

# Heats of Reaction of Natural Rubber With Sulfur

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An adiabatic copper calorimeter was used to determine the heats of vulcanization of pale crepe natural rubber with sulfur for mixtures varying in composition from 0 to 32 percent added sulfur. The side reaction that produces hydrogen sulfide was avoided by using reaction temperatures near 155 °C. Heats of reaction at 25 °C and at 155 °C are reported. The enthalpy change at 25 °C for compounds containing up to about 18 percent sulfur is given in joules per gram of vulcanizate by the equation,  $\Delta H_{25} = -21.1 \cdot S$  with a standard deviation of 11 J/g. Here  $S$  is the percentage of combined sulfur. Above 18 percent sulfur the heat of reaction at 25 °C remains approximately constant at  $380 \pm 8$  J/g. A comparison is made between the heat of vulcanization and the volume change on vulcanization, both as functions of combined sulfur, by making use of data in the literature.

Key words: Aneroid calorimeter; calorimeter; heat of vulcanization; heat measurements; rubber; rubber-sulfur reaction; volume change on vulcanization; vulcanization.

## 1. Introduction

The generally accepted theory of the vulcanization of natural rubber with sulfur is that a chemical reaction takes place in which intermolecular sulfur crosslinks are formed, giving the product a three-dimensional network structure. However, neither the details of this structure nor the mechanism of the chemical reaction is entirely understood, in spite of the vast amount of research work that has taken place in this field.

It has been known for many years that the vulcanization of natural rubber with sulfur involves an exothermic reaction, but very little careful work has been done to measure the quantity of heat involved. Most of the thermal studies have been only of a qualitative nature, in which thermometers or thermocouples have been imbedded in mixtures of rubber with vulcanizing ingredients and observed for temperature rise during the chemical reaction [1-14].<sup>1</sup> These rather crude experiments were made chiefly for the purpose of comparing the efficiencies of various types of accelerators, evaluating raw rubbers, or searching for the best temperature conditions for vulcanization.

However, several investigators have obtained quantitative data for the heat liberated from similar experiments involving differential calorimetry [15-22] and by means of direct measurements [23]. Indirect means have also been employed [24-26], in which measure-

ments of the heats of combustion have been made both on the reactants and the products of reaction, but this method has the disadvantage of requiring extremely high accuracy of calorimetric measurements because the heats of reaction are obtained as the differences between relatively large values of heats of combustion.

For a good review and discussion of the earlier work on the subject of the heat of reaction of the vulcanization process reference should be made to the articles of Oberto [17] and Hock and Schroeter [19]. The published results, however, have been anything but harmonious, even with respect to the general shape of the curve obtained when the heat of reaction is plotted as a function of the composition of the product. The present investigation was undertaken primarily with the hope that more precise calorimetric measurements might aid in bringing about a better understanding of the mechanism of the vulcanization process.

## 2. Method

A calorimeter of large heat capacity was designed and constructed so that samples of convenient size, at 25 °C, can be inserted into the calorimeter at vulcanization temperatures without lowering its temperature by more than a few degrees. In addition, this large heat capacity keeps the temperature change, arising from the vulcanization reaction, small enough for convenient measurement.

By using a reaction temperature of about 165 °C for the mixtures containing less than about 20 percent

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

sulfur the reaction rate was rapid enough to permit one sample to be run during a single day. However, it was found that for very high percentages of sulfur appreciable portions of the sample would be lost by the formation of  $\text{H}_2\text{S}$ . By lowering the reaction temperature to about  $145^\circ\text{C}$  this  $\text{H}_2\text{S}$  formation was reduced in all cases to negligible amounts. Of course, the time interval needed for complete reaction at this lower temperature was considerably lengthened, to as much as four days in some instances.

Since enthalpy is a function of the state of a system only, the heat of the vulcanization reaction at  $25^\circ\text{C}$  may be determined by subtracting the energy absorbed by the products of the reaction, in going from  $25.0^\circ\text{C}$  to the final equilibrium temperature of the reaction, from the energy absorbed by the reactants in going through the same temperature interval. Figure 1 is a schematic diagram which aids in the explanation of the experiments and in the derivation of the equations used to calculate the results of the experiments.

At a recorded time the reactants, a mixture of natural rubber and sulfur at temperature  $T_1'$ , are dropped into the calorimeter at temperature  $T_4'$ . The temperature of the calorimeter and its contents would then, exclusive of any heat of reaction, come to an equilibrium temperature  $T_2'$ . The heat liberated by the vulcanization reaction causes a rise in the temperature of the calorimeter and its contents to  $T_3'$ .

The products of the completed reaction are removed from the calorimeter and allowed to return to room temperature. The calorimeter temperature is then readjusted to a temperature near  $T_4'$ , but is measured as  $T_4''$  at the time that the reaction products at  $T_1''$  are inserted into it. The equilibrium temperature of the calorimeter and contents is now measured as  $T_2''$ . A measured quantity of electrical energy,  $q$ , is then added to the calorimeter to bring it up to a temperature  $T_3''$ , where should be quite near the previously measured temperature  $T_3'$ . The symbol  $T_v$  denotes the average

temperature of vulcanization,  $\Delta T_v$  the temperature rise which occurs during the vulcanization, and  $\Delta T_q$  the temperature change from adding the quantity of heat,  $q$ .

Sample temperatures  $T_1'$  and  $T_1''$  are measured to the nearest  $0.1^\circ\text{C}$ , and differences in the calorimeter temperature, e.g.  $T_4' - T_3'$ , to the nearest  $0.001^\circ\text{C}$ . Temperature  $T_2'$  needs not, and usually cannot, be measured because of lack of time for complete equilibrium before the vulcanization reaction begins.

From the first law of thermodynamics, the following general equation is obtained for the heat of the vulcanization reaction at  $25^\circ\text{C}$ ,

$$\Delta H_{25} = \int_{T_3'}^{T_4'} C dT - \int_{T_3'}^{T_4''} C dT + \int_{25}^{T_1'} c' dT - \int_{25}^{T_1''} c'' dT + \int_{T_3'}^{T_3''} c'' dT - q. \quad (1)$$

In this equation  $C$  represents the heat capacity of the empty calorimeter and  $c$  refers to the heat capacity of the sample plus its container. Single primes are used in referring to experiments involving the mixed reactants, and the double primes to those on the reaction products. When the temperatures  $T_1'$  and  $T_1''$  are adjusted to  $25^\circ \pm 0.1^\circ\text{C}$ , as was done in most of the experiments in the present investigation, the third and fourth terms on the right side of the equation are eliminated.

For reasons that will be explained later in the discussion, it is actually more meaningful to report the heats of reaction with reference to a higher vulcanization temperature than to  $25^\circ\text{C}$ . It can be seen from figure 1 that the heat of the reaction,  $\Delta H_v$ , at this higher temperature,  $T_v$ , can be obtained from

$$\Delta H_v = \int_{T_3'}^{T_4'} C dT - \int_{T_1'}^{T_v} c' dT - \int_{T_v}^{T_3''} c'' dT. \quad (2)$$

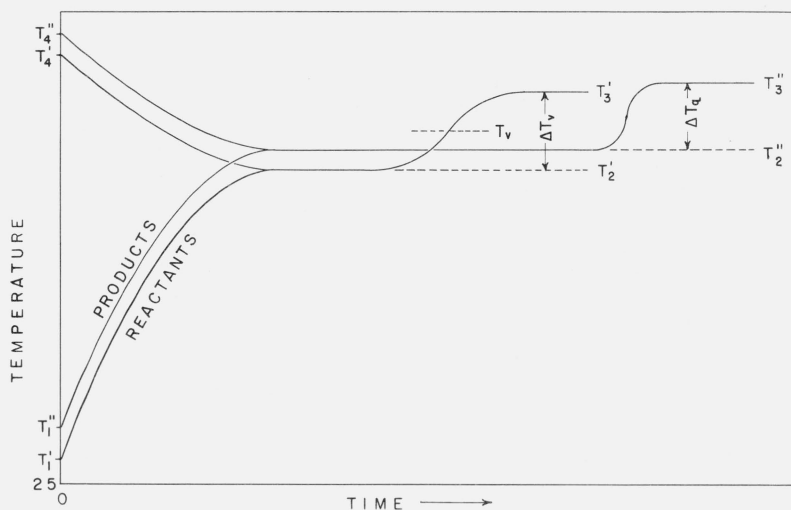


FIGURE 1. Diagram showing the course of the experiments for both the reactants and the products of reaction.

The diagram is not drawn to scale. See text for explanation

Here, the mean heat capacities of rubber, sulfur, and the sample container must be known between room temperature and the temperature of vulcanization. This can be determined for each of the materials separately in the same calorimeter by applying the equation

$$\int_{T_1}^{T_2} c dT = \int_{T_2}^{T_4} C dT. \quad (3)$$

### 3. Experimental Detail

#### 3.1. Calorimeter Assembly

A diagram of the apparatus is given in figure 2. A cylindrical block of copper, C, 6.7 cm in diameter and

22.2 cm long, is supported on glass wool in the bottom of a 1-liter wide-mouth dewar flask, D1. The block contains a circular well, W, about 3.8 cm in diameter, extending from the top to within 1.2 cm of the bottom. A copper tube of 2.5 cm inside diameter, with constantan heating-wire wound around it, is of such wall thickness that it fits snugly into the copper block. The heating-wires are represented by open circles. This whole unit then serves as the heater, H4, of the calorimeter. The space within this heater, which is about 20 cm in length, holds the sample container during an experiment. A small plug of glass wool is placed at the bottom of the well for protection of this container, which is made of glass.

The temperature of the calorimeter is measured by means of an 8-junction copper-constantan thermopile, whose junctions are represented by solid circles and are referred to as j2, j4, j6, and j8. The other four junctions are in similar positions 90 degrees from those shown in the diagram. A hinged lid, L1, covers the sample-well in order to prevent the loss of heat by convection currents from the sample compartment, which may be at a temperature several degrees higher than that of the calorimeter.

A copper jacket, S, having a 0.6-cm wall thickness surrounds the calorimeter and serves as a thermal shield. A hinged lid, L2, is placed at the top to allow introduction of the sample. Both the lids L1 and L2 can be opened simultaneously by pulling on the loop of fine wire, A. Three separate heaters, H1, H2, and H3 are wound on the side, top, and bottom of the jacket, respectively, as are shown by the open circles in the diagram. It was later found, however, that the bottom heater, H3, was unnecessary. Thermal insulation of the jacket from the surroundings is provided by two 4-liter dewar flasks, D2 and D3, one inverted over the other. An asbestos ring, R, acts as a cushion between the two flasks. In order to lower the sample into the calorimeter or to remove it, the top dewar D2 must, of course, be temporarily removed.

The thermal head between the shield and the calorimeter is measured by an 8-junction copper-constantan thermopile located in various positions as indicated by the closed circles J1 to J16. Several other thermocouples were used to balance the heat input to H1 and H2.

In the earlier experiments, the sample was initially equilibrated to room temperature in a large copper block inside a wide-mouth dewar and was quickly transferred into the calorimeter. Later, a vertical tube oven was mounted above the calorimeter, so that the sample container could be maintained at 25.0 °C and then dropped directly into the calorimeter.

##### a. Jacket Temperature Control

Except for a short interval of time when the upper dewar flask is removed, the jacket temperature is automatically held very nearly equal to that of the calorimeter by the jacket temperature controller. Figure 3 is a schematic diagram of the system, which also records the differential thermopile emf. A cam is attached to the shaft of the large drive gear of the potentiometer in such a position that it will just touch a

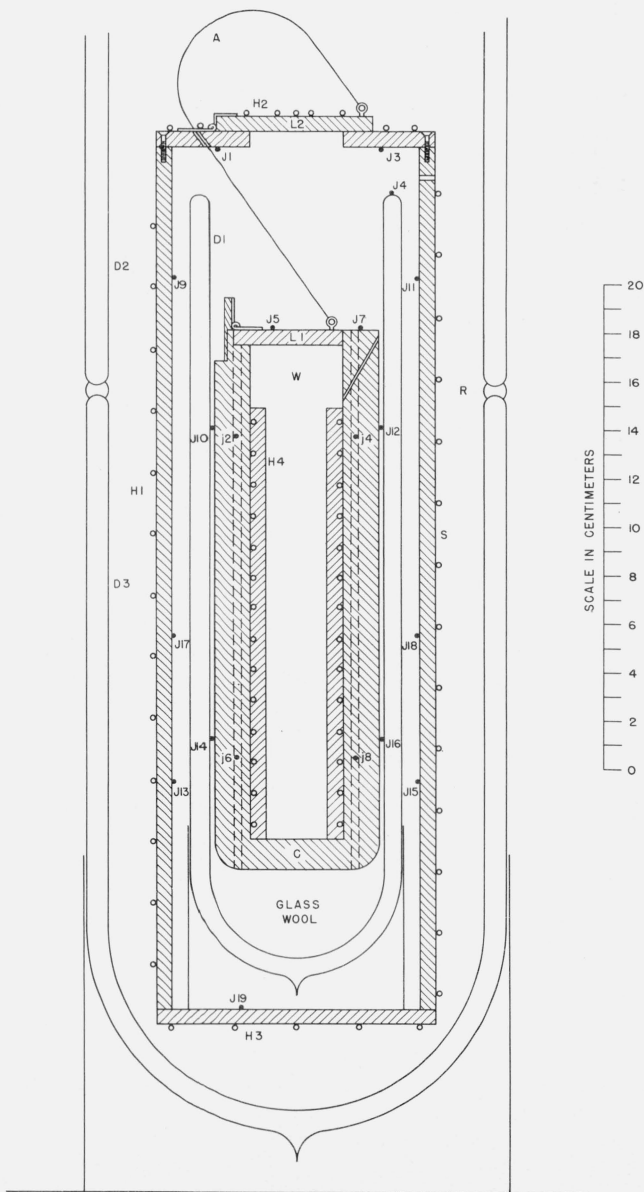


FIGURE 2. Diagram of the calorimeter used to measure the heats of vulcanization.

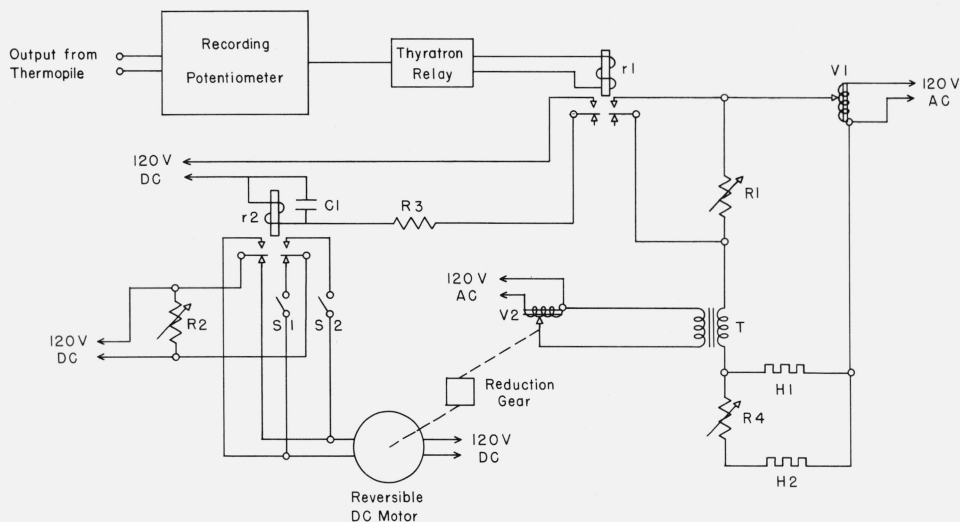


FIGURE 3. Schematic diagram of the apparatus that controls the differential temperature between the jacket and the calorimeter.

spring contactor when the input voltage exceeds zero (or any other desired value). This action shorts out the bias on a 2050 thyratron, which fires and thereby closes a double-pole-double-throw relay,  $r1$ . Closing of this relay does two things: first, the variable resistance,  $R1$ , that was initially in series with the jacket heaters,  $H1$  and  $H2$ , is shorted out; and second, the circuit to the coil of another double-pole-double-throw relay  $r2$ , is completed. The position of this second relay, determines the direction of rotation of a reversible d-c motor, which in turn operates, through a reduction gear, a variable transformer,  $V2$ , across the input of a 6-volt transformer,  $T$ . The output of this transformer is in series with the heaters. Two micro-switches,  $S1$  and  $S2$ , are used to limit the rotation of the transformer shaft. By adjusting the slack in the linkage between the reduction box and the variable transformer, or by adjusting the speed of the motor, a normal high-low heating period is allowed without any change in the transformer setting. This period was found to be about 40 s for the present setup. Should the demand for heater power change, as, for example, it does during the vulcanization, the setting of the transformer will automatically be changed to the proper value. The overall system provides high-low control with automatic reset.

With a zero emf input to the jacket temperature controller, it was found that the empty calorimeter would drop slowly in temperature, at a rate of about  $0.00012\text{ }^{\circ}\text{C}/\text{min}$ . By measuring this average rate of temperature change overnight on a number of occasions, an indication of the reliability of the jacket control was obtained. The standard deviation of 67 measurements of the rate was found to be  $8\text{ }\mu^{\circ}\text{C}/\text{min}$ . The rate of temperature change for the calorimeter plus a sample is equal to that for the empty calorimeter times the ratio of the heat capacity of the calorimeter to that of the calorimeter plus sample and sample container.

The cooling constant of the calorimeter was measured to be  $2.3 \times 10^{-3}\text{ min}^{-1}$  by utilizing various control point settings of the jacket temperature controller. If the upper dewar ( $D2$  in figure 2) is removed, the cooling constant is increased by about 10 percent.

#### b. Calibration of Calorimeter

The heat capacity of the empty calorimeter was determined by two different methods: (a) from measured additions of electrical energy, and (b) from the enthalpy change in a calorimetric standard sample of aluminum oxide.

The usual procedure was followed in the first method in that direct current from batteries was used, the energy being obtained from the product of the voltage, current, and time of current flow. Most of the voltage (120 volts) supplied by the batteries was dropped by resistors in series with the calorimeter heater, so that 0.1 to 0.2 amp would flow through the  $80\text{-}\Omega$  heater. The current was obtained from voltage measurements, using a Rubicon Type-B potentiometer, across a calibrated  $1\text{-}\Omega$  resistor in series with the heater. Durations of time were measured to 0.1 s with a timer run on the regular ac line voltage. Heating intervals of 45 to 90 min were used.

In the second method of calibration a known weight of standard sample of aluminum oxide, contained in a thin-walled copper tube, was dropped into the calorimeter; and the heat capacity of the latter was calculated from its observed temperature change and the known enthalpy changes in the copper tube and in the aluminum oxide. The value used for the specific heat of copper was that given in the International Critical Tables [27]. Values for aluminum oxide as a function of temperature are given by Furukawa, Douglas, McCoskey, and Ginnings [28, 29].

In order to convert the measured thermocouple voltage,  $e$ , for the 8-junction thermopile into degrees



Celsius when using an ice bath to maintain the reference junctions at 0 °C, the equation

$$e = 312.64t + 0.2925t^2 + 0.1784 \times 10^{-4}t^3 \quad (4)$$

was used. It was obtained from the calibration values of emf at 120, 140, and 160 °C for the spool of thermocouple wire used in the calorimeter. The derivative of this equation, evaluated at the mean temperature of the experiment, was divided into the emf difference to obtain the temperature difference. This procedure for converting  $\Delta e$  into  $\Delta t$  produces an error no larger than 10  $\mu$  °C.

Assuming the electrical and the  $\text{Al}_2\text{O}_3$  measurements to be equally valid, the linear regression of the heat capacity as a function of temperature was found to be, in J/°C,

$$C = 2494.2 + 1.53(t - 155.00), \quad (5)$$

with a standard deviation of 3.0 J/°C. This equation was obtained from eleven electrical and seven  $\text{Al}_2\text{O}_3$  measurements in the temperature range from 143 to 166 °C.

### 3.2. Samples and Container Materials

The samples were prepared from No. 1 pale latex crepe and commercial powdered rhombic sulfur. One kilogram of the rubber was thoroughly blended on a compounding mill. One-half of this rubber was mixed with sulfur to give a masterbatch containing 32.1 percent sulfur. The other half was used to add to portions of the masterbatch when mixtures of other compositions were required.

In preliminary experiments the samples were allowed to vulcanize while exposed to air in the calorimeter, but the susceptibility of the rubber to oxidation prevented a final equilibrium temperature from being reached. The samples in all later experiments were sealed in a glass container, and the air surrounding them was replaced by helium.

In spite of this treatment some reaction still took place within the rubber, as was shown by measurements of the enthalpy change of sulfur-free rubber between 25 and 165 °C. The initial average specific heat,  $\bar{s}$ , of seven such samples in this temperature range was  $2.154 \pm 0.007 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ \*; but when the same samples were run a second time the  $\bar{s}_{95}$  values were found to be higher by  $0.020 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ . No further increases were obtained on subsequent runs. Several variations in the methods of preparation of the rubber, including vacuum molding, did not eliminate the reaction that occurs the first time the sample is raised to the elevated temperatures. In measurements of the specific heats of organic polymeric materials Furukawa [30] has reported a similar evolution of heat above about 65 to 70 °C from polymers containing double bonds. Since the total heat evolved in this reaction of the rubber, which amounts to about 2.8 J/g

for the 140 °C difference in temperature, is small compared with that produced by the rubber-sulfur vulcanization reaction, no further attempt was made to eliminate it.

The recommended values [31] for the specific heat of natural rubber in the temperature range from about 50 to 175 °C, in  $\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ , are given by

$$s(\text{rubber}) = 1.917 + 0.00344(t - 25). \quad (6)$$

This equation gives a value of  $2.158 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$  for  $\bar{s}_{95}$ , which agrees very well with that determined by the measurements described earlier. Later in this paper calculations are made for the heats of vulcanization at 155 °C, which require specific heat values between 25 and 155 °C. We will use eq (6) which gives for  $\bar{s}_{90}$  a value of  $2.141 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ .

Sulfur is also part of the rubber sample, being present in a simple mixture prior to the vulcanization reaction and as part of the rubber-sulfur compound after the reaction. In calculating the heat of reaction at vulcanization temperatures, for example at 155 °C, from experimental data using eq (2) the difference in the heat content of the rubber-sulfur mixture must be known between 25 and 155 °C. For elemental sulfur West [32] reported a value of 174.1 J/g for  $H_{155} - H_{25}$ . Measurements by means of our own calorimeter gave good agreement with this, a value of 174.6 J/g. The former value, which is used for the present calculations, is equivalent to a mean specific heat of  $1.339 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$  at 90 °C. The mean specific heat of the rubber-sulfur mixture between 25 and 155 °C, in  $\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ , can therefore be obtained from

$$\bar{s}_{90}(\text{mixture}) = 2.141 - 0.00802 \cdot S \quad (7)$$

in which  $S$  is the percentage of sulfur in the mixture.

In order to evaluate the last integral in either eq (1) or eq (2), we need an estimate of the specific heats of the vulcanizates,  $s''$ , in the temperature range 145 to 165 °C. Direct measurement of  $s''$  was not possible in this temperature range because the vulcanization reaction continues to a slight extent when high percentage sulfur compounds are heated to these temperatures. First, we approximate the dependence of  $s''$  on the combined sulfur by measuring the mean specific heats of rubber vulcanizates between 25 and 155 °C and use this value at the higher temperatures. For compounds containing from 0 to 18 percent sulfur, the results, in  $\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ , can be represented by

$$\bar{s}_{90}'' = 2.156 - 0.478x \quad (8)$$

in which  $x$  is the fraction of an atom of combined sulfur per unit of  $\text{C}_5\text{H}_8$  in the compound. Compounds containing more than 18 percent sulfur gave  $\bar{s}_{90}''$  values which deviated from this relation and which appeared not to be given by a linear function of the combined sulfur.\* Secondly, we assume the temperature derivative of the compounds to be the same as

\*Earlier work in our laboratory [23] using a less precise calorimeter gave a value of  $2.16 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$  for the mean specific heat of natural rubber between 25 and 175 °C, which is equivalent to a  $\bar{s}_{95}$  of  $2.14 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$

\*For the cause of the deviation from linearity see section 4.2c.

that of rubber alone, which we derive as follows. An average value of  $s$  (rubber) at 155 °C was found to be  $2.435 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ . When this value is combined with our previously mentioned value of 2.174 at 95 °C, an average temperature derivative of  $0.0044 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-2}$  is obtained. We therefore estimate  $s''$  in the temperature range near 155 °C to be given by

$$s'' = 2.435 - 0.478x + 0.0044(t - 155). \quad (9)$$

It is also necessary to know the specific heat of the Pyrex glass that was used as a sample container. We measured its  $H_{165} - H_{25}$  to be 122.7 J/g which, when combined with the  $ds/dt$  of  $0.001311 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-2}$  determined by de Vries [33], gives the equation

$$s(\text{Pyrex}) = 0.7521 + 0.001311t \quad (10)$$

for the specific heat of Pyrex glass in  $\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ .

### 3.3. Illustrative Example

Details of the measurements are illustrated by the following history of one of the samples that was used in this study of the heat of reaction.

Five grams of the blended pale crepe were thoroughly mixed with 15g of the 32.1 percent sulfur masterbatch on a cold laboratory mill. This sample which contained 24.1 percent S, was removed in the form of a thin sheet and rolled into a cylinder. After its surface was lubricated with water, the sample was slipped into a 22-mm Pyrex glass tube which had a short capillary tube attached at one end. A plug of Pyrex glass wool was added above the sample, and the tube was sealed while the lower part of the tube containing the sample was cooled with ice water. The tube was then evacuated through the capillary for 6 hr at room temperature, then overnight at 70 °C, after which helium was admitted. The capillary was finally sealed close to its entrance to the tube and formed into a small hook which enabled the tube to be lifted by a loop of fine wire. The mass of the glass container was 57.41g.

Over a period of 24 hr the average rate of thermal emf change in the empty calorimeter was measured to be  $-0.0475 \mu\text{V}/\text{min}$ . At zero time the calorimeter thermopile emf was  $50,767 \mu\text{V}$ . The sample was quickly transferred from its 25 °C chamber into the calorimeter. This opening and closing of the calorimeter disturbs its temperature, so a correction was made to the initial emf reading. A number of experiments of opening the calorimeter just as is done when inserting the sample, but without actually inserting it, showed that the correction is  $-3 \mu\text{V}$ .

Corrections were also made for the heat exchange between the calorimeter and the jacket during the experiment. First, there is a correction for the interval when the jacket controller cannot maintain the differential emf at the control point setting. Figure 4 is a diagram prepared from an automatic recording sheet showing the differential emf. A reading to the left of the zero indicates that the jacket is at a lower temperature than the calorimeter. Each microvolt

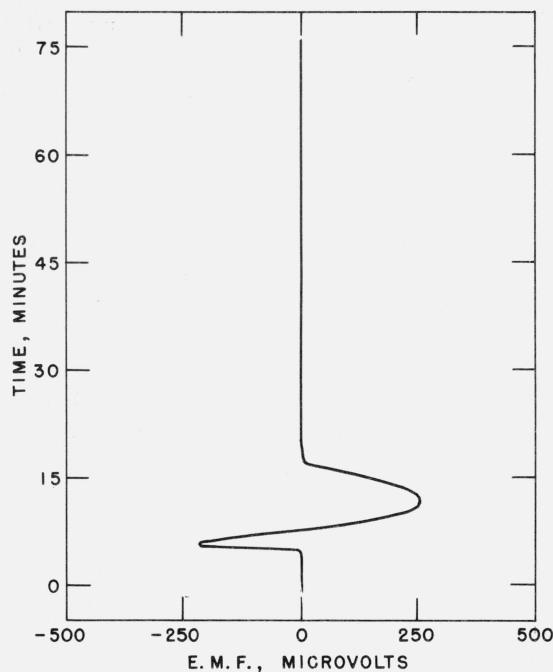


FIGURE 4. Automatic recording of the differential emf between the calorimeter and the jacket.

represents about  $0.0025 ^\circ\text{C}$ . As may be seen, the jacket temperature falls rapidly until the sample starts to cool the calorimeter. Then the calorimeter cools more rapidly than the jacket, in spite of the electric current in the jacket heater being completely off, until the sample approaches the calorimeter temperature. After a period of about 15 min the rates of change are slow enough so that the jacket temperature controller automatically keeps the differential thermopile voltage at a constant zero value for the rest of the experiment. The correction for the interval during which the jacket was out of control was calculated to be  $-1 \mu\text{V}$ . This value was obtained by multiplying the integrated area of the curve in figure 4 by the cooling constant of the calorimeter (sec. 3.1a).

The second correction, necessitated by the intrinsic heat transfer between calorimeter and jacket, even when the jacket is in temperature control, was derived in the following manner. On the third day of the experiment the observed rate of voltage change of the calorimeter thermopile had reached a value of  $-0.036 \mu\text{V}/\text{min}$ , which by comparison with the value of  $-0.0475 \mu\text{V}/\text{min}$ , noted just prior to the experiment, indicated that the reaction was essentially complete. The final calorimeter thermopile emf was read as  $50,210 \mu\text{V}$  after 4740 min of reaction time, and the sample was removed. Over the following day the average rate of voltage change with the calorimeter empty was found to be  $-0.0491 \mu\text{V}/\text{min}$ . This value was averaged with the rate determined just prior to the experiment, and the result multiplied by  $C/(C+c')$ , (in this case  $2475/2569$ ), to account for the increased heat capacity of the calorimeter when it contained the sample. This gives a value of  $-0.0465 \mu\text{V}/\text{min}$  for the drift rate of the calorimeter during the measurement on the

rubber. When this drift rate is multiplied by 4725 min, the time during which the jacket was in temperature control, a correction of +220  $\mu\text{V}$  is obtained. The total correction to be added to the final thermopile emf is thus 219  $\mu\text{V}$ , making the corrected final emf equal to 50.438  $\mu\text{V}$ .

The average temperature of the calorimeter during the experiment was 142.65  $^{\circ}\text{C}$ . At this temperature (by eq (5)) the heat capacity of the calorimeter is 2475 J/ $^{\circ}\text{C}$ . The derivative of eq (4) for this temperature gives a value of 397.2  $\mu\text{V}/^{\circ}\text{C}$  as the conversion factor for changing the observed emf difference of 326  $\mu\text{V}$  into the temperature difference  $T'_4 - T'_3$ . The calorimeter temperature change was 0.821  $^{\circ}\text{C}$ . Thus the first integral term of eq (1) is

$$\int_{T'_3}^{T'_4} C dT = 2475 \times 0.821 = 2032 \pm 100 \text{ J.}^*$$

The same procedure was carried out on the products, with the exception that 1321 J of electrical energy,  $q$ , was added to the calorimeter and sample in order to bring the final equilibrium temperature,  $T''_3$ , close to that attained by the reactants,  $T'_3$ . The observed calorimeter thermopile emf was corrected for heat exchange with the surroundings in the same manner as previously described. However, the rate of emf change recorded just prior to completion of the vulcanization run was used for the correction so that if the sample should still have been reacting to a slight extent the heat evolved would not be included in the enthalpy change of the products. Of course, the reaction must have been carried very nearly to completion in the first place or else a significant amount of additional sulfur would combine when the products are brought up to the calorimeter temperature. The total heat loss correction was found to be +5  $\mu\text{V}$ , giving a corrected emf change of 1368  $\mu\text{V}$ , which is equivalent to 3.437  $^{\circ}\text{C}$  for  $T''_4 - T''_3$ . The mean temperature of the calorimeter was 144.02  $^{\circ}\text{C}$ , at which temperature its heat capacity is 2477 J/ $^{\circ}\text{C}$ . The enthalpy change in the calorimeter during this experiment was

$$\int_{T''_3}^{T''_4} C dT = 2477 \times 3.437 = 8513 \pm 12 \text{ J.}$$

The final temperature of the run,  $T''_3$ , was 142.30  $^{\circ}\text{C}$ , as compared with the  $T'_3$  of 142.24  $^{\circ}\text{C}$  for the vulcanization experiment. The correction that must be applied to bring the reactants and the products to the same final temperature is calculated from the specific heat of the rubber vulcanizate, eq (9), and the specific heat of the Pyrex glass container, eq (10), as

$$\int_{T'_3}^{T''_3} c'' dT = [(20.00 \times 2.0) + (57.41 \times 0.93)]0.06 = 6 \text{ J.}$$

The two remaining terms in eq (1) that are necessary for calculating the heat of reaction are both zero

\*The value following the  $\pm$  symbol here and in the rest of this section is the estimated standard deviation of a single measurement. It results primarily from the previously given standard deviation of the drift rate and heat capacity of the calorimeter.

because the samples were at 25.0  $^{\circ}\text{C}$  when introduced into the calorimeter.

The total heat exchange during the vulcanization reaction calculated at 25  $^{\circ}\text{C}$  from eq (1) is thus

$$\Delta H_{25} = 2032 - 8513 + 0 - 0 + 6 - 1321 = -7796 \pm 101 \text{ J}$$

for the whole sample of rubber vulcanizate. Assuming that oxidation took place in the rubber to the same extent as measured previously for the rubber alone (2.8 J/g) a correction of 43 J is needed for the 15.2 g of rubber present in the sample. For the vulcanization reaction at 25  $^{\circ}\text{C}$ , therefore, the corrected value is -7753 J for the sample, or

$$\begin{aligned} \Delta H_{25} &= -388 \pm 5 \text{ J/g of vulcanizate} \\ &= -34.7 \pm 0.4 \text{ kJ/mole of } \text{C}_5\text{H}_8 \\ &= -51.7 \pm 0.7 \text{ kJ/atom of S.} \end{aligned}$$

In calculating the heat of the vulcanizing reaction at a temperature of 155  $^{\circ}\text{C}$  from eq (2)

$$\begin{aligned} \Delta H_{155} &= 2032 - 130[(20.00 \times 1.948) + \\ &\quad (57.41 \times 0.8701)] + 12.8[(20.00 \times 2.02) + \\ &\quad (57.41 \times 0.9469)] \\ &= -8314 \pm 101 \text{ J for the sample,} \\ &= -416 \pm 5 \text{ J/g of vulcanizate.} \end{aligned}$$

Subsequent analysis for free sulfur [34] in the vulcanizate showed the presence of 0.08 percent S, indicating that 24.0 percent sulfur had combined with the rubber, which is equivalent to an  $x$  value of 0.671 atom of S per  $\text{C}_5\text{H}_8$  unit.

## 4. Results and Discussion

### 4.1. The Vulcanization Reaction

As early as 1902 Weber [35], in vulcanizing rubber-sulfur mixtures containing from 33 to 50 percent sulfur, found that the amount of combined sulfur increased with time and higher temperatures but that under no condition was it possible to obtain a combined sulfur content of more than about 32 percent. Under normal conditions of vulcanization it was therefore assumed that sulfur adds chemically to the double bonds of the rubber hydrocarbon molecule until the saturation point is reached, which gives the formula  $(\text{C}_5\text{H}_8\text{S})_n$ . This assumption was strengthened when it was found that for every atom of sulfur that was added to a molecule of rubber in soft-rubber vulcanization a double bond was lost [36-38]. However, this loss of a double bond for each sulfur atom over the complete range of sulfur additions was later questioned by the infrared studies of Sheppard and Sutherland [39] and of Linnig and Stewart [40], who found that a considerable number of double bonds still remain in hard-rubber vulcanizates, even in those containing 32 percent combined sulfur.

Other studies of the rubber vulcanization process, both with and without accelerators and other additives, indicate that the molecular structure of the vul-

canizate is not as simple as it was once thought to be. Recent review articles, such as those of Moore and collaborators [41, 42], Scheele [43], and Saville and Watson [44], point out that although the primary purpose of the vulcanization process is to interlink the rubber molecules so as to form a three-dimensional network, other sulfur addition reactions take place that lower the efficiency of the desired reaction. The unaccelerated rubber-sulfur reactions are very inefficient in the formation of good vulcanizates because most of the sulfur atoms add as intramolecular monosulfides rather than as cross-links. The function of accelerators and other additives is not only to increase the rate of the chemical reactions but also to increase the efficiency of the crosslinking reactions by decreasing the intramolecular cyclic monosulfide formations. The crosslinks enter as long polysulfide chains, but as the reaction proceeds they decrease in length and finally end up primarily as monosulfide crosslinks. Even under the best conditions of acceleration 100 percent efficiency of crosslinking has not yet been achieved with sulfur vulcanizations. Although the system, rubber-sulfur without accelerators or other additives, is the least efficient of the vulcanizing formulas, it was chosen for the present study because of fewer complications from reactions involving other materials.

## 4.2. Heat of Vulcanization

### a. Reaction Conditions

Compromises had to be made in the selection of temperatures for conducting the vulcanization reactions. It was desired to have the reaction take place at as high a temperature as possible in order to decrease the overall time for completion and thus to reduce the error of measurement caused by heat leakage in the calorimeter. On the other hand, the reaction should not be forced to proceed too rapidly because of introducing undesirable side reactions, such as the production of hydrogen sulfide at the higher concentrations of sulfur.

Because of the low thermal conductivity of the rubber the exothermic vulcanization reaction causes the temperature of the reactants to become higher than that of the surroundings. When a rubber-sulfur mixture containing 24 percent sulfur, about the size and shape of the usual sample used in the vulcanization experiments, was placed in an oven maintained at 175 °C, the center of this sample attained a maximum temperature of 276 °C, which resulted in a large amount of hydrogen sulfide being formed. However, in a similar experiment in an oven at 143 °C the temperature rose to only 154 °C, which is low enough to avoid the H<sub>2</sub>S side reaction. For an 8 percent sulfur mixture in a 161 °C oven the temperature rose to only 169 °C. Similar results had previously been obtained by Daynes [11] and by Winspear and coworkers [14].

In a number of experiments on samples with a high sulfur content the sample containers were broken open and weighed immediately, and in no case was there a weight loss of more than 0.1 percent of that of the sample. Neither was there any odor present that

indicated an appreciable quantity of hydrogen sulfide gas in the container. It was found that for the rubber samples containing less than about 20 percent of sulfur, a calorimeter temperature of 165 °C was suitable and that the reaction under these conditions was usually complete within a single day. For samples containing higher percentages of sulfur, however, the calorimetric measurements were conducted at temperatures near 145 °C. These lower-temperature experiments required more time for the completion of the reaction, but this procedure was found to be necessary in order to prevent side reactions from taking place.

Although the evolution of hydrogen sulfide from a rubber-sulfur compound is increased by either an increase in temperature or sulfur content [45, 46], it can also be increased by subjecting the rubber to direct sunlight and, conversely, can be greatly reduced in darkness [47, 48]. Other studies [49] have shown that the production of hydrogen sulfide becomes much greater if a stream of air of some other gas is passed over the sample while it is being vulcanized or while the vulcanized product is held at elevated temperatures.

The conditions under which the samples were vulcanized in the present investigation were therefore optimum, in that no flow of gas was present over the sample, the samples were kept in complete darkness, and vulcanization temperatures were relatively low.

### b. Results of the Measurements

The results obtained from direct measurements of the heat of reaction of natural rubber with sulfur, for mixtures varying in composition from 0 to 32 percent added sulfur, are given in table 1. Figure 5 also presents the

TABLE 1. Results of experiment

Sulfur			Heat of Reaction	
Added	Combined		−ΔH <sub>25</sub>	−ΔH <sub>155</sub>
percent	percent	x <sup>1</sup>	kJ/C <sub>5</sub> H <sub>8</sub>	kJ/C <sub>5</sub> H <sub>8</sub>
1.01	1.00	0.021	1.04	1.08
2.01	1.99	.043	2.53	2.54
2.99	2.96	.065	3.79	3.94
4.00	3.96	.088	5.15	5.12
5.00	4.94	.110	6.26	6.40
6.01	5.89	.133	8.35	8.76
8.00	7.70	.178	12.18	12.30
10.03	9.54	.225	14.45	14.87
13.00	12.34	.301	21.52	22.01
16.06	15.46	.391	27.15	27.88
<sup>2</sup> 19.00	17.83	.468	32.49	33.64
16.04	15.82	.400	26.22	26.85
19.03	18.85	.494	31.34	32.56
<sup>3</sup> 24.08	23.98	.671	34.74	37.20
27.98	27.81	.820	36.92	39.96
32.08	31.09	.973	37.63	40.68
32.08	30.97	.969	37.49	41.01

<sup>1</sup> Atom of sulfur per C<sub>5</sub>H<sub>8</sub> unit.

<sup>2</sup> This sample and all previously listed ones were vulcanized at temperatures near 165 °C; all following ones near 145 °C.

<sup>3</sup> Used as illustrative example in section 3.3.

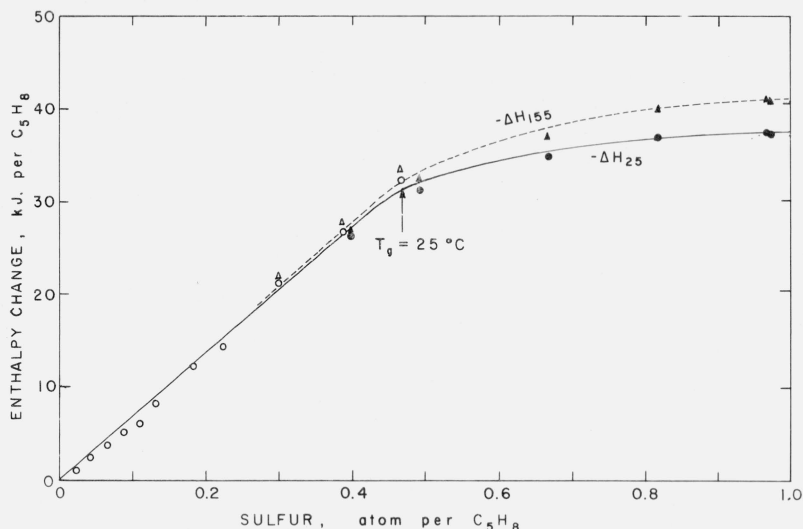


FIGURE 5. Heat of vulcanization of rubber-sulfur mixtures as a function of composition expressed as the fraction of an atom of sulfur per  $C_5H_8$  unit of the rubber.

results in graphical form, in which the enthalpy change in kilojoules per mole of  $C_5H_8$  units is plotted as a function of the fraction of an atom of combined sulfur in the vulcanizate, assuming that the rubber is all hydrocarbon. The solid circles and triangles represent measurements that were made with the vulcanization reaction taking place near 145 °C, and the open circles and triangles for those near 165 °C. The circles and the solid curve represent values for the heat of reaction calculated to 25 °C, while the triangles and broken curve are for the values at 155 °C.

Data from table 1 were also used to plot figure 6, which shows the heat of reaction as a function of sulfur concentration, but in this case the units for the abscissa and ordinate are different from those of figure 5. In this plot it seems as though the heat of vulcanization at 25 °C,  $\Delta H_{25}$ , levels off to a value of about  $-380 \pm 8$  J/g above 18 percent combined sulfur by weight. Below the 18 percent sulfur the heat change in J/g can be obtained, with a standard deviation of 11 J/g, from the formula

$$\Delta H_{25} = -21.2 \cdot S$$

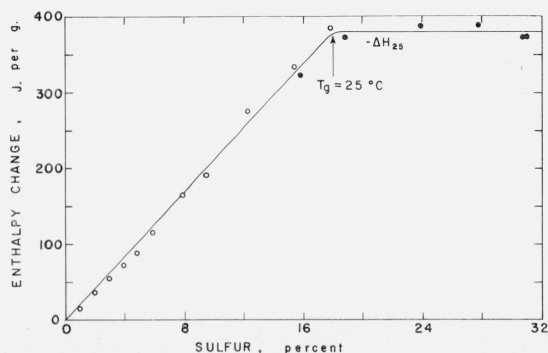


FIGURE 6. Heat of vulcanization of rubber-sulfur mixtures as a function of composition expressed as percent of sulfur by weight.

in which  $S$  is the percentage of combined sulfur by weight. McPherson [50] found that when variations were made in the temperature and time of vulcanization the same density values were always obtained provided the reaction had been run to completion. The same should probably be true for the enthalpy; however, there is some slight indication in our data (see fig. 6) that the 25 °C heat of reaction is greater when vulcanization takes place at 165 °C than when it occurs at 145 °C, at least for compounds containing about 16 percent combined sulfur.

#### C. Comment on $\Delta H_{25}$

The obvious change in slope of the  $-\Delta H_{25}$  curve at  $x \approx .47$  in figure 5 can be only partially accounted for. Martin and Mandelkern [51] have shown that the glass temperature,  $T_g$ , of a natural rubber vulcanizate is dependent on the percentage of combined sulfur. For a vulcanizate having a composition of 18 percent combined sulfur, which is equivalent to 0.466 atom of sulfur per  $C_5H_8$  unit, the  $T_g$  is about 25 °C. (This point is marked by a vertical arrow in figure 5.) At this temperature, and below this concentration of sulfur, both the raw rubber reactant and the vulcanized rubber product exist in liquid states above their glass transition temperatures. However, at the same temperature of 25 °C but above this sulfur concentration, the product of the reaction is in the glassy state, while the rubber reactant is in a liquid state. Therefore an abrupt change in slope would be expected in the curve for the heat of vulcanization at 25 °C at a concentration of 0.466 atom of S per  $C_5H_8$  because of the discontinuity at  $T_g$  in the specific heat curve of any vulcanized rubber having more than 18 percent combined sulfur.

The highest  $T_g$  value for any rubber-sulfur vulcanizate is about 95 °C, which is that for 32 percent sulfur or  $x=1.0$  [51]. Thus, a curve for  $\Delta H$  at any temperature above 95 °C would not be biased by a specific heat change at  $T_g$  in some of the products.



We chose to obtain  $\Delta H$  at 155 °C not only because all the reactants and products would be liquids at that temperature, but also because the heat corrections to bring the products to 155 °C from the final vulcanization temperature would be small. The experimental values for  $\Delta H_{155}$  are given in table 1 but are plotted in figure 5 only where the curves exhibit appreciable separation from each other. Since both the  $\Delta H_{25}$  and  $\Delta H_{155}$  curves are very similar to each other, it indicates that the  $T_g$  transition has only a small effect on the shape of the  $\Delta H_{25}$  curve. Apparently, its effect is overshadowed by a change in the shape of the curve due to another cause. This could be either a change in the type of chemical reaction taking place or the simultaneous occurrence of an endothermic reaction. It is probably only coincidental that these two different causes for a change of slope should arise at or near the same concentration of combined sulfur.

Bhaumik, Banderjee, and Sircar [21, 22] obtained a linear curve through the 0.466 S region and suggested that earlier work done at the National Bureau of Standards [23] must have allowed an endothermic reaction, the formation of hydrogen sulfide, to take place with the higher percentages of sulfur and thus cause the curve to deviate from the linearity that it has below about 18 percent of combined sulfur. Care was taken in the present investigation, however, not to permit this side reaction to take place, but the shape of the curve in figure 5 still resembles that obtained previously [23], indicating again that the curve does not have the same slope for the higher concentrations of combined sulfur as it does for the lower.

### 4.3. Vulcanization Volume Change

Further indication that changes of slope actually do take place in the curves for the heat of vulcanization as a function of combined sulfur both at 25 °C and 155 °C results from work done by McPherson [50] and by Martin and Mandelkern [51] on the measurement of the densities of rubber-sulfur mixtures at various concentrations and their vulcanizates. The changes of volume on vulcanization, shown in figure 7, were calculated from data obtained in the publication of the latter investigators [51]. From data given in table 1 and in figure 3 of their paper it was determined that the specific volumes of the unvulcanized rubber-sulfur mixtures,  $V_{25}$  (mix), in  $\text{cm}^3/\text{g}$  at 25 °C, can be obtained from the equation

$$V_{25}(\text{mix}) = 1.095 - 0.0060 \cdot S \quad (11)$$

in which  $S$  is the percentage by weight of sulfur. The specific volumes of the corresponding vulcanizates,  $V_{25}$  (vulc), given in column 3 of their table 1, after being corrected for the amount of free sulfur present, were subtracted from the  $V_{25}$  (mix) values obtained for the corresponding concentrations of sulfur and were then computed per gram of isoprene. The values of volume change on vulcanization are plotted as  $-\Delta V_{25}$  in figure

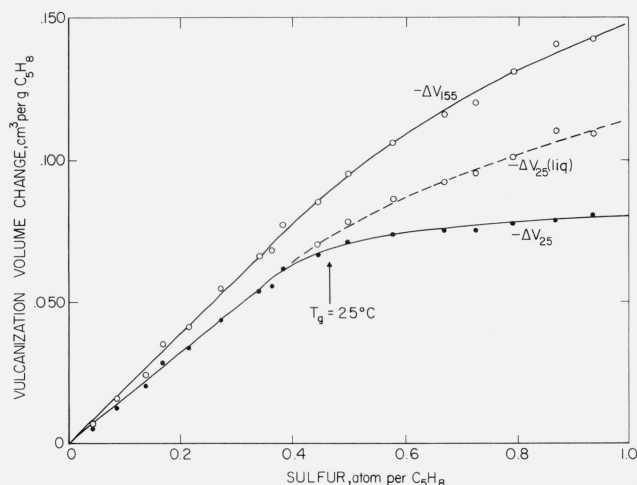


FIGURE 7. Change in volume of rubber-sulfur mixtures during vulcanization as a function of composition.

Data for the curves are taken from a paper by Martin and Mandelkern [51].

7 as a function of the bound sulfur recalculated to the fraction of an atom per  $\text{C}_5\text{H}_8$  unit.

It can be seen that the  $-\Delta V_{25}$  curve of figure 7 has a shape similar to that of the  $-\Delta H_{25}$  curve of figure 5 in that they both deviate from linearity at about the same sulfur concentration and that both the changes in volume and the changes in heat of vulcanization are much less per sulfur atom at the higher concentrations of sulfur.

The  $-\Delta V_{25}(\text{liq})$  curve of figure 7 was derived from the data plotted in figure 3 of reference 51 expressed in the same units as before. Now the vulcanization volume change is given with all the products in a liquid state but a change of slope at higher concentrations of sulfur is still observed. We also calculated the volume changes which would occur from vulcanization at 155 °C by making use of the volume-temperature derivatives given in tables 1 and 2 of Martin and Mandelkern's paper [51]. These changes are shown in figure 7 and labeled  $-\Delta V_{155}$ . The change in slope for  $x > .47$  is less obvious but still similar to that occurring in the plot of  $\Delta H_{155}$ .

In conclusion, both heat and volume measurements have shown that the vulcanization of natural rubber with sulfur does not proceed to 32 percent combined sulfur by means of a single type of chemical reaction. Other kinds of measurements will be needed to elucidate the detailed molecular combinations but any proposed theory for the vulcanization of this system should at least be compatible with these observations.

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