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## HEATS OF REACTION OF THE SYSTEM: RUBBER-SULPHUR

By Archibald T. McPherson and Norman Bekkedahl

## ABSTRACT

Heats of reaction of rubber with sulphur to form vulcanized compounds having empirical formulas lying between  $C_5H_8$  and  $C_5H_8S$  (0 to 32 weight percent of sulphur) were determined directly at  $175^\circ C$  in an isothermal calorimeter, which consisted essentially of an insulated copper block to which heat could be added with electrical energy or removed by adding cold steel balls. In a reaction experiment, the mixture of rubber and sulphur was placed in a cavity in the copper block and the temperature of the block was maintained constant by the addition or removal of measured quantities of heat energy until the reaction of vulcanization was complete. Differences in heat content between  $25$  and  $175^\circ C$ ,  $(H_{175} - H_{25})$ , for unvulcanized mixtures and vulcanized compounds of rubber and sulphur, were determined in the same calorimeter by dropping the sample at  $25^\circ C$  into the calorimeter at  $175^\circ C$ . For vulcanized compounds of rubber and sulphur, empirical formula  $C_5H_8S_x$ ,

$$(H_{175} - H_{25}) = 22.2 + 1.2 x$$

kilojoules per gram-mole of  $C_5H_8$  in the range from  $x=0$  to  $x=0.5$ , and

$$(H_{175} - H_{25}) = 24.1 - 2.6 x$$

in the range from  $x=0.5$  to  $x=1.0$ , where  $x$  is the number of atoms of sulphur per  $C_5H_8$  and varies from 0 to 1.0. For unvulcanized mixtures of rubber and sulphur ( $C_5H_8 + x S$ ),

$$(H_{175} - H_{25}) = 22.2 + 6.2 x$$

kilojoules per gram-mole of  $C_5H_8$ . The heat of the reaction of rubber with sulphur, which for the sake of simplicity may be represented as  $C_5H_8$  (solid)  $+ x S$  (solid)  $= C_5H_8S_x$  (solid), was found to be linear with  $x$  from  $x=0$  to  $x=0.5$ , at which point there is a discontinuity in the slope of the curve; and also linear with a different slope for the range  $x=0.5$  to  $x=1.0$ . In the composition range  $x=0$  to  $x=0.5$ , the increases in heat content for the reaction of vulcanization at  $175^\circ$  and  $25^\circ C$  are respectively,

$$\Delta H_{175} = -60.0 x, \text{ and}$$

$$\Delta H_{25} = -55.4 x,$$

kilojoules per gram-mole of  $C_5H_8$ . In the range  $x=0.5$  to  $x=1.0$ ,

$$\Delta H_{175} = -22.5 - 15.0 x, \text{ and}$$

$$\Delta H_{25} = -24.8 - 5.8 x,$$

kilojoules per gram-mole of  $C_5H_8$ .

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## I. INTRODUCTION

Previous investigators have employed two methods for determining the heat effects when rubber is vulcanized. In one method the heats of vulcanization are found by subtracting the heats of combustion of vulcanized rubber-sulphur compounds from the heats of combustion of the corresponding mixtures of rubber and sulphur before vulcanization.<sup>1</sup> This method is limited in precision by reason of the fact that the differences thus obtained are at most only a few percent of the measured heats of combustion. The other method, which has been used previously, involves the determination of the temperature rise which occurs when mixtures of rubber and sulphur are vulcanized. This method has, for the most part, been used for relative measurements, but Blake<sup>2</sup> has recently employed it for quantitative determinations of the heats of reaction of rubber with proportions of sulphur up to about 8 percent by weight. Recently Daynes<sup>3</sup> has employed a similar method for measurements over a wider range of composition.

This investigation was undertaken for the purpose of measuring the heats of reaction of rubber with different percentages of sulphur over the entire range of composition in which combination takes place. The study was exploratory in character, the aim being to make the measurements by direct means, with emphasis on simplicity rather than refinement of calorimetric procedure.

## II. DESCRIPTION OF CALORIMETER

The calorimeter in which the reaction of rubber and sulphur was conducted consisted essentially of an insulated copper cylinder which served as a constant-temperature bath. This cylinder was 2¼ inches in diameter and 9½ inches long, and in it 4 holes were bored, ¼, ⅝, ⅝, and 1 inch, respectively, in diameter, and 9 inches in depth. As shown in figure 1, the cylinder was mounted in a 1-liter dewar flask, which was surrounded by thermal insulation and placed in a double-walled container. This container was maintained at constant temperature, about 175° C, by means of vapors of boiling cymene.

The temperature of the calorimeter was indicated by a mercury-in-glass thermometer, which was placed in the smallest hole, designated as K in the figure. The thermometer was graduated to 0.1° C and

<sup>1</sup> Jessup and Cummings, *BS J. Research* **13**, 357 (1934) RP713. Blake, *Ind. Eng. Chem.* **22**, 737 (1930). Hada, Fukaya, and Nakajima, *J. Rubber Soc. Japan* **2**, 389-397 (1931); *Rubber Chem. Tech.* **4**, 507 (1931).

<sup>2</sup> *Ind. Eng. Chem.* **26**, 1283 (1934).

<sup>3</sup> H. A. Daynes, paper presented at meeting of Institution of the Rubber Industry, Dec. 10, 1934.

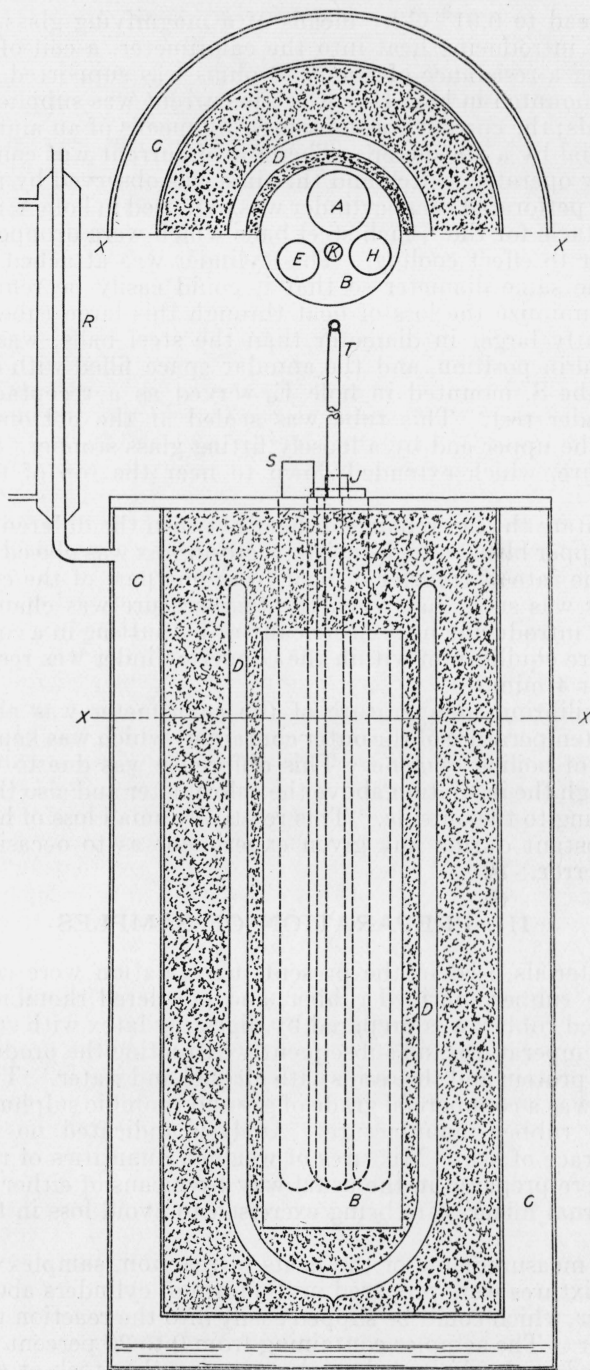


FIGURE 1.—Cross section of the calorimeter used for the determination of the heats of reaction.

A, cavity for the container of the steel balls; B, copper cylinder; C, cymene vapor bath; D, dewar flask; E, cavity for the sample tube; H, cavity for the calorimeter heater; J, tube leading to the container for the steel balls; K, cavity for the thermometer; R, reflux for the cymene vapors; S, sample tube; T, mercury thermometer.

could be read to  $0.01^{\circ}\text{C}$  by means of a magnifying glass. For the purpose of introducing heat into the calorimeter, a coil of nichrome wire having a resistance of about 40 ohms was supported on a glass tube and mounted in hole H. Electric current was supplied through copper leads; the current was measured by means of an ammeter, and the potential by a voltmeter. The flow of current was controlled by a manually operated switch and the time was observed by means of a watch. A perforated brass cylinder was mounted in hole A, and served as a receptacle for the  $\frac{1}{4}$ -inch steel balls which were dropped into the calorimeter to effect cooling. This cylinder was attached to a glass tube of the same diameter so that it could easily be removed. In order to minimize the loss of heat through this large tube a smaller tube, slightly larger in diameter than the steel balls, was mounted in it, sealed in position, and the annular space filled with insulation. A glass tube S, mounted in hole E, served as a receptacle for the sample under test. This tube was sealed at the bottom and was closed at the upper end by a loosely fitting glass stopper, not shown in the figure, which extended down to near the top of the copper cylinder.

To facilitate the interchange of heat between the different elements and the copper block, a high-melting ceresin wax was placed in all four holes. The rate of transfer of heat from one part of the calorimeter to another was such that when the temperature was changed a few degrees by introducing heat electrically or by putting in a cold sample, temperature equilibrium within the copper cylinder was reestablished within 3 or 4 minutes.

The equilibrium temperature of the calorimeter was about  $1^{\circ}\text{C}$  below the temperature of the outer container, which was kept constant by means of boiling cymene. This difference was due to the loss of heat through the insulation above the calorimeter and also through the tubes leading to the outside. This relatively small loss of heat was so nearly constant during any given experiment as to occasion no appreciable error.

### III. PREPARATION OF SAMPLES

The materials used in the present investigation were commercial pale crepe rubber, purified rubber, and powdered rhombic sulphur. The purified rubber was prepared by digesting latex with steam at an elevated temperature, and subsequently extracting the products of hydrolysis of protein and the resins with alcohol and water.<sup>4</sup> The sulphur employed was a commercial grade of ground rhombic sulphur intended for use in rubber manufacture. Analysis indicated no impurities except a trace of ash. Mixtures of weighed quantities of rubber and sulphur were prepared in the usual way by means of either a roll mill or an internal mixer, care being exercised to avoid loss in the mixing process.

For the measurements of the heats of reaction, samples of rubber-sulphur mixtures were prepared in the form of cylinders about 10 mm in diameter, which could be slipped easily into the reaction tube of the calorimeter. The samples containing from 0 to 20 percent of sulphur were formed in the desired shape by pressing the stock at about  $100^{\circ}\text{C}$  in a rod mold lined with aluminum foil to prevent sticking. Samples

<sup>4</sup> BS J. Research 8, 751 (1932) RP449.



of stocks containing more than 20 percent of sulphur could not be used as solid cylinders of 10 mm diameter, because local superheating along the axis of the cylinders occurred during the reaction between the rubber and the sulphur. These samples were made in the form of hollow cylinders by wrapping the rubber stock in sheet form around weighed glass tubes of about 4 mm outside diameter. Correction for the heat capacity of these tubes was made in computing the results.

The samples which were vulcanized in the course of determining the heats of reaction were subsequently employed for the measurement of the differences in heat content of the rubber-sulphur compounds between room temperature and the temperature of the calorimeter.

#### IV. METHOD OF DETERMINING HEATS OF REACTION

In order to determine the heats of reaction of rubber and sulphur at the vulcanizing temperature, about 175° C, by the method here employed, it was necessary not only to measure the heat effects at that temperature but also to measure the differences in heat content of the *unvulcanized* rubber-sulphur mixtures between the temperature of the room, approximately 25° C, and that of the calorimeter. Furthermore, to obtain the heats of reaction at 25° C it was necessary to measure also the differences in heat content of the *vulcanized* rubber-sulphur compounds between 175 and 25° C.

##### 1. MEASUREMENT OF DIFFERENCES IN HEAT CONTENT BETWEEN 25 AND 175° C

The experimental procedure in the measurement of differences in heat content was the following. Cymene was placed in the outer double-walled container of the apparatus and was heated to boiling by an electric hot plate. The copper cylinder was heated electrically to approximately the same temperature as the vapors of the boiling cymene and was allowed to stand for several hours until thermal equilibrium was established between the cylinder and the container. A sample of known weight and temperature, usually about 25° C, was slipped quickly into the sample tube of the calorimeter. The rubber samples were first dusted with talc to prevent their sticking to the sides of the glass tube. The weight of the talc used was not significant. Experiments in which the sample tube was opened and closed in the same manner without introducing a sample indicated that no significant quantity of heat was lost from the calorimeter in this operation. Heat was then added electrically to the copper cylinder in quantity sufficient to balance the heat taken up by the cold sample and bring it again to the previous equilibrium temperature. During this process the temperature variation was seldom greater than 1° C and the time of disturbance never over 4 minutes, so the results were probably not materially affected by the onset of the vulcanization reaction.

The difference in heat content of a sample between the temperature of the room and that of the calorimeter was found from the equation,

$$(H_c - H_r) = \frac{EIs}{m}$$

where  $H_c$  and  $H_r$  are the heat contents in joules per gram of the samples at the temperature of the calorimeter and of the room, respectively,  $s$  is the time of heating in seconds,  $E$  the potential in volts,  $I$  the current

in amperes, and  $m$  the weight of the sample in grams. Since the temperatures of the calorimeter and of the room are relatively close to  $175^\circ$  and  $25^\circ$  C, respectively, the difference in heat content between these temperatures,  $(H_{175} - H_{25})$ , can be computed from  $(H_c - H_r)$  without appreciable error.

## 2. MEASUREMENT OF HEATS OF REACTION

In determining the heat of reaction of a mixture of rubber and sulphur, a cylindrical sample was dusted with talc and dropped into the sample tube of the calorimeter. The quantity of heat required to restore the calorimeter to the equilibrium temperature was computed and was added electrically. With this heat added the calorimeter was ready for the measurement of the heat of reaction of the sample at the calorimeter temperature. Vulcanization proceeded with the liberation of heat. In order to determine this quantity of heat, steel balls at the temperature of the room were dropped into the calorimeter at such a rate as to keep the temperature constant. Since the balls were uniform in weight to within 0.1 percent it was only necessary to count them to obtain the mass of the metal added. The reaction, in all cases, was complete in about an hour, though observations of the temperature were made for at least one-half hour longer to insure that equilibrium had been reached.

The heat of reaction at the temperature of the calorimeter, in joules per gram of mixture, is given by the relation

$$\Delta H_{175} = \frac{-1.045N(0.510)(t_c - t_r)}{m}$$

where  $N$  is the number of steel balls added, 1.045 the weight in grams of each ball,  $m$  the weight in grams of the sample, and 0.510 the mean heat capacity in joules per gram per degree centigrade of the steel from  $25$  to  $175^\circ$  C, which were approximately the temperatures of the room and of the calorimeter,  $t_r$  and  $t_c$ , respectively.

The heat of reaction at  $25^\circ$  C was calculated from the equation

$$\Delta H_{25} = \Delta H_{175} + (H_{175} - H_{25})_{\text{unvulcanized}} - (H_{175} - H_{25})_{\text{vulcanized}}$$

where the last two terms represent differences in heat content between the temperatures indicated.

## 3. ILLUSTRATIVE EXPERIMENT

The data and results which were obtained in a typical experiment involving the measurement of heat of reaction and the differences in heat content between room temperature and vulcanizing temperature, of the reactant mixture and the product of reaction, are given in table 1.

TABLE 1.—Calculation of the heat of reaction of a sample of rubber-sulphur mixture

| State of sample.....                                                                   | Unvulcanized | Vulcanized |
|----------------------------------------------------------------------------------------|--------------|------------|
| Composition of sample:                                                                 |              |            |
| Rubber, percent by weight.....                                                         | 75.0         | 75.0       |
| Sulphur, percent by weight.....                                                        | 25.0         | 25.0       |
| Sulphur, atoms per $C_5H_8$ <sup>a</sup> .....                                         | 0.708        | 0.708      |
| Weight of sample in grams.....                                                         | 8.46         | 7.87       |
| Gram-mole of $C_5H_8$ in sample.....                                                   | 0.0933       | 0.0868     |
| Temperature of calorimeter, °C.....                                                    | 176.2        | 178.2      |
| Temperature of room, °C.....                                                           | 24.0         | 24.3       |
| Determination of $(H_{175}-H_{25})$ :                                                  |              |            |
| Current, amperes.....                                                                  | 0.775        | 0.770      |
| Potential, volts.....                                                                  | 30.8         | 30.9       |
| Time, seconds.....                                                                     | 105.         | 85.        |
| Quantity of heat added, joules.....                                                    | 2,506.       | 2,022.     |
| $(H_c-H_r)$ , j/g of sample.....                                                       | 296.         | 257.       |
| $(H_{175}-H_{25})$ , j/g of sample.....                                                | 292.         | 250.       |
| $(H_{175}-H_{25})$ , j/gram-mole of $C_5H_8$ .....                                     | 26,500.      | 22,700.    |
| Determination of heat of reaction at 175° C:                                           |              |            |
| Steel balls added, number.....                                                         | 38           | -----      |
| Steel added, weight in grams.....                                                      | 39.7         | -----      |
| Mean heat capacity of steel, j/g° C.....                                               | 0.510        | -----      |
| Total heat liberated by reaction, joules.....                                          | 3,081.       | -----      |
| $-\Delta H_{175}$ in j/g of sample.....                                                | 364.         | -----      |
| $-\Delta H_{175}$ in j/gram-mole of $C_5H_8$ .....                                     | 33,000.      | -----      |
| Determination of heat of reaction at 25° C:                                            |              |            |
| $(H_{175}-H_{25})_{unvulc.}-(H_{175}-H_{25})_{vulc.}$ in j/gram-mole of $C_5H_8$ ..... | 3,800.       | -----      |
| $-\Delta H_{25}$ in j/gram-mole of $C_5H_8$ .....                                      | 29,200.      | -----      |
| $-\Delta H_{25}$ in j/g of sample.....                                                 | 322.         | -----      |

<sup>a</sup> The computation of atoms of sulphur per  $C_5H_8$  was made as if the rubber were all  $C_5H_8$ .

## V. RESULTS OF CALORIMETRIC DETERMINATIONS

### 1. DIFFERENCES IN HEAT CONTENT BETWEEN 25 AND 175° C

The differences in heat content between 25 and 175° C for the various samples are given in table 2. The average value of  $(H_{175}-H_{25})$  for the rubber alone is 326 joules per gram, which is equivalent to a mean heat capacity of 2.17 joules per gram per degree centigrade over this range. This value is of the same order or magnitude as other

TABLE 2.—Differences in heat content between 25 and 175° C of rubber, sulphur, rubber-sulphur mixtures, and rubber-sulphur compounds

| Composition of sample |                |                |                      | Difference in heat content ( $H_{175}-H_{25}$ ) |          |
|-----------------------|----------------|----------------|----------------------|-------------------------------------------------|----------|
| Rubber                |                | Sulphur        |                      |                                                 |          |
| Condition             | Amount         | Amount         | Atoms per $C_5H_8^a$ |                                                 |          |
|                       | <i>Percent</i> | <i>Percent</i> |                      | (j/g)                                           |          |
| Purified.....         | 100            | 0              | 0                    | 331                                             |          |
| Do.....               | 100            | 0              | 0                    | 321                                             |          |
| Do.....               | 0              | 100            | -----                | 191                                             |          |
| Do.....               | 0              | 100            | -----                | 196                                             |          |
|                       |                |                |                      | Mixture                                         | Compound |
| Purified.....         | 95.5           | 4.5            | 0.100                | 318                                             | -----    |
| Crude.....            | 95.5           | 4.5            | .100                 | -----                                           | 309      |
| Purified.....         | 91.0           | 9.0            | .210                 | 314                                             | -----    |
| Crude.....            | 91.0           | 9.0            | .210                 | -----                                           | 304      |
| Purified.....         | 82.0           | 18.0           | .467                 | 301                                             | -----    |
| Crude.....            | 82.0           | 18.0           | .467                 | -----                                           | 273      |
| Do.....               | 78.0           | 22.0           | .599                 | 296                                             | -----    |
| Do.....               | 75.0           | 25.0           | .708                 | 301                                             | -----    |
| Do.....               | 75.0           | 25.0           | .708                 | 292                                             | -----    |
| Do.....               | 75.0           | 25.0           | .708                 | -----                                           | 250      |
| Do.....               | 75.0           | 25.0           | .708                 | -----                                           | 240      |
| Do.....               | 75.0           | 25.0           | .708                 | -----                                           | 250      |
| Purified.....         | 68.0           | 32.0           | 1.00                 | 278                                             | -----    |
| Crude.....            | 68.0           | 32.0           | 1.00                 | -----                                           | 220      |
| Do.....               | 68.0           | 32.0           | 1.00                 | -----                                           | 217      |
| Do.....               | 68.0           | 32.0           | 1.00                 | -----                                           | 212      |

<sup>a</sup> The computation of atoms of sulphur per  $C_5H_8$  was made as if the rubber were all  $C_5H_8$ .

determinations reported in the literature,<sup>5</sup> the more reliable of which lie between 2.0 and 2.2 joules per gram per degree centigrade. Strict comparison cannot be made between these different values since they relate to different temperature ranges. The difference in heat content for sulphur between 25 and 175° C was found to be 194 joules per gram. Calculations from data given in the literature<sup>6</sup> for the heat capacities of solid and liquid sulphur and the heat of fusion give a value of 191 joules per gram for this difference.

The differences in heat content between 25 and 175° C of both unvulcanized rubber-sulphur mixtures and vulcanized rubber-sulphur compounds are shown in figure 2 as functions of the sulphur content in percentage by weight. For the unvulcanized mixtures a straight line was drawn between the values at 0 and 100 percent of sulphur. This involves the assumption that the heat content of the mixture follows a simple additive relation and leaves out of consideration the heat of solution of rubber in sulphur and the interfacial energy between the rubber and the sulphur, both of which are probably very small.

Evidence of the linear relation between the differences in heat content of rubber-sulphur mixtures and the composition of such mixtures in percentage of sulphur by weight was obtained by observing the quantity of heat required to bring the calorimeter to the equilibrium temperature after a sample of mixture at room temperature had been added. This was not a precise determination because the liberation of heat by the vulcanization reaction became appreciable in a very few minutes, but, as shown in the figure, the observations are in fair agreement with the linear relation. The values for the rubber-sulphur compounds, also shown in figure 2, cannot be adequately represented by a single linear equation. However, two linear equations intersecting at the composition 19 percent of sulphur (0.5 atom of sulphur per  $C_5H_8$ ) fit the results fairly well. This method of representation was chosen since it is shown later in this paper that the heats of reaction indicate the formation of compounds above 19 percent of sulphur dissimilar to those formed at lower percentages of sulphur. It would be expected that a break in the heat-content curve would most probably occur at this point, and the curve was drawn accordingly. The shape of the curve, however, does not materially affect the values obtained for the heats of vulcanization.

Equations were derived from the curves drawn in figure 2 expressing the differences in heat content in kilojoules per gram-mole of  $C_5H_8$  for compositions in terms of molecular ratios.<sup>7</sup> For the unvulcanized mixtures,

$$(H_{175} - H_{25}) = 22.2 + 6.2x$$

kilojoules per gram-mole of  $C_5H_8$ , where  $x$  represents the number of sulphur atoms per  $C_5H_8$ . This equation holds true for all values of  $x$ . For the vulcanized rubber-sulphur compounds

$$(H_{175} - H_{25}) = 22.2 + 1.2x$$

<sup>5</sup> See Gee and Terry, *Brit. Assoc. Advancement Sci.* page 516 (1889); *Mem. Proc. Manchester Lit. Phil. Soc.* [4] **4**, 38 (1890-1891); Ruhemann and Simon, *Z. physik. Chem.* [A] **138**, 1 (1928); LeBlanc and Kröger, *Z. Elektrochemie* **34**, 241 (1928); and Boström, *Kolloidchem. Beihefte* **26**, 439 (1928).

<sup>6</sup> Lewis and Randall, *J. Am. Chem. Soc.* **33**, 476 (1911); Lewis and Randall, *Thermodynamics*. (McGraw-Hill Book Co., New York, 1923); and Monval, *Bul. soc. chim.* [4] **39**, 1349 (1926).

<sup>7</sup> It may be well to note that if the curves for the heat of reaction or heat content per gram of mixture are linear with the weight percent of sulphur, then the corresponding curves per mole of  $C_5H_8$  are linear with the number of atoms of S per  $C_5H_8$ .



kilojoules per gram-mole of  $C_5H_8$ , from  $x=0$  to  $x=0.5$ . From  $x=0.5$  to  $x=1.0$

$$(H_{175} - H_{25}) = 24.1 - 2.6x$$

kilojoules per gram-mole of  $C_5H_8$ . The observations agree with the values indicated by these equations with a maximum deviation of 0.6 and an average deviation of 0.2 kilojoule per gram-atom of  $C_5H_8$ .

The mean heat capacity between 25 and 175° C was determined for the steel balls used to absorb heat from the calorimeter in the measurements of the heats of the reaction. The average value obtained was 0.510 joule per gram per degree centigrade. Levin and Schottky<sup>8</sup> give data from which a value of 0.507 was computed for steel of 1 percent carbon content in the range of temperature covered by this investigation. The steel balls had approximately the same carbon content. The mean heat capacity of the glass used as a core for some

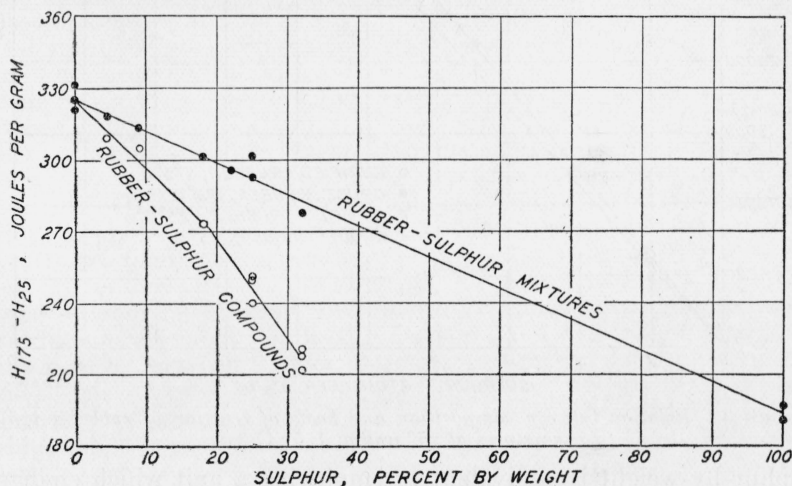


FIGURE 2.—Relation between composition and differences in heat content between 25 and 175° C of rubber-sulphur compounds and mixtures

of the rubber samples was also determined and was found to be 0.85 joule per gram per degree centigrade, which is in practical agreement with the value of 0.84 given in the literature for laboratory pyrex glass.<sup>9</sup> Since the calorimeter was operated isothermally its heat capacity was not required for the computation of the results. It was of interest, however, in connection with the precision of the method since this is dependent on the amount by which the temperature of the calorimeter is changed by the addition or removal of a given quantity of heat. The heat capacity was of the order of 2,300 joules per degree centigrade. This means that when a steel ball at 25° C was dropped into the calorimeter at 175° C the temperature was lowered by about 0.033° C.

## 2. HEATS OF REACTION AT 175° AND 25° C

The heats of reaction of different mixtures of rubber and sulphur at 175° and 25° C are given in table 3. The same results are shown graphically in figure 3, the heats of reaction in joules per gram-mole

<sup>8</sup> Ferrum 10, 193 (1913).

<sup>9</sup> International Critical Tables, 2, 93 (1927) (McGraw-Hill Book Co., New York, N. Y.)

of  $C_5H_8$  being plotted against the number of atoms of sulphur per  $C_5H_8$ . This method of expressing the results was adopted because it provides as a basic unit a fixed chemical quantity,  $C_5H_8$ . The convention followed by previous investigators of plotting the heats of reaction per gram of mixture against the composition in percentage of

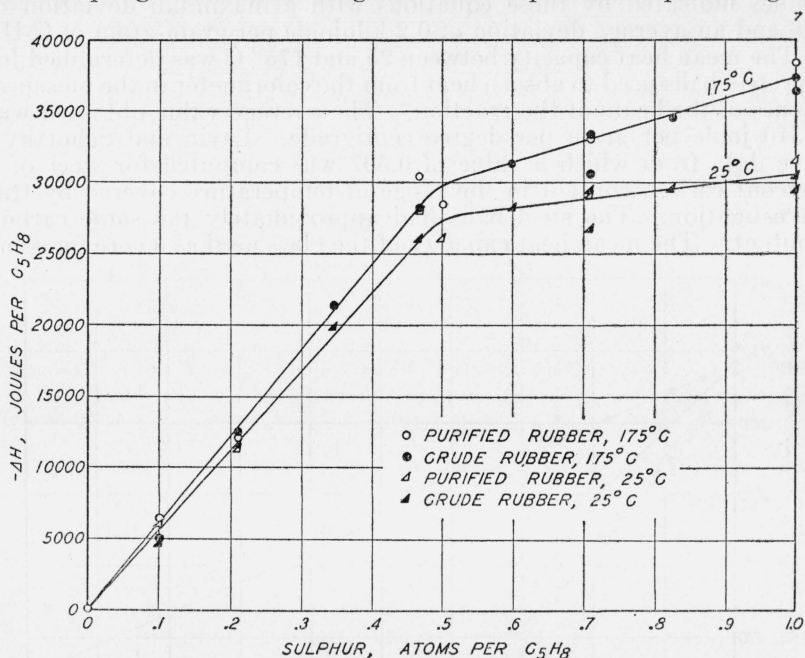


FIGURE 3.—Relation between composition and heats of reaction of rubber-sulphur mixtures at 25° and at 175° C.

sulphur by weight is equivalent to employing a unit which changes with composition.

TABLE 3.—Heats of reaction of rubber-sulphur mixtures.

| Composition of sample |         |         |                                 | Heats of reaction                |          |
|-----------------------|---------|---------|---------------------------------|----------------------------------|----------|
| Rubber                |         | Sulphur |                                 | (-ΔH)                            |          |
| Condition             | Amount  | Amount  | Atoms per $C_5H_8$ <sup>a</sup> | At 175° C                        | At 25° C |
|                       | Percent | Percent |                                 | Kilojoules/gram-mole of $C_5H_8$ |          |
| Purified              | 95.5    | 4.5     | 0.100                           | 6.4                              | 5.9      |
| Crude                 | 95.5    | 4.5     | .100                            | 5.0                              | 4.5      |
| Purified              | 91.0    | 9.0     | .210                            | 12.1                             | 11.1     |
| Crude                 | 91.0    | 9.0     | .210                            | 12.4                             | 11.4     |
| Do                    | 86.0    | 14.0    | .346                            | 21.3                             | 19.6     |
| Purified              | 82.0    | 18.0    | .467                            | 30.4                             | 28.1     |
| Crude                 | 82.0    | 18.0    | .467                            | 28.2                             | 25.9     |
| Purified              | 81.0    | 19.0    | .499                            | 28.5                             | 26.0     |
| Crude                 | 78.0    | 22.0    | .599                            | 31.3                             | 27.9     |
| Purified              | 75.0    | 25.0    | .708                            | 33.0                             | 28.7     |
| Crude                 | 75.0    | 25.0    | .708                            | 30.7                             | 26.4     |
| Do                    | 75.0    | 25.0    | .708                            | 33.4                             | 29.1     |
| Do                    | 72.0    | 28.0    | .826                            | 34.6                             | 29.3     |
| Purified              | 68.0    | 32.0    | 1.00                            | 38.4                             | 31.5     |
| Crude                 | 68.0    | 32.0    | 1.00                            | 36.4                             | 29.5     |
| Do                    | 68.0    | 32.0    | 1.00                            | 37.4                             | 30.5     |

<sup>a</sup> The computation of atoms of sulphur per  $C_5H_8$  was made as if the rubber were all  $C_5H_8$ .

The results plotted in figure 3 may be represented within experimental error by straight lines of different slopes. Discontinuity in the slope occurs for each curve at a composition corresponding to 0.5 atom of sulphur per  $C_5H_8$ . The two portions of the curve representing the heats of reaction at  $175^\circ C$  are described by the following equations:

$$\Delta H_{175} = -60.0 x$$

kilojoules per gram-mole of  $C_5H_8$ , from  $x=0$  to  $x=0.5$  atom of sulphur per  $C_5H_8$ , and

$$\Delta H_{175} = -22.5 - 15.0 x,$$

from  $x=0.5$  to  $x=1.0$ . Similarly the two portions of the curve for the heats of reaction at  $25^\circ C$  are described by the equations:

$$\Delta H_{25} = -55.4 x, \text{ and}$$

$$\Delta H_{25} = -24.8 - 5.8 x$$

kilojoules per gram-mole of  $C_5H_8$ , the values of  $x$  lying between  $x=0$  and  $x=0.5$  for the former equation, and between  $x=0.5$  and  $x=1.0$  for the latter. The observations agree with the values given in these equations with a maximum deviation of 2.3, and an average deviation of 0.6, kilojoules per gram-mole of  $C_5H_8$ .

The heats of reaction may also be expressed in terms of heat units per gram-atom of sulphur. Since the curve which gives the heat of reaction per gram-mole of  $C_5H_8$  as a function of the number of atoms of sulphur per  $C_5H_8$  consists of two straight lines corresponding to the two stages of reaction, the heats of reaction per atom of sulphur entering into the respective reactions are constant and are equal to the respective slopes of the two straight lines. The numerical values at  $175^\circ C$  are  $-60.0$  kilojoules per gram-atom of sulphur for the first stage reaction, which takes place from  $x=0$  to  $x=0.5$  atom of sulphur per  $C_5H_8$ , and  $-15.0$  for the second stage, which takes place from  $x=0.5$  to  $x=1.0$ . At  $25^\circ C$  the numerical values are  $-55.4 x$  and  $-5.8 x$  kilojoules per gram-atom of sulphur for the first and second stage reactions, respectively.

In calculating the composition of the samples in atoms of sulphur per  $C_5H_8$ , the rubber, whether crude or purified, was treated as if it were all rubber hydrocarbon. This procedure is warranted, in the present case, by the fact that there is no significant difference in the results for the two kinds of rubber, as shown in table 3 and figure 3. More precise measurements, however, would doubtless indicate a difference, since it is well known that not only the hydrocarbon but also the resins and proteins of crude rubber react with sulphur.

Some experiments were conducted in which rubber-sulphur compounds, vulcanized with less than the maximum amount of sulphur, were further vulcanized with additional sulphur. The quantity of heat liberated was in agreement with the value calculated by subtracting the heat of reaction of rubber with the initial percentage of sulphur from the heat of reaction with the final percentage as read from figure 3. In one such experiment vulcanized rubber containing 19 percent of sulphur ( $C_5H_8S_{1/2}$ ) was ground and mixed with additional sulphur to correspond to a composition of 32 percent ( $C_5H_8S$ ). Because of the bulk of the mixture the largest sample that could be used was less than half the ordinary size, and the precision was cor-

respondingly reduced. On vulcanization the heat liberated was 5.5 kilojoules per gram-mole of  $C_5H_8$ . Curve 3 indicates a value of about 30.0 kilojoules per gram-mole of  $C_5H_8$  for the vulcanization of rubber with 19 percent of sulphur. The addition of 5.5 kilojoules to this gives a value of 35.5 kilojoules per gram-mole of  $C_5H_8$ , which may be compared with the value 37.5 which is indicated by the curve for the compound containing 32 percent of sulphur.

## VI. COMPARISON WITH PREVIOUS INVESTIGATIONS

A comparison of the heats of reaction at 25° C, which are given in table 3, with the heats of reaction found in some previous investigations is shown in figure 4. In preparing this figure the convention of

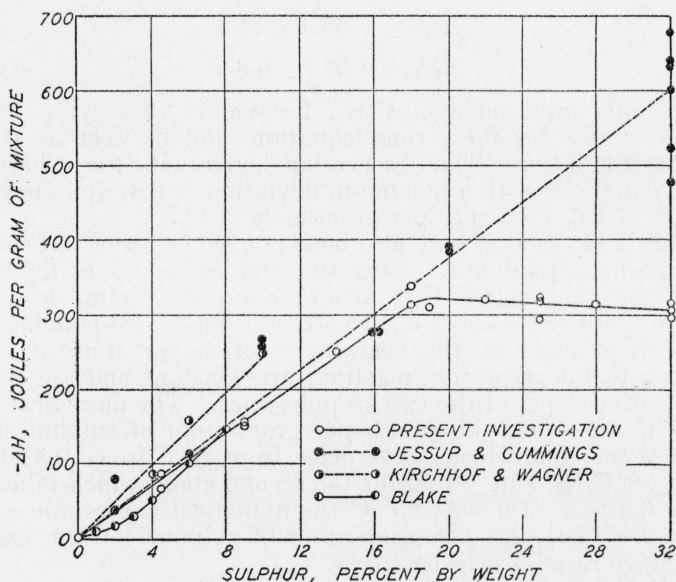


FIGURE 4.—Relation between composition and heats of reaction of rubber-sulphur mixtures determined by various investigators.

previous investigators has been followed in expressing the heats of reaction in joules per gram of mixture, and the composition in percentage of sulphur by weight.<sup>10</sup> The results of Kirchhof and Wagner<sup>11</sup> are somewhat higher than those of the present investigation and extend to only 10 percent of sulphur. These investigators were chiefly concerned with the effect of fillers and accelerators on the heats of vulcanization and reported only a few observations on mixtures of rubber and sulphur alone. The results of Blake<sup>12</sup> are lower than those of the present investigation and indicate that the heat of reaction is not a linear function in the range from 0 to 8 percent of sulphur.

<sup>10</sup> See footnote 7.

<sup>11</sup> *Gummi-Zeitung* **39**, 572 (1924-1925).

<sup>12</sup> *Ind. Eng. Chem.* **26**, 1283 (1934).



The results reported by Jessup and Cummings<sup>13</sup> agree well with the present results for the range from 0 to 19 percent of sulphur. Their curve exhibits no discontinuity in the slope at this point, hence their values for the compositions from 19 to 32 percent of sulphur are higher than the present values. This discrepancy at the higher percentages of sulphur may be due to differences in the conditions of vulcanization employed in the two investigations. The samples used by Jessup and Cummings were vulcanized for about 40 hours at 141° C in an autoclave containing inert gas under pressure, while in the present work the samples were vulcanized for about 1 hour at 175° C in a glass tube, one end of which was open to the air.

The results of an earlier investigation by Blake and of an investigation by Hada, Fukaya, and Nakajima<sup>14</sup> are considerably at variance with those here considered and are not shown in figure 4 because of the scale used.

A salient feature of this study is the change of slope obtained in the curve for the heat of vulcanization at the composition 0.5 atom of sulphur per  $C_5H_8$  (19 percent of sulphur by weight). This is an indication that the reaction of rubber with sulphur takes place in two stages, the first liberating a greater quantity of heat than the second. The suggestion of a two-stage reaction between rubber and sulphur is by no means novel, a variety of evidence for it having been presented by different authors.<sup>15</sup> In some instances the evidence relates to changes in properties which are associated with the fortuitous circumstance that the transition between soft and hard rubber occurs at room temperature at the composition, 0.5 atom of sulphur per  $C_5H_8$ . This evidence is shown not to hold when the properties under consideration are measured at other temperatures and pressures. Other types of evidence, however, such as the reaction between vulcanized rubber and alcoholic potash described by Whitby and Jane,<sup>16</sup> seem to constitute valid evidence for a two-stage reaction. Definite conclusions, however, cannot be drawn until the mechanism of the reaction of rubber with sulphur is established.

WASHINGTON, December 20, 1934.

<sup>13</sup> BS J. Research **13**, 357 (1934) RP713.

<sup>14</sup> Blake, Ind. Eng. Chem. **22**, 737 (1930). Hada, Fukaya, and Nakajima, Rubber Chem. Tech. **4**, 507 (1931).

<sup>15</sup> Blake, Ind. Eng. Chem. **22**, 737 (1930); **26**, 1283 (1934); Hada, Fukaya, and Nakajima, Rubber Chem. Tech. **4**, 507 (1931); Williams and Beaver, Ind. Eng. Chem. **15**, 255 (1923); Glancey, Wright, and Oon, Ind. Eng. Chem. **18**, 73 (1926); and Davies, Trans. Inst. Rubber Ind. **10**, 176 (1934). Curtis, McPherson, and Scott, in BS Sci. Pap. **22**, 398 (1927) S560, suggested the existence of definite compounds of rubber and sulphur on the basis of changes in electrical properties and density with composition. It was later shown by Kimura, Aizawa, and Takeuchi, J. Inst. Elec. Engrs., Japan, no. 485, 1274 (December 1928), and Kitchin, J. Am. Inst. Elec. Engrs. **48**, 281 (1929), and Kimura and Namikawa, J. Soc. Chem. Ind., Japan, **32** (supplemental binding), 196B (1929) that the agreement between changes in electrical properties and the compositions represented by simple empirical formulas was fortuitous and without basic significance.

<sup>16</sup> Trans. Roy. Soc. Canada [3], **20**, 121 (1926).