Compressibility and Other Thermodynamic Properties of Polymers

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Synopsis

Experimental methods for estimating the thermodynamic derivative, $(\partial T/\partial P)_S$, of both liquids and solids are described and discussed. The adiabatic heating parameter is shown to be useful, in conjunction with other more commonly measured properties, for estimating the heat capacity, $C_p = T(\partial S/\partial T)_P$, and the internal pressure, $P_i = (\partial U/\partial V)_T$. The principles for applying adiabatic heating measurements to the characterization of polymers are given with data for several common liquids and for filled and unfilled polyurethane rubbers.

INTRODUCTION

One type of adiabatic heating measurement of practical importance determines values of the thermodynamic derivative $(\partial T/\partial P)_S$. Almost all forms of stress that are applied to a body change its internal energy. These are evinced as temperature changes in the body in proportion to the dilatational component of the stress. Searle[1] gives an elementary, but particularly lucid discussion of the distinction between the ratios of the adiabatic and isothermal moduli for various stress fields. The case of hydrostatic compression is the easiest to implement experimentally and gives rise to the greatest temperature changes for a given level of applied stress. Such measurements are known[2-4] but have not been widely exploited.

The author has described various methods[5] for measuring both the adiabatic and isothermal compressibilities of a number of polymers and filled polymers. Such measurements, in conjunction with adiabatic heating data, give considerable insight into the thermodynamic nature of the material studied all without recourse to calorimetric measurements in the usual sense.

Relatively simple experimental techniques are described for measuring the adiabatic heating of rubbery polymers or plastics. Typical data for polyurethane rubber are used to illustrate means for estimating its specific heat and internal pressure. These are discussed primarily in terms of the experimental procedures which are required to produce data of nominal precision and accuracy; that, for example, which might be required for characterizing the properties of a polymer for engineering purposes. Refinements of the measuring techniques described here may very well permit more subtle material properties to be examined, such as the pressure and temperature dependence of its thermodynamic parameters.

ADIABATIC HEATING

Theory and Applications

Only hydrostatic compressions which occur in periods long compared with the relaxation time of the system will be considered. The relaxation time of the system may be defined for this purpose as the ratio of the longest dimension of the specimen to the speed of sound in the material. Hydrostatic compressions will also be regarded as reversible processes in which case isentropic and adiabatic are synonymous, since there seems to be little evidence to the contrary. Thus, we will be concerned only with systems for which entropy increases result primarily from heat losses or non-adiabatic conditions.

Practical applications of adiabatic heating require that the partial derivatives $(\partial T/\partial P)_S$ be evaluated in terms of familiar or measurable quantities. This derivative may be expressed in an equivalent mathematical form as:

$$(\partial T/\partial P)_S = -(\partial S/\partial P)_T/(\partial S/\partial T)_P \tag{1}$$

The equivalence of the relations involving the specific volume V and specific heat at constant pressure C_P,

$$-(\partial S/\partial P)_t = (\partial V/\partial T)_P \tag{2}$$

and

$$C_P \equiv T(\partial S/\partial T)_P$$

may be invoked to reduce the right side of eq. (1) to more commonly measured quantities including β, the bulk coefficient of thermal expansion, to give

$$(\partial T/\partial P)_S = T\beta/\rho C_P \tag{3}$$

where

$$\rho = 1/V$$

and

$$\beta = (1/V)(\partial V/\partial T)_P$$

Two basic experimental approaches may be contemplated for determining the derivative in eq. (3). Both involve the measurement of the relatively small temperature changes that result from pressure changes of considerable magnitude. For many polymers and rubbers, the adiabatic heating is about 0.7°C./1000 psi.

The first method may be thought of as a classical one, whereby pressure is applied to the test material in increments of sufficient extent to produce temperature changes that can be measured to some desired accuracy. The second method makes use of modern recording systems and involves the continuous measurement of temperature and pressure in autographic fash-

ion. In this way a continuous record of temperature versus pressure may be obtained, the slope of which defines the derivative in eq. (3).

There are certain theoretical limitations which must be considered in evaluating data obtained by either experimental approach. For example, the variation of the thermal expansion coefficient with pressure is related to the variation of the compressibility, $B = 1/\kappa$, in the following way:

$$(\partial\beta/\partial P)_T = -(\partial B/\partial T)_P \tag{4}$$

There is considerable experimental evidence to support the validity of this relation in principle. The specific heat is also expected to be pressure-dependent, as follows:

$$(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P \tag{5}$$

in addition to the well known variation of C_P with temperature, particularly for polymers at ordinary temperatures.

Thus, all the parameters in the right-hand member of eq. (3) are expected to be functions of both pressure and temperature. For polymers, the thermal expansion coefficient is the variable expected to be most affected by pressure and temperature changes. Bridgman[6] showed that the specific heat decreased about 0.2% per 1000 psi for a number of common liquids. Somewhat smaller changes might be expected for polymers with similar small variations in temperature and density, ρ.

The limitations which have been described for the adiabatic heating measurements are somewhat pedagogical in the practical use of the method. Both temperature and pressure changes may be measured in isentropic compression with extreme precision. Thus, the experimental range of pressure that is used may be restricted to the extent that the true value of the derivative is quite well approximated. Continuous records of temperature versus pressure, recorded in X–Y fashion by the autographic method, for example, are seldom detectably nonlinear. This means that the right-hand member of eq. (3) remains essentially constant.

Specific Heat Determinations

Excellent estimates of the specific heat may be obtained by arranging eq. (3) to show the specific heat as the dependent variable.

$$C_P = \frac{T\beta}{\rho(\partial T/\partial P)_S} \tag{6}$$

If the compressibility and thermal expansion of the test material are known, the specific heat may be estimated from eq. (6) without recourse to calorimetric measurements. This is of particular advantage for small amounts of materials as discussed by Burlew.[4] Another obvious point of interest concerns the small temperature range over which the parameter grouping of eq. (3) is measured. This, coupled with the experimental simplicity, suggests the adiabatic heating method as a means for examining

material properties at extremes of temperature, where their individual measurement is difficult.

Glass Transition Temperature Measurements

Polymers are known to pass through a transition with temperature between rubbery and glassy states. Different coefficients of thermal expansion are generally observed for the two states of the material. The temperature point at which the transition occurs, or the glass transition temperature, is commonly assessed from thermal expansion measurements. For many materials in the region of their glass transition temperature, the rates at which volume changes may occur are quite slow compared with the experimental heating or cooling rates which are available. Thus, equilibrium between volume and temperature may not be achieved, and the transition is not sharply defined. Adiabatic heating measurements would not be expected to suffer from these problems. This is not discussed further here but is suggested only as one of many potential applications of adiabatic heating which come to mind.

Ratio of Specific Heats or Bulk Moduli

It is now interesting to see how the adiabatic heating is intrinsically involved in the ratio of the adiabatic and isothermal bulk moduli, κ_S and κ_T. The familiar relation for the ratio of the specific heats at constant pressure and volume, C_p/C_V, is

$$\gamma = C_P/C_V = \kappa_S/\kappa_T = 1 + (TV\beta^2\kappa_T/C_V) \tag{7}$$

which may be written

$$\gamma = 1 + (\partial T/\partial P)_S\beta\kappa_S \tag{8}$$

since

$$(TV\beta^2\kappa_T/C_V) = (T\beta/\rho C_p)\beta\kappa_S \tag{9}$$

From eq. (8), it is clear that β may be determined indirectly from measured values of the adiabatic and isothermal bulk moduli and the adiabatic heating parameter, $(\partial T/\partial P)_S$. Equation (8) may also be used to estimate the value of the ratio of the specific heats or bulk moduli, γ, without specific knowledge of the specific heat.

Internal Pressure

The internal pressure P_i is a property of materials of considerable current interest to polymer scientists. It is defined as the change in internal energy U with volume at constant temperature.

$$P_i \equiv (\partial U/\partial V)_T \tag{10}$$

In terms of state variables, this is

$$P_i + P = T(\partial P/\partial T)_V \tag{11}$$

Bianchi et al.[7,8] have measured the derivatives in eq. (11) directly to determine P_i for silicone rubber, an ethylene–propylene copolymer, and other polymers. It was desirable to do this presumably because the polymers were studied under various states of stress and strain. In such instances, the more usual expression for internal pressure in terms of the thermal expansion coefficient appropriate to the unstrained state

$$P_i + P = T\beta\kappa_T \tag{12}$$

would not have been appropriate.

The internal pressure is of interest otherwise in polymer technology because of its close correlation with cohesive energy density. The extent of this empirical relationship is discussed by Sims[9] and others. When it is desirable to estimate the cohesive energy density by reference to calculated or direct measurements of internal pressure, it must be noted that both choices involve experimental determinations of the thermal expansion. This is accomplished in the direct determination of the derivative in eq. (11) under very difficult experimental conditions. It is the author's opinion that accurate measurements of the thermal expansion coefficient of polymers may be a more elusive thing than is usually supposed. Without debating this point, it will suffice to show that the internal pressure may be related to compressibility and adiabatic heating measurements as

$$P_i + P = T\left(1 - \frac{1}{\gamma}\right)\Big/\left(\frac{\partial T}{\partial P}\right)_S \tag{13}$$

The internal pressure is then calculable without direct experimental reference to the thermal expansion coefficient.

Grüneisen's Ratio

Grüneisen's ratio[10] expressed in terms of measurable quantities is

$$\gamma_G = -(V/C_p)(\partial P/\partial V)_T(\partial V/\partial T)_p \tag{14}$$

which stems from its basic definition in terms of the internal energy U by thermodynamic manipulation. The basic definition follows.

$$\gamma_G \equiv V(\partial P/\partial U)_V = V(\partial P/\partial T)_V/C_V \tag{15}$$

Equation (15) may be expressed in terms of familiar coefficients as

$$\gamma_G = \frac{\kappa_T\beta_p}{\rho C_V} \quad \text{or} \quad \frac{\kappa_S\beta_p}{\rho C_p} \tag{16}$$

Grüneisen's ratio has been found to have a very limited range of values ιor a wide variety of crystalline solids and metals. Because its definition is founded in the internal energy it is widely used in considering the compression of crystalline solids or metals by shock waves. In this regard, Rice et al.[11] discuss the relatively predictable variation of the value of Grüneisen's relation with large volume changes and the famous Mie-

Grüneisen equation of state. These form the basis for thermodynamic description of the high-pressure states of metals.

The adiabatic heating parameter may be used to estimate Grüneisen's ratio for polymers as it was for the internal pressure. These quantities are closely related, in that both depend upon the derivative $(\partial P/\partial T)_V$. The coefficients at the right of eq. (15) are observed to occur in a grouping similar to that which defines the adiabatic heating parameter, as in eq. (3). Thus eq. (16) which intrinsically contains the adiabatic heating derivative may be expressed as

$$\gamma_G = \kappa_S \beta_p / \rho C_p = (\kappa_S/T)(\partial T/\partial P)_S \qquad (17)$$

where T is the absolute temperature as in eq. (3).

Nominal values of Grüneisen's constant for metals center around 2.0. For a typical polyurethane rubber, values of 0.4–0.6 are more characteristic, which may be determined by calculating γ_G with nominal property values, either by eq. (16) or eq. (17). Nominal properties for aluminum, with eq. (15) predict Grüneisen's ratio as about 2.08, in agreement with values given by Rice et al.[11] This approach may be of some formal interest, because as previously indicated for the internal pressure, Grüneisen's ratio for polymers may be estimated from eq. (16) without direct knowledge of either thermal expansion or specific heat. This estimate is not as dependent upon precise knowledge of the compressibility as was the estimate for the internal pressure which involves the more experimentally critical ratio of the isothermal and adiabatic compressibilities.

EXPERIMENTAL METHODS

The measurement of temperature changes within the bulk of hydrostatically stressed solids is the primary consideration to be dealt with in this discussion. The measurements which are reported here were made with reasonable care. However, experimental errors will not be discussed in great detail, nor are extensive comparisons of the accuracy or precision of various experimental techniques attempted. The experimental methods and equipment which are discussed were devised primarily to study the properties of solid rocket propellants. These are mixtures of polymers or binders and highly reactive chemicals or oxidizers. Their dangerous nature requires considerable compromise with the experimental conditions which might otherwise be used to achieve accuracy. This is most true in the matter of specimen size, which had to be minimized for safety's sake. Other materials which were evaluated, therefore, suffered less than optimum characterization as a result of the design limitations of the system impressed by the propellant materials.

The basic work of Burlew[4] came to the author's attention only recently in reference to the article on adiabatic heating of Gill and West[3] referred to previously. These, and the measurements of Pushin and Grebenschikov[12] refer primarily to determinations on materials in the liquid state. While some data on standard liquids are given here, unfortunately these do not

include benzene and toluene which had been measured previously by Burlew. It is hoped that the application of this technique to solids is sufficiently interesting to the current technology of polymer characterization to warrant further study.

Temperature and Pressure Measurements

The effectiveness of several temperature-measuring devices has been examined experimentally in an apparatus for determining the adiabatic heating that occurs in solids subjected to hydrostatic stress. Semiconductors were found to have a pressure coefficient of resistance comparable with their thermal coefficient, for the ranges of pressure and temperature of interest in the measurement of the adiabatic heating of polymers. Fine resistance thermometers embedded in solids are affected by the compression of the solid in the manner of resistance strain gages. In both instances, the temperature and pressure effects are difficult to separate from one another. These measuring devices are therefore considered unsuitable for adiabatic heating measurements in solids. Similar difficulties are not experienced with fine-wire thermocouples. They are found to be quite applicable to the measurement of temperature at different or changing levels of hydrostatic stress within a pressurized solid. Hanneman and Strong[13] show that the e.m.f. of Chromel–Alumel couples, which were used here, are relatively insensitive to pressure effects.

Some consideration must be given to the widely different thermal properties of the thermocouple wire and the polymer specimen. The influence of the mass of the thermocouple and its thermal properties on the measurement of the temperature of the bulk of material surrounding it are important considerations in the adiabatic heating measurement. The experiment must be designed to minimize the effects of heat transfer which occur along the relatively conductive metal wires of the couple. This is effectively done in practice by immersing long lengths of the thermocouple wire in the test material. The small heat losses through the wires which occur during the measurements are distributed over the relatively large mass of the specimen. This can be implemented to the extent that thermal gradients along the wires are essentially eliminated. The temperature measurement in the vicinity of the thermocouple junction is then truly representative of the material temperature.

The mass of the thermocouple in the body of the test specimen must be regarded as an inhomogeneity or contaminant since its properties are ordinarily quite different from those of the surrounding material under test. A thermocouple of 0.003 in. diameter embedded in a cylindrical specimen 1.0 in. diameter introduces an inhomogeneity of mass or volume fraction less than 0.00004 for a typical polymer specimen. The presence of the thermocouple in this proportion then has a negligible effect on the otherwise uniform temperature changes that occur as the internal energy changes with pressure for a small volume of the material surrounding the thermocouple junction.

Analog transducers of the bonded strain-gage type were used to sense the pressure. The transducers were exposed directly to the test fluids and to the confining fluids in tests of solids. These were calibrated initially against free piston gages. Range calibration of the pressure scale was effected by standard shunt resistors connected across one arm of the strain gage bridge, in the normal fashion. The transducers used were accurate to 0.25%, and the accuracy of pressure measurements from autographic records was believed to be 0.5% or better.

Test Apparatus and Specimens

A basic system for measuring adiabatic heating is illustrated schematically in Figure 1. Figure 1a (on the left) applies to liquids and Figure 1b (on the right) to solids. In the case of liquids, the pressure chamber cavity is filled with the test fluid and may be pressurized in a variety of ways. The thermocouple in the fluid at the geometric center of the cavity then measures the concatenate temperature changes. For solids, the thermocouple is coaxially embedded in the specimen with the junction at the approximate geometric center by whatever means may be convenient. Liquids are generally used to transmit hydrostatic stress to the solid specimen. These confining fluids may be mixtures of liquids in proportions which have adiabatic heating values like those of the solid specimens being tested. Water and alcohol mixtures are effective for this purpose. The time during which adiabatic conditions obtain may be effectively increased in this way for specimens of limited size.

Satisfactory adiabatic heating records for solids can be obtained without the use of special confining fluids by using relatively large specimens. Pressurization directly from a gas source generally causes greater temperature changes at the exposed surfaces of the specimen than when confining fluids are used. This may cause an inflection in the temperature record
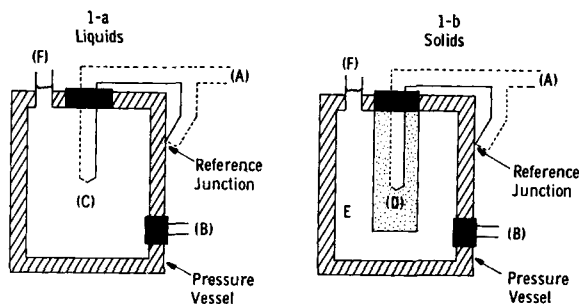

Fig. 1. Apparatus for adiabatic heating measurements of liquids and solids with hydrostatic stresses: (A) differential thermocouple (output to microvolt amplifier and recorder); (B) pressure transducer (output to millivolt amplifier–recorder); (C) test fluid; (D) test solid; (E) confining fluid; (F) pressure source. Initial temperature determined by referring test thermocouple output to standard reference junction. Temperature change measured differentially by referring test thermocouple to reference junction initially in equilibrium.
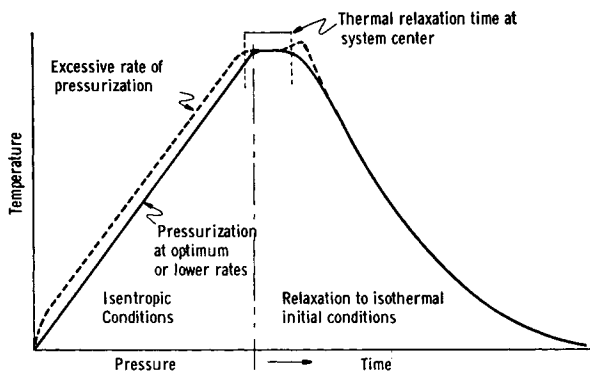
Thermal relaxation time at system center

Excessive rate of pressurization

Temperature

Pressurization at optimum or lower rates

Isentropic Conditions

Relaxation to isothermal initial conditions

Pressure ⟶ Time

Fig. 2. Typical autographic adiabatic heating records. Positive inflections of the temperature–time record may be observed when the adiabatic heating of the confining fluid exceeds that of the specimen. This is generally the case when compressed gases are used for pressurization. Similar behavior to that illustrated is observed for the depressurization cycle, after thermal equilibrium is achieved at pressure.

subsequent to the period of equilibrium which follows a pressure change. This effect which is exaggerated for illustration by the schematic representation of typical autographic adiabatic heating records in Figure 2, has no bearing on the results providing the temperature change is measured during the adiabatic period.

Polymer specimens 1.0 in. in diameter, having thermal diffusivities of about 0.001 cm.^{2}/sec., and containing thermocouples 0.003 in. in diameter are satisfactorily tested with pressurization rates of 100 psi/sec. Pressure changes of 1000 psi generally produce temperature changes in polymers of 1°F., an amount that can be precisely measured. Approximately 10-sec. periods are required to produce a satisfactory autographic record of pressure versus temperature. Adiabatic conditions in the region of the thermocouple junction embedded in a 1.0-in. diameter specimen are maintained for periods in excess of 100 sec. following a change in pressure. Under these circumstances, less responsive but more sensitive direct reading digital recording systems may be used for monitoring temperature and pressure changes separately, to achieve maximum precision in the measurements of both parameters. Autographic recording systems of the X–Y servomechanism type generally compromise the ultimate precision of one of the parameters. In this case the pressure change component of the measurement is recorded at reduced sensitivity to contain the continuous temperature versus pressure trace within the limited confines of the recorder's chart paper.

Adiabatic Heating

Adiabatic heating values representative of those ordinarily obtained by the methods described are given for several liquids and solids in Table I. Separate measurements of temperature and pressure change were used to

TABLE I
Calculated and Experimental Values of the Adiabatic
Heating from Hydrostatic Compression

	Calculated $(\partial T/\partial P)_S$, °F./$10^3$ psi	Experimental $(\partial T/\partial P)_S$, °F./$10^3$ psi	Temp., °C.	C_p, cal./g.-°C.	$1/V$, g./cm.^{3}	β, 10^{-6} °C.$^{-1}$
		Liquids				
Water	0.180	0.175	20	0.99883	0.99820	207
Glycerol	0.619		24	0.570	1.260	505
Glycerol (96%)	0.593	0.594	24	0.587	1.251	495
		Pure solids				
Polyurethane rubber		1.31	25	0.48[a]	1.054	751
CTPB rubber		1.25	25	0.49[a]	0.924	640
		Composites				
40.8 vol.-% glass beads in polyurethane rubber		0.83	25	0.30[a]	1.614	456
11.3 vol.-% glass beads in CTPB rubber		1.13	25	0.42[a]	1.087	583
Glass beads			20	0.185[b]	2.427[b]	

[a] Experimental values from $(\partial T/\partial P)_S$ measurements.
[b] Manufacturer's data.

TABLE II
Precision of Experimental Adiabatic Heating
Determinations for Various Liquids and Solids

	Measured mean value $(\partial T/\partial P)_S \times 10^{-3}$, °F./psi	Standard deviation $\sigma \times 10^{-3}$, °F./psi[a]	Number of measured values n
Water	0.175	0.004	10
Methyl alcohol (95%)	2.094	0.012	7
Glycerol (96%)	0.594	0.007	10
Polyurethane rubber	1.309	0.006	9
Typical composite solid propellant	0.632	0.01	11

[a] The standard deviation σ is calculated on the assumption that the errors of measurement are random errors. It seems reasonable to expect that systematic errors would be present in the measurements which would result in a consistent under estimate of the actual temperature change.

obtain the more precise experimental data reported for the liquids, water, 96% pure glycerol, and 95% pure methyl alcohol (Table II). Water was considered to be the principal contaminant in each. The properties of the glycerol were obtained from tables of its properties as a mixture with water. These values appropriate to the purity and test temperature were used to calculate a theoretical or expected value for the adiabatic heating derivative. These are shown in Table I for comparison with the experimental results. The data of Table II show that the experimental results are those expected from the theory within experimental error.

Pressure changes as great as 5000 psi were used to obtain adequate temperature changes for water, which has a relatively small adiabatic heating value. While these experimental results are centered around a mean value for water lower than that calculated from its properties, the statistical data in Table II do not allow the conclusion that the expected effects of pressure are evidenced in the results. The data for glycerol and methyl alcohol were obtained with pressure changes of about 1000 psi. The data for solids of Tables I and II came from autographic records of the temperature change upon pressurization. These were quite linear curves for a pressure range of 1000 psi and the slopes were determined from the coordinates of straight lines graphically overlaid on the records. Table II shows these results to be somewhat less reproducible than those obtained for liquids, but adequate for characterizing the materials.

The observed discrepancies between the theoretical and experimental adiabatic heating values for liquids are found to be generally of the order of the experimental error. It appears then that modifications or extensions of the form of expression (3) to include the pressure and temperature coefficients of the parameters would only be warranted for measurements of considerably greater precision than those reported. Ultimate applications of the most sensitive methods might very well be used to study such pressure dependence, although this has not been explored as it well might be.

Thermal Diffusivity

The physical arrangement of the specimen, pressure chamber, and confining fluid shown schematically in Figure 1b suggests a much greater quantity of confining fluid than was generally used in testing solid specimens. For adiabatic heating measurements, the amount of confining fluid is immaterial to the design except for thermal overshoot which was mentioned in the discussion of Figure 1. This has no influence on the adiabatic heating measurement, as noted, but is of some interest experimentally. For example, it was common practice to allow the system to come to thermal equilibrium following pressurization and obtain a pressure–temperature record upon depressurization. To minimize the amount of oil interface, and hence decrease the time needed to re-establish thermal equilibrium, the diameter of the cylindrical specimen was chosen to be only slightly less than that of the pressure vessel cavity. Thermal effects due to the gener-

ally higher adiabatic heating of the silicone oil confining fluids which were employed were then minimized.

The nature of the temperature decay in a specimen following a pressure step was observed to be exponential in time. The appearance of the temperature curve is indicated schematically at the right of Figure 2. The logarithm of the unattained temperature difference was found to be quite linear with time, once the decay was established. This is in accord with predictions from heat transfer theory for the temperature history at the center of an infinite cylinder at uniform temperature suddenly exposed to a temperature step on its boundaries. Further analysis showed that appropriate values for the thermal diffusivity of the specimen were obtained from the geometry and the temperature–time data, only if large values of surface resistance at the oil interfaces were accounted for, as anticipated.

Thermal diffusivity measurements obtained in this way have certain experimental advantages. A wide range of temperatures is allowed because of the ease with which the entire system may be conditioned. Temperature changes are induced in the specimen by the simple expedient of pressure change. Uniform temperatures in the specimen are assured by rapid pressurization. The problem of surface resistance may be reduced to negligible amounts by bonding the test specimen to the walls of the pressure vessel cavity. Then, upon a step change in pressure, the thermal conditions of the system are changed to those required for the simplest and most direct analysis of the heat transfer. As in other applications of adiabatic heating, the range of temperature over which an individual measurement of thermal diffusivity is characterized need not be more than a degree or two. The pressure dependence of the thermal diffusivity could also be explored. This, in conjunction with the pressure dependence of the specific heat and density, would allow the pressure dependence of the thermal conductivity to be estimated. This general approach may also have important applications to the changes in thermal properties with stretch ratio or other stress-induced anisotropy effects.

Specific Heat

The specific heat may be calculated from eq. (3) by using experimental values of the independent parameters. The determination of specific heat in this way is perhaps the most interesting application of adiabatic heating measurements. Data for a number of materials appropriate to this calculation are given as examples in Table I. The excellent agreement between experimental and theoretical values of adiabatic heating obtained for liquids qualitatively indicates the confidence with which the specific heat may be determined for solids.

Table I lists the specific heat values for composites of the polyurethane and CTPB rubbers, and glass microbeads. These were calculated from eq. (3) with the use of measured values of the independent parameters and are 0.30 and 0.42 cal./g.-°C., respectively. The variability of the results obtained in this way for composites are very likely a reflection of the uncer-

tainty with which the coefficient of thermal expansion, that is appropriate to the use of eq. (3), may be measured. Experimental values of thermal expansion for composites are affected by the internal stresses which may develop in the polymer matrix as a result of the shape, size, and amount of filler particles, and the various bulk moduli of the ingredients, with changing temperature.[14] It is interesting, therefore, to compare these values of specific heat, calculated from adiabatic heating data on the composites themselves, with estimates based on the individual values of specific heat for the composite ingredients.

The individual specific heats of the ingredients, shown in Table I for the polyurethane and CTPB rubber composite, may be combined with those of the glass filler and mass fractions of the ingredients to obtain values of 0.30 and 0.40 cal./g.-°C., respectively. In this instance, the specific heat values for the polymers, calculated from eq. (3), are not believed to suffer from inaccuracies in the determination of the coefficient of thermal expansion, to the same extent that the composites do. On the other hand, exact values of specific heat were not available for the glass-bead filler. Either source of uncertainty could have caused the observed discrepancy. Both methods produce useful values, however, in reasonable agreement with calorimetric data. This conclusion is based on the result of similar comparisons made on other composite materials[2] not discussed in this report. In general, either method of calculation can be used with these adiabatic heating methods for determining the specific heat of composites over a wide range of temperatures. The individual results are then specific to a very narrow range of temperature. This is an obvious advantage in characterizing the temperature dependence of the specific heat.

Thermodynamic Properties

Table III lists the properties of two polyurethane rubbers. These differed principally in the degree of crosslinking of the polymer network achieved upon polymerization. These polymers are identified in the table as binder specimens of crosslink density index 1.0 and 3.0. The number 1.0 indicates a degree of crosslinking somewhat lower than that generally used with these materials in composite solid rocket propellants. The higher index indicates a greater than usual amount of crosslinking. This casual description is used here since it is only intended to illustrate the variation of thermodynamic properties that are obtained for two similar rubbers whose primary structural differences are broadly indicated.

The adiabatic heating values of Table III were obtained by the experimental technique described previously. Compressibility values were calculated from contractions in the length of long specimens under hydrostatic pressure. This technique is described elsewhere.[15] Density and thermal expansion data were determined by hydrostatic weighing in a standard manner. The coefficients of thermal expansion listed are the least precise of the data.

TABLE III
Typical Polyurethane Rubber Data

Property at 295.2°K.	Binder specimen	
	Crosslink density index 1.0	Crosslink density index 3.0
Adiabatic heating, $(\partial T/\partial P)_S$, °F./1000 psi	1.264	1.201
Adiabatic bulk modulus $\kappa_S \times 10^{-6}$, psi	0.192	0.299
Isothermal bulk modulus $\kappa_T \times 10^{-6}$, psi	0.177	0.262
Density, ρ, g./cm.³	1.027	1.038
Bulk coefficient of thermal expansion $\beta_P \times 10^3$, °C.$^{-1}$	650	700
Derived quantities		
Internal pressure $(P_i + P)P \ll P_i$, psi	32,600	54,700
Gruneisen's ratio γ_G	0.46	0.68
Ratio of bulk moduli γ	1.085	1.141

From these data, several derived properties are calculated and given in Table III. They illustrate the various applications of adiabatic heating data which were alluded to in the text.

The values for internal pressure, P_i, calculated from eq. (13), and Grüneisen's ratio, γ_G, from eq. (17), are seen to be sensitive to the degree of crosslinking in the polymer network. The ratios of the bulk moduli listed are from the compressibility data and eq. (7), i.e., $\gamma = \kappa_S/\kappa_T$. These are 1.085 and 1.141 and are to be compared with values calculated from eq. (8) of 1.090 and 1.141 for the two materials compared in Table III, respectively. All derived values are given with an indicated precision in the last figure greater than that warranted from the original data. The materials on which Table III is based were not extensively characterized. The two rubbers were chosen from a group of materials tested for other purposes and are used here only to illustrate the principles outlined in the text.

SUMMARY AND CONCLUSIONS

The derivative $(\partial T/\partial P)_S$ is found to be precisely measured with relatively simple experimental techniques. Such measurements are shown to be feasible for solids as well as liquids, with particular applications to polymers and filled polymers.

Adiabatic heating data, in conjunction with compressibility measurements, are useful in characterizing the thermodynamic nature of rubbery solids. Direct measurements of heat capacity and thermal expansion may be avoided, particularly where wide ranges of temperature or small amounts of material are to be considered.

The attributes of adiabatic heating data for the characterization of the thermal or thermodynamic properties of materials in very narrow temperature ranges are recounted. The applications indicated or cited are likely only a few of those possible or warranting further study.

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