Second-Order Transitions of Rubbers at High Pressures[1]

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Pressure-volume-temperature data on rubber-sulfur vulcanizates are analyzed in connection with their bearing on the second-order, or glass, transition in rubber. The results show no measurable change in transition temperature with increasing pressure nor any noticeable discontinuity in compressibility at the transition. No evidence is found for an isothermal transition produced by pressure. Possible explanations for the absence of the pressure transition are discussed.

1. Introduction

In a previous report [1] [2] experimental pressure-volume-temperature (PVT) data were presented for rubber-sulfur vulcanizates in the ranges 10 to 28 percent of sulfur, 10° to 80° C, and 1,000 to 10,000 atm. No interpretations of these data were made in that report. In this study the significance of the data with respect to unresolved questions concerning the second-order, or glass, transition in rubbers are considered.

The glass transition (denoted here as T_g) defines a temperature or temperature interval in which marked changes in properties occur in high polymers, glasses, and other materials that may manifest a glassy state. There is considerable doubt as to whether the phenomena observed are representative of a true thermodynamic transition or merely of a very slow rate process in which attainment of equilibrium may be considered temporally impractical [2]. Resolution of these problems is of great theoretical importance, particularly with respect to the third law of thermodynamics [3] but is beyond the scope of this report. The widespread interest in the glass transition comes from its practical importance in commercial applications, and there is considerable literature on the subject, such as the extensive reviews by Boyer and Spencer [4], Berger [5], Morey [6], Kauzmann [7], and others.

There is no established isothermal volume change that takes place at T_g and similarly no latent heat, although C_p (and presumably C_v) change markedly. To a first approximation, therefore, it would appear that T_g should be independent of pressure. The interest in the effect of P on T_g is indicated by the numerous recent attempts to deduce this relationship from data given by Scott [8].

Scott [8] previously reported PVT data on rubber-sulfur vulcanizates over essentially the same temperature interval but to a maximum pressure of only 800 bars. These have heretofore represented the only available data on high polymers with a direct bearing on the relationship between P, V, and T_g. However, at the time the measurements were made the future significance of the discontinuities in slopes of isobars was not apparent, and the data are given only by

means of graphs and empirical equations that are somewhat difficult to use. With subsequent increasing interest in the nature of the processes responsible for the changes observed at T_g, the data of Scott have received major attention from recent workers. It would appear, in view of the way the results are presented and the fact that their future significance could not be anticipated, that several questionable conclusions have been derived recently from these data. The unsoundness of such conclusions is confirmed in most instances by the original numerical experimental data that have been made available through the cooperation of A. H. Scott [9]. The previously reported data at high pressures [1] are designed to cover essentially the same sulfur and temperature ranges studied by Scott [8] and to give an unequivocal answer to the interdependence of T_g and P, as well as other matters of interest here.

Rubber-sulfur vulcanizates were selected so that several specimens were expected to pass through T_g in the temperature interval used, although studies were made of specimens exhibiting no T_g in this temperature interval. These were added to round out the picture in so far as possible. However, very low sulfur contents could not be conveniently studied because of the action of the confining liquid—a light petroleum distillate—on such specimens. The numerical data obtained, and the empirical equations derived to fit the data, have been given previously [1].

It must be emphasized that subsequent interpretations of these data can be considered to apply only to the pressure interval studied (1,000 to 10,000 atm) and to the rubber-sulfur vulcanizate system of high sulfur content.

2. Results and Discussion

2.1. Isobaric Transition, T_g

Isobars calculated from the numerical data are shown for six vulcanizates in figures 1 to 6, in which specific volumes are plotted as ordinates. Each isobar is labelled with the corresponding pressure in units of thousands of atmospheres. In these figures the isobars are drawn as linear above and below T_g, which is taken to correspond to the intersection of these lines. In figures 1 and 2 no transition is observed, and they are included to illustrate other matters to be pointed out later. In figures 4 and 6, the transition temperature is not well defined; in the

former because of scatter of points, and in the latter because only a single point occurs at temperatures above T_g. In figures 3 and 5, T_g is considered to be sufficiently well defined to conclude, with due consideration of the experimental errors [1], that there is no evidence for any measureable change in T_g with changing pressure. It is suggested, therefore, that for these materials in this pressure range, T_g is not a function of pressure to a rather good degree of approximation.

It will be noted that some discrepancy exists between the values of T_g given here and those of Scott [8], from which these data were essentially derived. These discrepancies are to be attributed to uncertainties in deriving the specific volumes from the graphical data of Scott [8] and inherent variations to be expected in lines drawn through experimental points. Therefore, no significance may be attached to the actual values of T_g shown here. It is of the utmost importance to recognize that no factor appears to act on compression to produce any measurable change in T_g.

Specimens used in these studies will ultimately be analyzed and studied dilatometrically at 1 atm. No significant change in any conclusion presented here is to be expected as a result of any measurements at 1 atm. Slight revisions of specific volumes or values of T_g may be expected and these will be reported in due course.

From the fact that the isobars represent a family of divergent lines, shown best in figures 1 and 2, it is possible to deduce qualitatively the effects of pressure on expansivity and of pressure and temperature on compressibility. Such effects are interrelated by the geometry of the family of isobaric lines and the fact that the expansivity is proportional to the slope of the isobars and the isothermal compressiblity to the separation of the isobars at a given temperature. Qualitatively, the expansivities and compressibilities behave in a manner similar to that pointed out by Bridgman for solids and liquids [16].

From the empirical equations derived previously, the compressibility may be written as

$$-\frac{1}{V_0}\frac{\partial V}{\partial P} = \frac{1}{V_0}[a - bP + cP^2 + (a' - b'P + c'P^2)t + (-a'' + b''P - c''P^2)t^2], \quad (1)$$

where the coefficients are essentially positive. In all empirical equations it is noted that b' and c' may change signs rarely; but a'', b'', and c'' are found to reverse in sign somewhat more frequently. The change in compressibility with temperature is then

$$-\frac{1}{V_0}\frac{\partial^2 V}{\partial P \partial T} = \frac{1}{V_0}[a' - b'P + c'P^2 + 2(-a'' + b''P - c''P^2 t] \quad (2)$$

with similar considerations regarding the signs of the coefficients. At a given pressure it is apparent from eq (1) that the compressibility increases with increasing temperature, since $|a'| \gg |a''|, |b'| \gg |b''|, |c'| \gg |c''|$. From eq (2) it appears that at a given pressure, the rate of increase of compressibility with temperature is less at higher temperatures (that is, above T_g) than at lower temperatures (that is, below T_g).
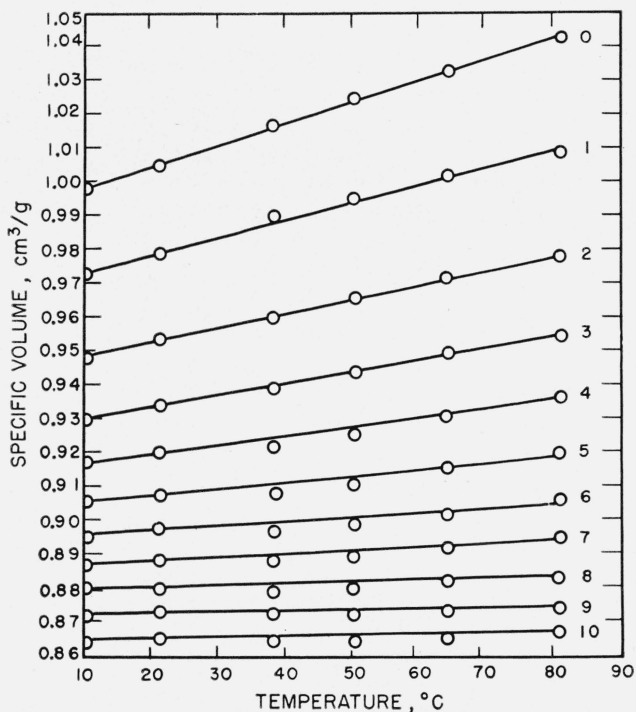

FIGURE 1. *Isobars for rubber-sulfur vulcanizate containing 10 percent of sulfur.*

The number opposite each isobar denotes the pressure in units of thousands of atmospheres.

FIGURE 2. *Isobars for rubber-sulfur vulcanizate containing 16 percent of sulfur.*

The number opposite each isobar denotes the pressure in units of thousands of atmospheres.
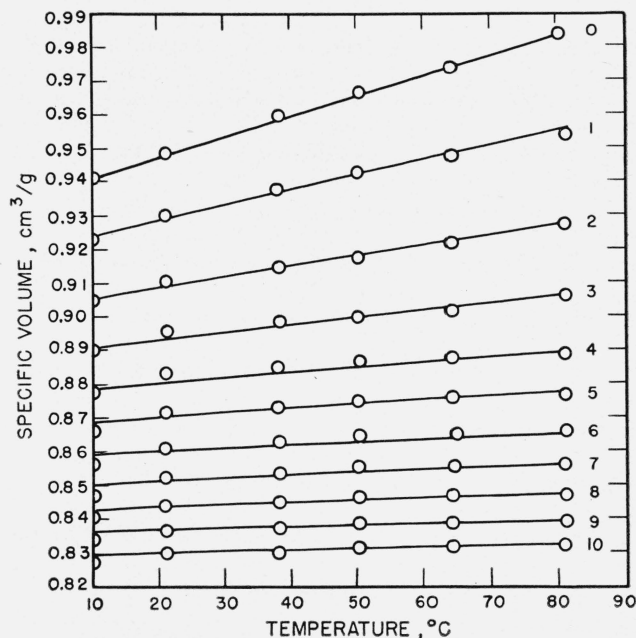
FIGURE 3. *Isobars for rubber-sulfur vulcanizate containing 18 percent of sulfur.*

The number opposite each isobar denotes the pressure in units of thousands of atmospheres.
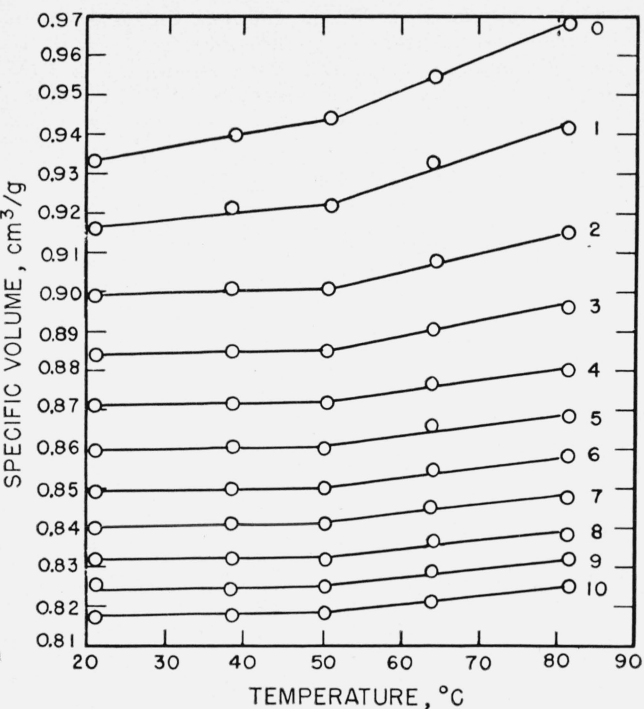
FIGURE 5. *Isobars for rubber-sulfur vulcanizate containing 22 percent of sulfur.*

The number opposite each isobar denotes the pressure in units of thousands of atmospheres.

FIGURE 4. *Isobars for rubber-sulfur vulcanizate containing 20 percent of sulfur.*

The number opposite each isobar denotes the pressure in units of thousands of atmospheres.
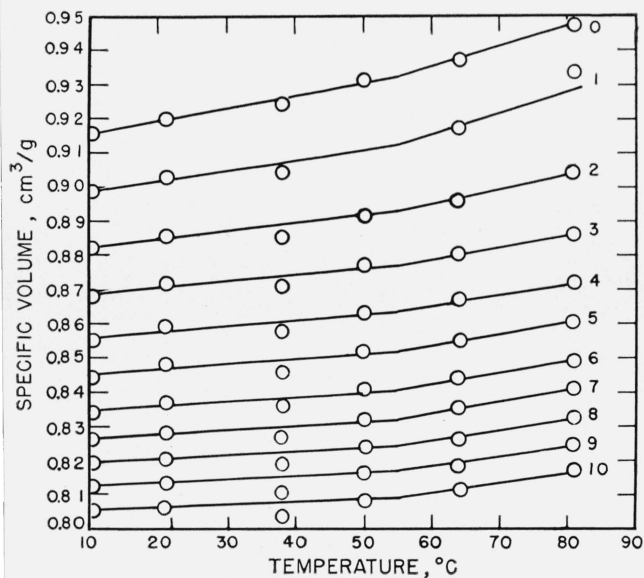
FIGURE 6. *Isobars for rubber-sulfur vulcanizate containing 25 percent of sulfur.*

The number opposite each isobar denotes the pressure in units of thousands of atmospheres.
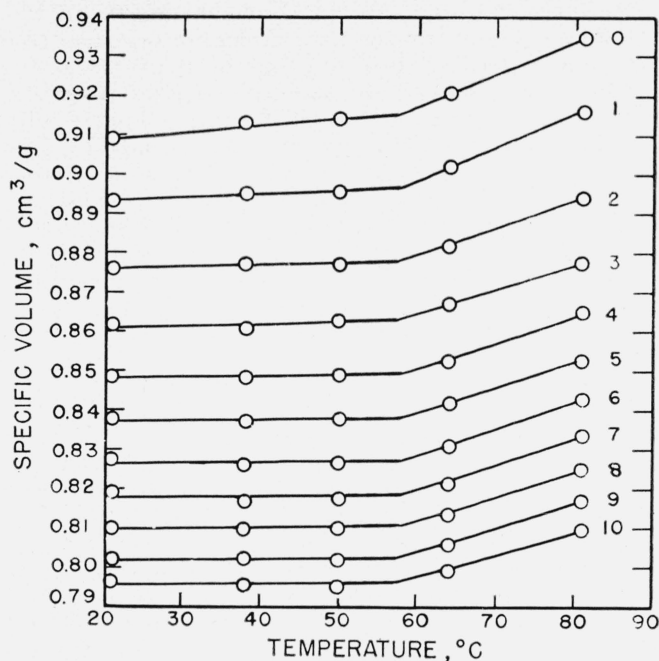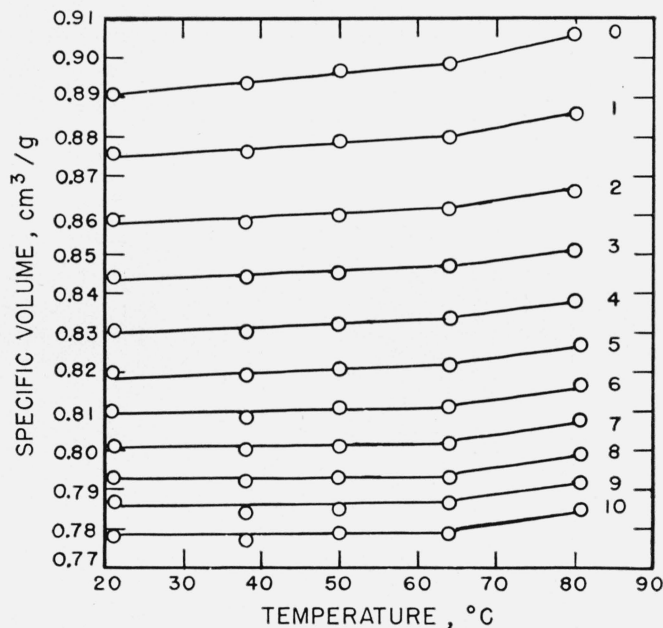
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However, for some specimens exhibiting T_g in this temperature interval, a'' is negative so that the reverse is true. This fact, together with the errors inherent in defining the smaller coefficients, renders a decision on the variation of compressibility with temperature somewhat uncertain. From the equations, however, it may be stated with confidence that any change in compressibility on passing through T_g is not large. From figures 3 to 6, it can be concluded that such an increase in compressibility would probably decrease with increasing pressure and that such an effect, if it exists, is larger at low pressures. Consideration of the experimental data furnished by Scott [9] yields the conclusion that existence of a change in compressibility on passing through T_g is very doubtful, and if present is certainly rather small. Because compressibility is generally not determined with the precision of expansivity and is a strong function of pressure and temperature, any conclusions involving small changes in such a property are subject to some uncertainty. There is little doubt that a change in compressibility of the order of 2 or 3 to 1 is not shown by these data.

Inasmuch as eq (1) and (2) do not readily permit an unequivocal general analysis, it is of interest to show the compressibility-temperature behavior numerically. Such calculations have been made for several vulcanizates with results similar to those shown for a flexible rubber (13 percent of S) and a rigid rubber (22 percent of S) which shows the marked isobaric transition of figure 5. The results of these calculations are shown graphically in figures 7 and 8, in which compressibility is plotted against tem-
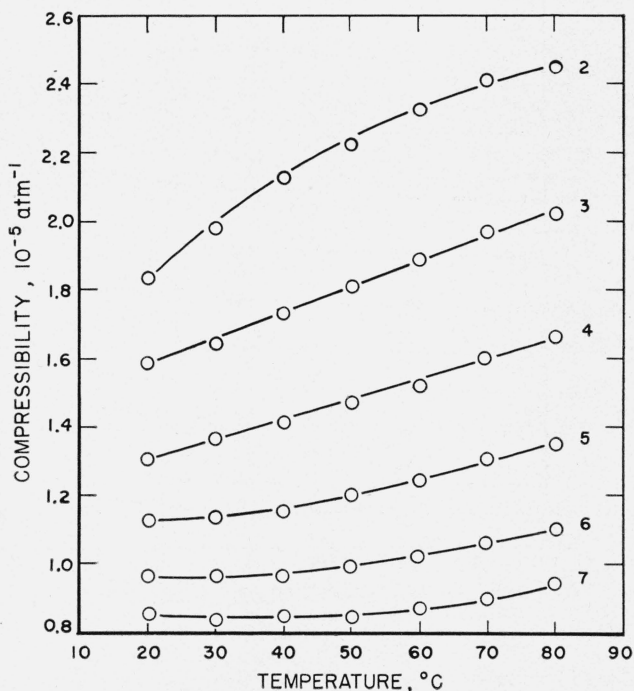
perature, the pressure being denoted on each curve in units of thousands of atmospheres. It will be noted that a discontinuity in compressibility at T_g is absent at all pressures in figure 8, the compressibility isobars being essentially as smooth as those for the 13-percent vulcanizate shown in figure 7 for comparison. Differences between the shapes of the curves in these figures are not of interest here, the principal point of interest being the essential smoothness of the curves. It is to be noted that any assumptions involved in calculations of the original data [1] have negligible effect on these curves, which are defined essentially by the *shapes* of the compression isotherms and not by their absolute magnitudes. Discontinuities in compressibility must show up as irregularities in the original experimental data irrespective of any extensive properties of the material. No such irregularities have ever been observed within the experimental errors of the measurements.

It is of interest to calculate the change of T_g with increasing pressure on the assumption that the phenomenon is representative of a true thermodynamic transition of second order. The equations defining this variation are

$$dP/dT=(Cp_1-Cp_2)/Tv(\alpha_1-\alpha_2), \qquad (3)$$

and

$$dP/dT=(\alpha_1-\alpha_2)/(\beta_1-\beta_2), \qquad (4)$$

where the terms have the usual significance [10]. Equation (3) has been evaluated by Gee [11], who found $dT/dP \approx 0.016$ deg/bar. Sufficient data are available here to evaluate eq (4). From eq (1), $\beta_1-\beta_2=\Delta\beta$ is found to be

$$\Delta\beta=(a'-b'P+c'P^2)(t_1-t_2)+(-a''+ \\ b''P-c''P^2)(t_1^2-t_2^2), \qquad (5)$$

FIGURE 7. *Compressibility isobars for rubber-sulfur vulcanizate containing 13 percent of sulfur.*

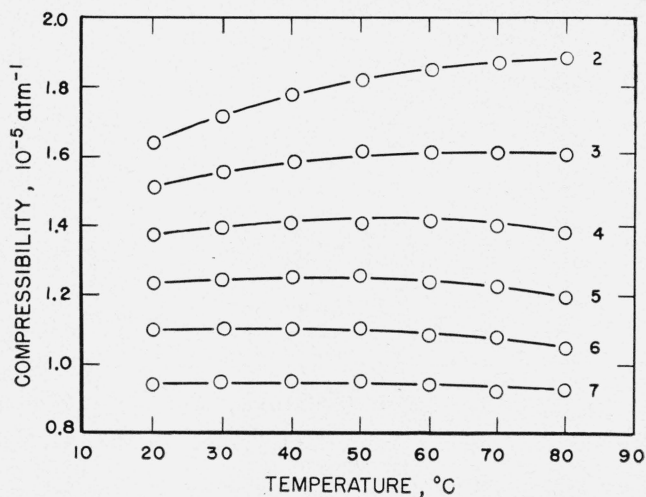The number opposite each isobar denotes the pressure in units of thousands of atmospheres.

FIGURE 8. *Compressibility isobars for rubber-sulfur vulcanizate containing 22 percent of sulfur.*

The number opposite each isobar denotes the pressure in units of thousands of atmospheres.

where t_1 and t_2 refer to temperatures slightly below and slightly above T_g. From the empirical equation [1], $\alpha_1-\alpha_2=\Delta\alpha$ is found to be

$$\Delta\alpha=2(a_0''+a''P-b''P^2+c''P^3)(t_1-t_2) \qquad (6)$$

whence, by substituting, eq (4) may be shown to be

$$dT/dP=(a'-b'P+c'P^2)+(-a''+b''P-c''P^2)$$
$$(t_1+t_2)/2(a_0''+a''P-b''P^2+c''P^3), \qquad (7)$$

which reduces at low pressures to

$$dT/dP\approx a'-a''(t_1+t_2)/2a_0''. \qquad (8)$$

Considering the 22-percent-rubber-sulfur vulcanizate in particular, although all other rubbers are quite comparable, t_1+t_2 may be taken to be approximately 1×10^2, while a'' is $+3.6\times10^{-10}$, a' is 1.3×10^{-7} and $2a_0''$ is 1.4×10^{-5}. The value of dT/dP is then of the order of 7×10^{-3} deg/atm. This corresponds to a change of T_g of the order of 7 deg C/1,000 atm at low pressures. It is not apparant that the orders of magnitude of numerator and denominator of eq (7) do not change with increasing pressure. However, simple numerical computations, using the coefficients of the empirical equations, show that such is the case. On the basis of these data, a change of T_g of the order of 70 deg C is predicted from eq (4); and from the value given by Gee [11] for eq (3), the corresponding change would be approximately 160 deg C/10,000 atm. It is obvious that no such change occurs in figures 3 to 6; and indeed, any change in T_g with pressure, if present at all, would appear to be less than 1 deg C/10,000 atm. The discrepancy between predicted and observed change in T_g with varying P would appear to lend support to the suggestions that the phenomena occurring at T_g are not representative of a true thermodynamic transition of second order [2, 4].

2.2. Isothermal Compression

Typical isotherms are shown in figure 9, and because all other isotherms are essentially similar, there seems no reason for their reproduction here. All isotherms are inherently smooth, and it must be concluded that a second-order, or glass, transition pressure, P_g, does not exist in these data. The existence of P_g would appear to be of importance from both theoretical and practical viewpoints and possible reasons for failure to observe such a phenomenon must be considered.

First, occurrence of such a transition at low pressures, that is, below 1,000 atm, may be essentially ruled out, since Scott [8] observed no such transition up to 800 bars.

Second, the effect of the confining liquid on the transition may be discarded as measurements of the amount of such liquid absorbed yielded results of such small magnitude as to invalidate this possibility.

Third, the small magnitude of any change of compressibility occurring on traversing P_g might render observation of such a phenomenon most difficult, particularly since the compressibility is strongly pressure dependent. The difficulties arising from this possibility cannot be minimized and are very real. However, it would appear from the very real similarity of the compression curves of all polymers studied to date without regard to T_g or the chemical structure of the polymer that it is very improbable that any such P_g exists.

All previous studies of this nature have reported smooth PV relationships. Adams and Gibson [12] used essentially the same experimental apparatus applied here; Bridgman [13] however, has evolved a different method requiring no confining liquid and has reported some irregularities. Tammann and Jellinghaus [14] studied glasses at various temperatures through the transition range at pressures as high as 2,000 kg/cm^2 and likewise reported data showing no isothermal irregularities.

The report of Bridgman deserves special consideration. The data from which this report originated were made available through the cooperation of P. W. Bridgman [15]. From these data it would appear that the isotherms themselves are also smooth, but irregularities appear in the differences of the experimental data. Because all rubbers studied which had
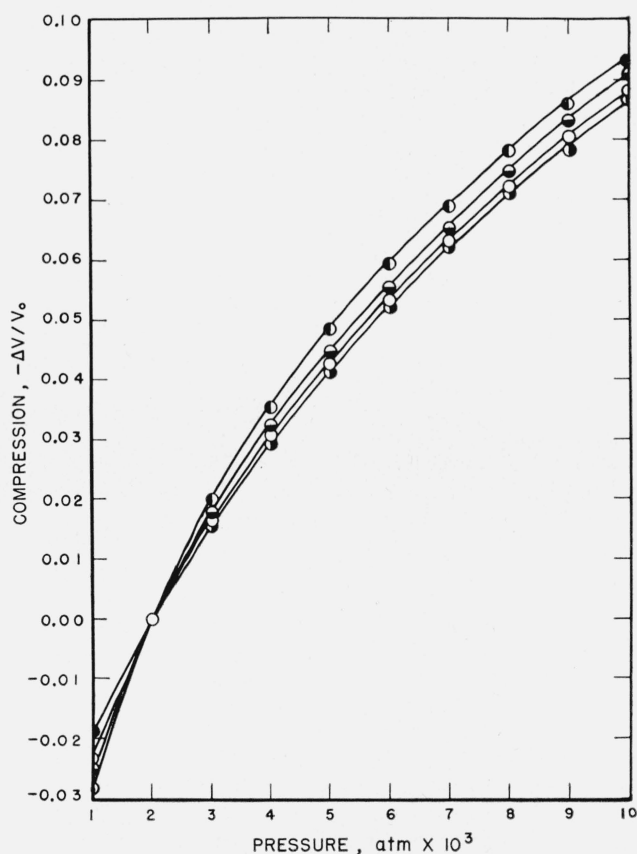

FIGURE 9. *Compression isotherms of rubber-sulfur vulcanizate containing 18 percent sulfur.*

◑, 21.0° C; ○, 50.2° C; ◕, 64.0° C; ◐, 81.5° C.

similar rubber content did not exhibit similar behavior, it appears most probable that the irregularities did not arise from the polymer alone. This is not believed to be typical of the transitions considered here.

It is concluded therefore, that there is no good evidence for a P_g comparable to T_g. No absolute requirement for such a P_g exists because P and T are independent and observed behavior in the V-T plane does not imply a definite behavior in the P-V plane. However, since V is considered to be of great importance in determining the behavior of condensed phases, and values of V smaller than those expected at $T=0°$ K by thermal contraction alone can be produced by these pressures, it is of interest to evaluate internal-energy changes due to isothermal compression over this pressure range and by isobaric expansion over a temperature interval that includes T_g. These energy changes may be evaluated by the easily derivable relationships

$$(\Delta E)_T = -TV_0 \int_{P_1}^{P_2} \alpha dP + V_0 \int_{P_1}^{P_2} \beta P dP \qquad (9)$$

$$(\Delta E)_P = \int_{T_1}^{T_2} C_p dT - PV_0 \int_{T_1}^{T_2} \alpha dT \qquad (10)$$

where the quantities have the usual thermodynamic significance. These equations were evaluated for natural rubber in which $T_g \approx 200°$ K. The temperature limits were $300°$ and $175°$ K, which include T_g, and the corresponding pressure limits were 1 and 10,000 atm, respectively. The following assumptions were required in evaluating eq (9) and (10):

1. β for natural rubber was assumed to have the same pressure dependence found for the 10-percent-sulfur vulcanizate studied.

2. α was assumed to be a linear function of pressure, with a pressure dependence similar to that found for liquids by Bridgman [16].

3. Quasi-equilibrium was assumed at T_g so that eq (10) could be applied. This assumption is borne out by experimental data [17].

4. α was assumed to be continuous in a mathematical sense at T_g.

Using Bekkedahl's data for specific heats [18] and expansivities [19], together with the above assumptions, the following values are obtained:

$$(\Delta E)_T = -103 \text{ j/g}.$$

$$(\Delta E)_P = -200 \text{ j/g}.$$

These values are of the same order of magnitude for natural rubber where T_g is far below room temperature. If harder rubbers are considered, the lower limit of temperature required on the integrals of eq (10) to encompass T_g becomes higher, and for very hard rubbers the value of $(\Delta E)_P$ reverses in sign as T_g becomes greater than room temperature. The value of $(\Delta E)_T$, however, will remain relatively unchanged. It is clear therefore that for the rubbers studied here that $|(\Delta E)_T|$ is certainly not necessarily

smaller than $|(\Delta E)_P|$. Therefore, a quantitative difference in internal energy changes cannot be used to account for the absence of P_g on isothermal compression. It must be emphasized that the source of the respective internal-energy changes has not been considered. On isothermal compression, it is most probable that the decrease in internal energy arises principally from change in potential energy [16], whereas in isobaric contraction, the decrease is to be attributed principally to kinetic sources. It appears reasonable to suppose that the transition is not caused by potential effects, particularly because recent theories of the causes of the transition in polymers [4, 17] emphasize the retarded viscous-response concept. The latter of these, however, deduces the viscous-response concept from an hypothesis of critical free volume. The free-volume concept would appear to require some modification because free volumes attained in the present studies, although considerably less than those expected at $0°$ K by thermal contraction alone, produce no isothermal transition and appear to have no effect on the isobaric transition. In the light of the present evidence no extension of such concepts appears justified.

Important quantitative conclusions differing from those of this report have been deduced from the data obtained in previous studies at elevated pressures. Although the measurements were made by Scott [8] and Tamman and Jellinghaus [14], pertinent conclusions of interest here have been reached by later workers from a study of the reported data. Such conclusions are frequently erroneously attributed to the original authors, and, in most instances, appear to be highly questionable. It is necessary, therefore, to examine those previous data critically and to evaluate such conclusions drawn therefrom that differ from those of this report.

The frequently quoted results of Scott [8], who studied rubbers to a maximum pressure of 800 bars, are cited chiefly with respect to the behavior of the 19.5-percent-rubber-sulfur vulcanizate that undergoes a glass transition in the temperature interval
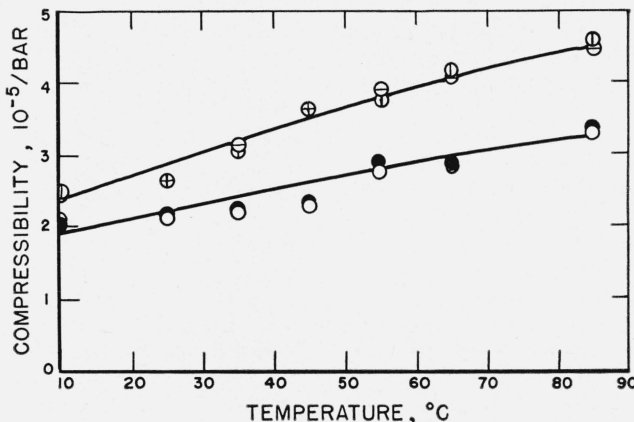

FIGURE 10. *Compressibility isobars calculated from data of Scott [8] for rubber-sulfur vulcanizate containing 19.5 percent of sulfur.*

⊖, 100 bars, decreasing pressure; ⊕, 100 bars, increasing pressure; ○, 700 bars decreasing pressure; ●, 700 bars, increasing pressure.

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TABLE 1. *Pressure-volume-temperature data for natural rubber-sulfur vulcanizate containing 19.5 percent of sulfur [9]*

10° C		25° C	
Pressure	Relative volume	Pressure	Relative volume
Bars	*ml*	*Bars*	*ml*
1	1.00000	1	1.00000
198	.99503	191	.99509
394	.99055	391	.99034
600	.98597	597	.98567
813	.98154	808	.98119
641	.98513	637	.98478
432	.98936	419	.98966
214	.99461	216	.99455
1	.99982	1	1.00005
25° C		**35° C**	
1	1.00000	1	1.00000
189	.99504	188	.99438
394	.99007	373	.98938
601	.98528	587	.98421
813	.98072	809	.97927
630	.98457	630	.98318
424	.98918	422	.98809
227	.99404	218	.99336
1	.99992	1	1.00008
45° C		**55° C**	
1	1.00000	1	1.00000
193	.99300	188	.99298
389	.98670	386	.98629
580	.98125	588	.97997
818	.97557	803	.97377
630	.97987	622	.97869
418	.98558	418	.98517
230	.99169	219	.99149
1	.99991	1	.99986
65° C		**85° C**	
1	1.00000	1	1.00000
193	.99194	189	.99131
388	.98499	386	.98329
589	.97820	591	.97544
818	.97162	821	.96794
622	.97712	629	.97410
429	.98351	416	.98173
227	.99084	209	.99000
1	.99997	1	.99929
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TABLE 2. *Compressibilities of natural-rubber-sulfur vulcanizate containing 19.5 percent of sulfur*

10° C		25° C	
Pressure	Compressibility	Pressure	Compressibility
Bars	*1/Bar*	*Bars*	*1/Bar*
99	2.52×10^{-5}	95	2.64×10^{-5}
296	2.28	292	2.43
497	2.21	497	2.31
707	2.08	707	2.15
727	2.09	722	2.11
536	2.02	527	2.24
323	2.40	325	2.47
108	2.45	114	2.60
25° C		**35° C**	
96	2.59×10^{-5}	94	3.01×10^{-5}
291	2.37	280	2.70
494	2.27	480	2.41
703	2.12	698	2.28
723	2.10	720	2.18
528	2.19	526	2.36
317	2.41	320	2.58
108	2.56	110	3.10
45° C		**55° C**	
96	3.64×10^{-5}	94	3.75×10^{-5}
291	3.21	287	3.37
487	2.85	487	3.13
699	2.38	696	2.88
724	2.27	712	2.72
524	2.69	520	3.17
324	3.25	319	3.18
116	3.59	110	3.84
65° C		**85° C**	
97	4.20×10^{-5}	95	4.61×10^{-5}
290	3.56	287	4.07
488	3.37	488	3.83
704	2.87	706	3.26
720	2.81	725	3.21
526	3.31	523	3.58
328	3.63	212	3.99
114	4.04	105	4.44

reported. The original experimental data on this vulcanizate were made available by A. H. Scott [9], and are reproduced in table 1. From these data the compressibilities $(-\Delta V/V_0 \Delta P)$ were calculated by first differences. These compressibilities are given in table 2, and a plot of compressibility versus temperature is shown in figure 10 for interpolated pressures of 100 and 700 bars. No appreciable discontinuity in compressibility is manifest at either pressure, and similar results will be obtained at other pressures as is evident by an inspection of the data of table 2.

The generally accepted conclusion that Scott's data show an increase in T_g with increasing pressure is also subject to question. The isobars given by Scott [8] are insufficiently detailed to warrant definite conclusions. *It must be emphasized that if the widely quoted 15 deg C rise in T_g at 800 bars for the 19.5-percent vulcanizate is literally accepted, one must be prepared to ignore completely similar data for the 18.8-percent vulcanizate, which by similar rigorous interpretation, show no change in T_g in the same pressure interval.*

Numerous qualitative and quantitative deductions have also been drawn from the data of Tammann and Jellinghaus [14], who investigated glasses at 100-kg/cm² pressure intervals to a maximum pressure of 2,000 kg/cm². Isothermal measurements were made at approximately 10-deg-C intervals covering a range that included T_g. These data have been widely quoted as showing a pronounced change in compressibility on passing through T_g. The authors estimated their experimental error through a measurement on water that was compared with the early (1893) data of Amagat [20]. By such a comparison they report an average error of 3×10^{-4} ml/g and a maximum error of 1.1×10^{-3} ml/g in *specific volume*.

Cursory examination of the specific-volume data does lead to indications of a marked change in compressibility at T_g as widely accepted. However, study of the isothermal first differences of the experimental data reported discloses a considerable scatter.

The first differences correspond to the ΔV values experimentally measured, and it is these values which determine compressibility. The estimated average error of 3×10^{-4} ml/g in specific volume now amounts to a large proportion of the ΔV value. These considerations apply to the isothermal data; and if it is no x required to estimate the temperature coefficient of compressibility, it is necessary to compare the ΔV values for a given pressure at the various temperatures. The change in compressibility at T_g is precisely this temperature coefficient of compressibility that is clearly subject to considerably more uncertainty than the compressibility itself. To illustrate the problem, the first differences of the reported data on salicin glass [14], which represent ΔV values for each 100 kg/cm^2, are plotted against pressure for four temperatures in figure 11. The vertical dimension of each point is taken as 3×10^{-4} ml/g in accordance with the author's estimated average error in specific volume and is indicated by the barred line. In a statistical sense this estimate for error in the differences is probably considerably too low, but all pertinent conclusions are obvious, even with the underestimated error.

The vertical separation of the points at a given pressure will be a measure of the effect of temperature on compressibility. It is to be anticipated that compressibility will increase with increasing temperature. However, in only 8 of the 20 pressures shown is the order of the points in the order of increasing temperature. The other 12 cases contain at least one instance of an inversion indicating at least one instance of greater compressibility at a lower temperature. In any event, inspection of the amount and degree of overlapping and inversion in figure 11 indicates the questionable nature of any conclusions concerning compressibility as related to
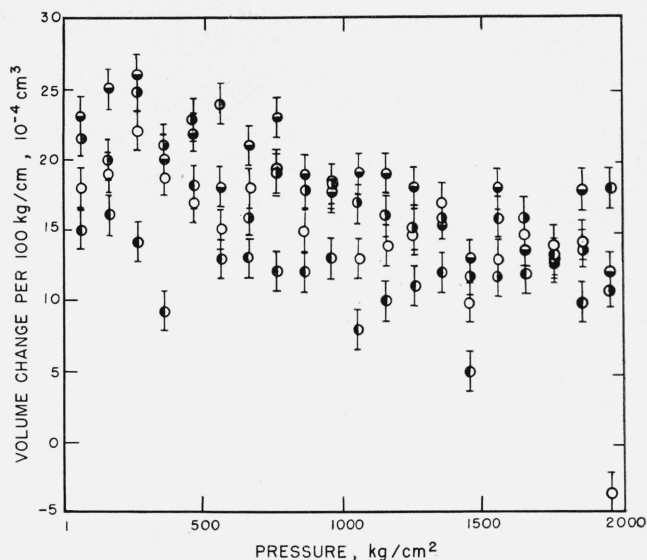

Fig. 11. *Volume changes for salicin glass calculated from data of Tammann and Tellinghaus [14]*

The uncertainties indicated are the errors estimated by the authors in the *specific volume.* ◑, 20° C; ○, 40° C; ◐ 50° C; ◓, 60° C.

temperature. It may be noted that instances of inversion of compressibility with temperature also occur in the data shown in figure 8. The amounts of such inversions are of a much smaller order than most of those indicated in figure 11 and are within the experimental errors of the present measurements.

A tabulation of compression values $(\Delta V/V_0)$ for three intervals (1 to 1,000; 1,000 to 2,000; and 1 to 2,000 kg/cm^2) is given in table 3 as calculated from the reported specific volumes of the three glasses

TABLE 3. *Compression values for glasses*

Selenium glass. $t_g = 29.8°$ C						
Pressure interval	Compression, $-\Delta V/V_0$					
	10° C	20° C	30° C	40° C	50° C	60° C	70° C
kg/cm^2							
1 to 1,000	0. 002120	0. 002155	0. 002350	0. 002756	0. 002783	0. 002839	0. 002866
1,000 to 2,000	.001600	.001726	.001654	.001606	.002003	.002122	.002015
1 to 2,000	.003720	.003881	.004004	.004362	.004786	.004961	.004881

Salicin glass. $t_g = 43$ to 44° C						
	20° C	30° C	40° C	50° C	60° C	70° C
1 to 1,000	0. 001350	0. 001548	0. 001795	0. 002068	0. 002137	0. 002187
1,000 to 2,000	.001250	.001318	.001196	.001412	.001593	.001733
1 to 2,000	.002600	.002866	.002991	.003480	.003730	.003920

Colophony glass. $t_g = 29.5°$ C					
	10° C	18° C	28° C	40° C	50° C	60° C
1 to 1,000	0. 002250	0. 002343	0. 002366	0. 003205	0. 003499	0. 005907
1,000 to 2,000	.001900	.001874	.001865	.001883	.002116	.002299
1 to 2,000	.004150	.004217	.004231	.005088	.005615	.006206

studied [14]. These data show that any conclusions regarding the change in compressibility at T_g must be qualified at least as to the pressure range and in view of the results of figure 11 should be drawn with extreme caution.

It can be concluded solely from a detailed examination of the data of these investigations that the interpretations, which have been subsequently advanced in connection with questions concerning the effect of pressure on the glass transition, are not unequivocally established by these data. It is therefore suggested that as a result of this and the previous studies that there is no valid evidence for a discontinuity of compressibility at T_g nor for any appreciable effect of pressure on T_g in the rubber-sulfur system of high polymers.

3. References

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