J. Chem. Eng. Data 1994, 39, 467–469

PVT Measurements on Fullerite from 30 to 330 °C and at Pressures to 200 MPa

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Specific volumes of C_{60}/C_{70} (3:1) fullerites are measured up to 330 °C and 200 MPa using a dilatometer-type PVT (pressure–volume–temperature) apparatus. The compressibility and thermal expansion of fullerites are found to be much higher than those of graphite. This is consistent with a lower degree of molecular and supermolecular (crystal) packing in fullerites compared to graphite.

Introduction

Fullerene molecules (bucky balls) are ball-like cage analogues of carbon. Their molecular packing and crystal packing (e.g., face-centered cubic (fcc) for C_{60}) are less dense than those of graphite and diamond. This is consistent with the difference in density between fullerites and graphite or diamond. Here we use the term "fullerenes" for the molecules, and "fullerites" for the solids. For example, the densities of graphite and diamond are 2.267 and 3.515 g·cm^{-3} at 20 °C, respectively (*1*), while the density of C_{60} is only 1.65 g·cm^{-3} (*2, 3*). Larger fullerites are even less dense (*2, 3*). This is because there is more free volume between the cages and inside the cages. Therefore, the compressibility and thermal expansion of such materials are expected to be much higher than those of graphite and diamond, which are known to be very low. This is consistent with the isothermal bulk modulus of $K/\text{GPa} = 18.1 + 5.7P/\text{GPa}$ determined by Duclos et al. (*4*) on the basis of the ambient-temperature compressibilities of C_{60} fullerite up to 20 GPa. Also, Fischer and co-workers (*5*) report that the ambient-temperature volume compressibility of solid C_{60} is 7.0×10^{-5} MPa^{-1}, which is 3 and 40 times greater than those of graphite and diamond, respectively.

However, there is a solid–solid phase transition (*simple cubic* to *face-centered cubic*) for C_{60} at −13 °C at ambient pressure (*6, 7*), which shifts to higher temperatures with increasing pressure at a rate of 0.117 K·MPa^{-1}, as measured by Kriza and co-workers (*8*). This means that, above 350 MPa at ambient temperatures, the phase structure (crystal form) of C_{60} fullerite is different from that at lower pressure. Therefore, the volume changes resulting from changes in pressure have a contribution from the phase transition (similar to melting expansion), in addition to the compressibility contribution. This may indicate that there is a significant error in the results of Fischer and co-workers (5).

High-pressure IR spectra (*9, 10*) show that intramolecular vibrations shift with increasing pressure, due to the reduction in intermolecular distance. Furthermore, the frequency shifts are found to be reversible up to 3200 MPa, which suggests that the fullerene cages do not collapse and rearrange themselves below 3200 MPa.

Thus, further measurements on the compressibility, expansivity, and phase behavior of fullerites at both elevated temperature and pressure are necessary. It is the objective of this report to determine the fullerite compressibility and phase behavior at higher temperatures from high-pressure, high-temperature PVT data, and to compare them to those of graphite.

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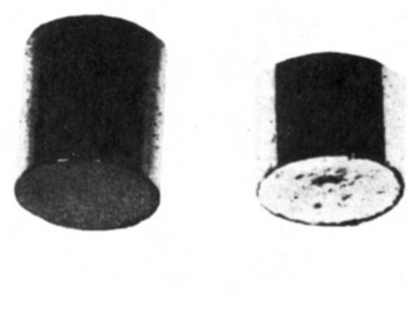

Figure 1. Photographs of fullerite and graphite cylinders.

Experimental Section

Fullerites used in this work are prepared by the carbon electrical arcing technique, and isolated by toluene extraction. The samples contain about 75 mol % C_{60} and 25 mol % C_{70} as determined by high-resolution ^{13}C NMR. Graphite is a spectroscopy grade powder (SP-1) from Union Carbide. Sample powders are dried under vacuum at 100 °C for 24 h. Cylindrical samples (diameter 10.0 mm) are formed in a SPECAC die by slowly applying a total force of 2500 kg over a cross-section of 0.785 cm^2 ($P \approx 315$ MPa) under vacuum. The densities of the cylinders are estimated from their lengths and diameters measured with a micrometer) and their masses (measured with an analytical balance).

Pressure–volume–temperature (PVT) properties of fullerites and graphite are determined in a dilatometer-type PVT apparatus (*11*) manufactured by Gnomix, Inc. (Boulder, CO). A cylindrical sample with a total volume of about 1 cm^3 is placed in a chamber with a flexible bellows. The volume in the chamber not taken by the sample is filled with mercury, after evacuation to 4-kPa vacuum. Isothermal compression experiments are conducted in the temperature range of 30–350 °C and pressure range of 10–200 MPa, and extrapolated to 0 MPa. The temperature interval is 20 °C, and the residence time at each pressure is 60 s. The manufacturer-quoted accuracy is 0.001–0.002 cm^3·g^{-1}, but the resolution is about 10 times better.

Results and Discussion

Pictures of the compressed fullerite and graphite samples are shown in Figure 1. The fullerite density, d_f, is found to be 1.58 g·cm^{-3}, and the graphite density, d_g, is found to be 2.15 g·cm^{-3}, at ambient conditions. These values are close to the literature values of 1.65 and 2.267 g·cm^{-3}, respectively (*1–3*), which is our test for achieving good, void-free samples for subsequent PVT experiments.

PVT results for fullerites given in Table 1 and plotted in

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Table 1. Isothermal PVT Results for C_{60}/C_{70} (3:1) Fullerites (V_0 = 0.632 $cm^3 \cdot g^{-1}$ at 25 °C and 0.1 MPa, Specific Volume at Given t and P is $V_0 + \Delta V$)

t/°C	P/MPa	$\Delta V/(cm^3 \cdot g^{-1})$	t/°C	P/MPa	$\Delta V/(cm^3 \cdot g^{-1})$	t/°C	P/MPa	$\Delta V/(cm^3 \cdot g^{-1})$	t/°C	P/MPa	$\Delta V/(cm^3 \cdot g^{-1})$
30.0	0	0.0017	110.9	0	0.0042	191.0	0	0.0201	270.1	0	0.0389
30.0	10	0.0002	110.9	10	0.0031	191.1	10	0.0182	270.2	10	0.0349
30.0	20	−0.0015	111.2	20	0.0020	191.6	20	0.0165	271.1	20	0.0311
29.8	30	−0.0028	111.4	30	0.0009	191.7	30	0.0147	271.7	30	0.0279
29.9	40	−0.0038	111.5	40	−0.0003	191.7	40	0.0130	272.0	40	0.0253
30.0	50	−0.0048	111.6	50	−0.0014	191.7	50	0.0115	272.3	50	0.0228
30.0	60	−0.0058	111.7	60	−0.0023	191.7	60	0.0100	272.4	60	0.0207
30.0	70	−0.0068	111.8	70	−0.0033	191.9	70	0.0086	272.5	70	0.0187
29.9	80	−0.0077	112.0	80	−0.0042	192.1	80	0.0072	272.8	80	0.0168
29.9	90	−0.0086	112.1	90	−0.0051	192.2	90	0.0059	272.9	90	0.0152
29.8	100	−0.0095	112.2	100	−0.0060	192.5	100	0.0045	273.2	100	0.0137
29.9	110	−0.0103	112.3	110	−0.0069	192.6	110	0.0034	273.6	110	0.0121
29.9	120	−0.0112	112.3	120	−0.0077	192.9	120	0.0021	273.7	120	0.0107
30.0	130	−0.0119	112.2	130	−0.0084	193.1	130	0.0009	273.7	130	0.0093
30.0	140	−0.0127	112.3	140	−0.0091	193.4	140	−0.0002	273.7	140	0.0081
30.0	150	−0.0134	112.3	150	−0.0099	193.6	150	−0.0013	273.8	150	0.0068
29.9	160	−0.0141	112.3	160	−0.0106	193.8	160	−0.0025	274.0	160	0.0056
29.9	170	−0.0148	112.3	170	−0.0113	194.0	170	−0.0035	274.1	170	0.0044
29.9	180	−0.0155	112.3	180	−0.0121	194.1	180	−0.0045	274.3	180	0.0034
29.9	190	−0.0162	112.4	190	−0.0127	194.3	190	−0.0055	274.5	190	0.0023
29.9	200	−0.0168	112.3	200	−0.0134	194.3	200	−0.0064	274.7	200	0.0011
51.1	0	0.0008	130.9	0	0.0079	210.9	0	0.0256	289.9	0	0.0443
51.1	10	−0.0003	130.9	10	0.0066	210.9	10	0.0233	298.8	10	0.0392
51.1	20	−0.0014	131.2	20	0.0054	211.5	20	0.0211	290.5	20	0.0345
50.9	30	−0.0026	131.3	30	0.0041	211.8	30	0.0190	291.2	30	0.0305
50.8	40	−0.0037	131.5	40	0.0028	211.7	40	0.0171	291.7	40	0.0276
50.7	50	−0.0048	131.7	50	0.0016	211.9	50	0.0153	292.2	50	0.0251
50.7	60	−0.0058	131.8	60	0.0005	212.1	60	0.0137	292.5	60	0.0227
50.7	70	−0.0067	132.0	70	−0.0005	212.2	70	0.0122	292.7	70	0.0206
50.7	80	−0.0076	132.2	80	−0.0015	212.4	80	0.0108	293.1	80	0.0186
50.7	90	−0.0084	132.3	90	−0.0025	212.6	90	0.0094	293.2	90	0.0168
50.7	100	−0.0093	132.4	100	−0.0034	212.8	100	0.0079	293.5	100	0.0150
50.7	110	−0.0102	132.6	110	−0.0043	212.7	110	0.0064	293.6	110	0.0133
50.7	120	−0.0110	132.7	120	−0.0052	212.7	120	0.0050	293.7	120	0.0119
50.7	130	−0.0117	132.8	130	−0.0061	212.9	130	0.0036	294.1	130	0.0104
50.7	140	−0.0125	132.9	140	−0.0069	213.0	140	0.0023	294.3	140	0.0090
50.7	150	−0.0132	133.0	150	−0.0077	213.2	150	0.0010	294.5	150	0.0078
50.7	160	−0.0140	132.9	160	−0.0084	213.5	160	−0.0002	294.3	160	0.0064
50.7	170	−0.0146	132.9	170	−0.0092	213.8	170	−0.0014	294.3	170	0.0051
50.6	180	−0.0153	132.9	180	−0.0100	214.0	180	−0.0025	294.4	180	0.0040
50.7	190	−0.0160	132.9	190	−0.0107	214.3	190	−0.0036	294.5	190	0.0028
50.8	200	−0.0167	132.9	200	−0.0114	214.4	200	−0.0046	294.7	200	0.0016
71.4	0	0.0014	150.8	0	0.0112	230.7	0	0.0301	310.1	0	0.0500
71.3	10	0.0003	150.8	10	0.0098	230.6	10	0.0273	310.1	10	0.0437
71.5	20	−0.0009	151.3	20	0.0084	231.4	20	0.0247	311.0	20	0.0378
71.5	30	−0.0021	151.4	30	0.0071	231.8	30	0.0223	311.6	30	0.0335
71.5	40	−0.0032	151.4	40	0.0057	231.9	40	0.0203	312.1	40	0.0302
71.4	50	−0.0042	151.5	50	0.0044	232.0	50	0.0182	312.6	50	0.0273
71.4	60	−0.0053	151.6	60	0.0032	232.3	60	0.0164	313.0	60	0.0243
71.4	70	−0.0062	151.9	70	0.0021	232.4	70	0.0148	313.5	70	0.0221
71.5	80	−0.0071	152.0	80	0.0010	232.6	80	0.0132	313.7	80	0.0199
71.5	90	−0.0080	152.2	90	−0.0001	232.9	90	0.0118	313.8	90	0.0180
71.5	100	−0.0089	152.5	100	−0.0011	232.9	100	0.0103	313.9	100	0.0161
71.5	110	−0.0097	152.7	110	−0.0021	232.9	110	0.0089	314.0	110	0.0143
71.4	120	−0.0106	152.9	120	−0.0031	232.9	120	0.0076	314.2	120	0.0127
71.5	130	−0.0113	153.0	130	−0.0040	233.1	130	0.0063	314.5	130	0.0111
71.5	140	−0.0121	153.1	140	−0.0048	233.1	140	0.0049	314.7	140	0.0096
71.5	150	−0.0128	153.3	150	−0.0057	233.3	150	0.0036	314.8	150	0.0081
71.5	160	−0.0135	153.5	160	−0.0065	233.5	160	0.0023	314.7	160	0.0068
71.5	170	−0.0142	153.7	170	−0.0073	233.7	170	0.0010	314.8	170	0.0055
71.5	180	−0.0149	153.7	180	−0.0082	234.0	180	−0.0001	314.9	180	0.0042
71.5	190	−0.0155	153.7	190	−0.0090	234.3	190	−0.0013	315.1	190	0.0029
71.4	200	−0.0162	153.7	200	−0.0098	234.6	200	−0.0025	315.2	200	0.0018
91.1	0	0.0025	170.9	0	0.0153	250.4	0	0.0342	330.7	0	0.0570
91.2	10	0.0013	170.9	10	0.0136	250.3	10	0.0309	330.8	10	0.0484
91.5	20	0.0002	171.4	20	0.0120	251.2	20	0.0278	331.5	20	0.0403
91.6	30	−0.0009	171.5	30	0.0104	251.9	30	0.0251	332.2	30	0.0354
91.7	40	−0.0020	171.5	40	0.0090	252.1	40	0.0228	332.7	40	0.0315
91.6	50	−0.0031	171.5	50	0.0075	252.4	50	0.0206	333.4	50	0.0284
91.6	60	−0.0041	171.8	60	0.0062	252.5	60	0.0187	333.8	60	0.0255
91.8	70	−0.0050	171.9	70	0.0049	252.5	70	0.0168	334.3	70	0.0230
91.8	80	−0.0059	172.0	80	0.0037	252.6	80	0.0151	334.6	80	0.0207
91.8	90	−0.0067	172.2	90	0.0025	252.7	90	0.0135	334.8	90	0.0182
91.8	100	−0.0076	172.4	100	0.0014	253.0	100	0.0119	334.9	100	0.0162
91.8	110	−0.0084	172.6	110	0.0003	253.1	110	0.0106	335.0	110	0.0142
91.9	120	−0.0092	172.9	120	−0.0008	253.4	120	0.0092	335.0	120	0.0125
91.8	130	−0.0099	173.0	130	−0.0017	253.6	130	0.0079	335.2	130	0.0108
91.8	140	−0.0106	173.2	140	−0.0028	253.5	140	0.0066	335.3	140	0.0093
91.8	150	−0.0113	173.4	150	−0.0038	253.5	150	0.0053	335.6	150	0.0077
91.8	160	−0.0120	173.5	160	−0.0047	253.7	160	0.0041	335.8	160	0.0063
91.8	170	−0.0128	173.6	170	−0.0056	253.8	170	0.0030	336.0	170	0.0049
91.8	180	−0.0134	173.8	180	−0.0064	254.0	180	0.0018	335.9	180	0.0036
91.8	190	−0.0141	174.0	190	−0.0073	254.1	190	0.0006	335.9	190	0.0023
91.9	200	−0.0147	174.1	200	−0.0081	254.4	200	−0.0006	335.9	200	0.0010

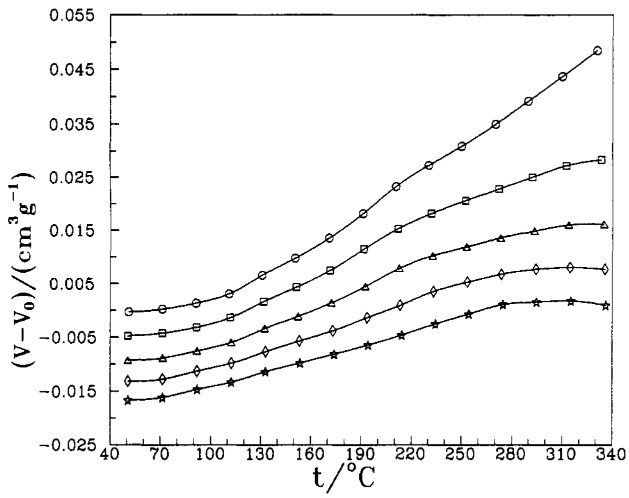

Figure 2. Isobars for fullerites. From top to bottom, 10, 50, 100, 150, and 200 MPa.

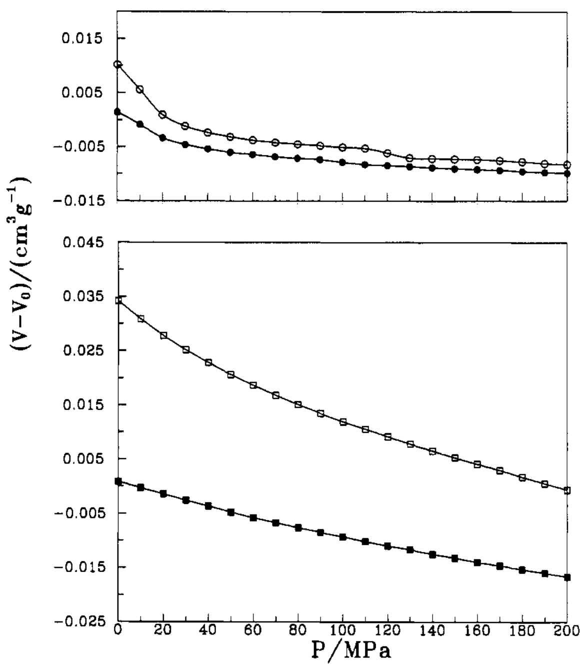

Figure 3. Comparison of isothermal compressibility of fullerites (bottom two curves with open squares for 250 °C and filled squares for 50 °C) and graphite (top two curves with open circles for 250 °C and filled circles for 50 °C).

Figure 2 indicate considerable compressibility and thermal expansion. These results are measured isothermally starting at low temperatures. Compressibility is found to be reversible; i.e., after reducing pressure at each temperature, the specific volume is restored to its initial low-pressure value. This means that the major contribution to the compressibility is from the material, not from possible porosity.

Within the temperature range of 40–340 °C, there is no significant phase transition found at both ambient pressure and 200 MPa. Thermal expansion at each pressure shows an almost linear increase, as demonstrated in Figure 2.

Figure 3 presents a comparison of two isotherms for fullerites and graphite with the same scales for the y axes. Fullerites are much more compressible than graphite (ΔV = −0.018 versus −0.011 $cm^3 \cdot g^{-1}$ at 50 °C and −0.035 versus −0.018 $cm^3 \cdot g^{-1}$ at 250 °C, respectively). Also, there is a large difference in thermal expansion. For example, for fullerites, the volume expansion is +0.031 $cm^3 \cdot g^{-1}$ in going from 50 to 200 °C at 10 MPa. By contrast, the corresponding expansion for graphite is only +0.007 $cm^3 \cdot g^{-1}$. A few average compressibility (β) and thermal expansion (α) values are given in Table 2. They are calculated from the following formulas:

Table 2. Compressibility and Thermal Expansion of Fullerites and Graphite

	α/K^{-1} (50–250 °C)		β/MPa^{-1} (0–200 MPa)	
	P = 0.1 MPa	P = 200 MPa	t = 50 °C	t = 250 °C
fullerites	2.7×10^{-4}	1.3×10^{-4}	1.4×10^{-4}	2.6×10^{-4}
graphite	0.9×10^{-4}	0.2×10^{-4}	1.2×10^{-4}	1.9×10^{-4}

$$\alpha = \frac{1}{V_0}\left(\frac{\Delta V}{\Delta T}\right)_P \quad (1)$$

$$\beta = \frac{1}{V_0}\left(\frac{\Delta V}{\Delta P}\right)_T \quad (2)$$

A previous study suggests that fullerites are extremely hard (*4*). We find that this can only be true to extremely high pressures. At low and moderate pressures (up to several hundred megapascals), the free volumes between the carbon cages should contribute tremendous compressibility and thermal expansion, as shown in our data.

Conclusions

On the basis of specific volumes for C_{60}/C_{70} (3:1) fullerites and graphite, measured up to 340 °C and 200 MPa, fullerite compressibilities and thermal expansions are found to be much higher than those of graphite. While graphite exhibits little isobaric thermal expansion at pressures above 10 MPa, fullerites exhibit significant and monotonic expansion. This is consistent with a lower degree of molecular and supermolecular packing in fullerites compared to graphite.

Acknowledgment

We thank B. Liang and J. Millar for conducting the ^{13}C NMR measurements.

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Received for review August 17, 1993. Accepted February 3, 1994.®

® Abstract published in *Advance ACS Abstracts,* March 1, 1994.