **10**, 525 (1933); RP546.

It will be seen from table 6 that the results obtained by the various observers are distributed over a range of about 4.5 percent. This is not surprising in view of the fact that most of the results were obtained on rubber which contained considerable amounts of impurities, and in view of the differences in the results obtained in the present work on different samples containing much smaller amounts of impurities.

Measurements of the heat of combination of rubber and sulphur have been made by Blake,²² and by Hada Fukaya, and Nakajima.²³ The results obtained by these observers, together with the results of the present work, are shown in figure 2.

Blake determined the heat of combination as the difference in the heats of combustion of vulcanized and unvulcanized samples. No details of calorimetric measurements and no analyses of the products of combustion are given.

Hada, Fukaya, and Nakajima determined heats of combustion of vulcanized compounds and calculated the heats of combustion of unvulcanized mixtures from their own value for the heat of combustion of rubber and Thomsen's data on

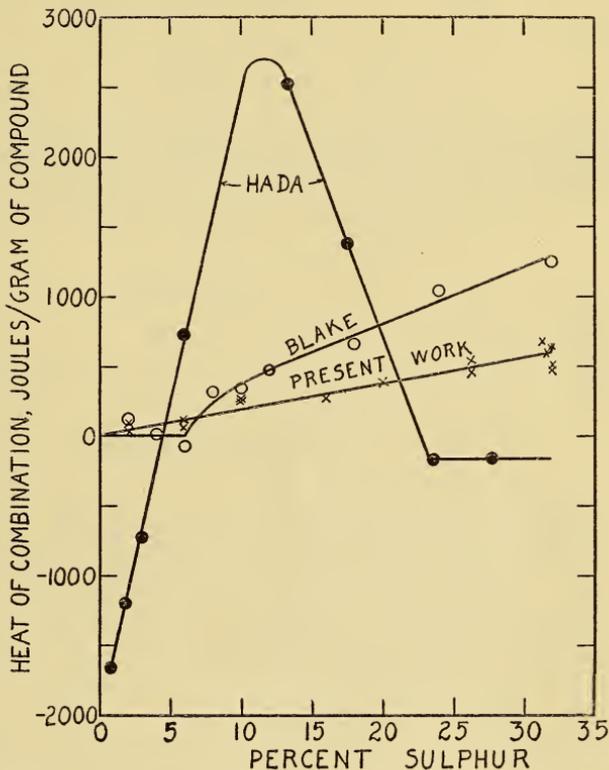


FIGURE 2.—Heat of combination of rubber with rhombic sulphur.

the heat of combustion of sulphur. Resins were removed from the rubber by acetone extraction, and corrections were applied for the heat of reaction of sulphur with protein. No details are given regarding calorimetric measurements. As may be seen from figure 2, the results obtained differ radically from those of Blake and those of the present work.

In conclusion, the authors wish to acknowledge their indebtedness to A. T. McPherson, under whose general direction this work was done.

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²² Ind. Eng. Chem. 22, 737(1930).

²³ Rubber Chem. Tech. 4, 507(1931).