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Dependence of the Specific Volume of RX-08-FK High-Energy Paste on Temperature and Pressure

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We have measured the volumetric behavior of paste extrudable explosive RX-08-FK using two methods: high-precision dilatometry at atmospheric pressure and temperatures from −30 to +85 °C and compression testing in a specially designed piston-type rheometer in which the orifice was replaced with a blank. Compression measurements were made at six temperatures from −54 to +74 °C and at many pressures up to 70 MPa. The volume coefficient of expansion of the paste at 1 atm is very nearly constant over the temperature range tested, averaging $(3.643 \pm 0.005) \times 10^{-4}\ \mathrm{K}^{-1}$. In compression tests, at a given volume, the observed pressure was 3–15 MPa higher when pressure was rising than when it was falling, possibly because of O-ring drag. The specific volume of the paste over the field of temperature and pressure was well described by a simple equation of state: $v/(\mathrm{cm}^3\ \mathrm{g}^{-1}) = 0.50977 + 0.16683(T/\mathrm{K})/(P/\mathrm{MPa} + 801.41)$, $s_e(v/(\mathrm{cm}^3\ \mathrm{g}^{-1})) = 0.00026$.

Introduction

The high-energy paste explosive RX-08-FK offers promise for safe weapon systems in which the paste is transferred to the weapon just before deployment. Accurate design of such systems and the paste-transfer mechanisms requires knowledge of both the paste's flow behavior and the dependence of its specific volume (or density) on pressure and temperature. To measure these properties on RX-08-FK, a program of experiments was undertaken at Pantex, using a Lawrence Livermore National Laboratory (LLNL)-designed, second-generation, double-piston capillary rheometer. The volume measurements are reported here, while the flow measurements are the subject of a second paper, in preparation.

Measurements of the thermal expansion (at 1 atm) of RX-08-FK were also made in a capillary dilatometer. We think that these measurements are more precise and accurate than those obtained in the rheometer. We have therefore given them more emphasis in the overall data analysis, as we discuss later.

Before these volume measurements were made, we had only a few density determinations made at room temperature, and these few were not satisfying because they averaged about 1% below the theoretical maximum density (TMD). The TMD was computed from the known densities of the components and their mass percentages in the compound, under the reasonable assumption that all the individual volumes are additive. Later in the report we discuss possible reasons for this discrepancy and for our decision to use the TMD, 1.7523 g/cm^3, in calculating specific volumes from the dilatometry and compression-test measurements.

A few of the measurements given here were presented at a conference at Karlsruhe, Germany, in July 1990, in a survey paper titled *Paste Extrudable Explosives: Their History and Their Current Status* (*1*).

In their report on another set of measurements made on significantly different mixes of RX-08-FK, Flowers and Brasher (2) reported two values for the bulk modulus of their paste but did not give the actual measurements from which they estimated the moduli. Their values are about 40% of ours; we discuss this discrepancy.

Experimental Setups and Measurements

Paste Composition. RX-08-FK is an intimate mix of five nominal components. The components are octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), formal mixture number 1 (FM-1), ethyl 4,4-dinitropentanoate (EDNP), amorphous silica (Cab-O-Sil EH-5, from the Cabot Corp., is used), and ethylene glycol. FM-1 (*3*) is itself a mixture of three related formals: 50% 1-[(2-fluoro-2,2-dinitroethoxy)methoxy]-2,2-dinitropropane (MF-1) and 25% each of 1,1′-(methylenedioxy)bis[2,2-dinitropropane] (BDNPF) and 1,1′-(methylenedioxy)bis[2-fluoro-2,2-dinitroethane] (FEFO). The HMX used is a special grade of material, called LX-04 grade, which has a median particle-size distribution of 55 μm. Their weight percents are HMX, 72.8%; FM-1, 14.8%; EDNP, 10.3%; Cab-O-Sil EH-5, 2.0%; and ethylene glycol, 0.1%. The structural formulas for the first five compounds are shown in Figure 1; see ref 1 for a more detailed discussion of each component.

Dilatometry. These measurements were made according to ASTM Test D 864 (*4*), with valuable guidance from the report of Bekkedahl (*5*). The dilatometer we used differs somewhat from that shown in ref 4 and is sketched in Figure 2. It is made entirely of Pyrex glass, with mercury as the confining fluid. The measuring element is a capillary, 1 mm in bore and 60 cm in height, with 1-mm graduations (Ace Glass Co. Model 8698-10). In the traditional dilatometer, intended for measuring volume coefficients of expansion of solid specimens, the sample chamber is joined directly to the bottom of the capillary. This method is unsuitable for liquid samples, which would float over the mercury and flow up into the capillary. The inverted sample chamber shown in Figure 2 prevents this problem. Another difference is that in the traditional dilatometer the sample chamber is fused to the capillary after the sample is loaded, whereas in ours the reusable sample chamber is fitted with a convenient ground spherical joint, sparingly lubricated with silicone high-vacuum grease and tightly clamped. This design avoids possible overheating of the sample and loss of volatiles during glass fusion. It also provides better precision by minimizing the volume of mercury needed. The capillary was calibrated as described in ref 5. With the sample in the dilatometer and the chamber clamped, the system was evacuated and back-

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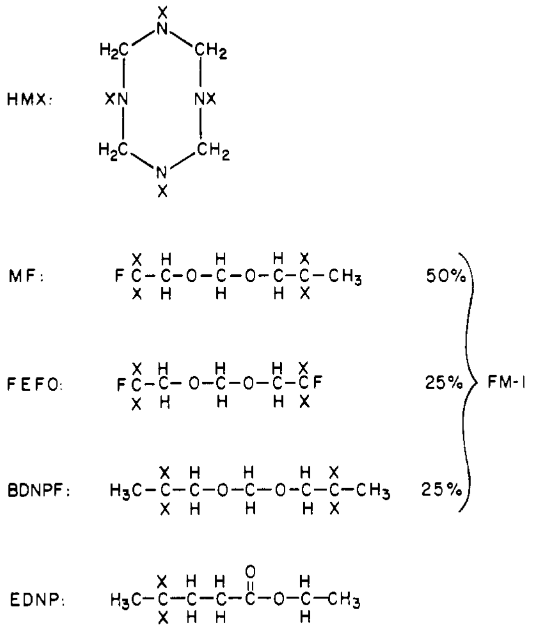

Figure 1. Structural–chemical formulas of main ingredients of RX-08-FK. The symbol -X stands for the radical $-NO_2$.

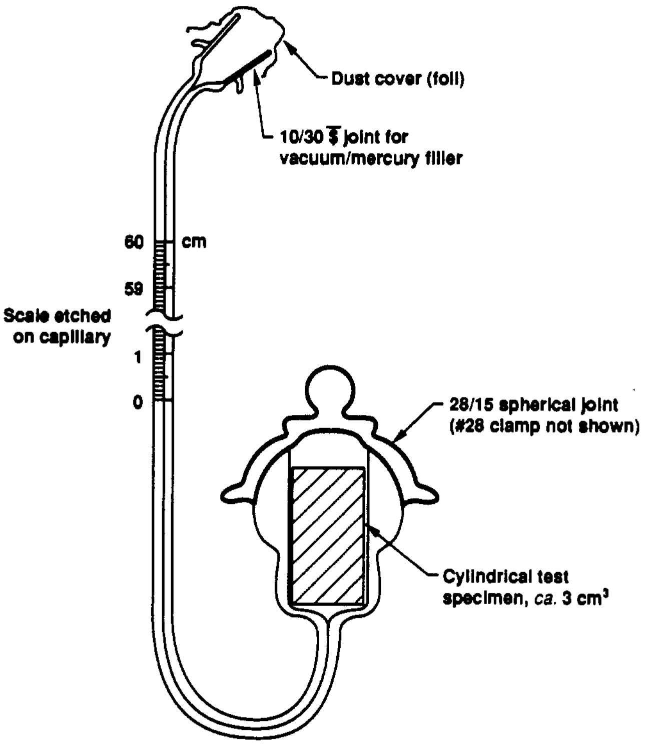

Figure 2. Sketch of Pyrex dilatometer, showing its inverted and reusable sample chamber.

filled with mercury using a handy loading fixture. Great care was taken to evacuate all air from the sample and chamber, and to clear all droplets of mercury from the empty portion of the capillary.

The loaded and mercury-filled sample chamber was immersed to the 2-cm mark in a programmable Neslab bath filled with a 50/50 solution of ethylene glycol and water. The bath has a range of −30 to +90 °C and can hold a set temperature to ±0.1 °C. The sample of RX-08-FK was held at −30 °C for 10 h and then heated at 0.5 K/min, with capillary readings taken at 3 K intervals. Subsequently, it was held at 90 °C for 45 min and then cooled at 0.5 K/min to −30 °C, with readings taken at 3 K intervals. It was left overnight (14 h) at −30 °C, and the heating sequence was repeated. The capillary readings were corrected for calibration error and for expansion/contraction of glass and mercury and converted to sample volumes. From these, using the theoretical density, specific volumes and densities were calculated. The data for the three runs on RX-08-FK are given in Appendix 1 of the supplementary material. Further details of the procedure are available from J.D.L.

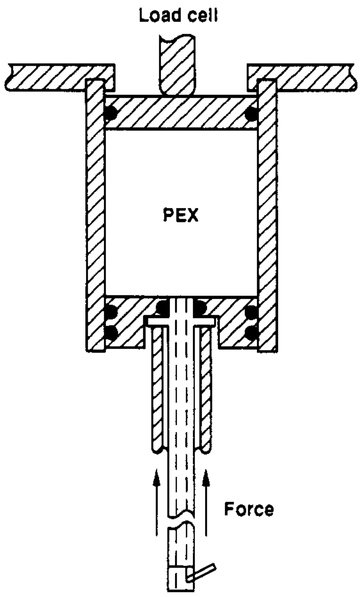

Figure 3. Schematic diagram of Pantex capillary rheometer (with long orifice in position).

Compression Measurements. The capillary rheometer used in this work is shown schematically in Figure 3. It differs from most other capillary rheometers in that it has two floating pistons. Also, it is the lower piston, carrying the capillary tube, that moves (upward) during a flow test. In the sketch, it is shown with a capillary in position for a flow test. In the work reported here, this tube was replaced with a solid bar that sealed the outlet. The rheometer was designed for insertion into a 50-kN, servohydraulic Instron biaxial testing machine, together with an environmental chamber that controlled the atmosphere and temperature of the rheometer. Details of the 2.5-cm-diameter sample reservoir and the pistons are given in LLNL Drawings AAA88-102806-0B, AAA88-100544-00, AAA71-116531-0C, and AAA88-100545-0B. (Note: Although stainless 316B is called for as the material of construction in the drawings, 304 was substituted to reduce the cost.)

As the lower piston is driven upward by the Instron's mechanism, the piston movement is measured by a position transducer. Touching the top piston is the foot of a force transducer whose reading is converted to pressure on the sample. As the sketch shows, the pistons, which clear the cylinder by 0.038 mm on its 14.17-mm radius, are sealed by O-rings.

To ensure that samples loaded into this rheometer would be free of air bubbles, we used a special deaerating loader, sketched in Figure 4. Loading was done at room temperature, using low hydraulic pressure. The loader consists of an upper and lower chamber that are separated by an orifice plate. Ports are available for vacuum and discharge. Operation was simple. With both pistons fully retracted, the paste was loaded into the upper chamber. The system was closed and evacuated to below 0.05 Pa, and the paste was slowly pressed through the small holes of the orifice plate into the evacuated lower chamber. Trapped air bubbles were exposed and removed in this process. The vacuum port was then closed, the discharge port was opened, and the paste was extruded into the rheometer cylinder while vacuum was maintained.

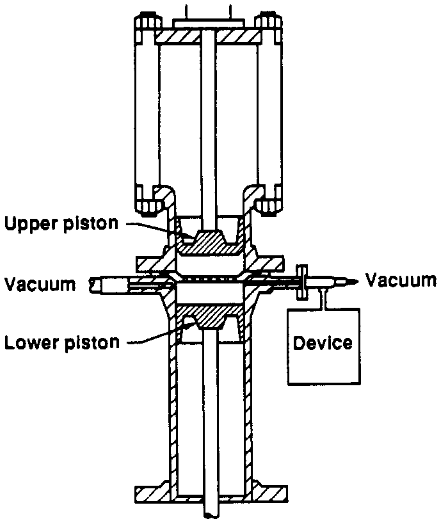

Figure 4. Schematic of the deaerator/loader used to load paste samples into rheometer chambers.

The loaded cylinder was carried to an environmental chamber set for the desired working temperature and left for at least 2 h, but usually overnight. (Estimating thermal diffusivity for the paste of 0.000 656 cm^2/s, we calculated that in 1 h the center of the 2.5-cm-diameter paste cylinder would be within a few tenths of a Celsius degree of the environmental temperature.) Prior to transferring it to the rheometer, that instrument was brought to the working temperature by blowing temperature-controlled nitrogen into its environmental chamber for at least 1 h. Transporting the preloaded, warmed (or chilled) cylinder and setting up for the test run took about 15 min. The loaded rheometer was then allowed to stand in the temperature-controlled environment for 15 min or more before commencing the test. Cylinders having nominal diameters of 2.5 and 5 cm were available, but only the 2.5-cm cylinder was used in the compression tests. Signals from the transducers were transmitted to a computer that stored them for later retrieval.

In making the compression tests, the lower cylinder was raised at velocities near 0.17 mm/s and position and pressure readings were recorded at 0.4-s intervals. This was continued until the pressure reached about 70 MPa (88% of the rated capacity of the force transducer), and then the ram was lowered while again taking 0.4-s readings of position and pressure until the pressure fell to zero (gauge). The records of these readings, for the six runs made at −54, −35, −10, 21.1, 50, and 74 °C, are in Appendix 2 of the supplementary material. This temperature range is specified for weapon service.

In this work, our original focus was on the bulk modulus of the paste and its reciprocal, the compressibility. Bulk modulus B is defined by the equation

$$B = -V(\partial P/\partial V)_T = -(\partial P/\partial \ln V)_T \quad (1)$$

where V is the measured sample volume at pressure P and temperature T.

As the pressure rises in the rheometer, the reservoir expands radially. Small, but not negligible, changes in cell dimensions also occur with temperature. The Instron reports the piston position, X (mm), with respect to the Instron's frame and the earth. However, the Instron, though very sturdy, deforms slightly (and not quite linearly) as the pressure rises, so a small correction must be made to each observed deflection for this "machine compliance". From the original dimensions and the modulus of the 304 stainless steel (193 GPa), we derived the following family of equations giving the paste volume:

$$V/\text{mm}^3 = 68274.6 - 630.04(X/\text{mm}) + 8.9269(P/\text{MPa}) - 0.026323(P/\text{MPa})^2 \quad (\text{at } -54\ °\text{C}) \quad (2a)$$

$$V/\text{mm}^3 = 68763.7 - 630.31(X/\text{mm}) + 8.9394(P/\text{MPa}) - 0.026334(P/\text{MPa})^2 \quad (\text{at } -35\ °\text{C}) \quad (2b)$$

$$V/\text{mm}^3 = 69401.7 - 630.66(X/\text{mm}) + 8.9557(P/\text{MPa}) - 0.026349(P/\text{MPa})^2 \quad (\text{at } -10\ °\text{C}) \quad (2c)$$

$$V/\text{mm}^3 = 70196.7 - 631.06(X/\text{mm}) + 8.9756(P/\text{MPa}) - 0.026366(P/\text{MPa})^2 \quad (\text{at } 21.1\ °\text{C}) \quad (2d)$$

$$V/\text{mm}^3 = 70934.6 - 631.51(X/\text{mm}) = 8.9949(P/\text{MPa}) - 0.026384(P/\text{MPa})^2 \quad (\text{at } 50\ °\text{C}) \quad (2e)$$

$$V/\text{mm}^3 = 71550.9 - 631.82(X/\text{mm}) + 9.0104(P/\text{MPa}) - 0.026397(P/\text{MPa})^2 \quad (\text{at } 74\ °\text{C}) \quad (2f)$$

For each temperature, $P = 0$ and $X = 0.1055$ mm will give the initial zero-pressure volume. The 0.1055 mm appears to be a very small machine slack in the Instron (see plot of compliance-test data in Appendix 3 of the supplementary material). Appendix 3 also gives the derivation of these equations and a sample volume calculation.

The volumes were converted to their natural logarithms so that we could plot, as suggested by eq 1, P vs $\ln V$ and observe the behavior of B, the slopes of these plots. The $\ln (V/\text{cm}^3)$ values ranged very narrowly in each run (from 4.2392 to 4.2484 at 21.1 °C, for example), so to prevent serious rounding errors in curve fitting the values were coded by converting to

$$u = 10^5(\ln V - k) \quad (3)$$

The k values chosen ranged from 4.21 to 4.25 (see Table A3-1 in Appendix 3 of the supplementary material). The u values and the sample volumes form the fourth and fifth columns in the tables of Appendix 2 of the supplementary material.

Results and Treatment of Data

Dilatometry. Our initial goal was determination of the paste's volume coefficient of expansion at atmospheric pressure. The coefficient is defined by the equation

$$\alpha = (1/V)\, \mathrm{d}V/\mathrm{d}T = (1/v)\, \mathrm{d}v/\mathrm{d}T = \mathrm{d} \ln V/\mathrm{d}T = \mathrm{d} \ln v/\mathrm{d}T \quad (4)$$

where v is the paste's specific volume.

The data in Appendix 1 of the supplementary material reveal that the volumes observed in the two heating runs agreed very closely, within 0.0004 cm^3. In the cooling run, volumes agreed closely with those of the heating runs in the central part of the temperature range, but tended to be slightly higher, by as much as 0.0015 cm^3, at the ends of the range. We have no explanation for these small differences (0.05% or less).

We expected that the coefficient of expansion might not vary over this limited range of temperature. Figure 5 is a plot of $\ln V$ vs T, as suggested by eq 4, and indeed it appears to be linear. Points for all three runs are included, and the line is the least-squares fit to the entire set. Its slope, the coefficient of expansion, is 3.6432×10^{-4} K^{-1}. The mass of each sample was computed from the measured volume at 21.1 °C and the theoretical density at that temperature, 1.7523

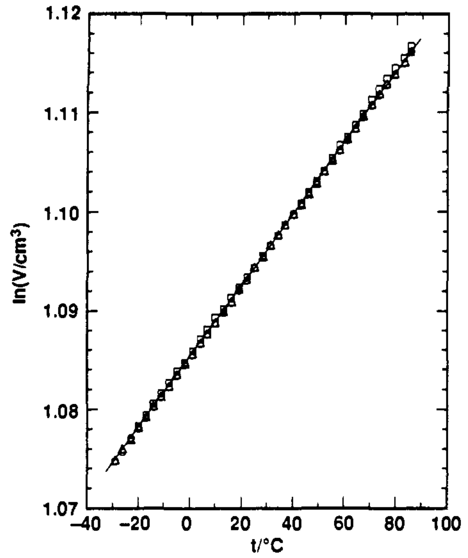

Figure 5. Natural logarithm of sample volume vs temperature for all three runs of RX-08-FK paste in dilatometer (heating rate 0.5 °C/min): ○, first heating; □, first cooling; △, second heating.

g/cm³, and then all the volumes were converted to specific volumes. The equation of the line, so converted, is

$$\ln (v/(\mathrm{cm}^3\,\mathrm{g}^{-1})) = -0.66704 + 3.6432 \times 10^{-4}(T/\mathrm{K}) \qquad (5)$$

The corresponding equation for specific volume at 1 atm is

$$v/(\mathrm{cm}^3\,\mathrm{g}^{-1}) = 0.50812e^{0.00036432(T/\mathrm{K})} \qquad (6)$$

The standard error of the volume coefficient of expansion is 5.0×10^{-7} K^{-1}, or 0.14% of the coefficient. The standard error of estimate for the specific volume is 0.000 10 cm³/g (±0.018%).

We also fitted lines to the three individual data sets. There were some slight differences among them, perhaps reflecting the effects of unidentified factors operating from one run to the next. Their contributions are reflected in the slightly larger overall error of the combined regression.

Although the volume equations are exponential in form, the exponential coefficients are very small, suggesting that volume is nearly linear with temperature. In fact, if the specific volumes calculated from eq 3 are plotted against temperature, the plot appears linear. The simpler linear equation provides a very satisfactory approximation and will be used later in fitting an overall equation of state to these data and those from the compression experiments.

Compression Results and Analysis. Figures 6–8 are plots of P vs V, for the compression runs made at −35, 21.1, and 74 °C, respectively. The plots for the other three temperatures are very similar to these. While several hypotheses can be entertained as to the cause of the divergence of the curves for rising and falling pressure, we think it is most credibly due to drag of the O-rings on the lower piston. The undeformed thickness of the O-ring is 2.56 mm, while the retaining recess and clearance total 1.95 mm, so they are compressed about 25% in service. For a given transmitted pressure, the piston rises slightly less than it would if the O-ring drag were absent; X, in eq 2, is less, and V is larger. When the direction of piston motion is reversed, so is the drag effect. The difference is less at the higher pressures when reservoir expansion reduces the deflection of the O-rings and their drag. In all cases the volume differences are small, 0.3% or less.

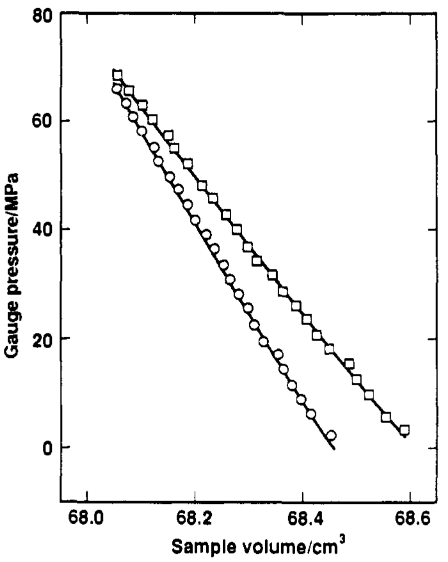

Figure 6. Observed pressure as a function of sample volume as lower, blocked-off piston of rheometer moves upward (□) and then downward (△), for t = −35 °C.

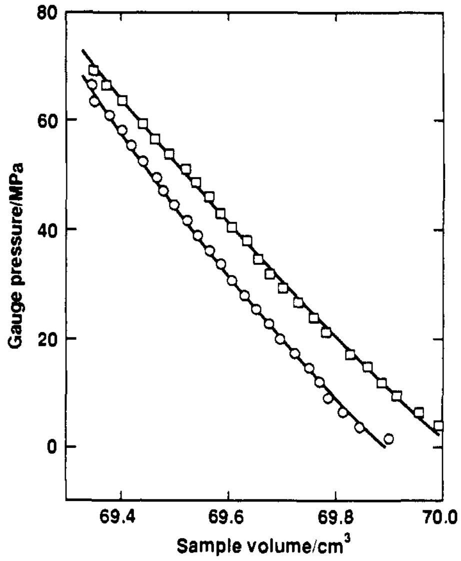

Figure 7. P vs V for 21.1 °C. Over the narrow ranges of volume in Figures 6–8, ln V and V are very nearly proportional. Note that the gap between volumes at rising (□) and falling pressure (○) is a little less here than in Figure 6.

By eq 1, the bulk modulus, B, is equal to the slope of P vs ln V at a given temperature. (Because the volume changes are so small over the pressure range, the P vs V curves are very nearly identical with P vs ln V.) The slopes of the curves in Figures 5–7 steepen considerably as pressure rises and are a little steeper, at any pressure, for the measurements at rising pressure than when pressure is falling. The curves drawn on these plots, which fit the data very well, are quadratic least-squares fits of P vs ln V. From the first-derivative equations of those fits, we were able to estimate values of B at various pressures and the six temperatures. By averaging the B values so obtained, at a given pressure, for rising and falling test pressures, we obtained estimates that were in fair agreement with those derived from the equation of state, to be discussed later. These mean values are listed in Table I.

Equation of State. Perhaps the most useful information to be derived from these experiments is an equation that gives the specific volume of the paste (or its density) as an explicit function of temperature and pressure. Of the many published equations of state, a simple one that has satisfactorily represented the specific volumes of several amorphous polymers is that of Spencer and Gilmore (*6*), which was

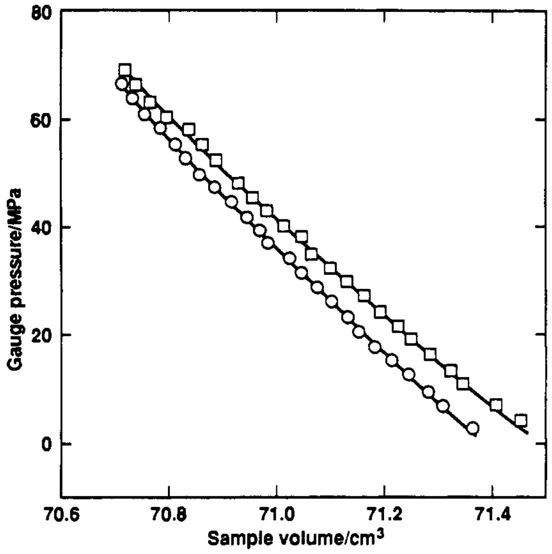

Figure 8. P vs V for 74 °C. Slopes of both curves here are less steep than those of Figure 7, which in turn are less steep than those of Figure 6, indicating expected diminution in bulk modulus with rising temperature.

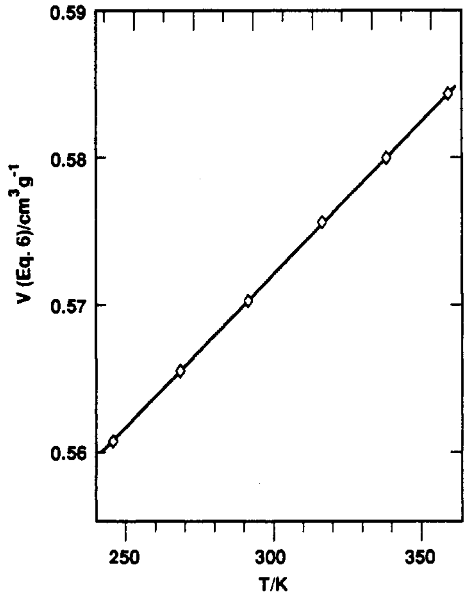

Figure 9. Specific volumes measured by dilatometry, as estimated from the exponential equation (eq 6). They appear to be closely linear with temperature.

simplified from the familiar van der Waals equation for gases. Their equation for specific volume is

$$v = RT/[M(p + \pi)] + b \qquad (7)$$

where R is the universal molar-energy constant, T is the absolute temperature, M is the molecular weight of an "interaction unit", p is the applied absolute pressure, π is the internal pressure, and b is the "unfree" volume of the molecules themselves.

M, π, and b are empirical constants that must be evaluated by fitting the p–v–T data. Interestingly, the M values found by Spencer and Gilmore (SG) for the five polymers they investigated were all very close to the respective mer weights (e.g., 104 for polystyrene), even though the interaction unit, a concept introduced earlier by Eyring and his co-workers (*7*) to model the flow of polymer melts, was thought to consist of about 25 mer units.

Each of these polymer melts was essentially a homogeneous solution of homologous compounds. Our paste is very different, a stable suspension containing about 70% by volume of finely divided solids (*1*) and no polymeric compounds. When we tried to impose its average molecular weight, 267.2, upon the fitting of our P–v–T data, the compressibility was too high.

We therefore tried a different approach. From eq 6, above, specific volumes were calculated for six temperatures distributed evenly over the entire temperature range of the dilatometry measurements, −29 to +85 °C. These were plotted, as in Figure 9, and the plot was found to be very closely linear, as we had expected. The equation of the line is

$$v/(\mathrm{cm^3\ g^{-1}}) = b + kT = 0.50972 + 2.083 \times 10^{-4}(T/\mathrm{K}) \qquad (8)$$

Comparing eq 8 with eq 7 shows that b is the same in both; on the other hand, if eq 7 is to be compatible with the dilatometry data, k must be equal to $R/M(p + \pi)$ for p = 0.101 MPa (1 atm).

To incorporate the compression data into this fitting, the sample volumes must first be converted to specific volumes. If we knew the volume of paste loaded each time, the mass loaded could be calculated from the specific volume of the paste, at the test temperature, as measured by dilatometry. We feel that the actual volumes loaded, for each temperature, are most realistically estimated from the quadratic equations fitted to the P vs ln V data, solving them for V at P(gauge) = 0 MPa. The initial volumes (cm^3) at the several temperatures are given in Table II.

Again using the fitted quadratics and the coefficients for rising and falling pressures, we computed mean sample volumes and, from the above masses loaded, mean specific volumes, for 25 gauge pressures from 1 to 69 MPa. Each of these values, listed in Table III, corresponds closely to a pair of original data points, for rising and falling pressures, listed in Appendix 2 in the supplementary material.

To fit the equation of state to the 150 mean volumes of Table III, we first found some preliminary values of the three parameters using graphical methods. These values were b = 0.509 84 cm^3/g, R/M = 0.169 43 (cm^3·MPa)/(g·K), and π = 815.44 MPa. We then applied the NONLIN program of SYSTAT (*8*), using these values as starters, to obtain the final EOS:

$$v/(\mathrm{cm^3\ g^{-1}}) = 0.50977 + 0.16683(T/\mathrm{K})/(P/\mathrm{MPa} + 801.41) \qquad (9)$$

Because P is the gauge pressure, 801.41 in eq 9 corresponds to π = 801.31 MPa. Equation 9 should not be confused with the *detonation* equation of state given in ref 1 for RX-08-FK, which relates the volume of combustion gases generated per unit mass of paste to pressure and temperature.

The three preliminary parameter values were all within 1 standard error of those obtained with NONLIN. (The NONLIN fit was rerun with very different starting values and again converged to the same final ones.)

From eq 7, 0.166 83 = R/M and, since R = 8.3144, M = 49.838. This value of M is much lower than the molecular weight of any constituent of the paste. However, because the paste consists mostly of solid particles rather than molecules, molecular motion and molecular weight are inapplicable concepts.

How well do the specific volumes computed from the EOS agree with the measured ones? The (corrected) coefficient of determination (R^2) for the fit is 0.999 22, which means that, of the total variation exhibited by the 150 mean experimental volumes, all but 0.078% is accounted for by the EOS. The standard error of estimate for the fit is 0.000 26

Table I. Mean Bulk Moduli B of RX-08-FK from Slopes of P vs ln V Curves

	B/GPa					
t, °C	P = 0 MPa	P = 15 MPa	P = 30 MPa	P = 45 MPa	P = 60 MPa	P = 75 MPa
−54	8.68	9.71	10.57	11.33	12.02	12.66
−35	9.41	9.71	10.00	10.29	10.56	10.83
−10	9.90	10.12	10.34	10.55	10.76	10.96
21.1	6.50	7.28	11.63	8.63	9.23	9.80
50	6.98	7.35	7.69	8.02	8.33	8.62
74	5.83	6.30	6.73	7.14	7.53	7.90

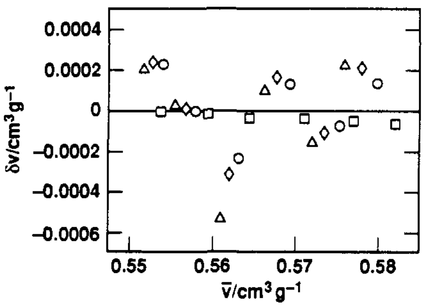

Figure 10. Deviations of specific EOS-estimated volumes from the mean measured volumes vs measured volumes for 24 cases spanning the experimental range: □, P = 0 MPa; ○, P = 23.7 MPa; ◇, P = 46.3 MPa; △, P = 69.0 MPa.

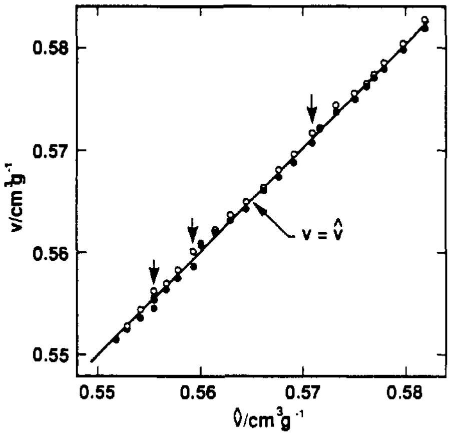

Figure 11. Actual measured volumes at rising and falling pressures for the same conditions as in Figure 10 vs volume given by EOS. In only three of the 24 cases (arrows) was the difference between volumes greater than 0.001 cm³/g.

cm³/g, about 0.04% of the specific volume. The relative error in density is the same.

A visual impression of the goodness of the EOS fit is given in Figure 10, in which, for 24 conditions over the range of the work, the EOS residuals are plotted against their mean measured partners.

Figure 11 shows that the differences between the measured volumes at rising and falling pressure are considerably larger than those between the mean measured volumes and volumes given by the EOS. As Figures 4–6 show, the former differences were more serious at low pressures than high ones. At 35 MPa, however, they averaged +0.0005 cm³/g, or twice the standard error of the EOS fit. In any practical application of the EOS to paste transfer, the question of the difference between the applied pressure and the paste pressure is again likely to arise, dwarfing the fitting error of the EOS.

The volume behavior of the paste is monotonic in both temperature and pressure, so eq 9 should provide accurate specific volumes over the entire experimental range and should be nearly as reliable for pressures up to 80 MPa and temperatures to 100 °C. (The excellent temperature stability of RX-08-FK is quantified in ref 1.)

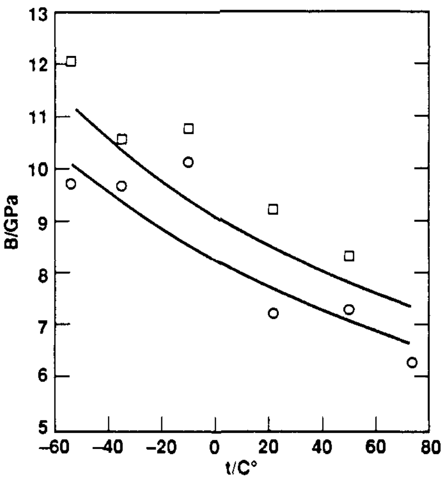

Figure 12. Mean bulk moduli, B, calculated from slopes of P vs ln V (plotted points) vs Celsius temperature, shown with curves computed from eq 10: □ and upper curve, P = 60 MPa; ○ and lower curve, P = 15 MPa. We could find no explanation for the unexpectedly high slopes at −10 °C.

McKelvey (9) has shown how the SG EOS can be used to estimate the bulk modulus by taking the appropriate derivative. In our case, the equation is

$$B/\mathrm{GPa} = 10^{-3}(P/\mathrm{MPa} + 801.41)[1 + 3.0556(P/\mathrm{MPa} + 801.41)/(T/\mathrm{K})] \quad (10)$$

Clearly, by this equation, B is monotonic (+) in P and monotonic (−) in T. In Figure 12 we have plotted curves of B vs T, computed from eq 10, for P = 60 and 10 MPa. Also plotted are the mean B values calculated from the slopes of the P vs u equations, at rising and falling pressures. As we said earlier, there is not only considerable scatter of the slope-derived values, but, as these plots show, they are not monotonic in temperature. Also, we cannot explain why the slope-derived values seem to exhibit stronger dependence on pressure than the values given by eq 10. Because of the erratic behavior of the slope-derived values and because the EOS provided such a close fit to the specific volumes over the whole experimental range, we suggest that designers rely on eq 10 for bulk-modulus values, when needed, rather than on the slope-derived ones.

We mentioned in the Introduction that Flowers and Brasher (2) have reported smaller bulk moduli for a similar but not identical paste. The chemical composition of the paste was that of RX-08-FK, but the HMX particle-size distribution was substantially different, and a different solvent was used in processing the mix. Also, Flowers and Brasher used the 5-cm-diameter cylinder in their work, whereas we used the 2.5-cm cylinder. Specifically, they reported that, at P = 20 MPa, the modulus was 2.9 GPa at ambient (approximately 21 °C) and 3.2 GPa at 45 °C. These can be compared with our mean slope-estimated values for the same pressure of 7.5 GPa at both 21 and 50 °C, or with the values from eq 9 of 7.8 GPa at 21 °C and 7.3 GPa at 45 °C.

Table II. Initial Volume and Mass of RX-08-FK As Estimated by P vs ln V Curves

	V/cm^3					
	t = −54 °C	t = −35 °C	t = −10 °C	t = 21.1 °C	t = 50 °C	t = 74 °C
pressure rising, R	68.206	68.607	69.381	70.012	70.914	71.473
pressure falling, F	68.025	68.453	69.308	69.882	70.852	71.371
mean of R and F	68.116	68.530	69.345	69.947	70.888	71.422

	t = −54 °C	t = −35 °C	t = −10 °C	t = 21.1 °C	t = 50 °C	t = 74 °C
m/g, adjusted mass loaded	122.650	122.521	122.834	122.497	121.849	122.713

Table III. Mean Specific Volumes[a] v of Paste, cm^3/g

	v/(cm^3 g^{-1})					
P/MPa	t = 219.16 K	T = 238.16 K	T = 263.16 K	T = 294.26 K	T = 323.16 K	T = 347.16 K
1.0	0.555 29	0.559 27	0.564 48	0.570 92	0.578 95	0.581 92
3.8	0.555 09	0.559 10	0.564 32	0.570 68	0.576 72	0.581 65
6.7	0.554 90	0.558 93	0.564 15	0.570 44	0.576 49	0.581 36
9.5	0.554 72	0.558 76	0.564 00	0.570 20	0.576 26	0.581 10
12.3	0.554 54	0.558 59	0.563 84	0.569 98	0.576 04	0.580 83
15.2	0.554 36	0.558 42	0.563 68	0.569 75	0.575 81	0.580 56
18.0	0.554 19	0.558 26	0.563 52	0.569 53	0.575 59	0.580 30
20.8	0.554 03	0.558 09	0.563 36	0.569 32	0.575 37	0.580 05
23.7	0.553 86	0.557 92	0.563 20	0.569 10	0.575 15	0.579 79
26.5	0.553 71	0.557 76	0.563 05	0.568 89	0.574 94	0.579 54
29.3	0.553 56	0.557 60	0.562 90	0.568 69	0.574 73	0.579 30
32.2	0.553 40	0.557 44	0.562 74	0.568 48	0.574 51	0.579 05
35.0	0.553 25	0.557 28	0.562 59	0.568 28	0.574 31	0.578 81
37.8	0.553 11	0.557 12	0.562 43	0.568 09	0.574 10	0.578 58
40.7	0.552 96	0.556 96	0.562 28	0.567 89	0.573 89	0.578 34
43.5	0.552 82	0.556 80	0.562 13	0.567 70	0.573 69	0.578 11
46.3	0.552 68	0.556 65	0.561 98	0.567 52	0.573 48	0.577 88
49.2	0.552 54	0.556 49	0.561 82	0.567 33	0.573 28	0.577 65
52.0	0.552 40	0.556 34	0.561 67	0.567 15	0.573 08	0.577 43
54.8	0.552 27	0.556 19	0.561 53	0.566 97	0.572 88	0.577 21
57.7	0.552 13	0.556 03	0.561 37	0.566 79	0.572 68	0.576 98
60.5	0.552 00	0.555 88	0.561 23	0.566 61	0.572 49	0.576 77
63.3	0.551 87	0.555 72	0.561 08	0.566 44	0.572 29	0.576 55
66.2	0.551 74	0.555 58	0.560 93	0.566 26	0.572 09	0.576 33
69.0	0.551 62	0.555 43	0.560 78	0.566 10	0.571 90	0.576 12

[a] These volumes are thought to be correct to four places, but could be off by as much as ±0.0005 cm^3/g because of uncertainty in the densities of the principal components of the paste. Five places were retained to prevent rounding errors in comparing these volumes with volumes calculated from the equation of state.

From eq 9 and the definition of the volume coefficient of expansion α, one can derive the following equation for that property (*9*):

$$\alpha/\mathrm{K}^{-1} = 1/[T/\mathrm{K} + 3.0556(P/\mathrm{MPa} + 801.41)] \quad (11)$$

By dilatometry we found the value of α to average 3.643 × 10^{-4} K^{-1} from −30 to +85 °C, whereas eq 11 clearly has it inversely related to T. Taking P = 0 MPa (1 atm absolute), the values of α given by eq 11 at three temperatures are 0.000 371 5 at −30 °C, 0.000 364 7 at 27 °C, and 0.000 358 2 at 85 °C. The mean of these three equally spaced point values is 3.648 × $10^{-4}K^{-1}$, only 0.1% more than the dilatometry value!

Summary and Conclusions

The mean volume coefficient of thermal expansion of RX-08-FK at one atmosphere was found to be (3.643 ± 0.005) × 10^{-4} K^{-1} from dilatometry measurements over the temperature range from −30 to +85 °C. We combined these measurements with measurements of paste compression in the Pantex rheometer, at six temperatures from −54 to +74 °C and at applied pressures from atmospheric pressure to 70 MPa, to develop an equation of state that represents the paste's specific volume (and density) with a standard error of 0.04%. The main uncertainty in the results is the slight difference, about 0.0005 cm^3/g, between volumes measured during rising pressures (upward motion of the active piston) and falling pressures (downward motion). We think it likely that these differences are due to drag of the piston's O-rings on the chamber wall. Additional error of the same size is possible because of uncertainties in the densities (at ambient conditions) of some components of RX-08-FK. It is safe to extrapolate the EOS by 15% of the pressure and temperature ranges. Equation 10 should probably be used to estimate bulk moduli (and their reciprocals, compressibilities) for this paste. Equation 11 should be used to estimate volume coefficients of expansion at pressures above atmospheric pressure.

Caution. A person using the data and equations of this report, e.g., for estimating paste mass from volume in a PEX-extrusion system, may obtain more accurate estimates by making adjustments for variations like those encountered in our measuring system. Containers and piping may expand with rising temperature and pressure, and pistons may drag.

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Glossary

B	bulk modulus, GPa
b	"unfree" volume in SG's equation of state, cm^3/g (eq 7)
m	sample mass, g
M	molecular weight, g/gmol
P	gauge pressure, MPa
p	absolute pressure, MPa ($p = P + 0.101$)
T	absolute temperature, K
t	temperature, °C
V	sample volume, cm^3
v	specific volume of paste, cm^3/g
X	rheometer-piston position (displacement), mm
α	volume coefficient of expansion, K^{-1} (eqs 4 and 11)
π	internal pressure, MPa (eq 7)
BDNPF	1,1′-(methylenedioxy)bis[2,2-dinitropropane]
EDNP	ethyl 4,4-dinitropentanoate
FEFO	1,1′-(methylenedioxy)bis[2-fluoro-2,2-dinitroethane]
FM-1	formal mixture number 1 (50% MF-1, 25% BDNPF, 25% FEFO)
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; LX-04 grade HMX refers to a specific particle size distribution having a median particle size of approximately 55 μm
MF-1	1-[(2-fluoro-2,2-dinitroethoxy)methoxy]-2,2-dinitropropane

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Supplementary Material Available:

Appendix 1 containing tables listing data from dilatometry runs, Appendix 2 containing tables listing data from capillary rheometer compression tests, and Appendix 3 containing a texual explanation of the treatment of compression data, a table listing quadratic-fit coefficients for P vs u, and a figure showing the response of an Instron tester during compression (21 pages). Ordering information is given on any current masthead page.

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