

Volume Dilatometry¹

By Norman Bekkedahl

The volume dilatometer, although inexpensive and simple in construction and principle, is found to be a valuable research tool, not only for obtaining data on volume coefficients of thermal expansion, but also for studying phase changes in solids and liquids. The preparation and operation of the volume dilatometer are described in detail. An illustrative calculation is given using data obtained from volume-temperature measurements on a sample of butyl rubber from about -30° to $+90^{\circ}$ C, using mercury as a confining liquid in the dilatometer.

I. Introduction

Dilatometers have been employed in various forms for the measurement of expansivity of both solids and liquids. Linear dilatometers of various types have frequently been used to advantage in determining the expansivity of metals and other solid materials. They cannot, of course, be used for measuring the expansivity of liquids, nor can they be relied upon to give correct results for nonrigid solid materials. In the latter instance, however, the volume dilatometer can be used successfully.

In addition to the simple determination of thermal expansivity of solids and liquids, this instrument has been used to great advantage in the study of phase changes. In experiments performed on unvulcanized natural rubber at this Bureau, it was found necessary, because of time lags in transitions, to study the phase changes of rubber by means of the dilatometer [5]² before satisfactory calorimetric measurements of specific heats could be made. The volume dilatometer offered a convenient means for studying rates of crystallization of vulcanized rubber [6], unvulcanized rubber [5, 24, 39], of glycerine [35], and also of sugar from a saturated solution [19]. Change of volume of rubber compounds has been studied while they are in the process of being stretched [18, 22]. In the dilatometric work of

Holt and McPherson [18] on the crystallization of rubber upon stretching, this method proved simpler and produced more useful information than was obtained by the more elaborate X-ray techniques [1, 23]. Mondain-Monval [26] determined the various transition temperatures for sulfur and for selenium. Several investigators used dilatometers to study volume changes during polymerization [14, 30, 33] and other reactions [15]. The quantity of bound water in solids has been determined accurately by similar procedures [2, 8].

Second-order transitions have been studied by this simple method. Raw rubber, using alcohol as a confining liquid in the dilatometer, was found to undergo this type of transformation at about -70° C [5], whereas vulcanized rubber showed a corresponding change at higher temperatures, depending on the degree of vulcanization [5, 37, 38]. Various investigators have obtained considerable information on the characteristics of the second-order transition by studying volume-temperature relationships for polystyrene and other plastic materials [3, 7, 13, 21, 27, 32]. Some of these authors, and also others [3, 20, 27, 32, 36], have studied the nonequilibrium features of this type of transition. Boyer and Spencer [7] found the volume technique valuable in investigating the nature of polymeric mixtures and the homogeneity of copolymers. Jenckel and Ueberreiter [20, 21] likewise studied various substances, determining the effects of different molecular weights of polymers and also the effects of addition compounds on the temperature of this transition.

¹ This work was financed, in part, by funds transferred from the Office of Naval Research.

² Figures in brackets indicate the literature references at the end of this paper.

In previous papers on volume dilatometers [5, 6, 10, 12, 13, 15, 16, 19, 21, 28, 33, 36, 38, 39], the emphasis has always been on the results obtained, and the descriptions of methods of operation have usually been very brief or missing completely. Standard texts on measurements in physical chemistry do not include descriptions of the construction and operation of volume dilatometers. This paper has, therefore, been written in considerable detail. The construction, operation, and method of calculating the results are described in full. The practices are similar to, but include marked improvements over, those previously used in this laboratory for investigations on rubber [5, 6, 39]. Illustrative data are given, together with detailed calculations, yielding, for the first time, information on the expansivity of a butyl rubber pure-gum vulcanizate.

II. Sample

A number of samples of different types of rubber in different compounding formulas have been measured for expansivities by means of volume dilatometers. However, only one of these samples was chosen for use in this article to illustrate the procedures of volume dilatometry and the methods of calculating the results from the data. This sample was a vulcanized gum stock of butyl rubber, compounded according to the formula

GR-I synthetic rubber (butyl)	100	parts
Zinc oxide	1.0	part
Sulfur	1.5	parts
Butyl zimate	1.0	part
Total	103.5	parts

The compound was cured in the form of sheets of 2-mm thickness for 60 minutes at 153° C.

III. Preparation of Dilatometer

The dilatometer is made solely from glass tubing and a glass capillary. The tubing from which the bulb of the dilatometer is made can be of any size convenient to fit the size and shape of the sample. The size of the capillary depends on the range of volume expected to be covered in a given set of measurements, which in turn depends on the size of the sample, its expansivity, and the range of temperature to be covered. The greater the uniformity of bore throughout the length of the tube,

the simpler are the calculations and more reliable are the results.

1. Calibrating the Capillary

The capillary used to make the dilatometer described here was approximately 500 mm in length and about 2 mm in inside diameter. The thickness of the wall of the capillary was about 3 mm. It was made from Pyrex glass by the Corning Glass Company and was described as "specially selected as to uniformity." It was graduated along its entire length in millimeters.

The capillary is calibrated by weighing mercury, at a known temperature, that had occupied known portions of the tube. In order to determine this volume with considerable accuracy, the zero (lower) end of the capillary is sealed to one arm of a capillary stopcock, the other arm of which is drawn to a smaller opening, thus forming a burette. In order to prevent air from being trapped in the stopcock, the mercury is introduced into the capillary by "sucking" it up through the stopcock and into the capillary by means of a vacuum pump.

After the level of the mercury in the completely filled capillary is recorded, a portion of the mercury, say from about 50 to 75 mm in length, is run out into a container and weighed. The volume of the capillary between these two levels is determined from the weight of the mercury and tables of its density [34]. This same operation is then repeated, beginning at each new level of the mercury in the capillary, until some level near the bottom of the capillary is reached. Care should be taken, however, not to work too close to the seal because of a possible abnormal size of the capillary in this region. From the volume of mercury occupying the space between the highest and the lowest levels, the average change of volume per unit length, in milliliters per millimeter, is calculated. For the capillary used in these experiments the value was determined to be 0.003720 ml/mm.

Using the lowest recorded level of the capillary as a reference point, or as zero volume, the nominal volumes of the capillary at the other levels of calibration are calculated, assuming complete uniformity of internal diameter throughout the length of the capillary. At the various levels of calibration, these nominal or uncorrected volumes are compared with the actual volumes as obtained

by calibration. The differences between these two sets of values give the corrections of the capillary at these readings. If the true volume is greater than that obtained by assuming uniformity of bore, then the correction is positive; and if it is less, then the correction is negative.

From these data a graph is prepared in which the correction for nonuniformity of the capillary is plotted as a function of the reading of the capillary graduations. Corrections are zero, of course, at the highest and lowest levels of calibration of the capillary. From this curve is determined the correction to be applied to the linearly calculated volumes for any given level of capillary. For the capillary used in the present investigation the correction curve is shown in figure 1. For

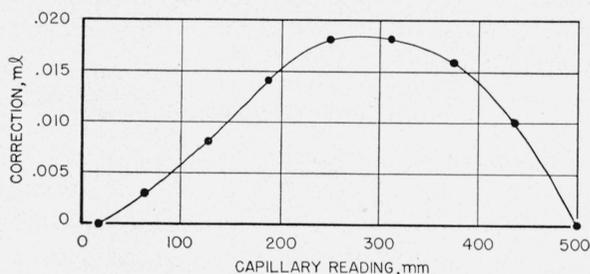


FIGURE 1. Corrections to be applied to the volume of the capillary at various heights to account for irregularity in cross section.

reasons that will be seen later in this paper, it is advisable to estimate the readings of the capillary to the nearest 0.5 mm and the weight of the mercury to the nearest 10 mg. From these calculations the volumes can be obtained to the nearest 0.002 ml.

2. Adding the Sample

The stopcock is removed from the capillary, and the zero end of the capillary is then sealed to one end of the 20-mm tube (see fig. 2, A and B). Into the large, open end of the glass tube is inserted the weighed sample. In this experiment, the sample of rubber was introduced in the form of strips cut from vulcanized sheets. These strips were cut in various widths, so as to fill up the cross-sectional area of the tube. The weight of the rubber sample was 27.321 g.

After the sample, there is inserted a hollow bulb made from the same type of glass as the dilatometer. The arrangement up to this point, which can be seen in figure 2, C, is sealed off just

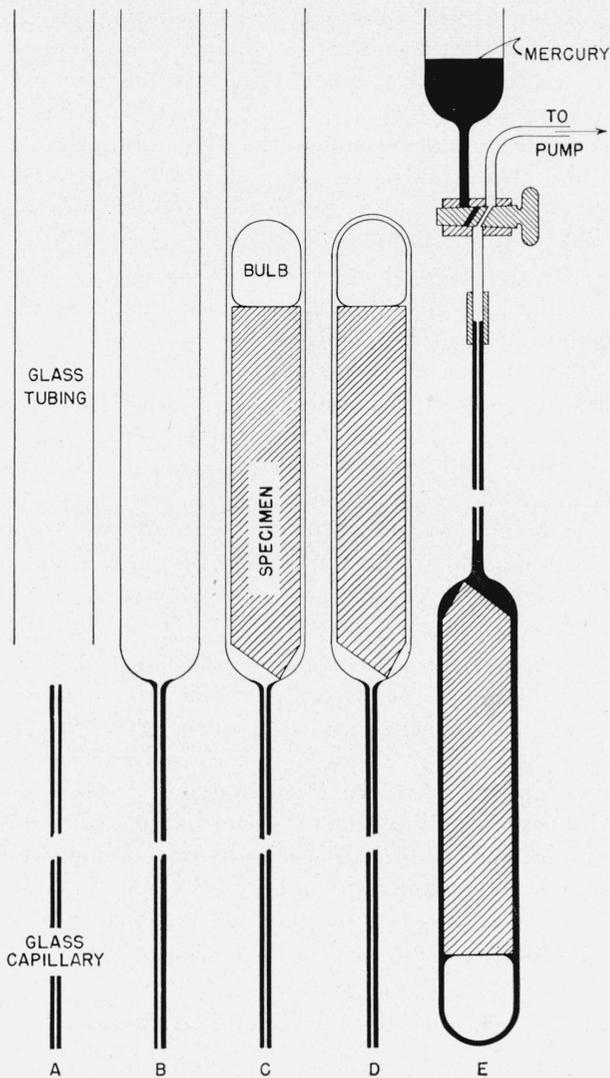


FIGURE 2. Steps in the construction and filling of a volume dilatometer.

above the hollow bulb, forming the completed dilatometer illustrated in figure 2, D. The sole object of the small, hollow bulb is to allow the sealing of the dilatometer without unduly heating the specimen and without increasing the net volume of the dilatometer. Sealing the dilatometer at the same distance from the specimen without the presence of the bulb may avoid overheating the sample, but it leaves more space to be occupied by the confining liquid, thus decreasing the precision of measurement. As the hollow bulb is made of the same material as the rest of the dilatometer, no correction need be made for its volume or its expansivity. The insertion of the bulb is therefore equivalent to reducing the net

volume of the dilatometer. Depending on the shape of the specimen, the volume of a sample in a dilatometer constructed in this manner may occupy as much as 75 percent or more of the total volume of the dilatometer. The dilatometer in this form is then weighed. For the experiment described here the weight of the dilatometer including the sample was 122.22 g.

In an effort to eliminate the process of heat-sealing the glass bulb, one of the experimental dilatometers was prepared a little differently. Its bulb was made up of two parts, the bottom and the top halves joined to each other by means of a ground joint held together by springs. Although this bulb gave no real trouble, it required considerable care to keep it tightly closed, and less confidence was felt in the ground-glass joints through which there was always the possibility of a leak.

Still another variation from the above-described dilatometers has been found necessary when the sample under investigation is soft enough to flow and is less dense than the confining liquid. In one experiment a soft polymeric material, under upward pressure from the mercury, was forced into the capillary on a rising temperature but would not return to the bulb on cooling. For use with substances of this type the capillary can be given a U-bend near the bottom, thus inverting the bulb.

3. Choosing the Confining Liquid

A confining liquid to be used in the dilatometer in order to be entirely suitable for the purpose, must satisfy certain requirements. It must exist in the liquid state over the entire range of temperature in which measurements are desired. It must have a vapor pressure sufficiently low that none of the liquid is lost by evaporation during the course of experiment. Its viscosity must not become unduly high at the lower temperatures. It must have little or no swelling action on the specimen. Its expansivity must be known accurately over the entire range of temperature for which it is to be used. In the present investigation mercury was used as the confining liquid because it satisfied all these requirements. Mercury is to be strongly recommended for use in all investigations not requiring measurements below -39°C .

In earlier work on rubber in this laboratory other confining liquids have been used [5]. Water is satisfactory near room temperature, but the relatively small range of temperature between its freezing and boiling points greatly limits its usefulness. There are a number of organic liquids that are suitable for use at low temperatures. Acetone and the alcohols have been used. However, these liquids produce some swelling of natural rubber over long periods of time. This swelling was not observed to produce any change in expansivity, but in one instance swelling by acetone probably displaced the second-order transition of unvulcanized natural rubber to a lower temperature [5]. It is recommended that methyl alcohol be used in work at temperatures below -39°C . Some of the new liquid silicones may also prove to be useful in this range of temperature.

4. Adding the Confining Liquid

The dilatometer is placed in its normal upright position (see fig. 2, E) for the insertion of the confining liquid. Into the capillary is inserted a fine wire, about 0.4 mm in diameter, of such length that it reaches into the bulb of the dilatometer and rests against the specimen. The composition of the wire must be such that it is inert to both the sample and the confining liquid. The wire is then cut off at a point about 5 cm above the top of the capillary. The object of this wire is only to allow any entrapped air to pass more freely through the confining liquid in the capillary, and it is removed before measurements are made. A three-way stopcock is connected, by means of a short length of heavy-walled rubber tubing, to the top of the capillary, allowing the top of the wire to enter into the tube of the stopcock. A diagram of these connections can be seen in figure 2, E; but in order not to make the drawing too involved the wire is not shown. Through the three-way stopcock the dilatometer can be connected either to a mercury reservoir or to an efficient mechanical-type vacuum pump.

The dilatometer is first connected to the vacuum pump in order to remove the air from the confining spaces of the dilatometer and also from the sample. This operation sometimes requires but a few minutes, and other times it takes several days, depending on the quantity of gas dissolved in the speci-

men. Gases must be removed quantitatively, because their expansivities are usually much different from that of the sample, and their volume changes are also greatly dependent on variations in pressure exerted upon them. After the dissolved or entrapped air is thought to be removed, the stopcock is turned in order to allow the confining liquid to enter the dilatometer, including part of the capillary.

Any small amount of gas entrapped in the dilatometer can be determined quantitatively. The level of the liquid in the capillary is measured when the dilatometer is at atmospheric pressure. Then, at the same temperature, a vacuum is applied to the capillary tube. The presence of entrapped air in the dilatometer causes the level to rise to a steady state in the capillary. The amount of rise, however, depends not only on the quantity of gas entrapped and the pressure change, but also on the compressibility of the materials in the dilatometer and of the dilatometer itself. The increased level of the liquid is noted.

For the dilatometer and its contents described in this investigation the increase in height of the mercury upon application of the vacuum was 1 mm, which is equivalent to a volume of 0.0037 ml. From the volume compressibility of soft vulcanized rubber, about 50×10^{-6} per bar [31], the volume of the rubber in the dilatometer increases by about 0.0015 ml for a decrease in pressure of one atmosphere. Similarly the volume of the mercury increases by about 0.0001 ml. A decrease of pressure inside the dilatometer also tends to decrease the volume of the dilatometer by an amount that has not been calculated. All three of these factors, therefore, cause the level of the mercury to rise in the capillary when the dilatometer is subjected to a reduced pressure. This means that the increase in volume arising from these factors must be subtracted from the total observed increase in volume in order to calculate the volume of any gas inside the sample. The value thus obtained is 0.0021 ml or less.

The reading for the mercury level in the capillary at room temperature was 368 mm above the zero. If it is assumed that the gas bubble was near the middle of the specimen, about 90 mm below the reference zero, a hydrostatic pressure of 458 mm of mercury was exerted on this bubble of gas while vacuum conditions existed above the mercury. Under normal atmospheric conditions the

pressure on the gas bubble was therefore about 1,218 mm of mercury. From the gas laws,

$$V_a = \frac{458}{1,218} \cdot V_v,$$

in which V_a is the volume of the gas bubble with atmospheric pressure on the mercury and V_v the volume with vacuum. The difference in these volumes was measured in the capillary as

$$V_v - V_a = 0.0021 \text{ ml.}$$

Solving the two equations for the volume V_a , one arrives at a value of 0.0013 ml of gas in the dilatometer. Experience has shown that this small quantity of gas is negligible. After volume-temperature measurements for the dilatometer are completed, the resulting data may be used to calculate the error caused by this quantity of gas.

After adjustment of the level of the liquid in the capillary, the dilatometer is again weighed in order to determine the quantity of confining liquid. If some of the confining liquid must be removed from the capillary, it can easily be done by inverting the dilatometer and playing the wire inside the capillary. The weight of the dilatometer, including the sample and the liquid used in the present investigation, was 386.93 g, of which 264.71 g were therefore mercury.

If a confining liquid is used that is too volatile to be added conveniently by the above procedure employing a vacuum, the liquid can be added by subjecting the dilatometer bulb alternately to high and low temperatures. In this case, a funnel containing the confining liquid is fastened to the top of the capillary.

IV. Experimental Procedure

The assembly of apparatus used for making these measurements is quite simple. A cylindrical flask of about 6-liter capacity contains the baths of alcohol and of water that are used, depending on the temperature range of the experiment. For temperatures below 0° C it is recommended that a vacuum-jacketed cylinder be used as the container for the bath. This type of bath container is not actually necessary for proper operation but provides easier control of temperature. Measurements may be conducted on several dilatometers in the bath during the same run. An efficient stirrer is required to maintain uniform tempera-

ture throughout the bath. Heat may be furnished the bath by means of an electrical immersion heater controlled by a variable-ratio autotransformer. The temperature of the bath can be measured by calibrated thermometers capable of reading to the nearest 0.1°C .

A determination of the density of the sample must be made in order to obtain the volume of the specimen in the dilatometer. The preparation of the rubber sample for the density measurements and the method of determining the density were the same as those described in detail in another article [40]. This method of hydrostatic weighings is an excellent method for measurement of density [4] if a liquid is available whose density is accurately known, and if the liquid has no solvent action on the sample to be measured. Utilizing an analytical balance having a sensitivity of 0.1 mg , density values can be obtained that are reproducible to about 0.0002 g/cm^3 or better.

For each set of measurements of volume-temperature in the dilatometer there must be recorded the room temperature, the reading of the dilatometer-stem at the surface of the bath, and also the reading of the thermometer-stem at the bath level. These data are necessary for the subsequent stem corrections for both the dilatometer and the thermometer.

With the stirrer operating and a constant and uniform temperature attained, readings are first made of the liquid levels of the dilatometer capillary and of the thermometer. Dry ice is then added to the alcohol bath in order to cool to the proper temperature. With mercury as a confining liquid, the lower temperature of measurement is limited to about -39°C because of the freezing of mercury. After the bath and dilatometer have remained at the lower temperatures sufficient time to be sure of temperature equilibrium, measurements are made of capillary and thermometer readings. The temperature is then allowed to rise slowly, usually less than 0.5°C per minute. A faster rate of heating may cause a lag of temperature between the sample and the bath. The safe rate of heating can easily be checked by adding powdered dry ice in a quantity just sufficient to hold the temperature constant. If the capillary reading at this constant temperature checks with the equivalent one made on a rising temperature the rate of heating can be considered safe. If the test indicates a lag of

temperature in the dilatometer the heating rate should be reduced. The maximum allowable rate is, of course, dependent on the heat conductivity of the confining liquid and the sample, and also on the size and shape of the specimen in the dilatometer. The rate of heating can be regulated very easily by either the controlled addition of dry ice or by the controlled application of current in the heater.

When the temperature is reached where the liquid of the dilatometer approaches the top of the capillary, the heating is discontinued and the temperature allowed to attain that of the room, at which time the temperature and volume readings are again noted. A rough graph is plotted between the temperature and the capillary readings. The two values obtained at room temperature, before and after the run, should both lie on the smooth curve obtained from data of the run unless there has been introduced some disturbing influence, such as the transformation to a different phase of the material or the formation of gas in the dilatometer.

Where data are desired at temperatures higher than those attained in the previous experiment, confining liquid must be removed from the dilatometer in order to bring the level nearer the bottom of the capillary. The dilatometer and contents need not be reweighed after this operation, as the volume of the dilatometer has already been established from previous data. Experimental data above room temperature are then taken in the same manner as in the previous run.

1. Calculations

Table 1 includes all the data taken from the present experiment that are necessary for calculation of results, with the exception of the calibrations of the capillary tube, which are shown in figure 1. The experimental data in the table begin with the weight of the sample, on line 1, and continue through line 11, the capillary readings as measured. All figures in the table below this latter line are calculated from the previously listed data.

In the bottom line of the table are recorded the corrected temperatures. These figures include the previously determined corrections for the inaccuracies of the thermometer and also the corrections for emergent stem. The latter corrections are made according to the usual procedure [11], taking

TABLE 1. Experimental data and calculated values for the volumes and densities of a sample of butyl gum rubber in a dilatometer

1	Weight of sample.....	27.321 g.							
2	Weight of sample and dilatometer.....	122.22 g.							
3	Weight of sample, dilatometer, and mercury (first series).....	386.93 g.							
4	Temperature of room during dilatometric measurements.....	27° C.							
5	Capillary stem reading at level of bath.....	100 mm.							
6	Thermometer stem reading at level of bath.....	50° C.							
7	Capillary size, assuming uniform.....	0.003720 ml/mm.							
8	Density of sample at 25° C ¹	0.9333 g/cm. ³							
9	Capillary calibration.....	Figure 1.							
		First series				Second series			
10	Thermometer readings (measured)..... °C.....	-23.7	-4.8	10.2	-----	41.3	53.9	67.2	81.0
11	Capillary readings (measured)..... mm.....	(368.0)	111.0	212.5	290.5	(80.5)	163.0	227.0	297.0
12	Capillary readings (stem-corrected)..... mm.....	368.0	111.0	212.0	290.0	80.5	163.0	227.5	298.0
13	Capillary volumes (uncorrected for irregularity)..... ml.....	1.369	0.413	0.789	1.079	0.299	0.606	0.846	1.109
14	Corrections for irregularity (fig. 1)..... ml.....	+0.016	+0.006	+0.016	+0.018	+0.004	+0.012	+0.017	+0.018
15	Capillary volumes (corrected for irregularity)..... ml.....	1.385	.419	.805	1.097	.303	.618	.863	1.127
16	Total volume of contents (uncorrected)..... ml.....	48.834	47.868	48.254	48.546	47.752	48.067	48.312	48.576
17	Total volume of contents (corrected for glass expansion)..... ml.....	48.834	47.845	48.240	48.539	47.752	48.075	48.326	48.596
18	Volumes of mercury..... ml.....	19.560	19.385	19.457	19.508	18.478	18.533	18.575	18.620
19	Volumes of sample..... ml.....	29.274	28.460	28.783	29.031	29.274	29.542	29.751	29.976
20	Densities of sample..... g/cm. ³	¹ 0.9333	0.9600	0.9492	0.9411	¹ 0.9333	0.9248	0.9183	0.9114
21	Specific volumes of sample..... cm ³ /g.....	1.0715	1.0417	1.0535	1.0626	1.0715	1.0813	1.0889	1.0972
22	Temperatures (corrected)..... °C.....	(25.0)	-24.2	-5.0	10.3	(25.0)	41.3	53.9	67.3

¹ Hydrostatic weighings.

into account the coefficients of expansion of both the glass and the liquid inside the thermometer.

The corrections for the emergent stem of the dilatometer are made in a manner similar to that used for the emergent stem of the thermometer. The difference between the expansivity of mercury used in the present dilatometer [34] and that of Pyrex glass [9, 17, 29] is 0.00017 per degree C. In table 1, line 12, are given the capillary readings after correction for emergent stem. The formula by which they are corrected is

$$\text{correction} = K(t - t_r)(R - R_b),$$

in which K is the coefficient previously described (0.00017, if mercury is used in Pyrex glass), t is the temperature of the bath in degrees centigrade, t_r is the temperature of the liquid in the emergent stem, which is practically the same as that of the room, R is the reading of the level in the capillary in millimeters, and R_b is the capillary stem-reading at the level of the bath. These corrections are made to the experimental readings to the nearest 0.5 mm.

From the stem-corrected dilatometer capillary readings (table 1, line 12) and the average size of the capillary in milliliter per millimeter (line 7), the capillary volumes, uncorrected for irregularity

(line 13), are calculated for all of the temperatures of measurement recorded in the table. To these figures are added the corrections for nonuniformity of bore of the capillary (line 14), giving the corrected volume of mercury in the capillary (line 15). For the capillary used in these experiments the corrections (see fig. 1) are all positive, which indicates a continuous decrease in the diameter of the tube in going up the capillary. Any abnormal size of the capillary near the zero reading or below the calibrated portion of the capillary will cause no error in the calculations, as the difference caused by this abnormality is taken care of in the calculations for the size of the bulb of the dilatometer.

A curve plotted from the original data, capillary readings versus temperature, showed that the mercury in the dilatometer stood at 368.0 mm at 25° C. Since the values for temperature and dilatometer readings in the first column of figures were obtained from the graph and not directly from measurements, they are placed in parentheses. A similar situation exists in the fifth column of figures, the level of the mercury being different because some of the confining liquid had been removed, and the total volume was therefore changed. There is, of course, no stem correction to be made at room temperature. From the zero reading of the capillary, which is used as a

reference point, the volume occupied by the mercury of the stem, assuming a uniform bore throughout, is 368.0×0.003720 , or 1.369 ml. From the calibration curve for the capillary, which was made previous to the preparation of the dilatometer and shown in figure 1, the correction at this height for nonuniformity of bore is found to be +0.016 ml. Therefore, the true volume of mercury in the capillary at 25° C is 1.385 ml.

The volume of the dilatometer contents is determined from the weights and densities of the specimen and the confining liquid. For the present experiment the density of the sample of vulcanized butyl gum rubber was measured by means of hydrostatic weighings in distilled water and found to be 0.9333 g/cm³ at 25° C. The 27.321-g specimen therefore occupies a volume of 29.274 cm³ at 25° C. At this same temperature the density of mercury is 13.5340 g/ml, and therefore the 264.71 g of confining liquid used in the first series of experiments occupies a volume of 19.560 ml at 25° C. This gives a total volume of 48.834 ml for the contents of the dilatometer at 25° C.

The weight of mercury of 264.71 g was that used only for the first series of experiments, performed below room temperature, and therefore could not be used in calculating the results tabulated in the second series, which were made above room temperature. The experiment described in the second series was made after some mercury had been removed in readjusting the level of the confining liquid in the capillary. At 25° C, the mercury level after readjustment stood at 80.5 mm in the dilatometer capillary. This height corresponds to a volume in the capillary of $0.299 + 0.004$, or 0.303-ml corrected volume. The capillary volume at 25° C in the first series was calculated to be 1.385 ml. Therefore, the amount of mercury removed was 1.082 ml, or 14.644 g. This left a weight of mercury of 250.07 g in the dilatometer for the second series of experiments.

The volume of the contents of the dilatometer (mercury plus sample) in the first series of measurements was calculated to be 48.834 ml at 25° C. Subtracting the volume of the mercury in the capillary at this temperature, 1.385 ml, leaves a volume of 47.449 ml for the bulb at 25° C. In order to determine the total volume of the contents at other temperatures, the bulb volume of 47.449

ml is added to the corrected capillary volumes. This total volume (table 1, line 16) must, of course, be corrected further for the expansion or contraction of the glass of the dilatometer itself. The corrected volumes at other temperatures, V_t , may be calculated from the equation

$$V_t = V_{25} [1 + 0.000010 (t - 25)],$$

in which V_{25} is the total volume of the dilatometer contents at 25° C, t is the temperature in degrees centigrade, and 0.000010 is the volume coefficient of expansion of laboratory Pyrex glassware [9, 17, 29]. These corrected volumes are recorded in line 17 of the table.

The volumes of the mercury at the different temperatures (table 1, line 18) are calculated from the densities of mercury given in International Critical Tables [34]. It was found that, for the range of temperatures covered in these experiments, the volumes of mercury could be calculated to a precision of nearly one part in 100,000 by means of the equation,

$$V = M (0.073554 + 0.0000134 t),$$

in which V is the volume of the mercury in the dilatometer in milliliters, M is its weight in grams, 0.073554 is its specific volume in milliliters per gram at 0° C, 0.0000134 is the temperature coefficient for its specific volume, and t is the temperature in degrees centigrade.

The volumes of mercury (table 1, line 18) are subtracted from the corrected total volumes (line 17) in order to obtain the volumes of the sample at the various temperatures (line 19). The calculations for the densities (line 20) and the specific volumes (line 21) are then made from the calculated volumes and the weight of the sample in the dilatometer.

Table 1 illustrates the method of calculating the specific volumes and densities of the specimen at different temperatures. It contains only a representative portion of all the capillary and temperature data recorded in the experiments. The results calculated in the table, together with the results calculated from all the other data not recorded here, are reproduced in figure 3, which shows a graph in which the densities and the specific volumes of the sample of rubber are plotted as a function of the temperature. The

slope of these curves gives the changes in density and specific volume with respect to temperature,

$$\frac{d\rho}{dT} \text{ and } \frac{dV}{dT}$$

A differentiation with respect to temperature of the equation, $\rho = m/V$, where m is the mass of the sample, gives

$$\frac{d\rho}{dT} = \frac{d}{dT} \left(\frac{m}{V} \right) = -\frac{m}{V^2} \left(\frac{dV}{dT} \right)$$

From this, one may obtain the equation

$$\frac{1}{\rho} \left(\frac{d\rho}{dT} \right) = -\frac{1}{V} \left(\frac{dV}{dT} \right)$$

It will be noted that all of the values of specific volume are represented in the graph by a straight line. The points representing the densities, however, fall on a curve that is slightly concave upward. Since $\rho = m/V$, it is evident that ρ and V cannot simultaneously vary linearly with T at any given temperature. If one of these varies linearly, the other must vary hyperbolically. Instead of drawing a curve to try to fit all of the values of density, a straight line was drawn that represents its tangent at a temperature of 25° C. The object of this curve is to calculate the density coefficient at room temperature. From a large-scale drawing of the same graph, both the specific volume and the density curves show the coefficients

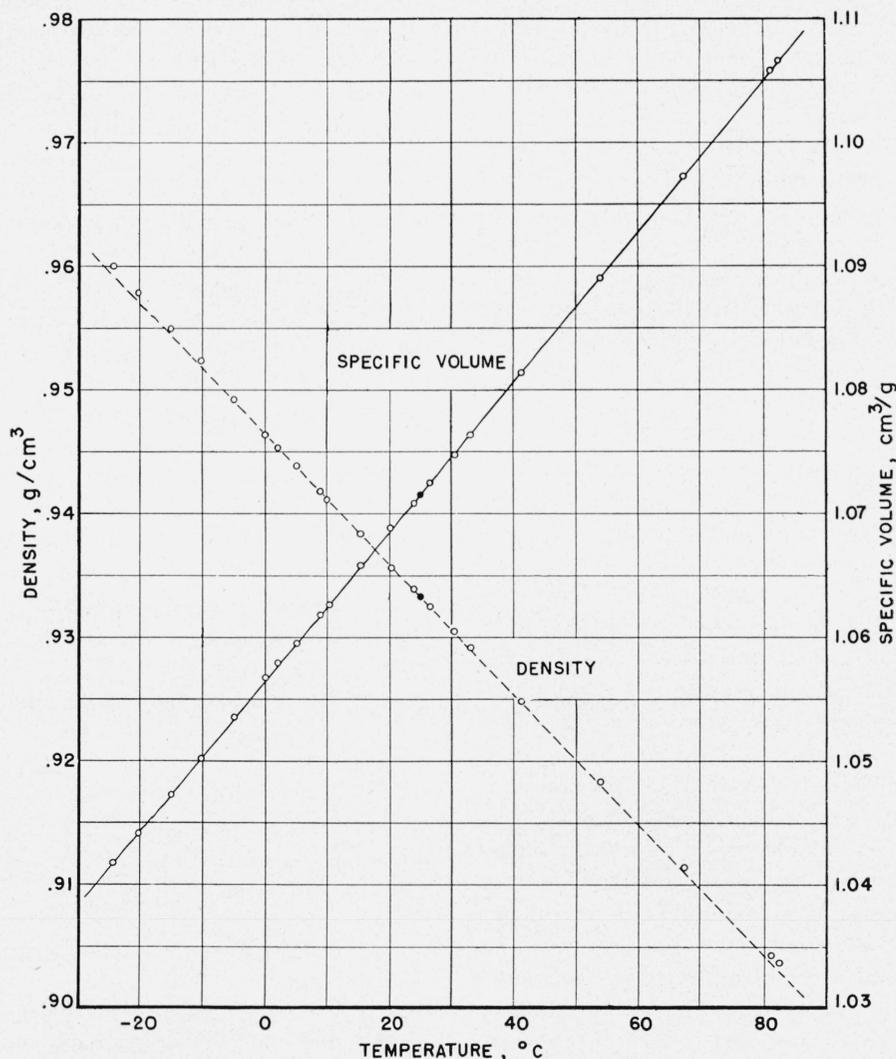


FIGURE 3. Specific volume in cm^3/g and the density in g/cm^3 of a butyl gum rubber at different temperatures. These values are obtained from volume measurements in a dilatometer and are based on a density measurement at 25° C by means of hydrostatic weighings.

$(1/V) (dV/dT)$ and $-(1/\rho) (d\rho/dT)$ to be 0.000567/deg C at 25° C. This value is about 15 percent lower than that found for pure-gum vulcanizates of natural rubber [6].

2. Precision of Measurements

The values of the densities of a sample determined in a dilatometer at different temperatures can be of no greater precision or accuracy than the density value used as reference. For samples such as that used in these experiments and the method used to measure the density, the reproducibility of values of this constant is about ± 0.0002 , or about two parts in 10,000. Therefore all other measurements should, if possible, be carried out to insure this continued precision. In order to do this, the weight of the specimen should be measured to the nearest 1 mg. The mercury, and thus the dilatometer too, should be weighed to the nearest 10 mg. The readings of the capillary of the dilatometer should be estimated to the closest 0.5 mm, which is equivalent to about 0.002 ml. The accuracy of the temperature should be within 0.1 deg, as an error of 0.1 deg is equivalent to about 0.002-ml volume change for the contents of the dilatometer. The corrections for the capillary must, of course, fall within these same limits.

It seems, therefore, that the limiting factors in the precision of the method are the ability to make precise measurements of temperature and of height of mercury in the capillary. The precision of these measurements could, of course, be stepped up to some degree, but this would serve no useful purpose unless the density values were more reliable. From the position of the individual specific volume values with relation to the curve in figure 3, it would appear that the expansivity values are good to within 1 percent. This is equivalent to an error of ± 0.0003 in the density or specific-volume values at the extreme ends of the curves.

In order to obtain precise results in expansivities the samples must be free from gases. The error caused by the presence of small amounts of gas can, however, be calculated. For example, it has been demonstrated that in the experiments described in this article there was about 0.0013 ml of gas in the dilatometer at room temperature. At the lowest temperature at which measurements were made, -23.7° C, the capillary reading was

111 mm above the zero. If, as before, the bubble is assumed to be in the center of the sample, 90 mm below the zero reference, the pressure on the bubble of gas would be 961 mm of Hg. At 25° C it was found to be 1,218 mm. The 0.0013 ml of gas in the dilatometer at 25° C had therefore been changed at -23.7° C to

$$0.0013 \times \frac{273-23.7}{273+25} \times \frac{1,218}{961} = 0.0014 \text{ ml.}$$

The difference in volume of the gas between 25° C and -23.7° C is therefore only 0.0001 ml, which is beyond the limits of experimental measurement. The effect of this quantity of gas can therefore be disregarded. The same holds true for those experiments performed above room temperature for the same dilatometer and contents.

The precision of this type of a dilatometer can, of course, be increased to beyond that described here. In order to do this one must be able to measure more accurately the temperature and the volume. The temperature-measuring instrument must be able to read smaller intervals of temperature and to have greater accuracy. The rate of heating must be made slower and more uniform, or it may be advisable to make measurements at constant temperatures and increase the temperature stepwise. The volume could be read more precisely if a capillary of smaller diameter were used. This, however, introduces more trouble in adding the confining liquid and regulating the level in the capillary before measurements are started. Madorsky [25] inserted wire of known and uniform diameter into the larger capillaries of his dilatometers, thus making them more sensitive. The range of temperature that a dilatometer can cover in a single experiment is, however, greatly decreased when using smaller capillaries. Gibson and Loeffler [16] and Burlew [10] used dilatometers of a different design and were able to weigh the mercury equivalent to the change in volume, thus increasing their precision. Their dilatometers were simplified by the fact that they were made for liquids only.

V. Summary and Conclusions

A somewhat detailed description has been given of the construction, calibration, and operation of a simple volume dilatometer, and also of the method of calculating specific volumes, densities,

and expansivities of solids or liquids from data obtained by measurements employing this type of dilatometer. The instrument is a relatively simple and inexpensive piece of equipment to construct. It can give volume expansivity measurements to a precision of about 1 percent. Its use provides an excellent method for the study of transitions. Illustrative data are given showing that the expansivity $(1/V) (dV/dT)$ of a pure gum vulcanizate of butyl rubber at 25° C is 567×10^{-6} per deg C, about 15 percent lower than that for natural rubber.

VI. References

- [1] M. F. Acken, W. E. Singer, and W. P. Davey, X-ray study of rubber structure, *Ind. Eng. Chem.* **24**, 54 (1932). Reprinted in *Rubber Chem. Tech.* **5**, 30 (1932).
- [2] A. B. C. Anderson and N. E. Edlefsen, Volume-freezing point relations observed with new dilatometer technique, *Soil Sci.* **54**, 221 (1942).
- [3] T. Alfrey, G. Goldfinger, and H. Mark, The apparent second-order transition point of polystyrene, *J. Applied Phys.*, **14**, 700 (1943).
- [4] N. Bauer, Determination of density, chapter III in Weissberger's "Physical methods of organic chemistry", **1**, 69. (Interscience Publishers, Inc., New York, N. Y. 1945).
- [5] N. Bekkedahl, Forms of rubber as indicated by temperature-volume relationship, *J. Research, NBS* **13**, 411 (1934) RP717. Reprinted in *Rubber Chem. Tech.* **8**, 5 (1935).
- [6] N. Bekkedahl and L. A. Wood, Crystallization of vulcanized rubber, *Ind. Eng. Chem.* **33**, 381 (1941). Reprinted in *Rubber Chem. Tech.* **14**, 347 (1941).
- [7] R. F. Boyer and R. S. Spencer, Thermal expansion and second-order transition effects in high polymers. I. Experimental results, *J. Applied Phys.* **15**, 398 (1944). Reprinted in *Rubber Chem. Tech.* **17**, 802 (1944).
- [8] T. F. Buehrer and M. S. Rose, Bound water in normal and puddled soils, *Univ. of Arizona Agricultural Experiment Station Technical Bulletin No. 100*, June 20, 1943.
- [9] R. M. Buffington and W. M. Latimer, The measurement of coefficients of expansion at low temperatures, *J. Am. Chem. Soc.* **48**, 2305 (1926).
- [10] J. S. Burlew, Coefficient of thermal expansion of benzene and of toluene measured with a new type of weight dilatometer, *J. Am. Chem. Soc.* **62**, 690 (1940).
- [11] J. Busse, Liquid-in-glass thermometers, chapter in "Temperature; its measurement and control in science and industry", p. 228. (Reinhold Publishing Co., New York, N. Y. 1941.)
- [12] H. F. Church and B. E. Wayne, Method for determining the cubical coefficient of thermal expansion of solids and liquids, *J. Rubber Research* **17**, 124 (1948).
- [13] R. F. Clash, Jr., and L. M. Rynkiewicz, Thermal expansion properties of plastic materials, *Ind. Eng. Chem.* **36**, 279 (1944).
- [14] M. L. Corrin, Kinetic treatment of emulsion polymerization, *J. Polymer. Sci.* **2**, 257 (1947).
- [15] A. Furst, An improved dilatometer, *J. Chem. Education* **18**, 335 (1941).
- [16] R. E. Gibson and O. H. Loeffler, Pressure-volume-temperature relations in solutions, *J. Am. Chem. Soc.* **61**, 2515 (1939).
- [17] P. Hidnert, Comparative tests of chemical glassware. Values reported by Wichers, Finn, and Clabaugh. *J. Research, NBS* **26**, 537 (1941) RP1394.
- [18] W. L. Holt and A. T. McPherson, Change of volume of rubber on stretching; effect of time, elongation, and temperature, *J. Research, NBS* **17**, 657 (1936) RP936. Reprinted in *Rubber Chem. Tech.* **10**, 412 (1937).
- [19] B. Ingelman, The dilatometer method for studying the rate of crystallization of saturated solutions of sugar, "The Svedberg" (Mem. Vol.) **1944**, 155 (Almquist and Wiksells Boktryckeri A. B., Uppsala, Sweden, 1944).
- [20] E. Jenckel, The cooling processes in glasses and artificial resins, *Z. Elektrochem.* **43**, 796 (1937).
- [21] E. Jenckel and K. Ueberreiter, Polystyrene glasses of different chain lengths, *Z. physik. Chem.* **A182**, 361 (1938).
- [22] H. C. Jones and H. A. Yiengst, Dilatometer studies of pigment-rubber systems, *Ind. Eng. Chem.* **32**, 1354 (1940); reprinted in *Rubber Chem. Tech.* **14**, 113 (1941).
- [23] J. D. Long, W. E. Singer, and W. P. Davey, Fibring of rubber. Time lag and its relation to structure. *Ind. Eng. Chem.* **26**, 543 (1934). Reprinted in *Rubber Chem. Tech.* **7**, 505 (1934).
- [24] V. E. Lucas, P. H. Johnson, L. B. Wakefield, and B. L. Johnson, Dilatometric measurement of molecular regularity in polymers, *Ind. Eng. Chem.* **41**, 1629 (1949).
- [25] I. Madorsky, National Bureau of Standards, unpublished work.
- [26] P. Mondain-Monval, Studies in allotropy and crystallization of vitreous substances, *Ann. chim.* [11] **3**, 5 (1935).
- [27] W. Patnode and W. J. Scheiber, The density, thermal expansion, vapor pressure, and refractive index of styrene, and the density and thermal expansion of polystyrene, *J. Am. Chem. Soc.* **61**, 3449 (1939).
- [28] M. O. Samsøen, Study of the vitreous state and the expansion of glasses, *Ann. phys.* **9**, 35 (1928).
- [29] J. B. Saunders and A. Q. Tool, Effect of heat treatment on the expansivity of a pyrex glass, *BSJ Research* **11**, 799 (1933) RP626.
- [30] G. V. Schulz and G. Harborth, A dilatometric method for observing the progress of polymerization, *Angew. Chem.* **A59**, 90 (1947).

- [31] A. H. Scott, Specific volume, compressibility, and volume thermal expansivity of rubber-sulfur compounds. *J. Research, NBS*, **14**, 99 (1935) RP760. Reprinted in *Rubber Chem. Tech.* **8**, 401 (1935).
- [32] R. S. Spencer and R. F. Boyer, Thermal expansion and second-order transition effects in high polymers. III Time effects. *J. Applied Phys.* **17**, 398 (1946).
- [33] H. W. Starkweather and G. B. Taylor, The kinetics of polymerization of vinyl acetate, *J. Am. Chem. Soc.* **52**, 4708 (1930).
- [34] V. Stott and P. H. Bigg, Density of liquid mercury, *International Critical Tables* **2**, 457 (McGraw-Hill Book Co., New York, N. Y., 1926).
- [35] G. Tammann and E. Jenckel, The crystallization velocity and the number of nuclei in glycerine and their dependence on temperature, *Z. anorg. allgem. Chem.* **193**, 76 (1930).
- [36] G. Tammann and A. Kohlhaas, The limits of the softening interval of glasses and the abnormal change of specific heat and volume in the softening region, *Z. anorg. allgem. Chem.* **182**, 49 (1929).
- [37] K. Ueberreiter, The freezing of normal liquids and liquids with "fixed" structures such as rubber and synthetic resins, *Z. physik. Chem.* **B45**, 361 (1940).
- [38] K. Ueberreiter and K. Klein, The dilatometer in plastics research, *Chemische Technik* **15**, 5 (1942).
- [39] L. A. Wood and N. Bekkedahl, Crystallization of unvulcanized rubber at different temperatures, *J. Applied Phys.* **17**, 362 (1946); *J. Research NBS* **36**, 489 (1946) RP1718. Reprinted in *Rubber Chem. Tech.* **19**, 1145 (1946).
- [40] L. A. Wood, N. Bekkedahl, and F. L. Roth, Measurement of densities of synthetic rubbers, *Ind. Eng. Chem.* **34**, 1291 (1942); *J. Research NBS* **29**, 391 (1942) RP1507. Reprinted in *Rubber Chem. Tech.* **16**, 244 (1943).

WASHINGTON, March 15, 1949.