Semiempirical equation of state and the Grüneisen parameter for polymers and rare gas solids

S. Saeki, M. Tsubokawa, J. Yamanaka and T. Yamaguchi
Department of Materials Science and Engineering, Fukui University, Fukui 910, Japan
(Received 10 July 1990; revised 2 October 1990; accepted 15 October 1990)

The temperature dependence of the specific volume for polyethylene (PE) and poly(cyclopentyl methacrylate) (PC5MA) over 100–300 K for PE and 10–140 K for PC5MA, and for the rare gas solids argon (Ar), krypton (Kr) and xenon (Xe) over 4–83 K for Ar, 4–115 K for Kr and 5–150 K for Xe has been studied. Also, the pressure dependence of the specific volume for PE and poly(methyl methacrylate) (PMMA) over the pressure range up to 30 kbar for PE and 2 kbar for PMMA and for rare gas solids up to 30 kbar at low temperatures (4–150 K) has been studied. The temperature and pressure dependences have been examined using an equation derived by the homogeneous function method. The relationship for the temperature dependence used in this work is given by

$$\ln T = A_1 Z^{n_1} \qquad T \geqslant 1$$

and that for the pressure dependence by

$$V_0/V = B_1(T)(P + P_L(T))^{m_1}$$

where A_1, n_1 and m_1 are constants, $B_1(T)$ and $P_L(T)$ are functions of temperature, V_0 is the volume at atmospheric pressure and Z is defined by $Z = \{V - V(0)\}/V$ where $V(0)$ is V at 0 K. Values of n_1 for polymers and rare gas solids are in the range of 0.099–0.17 with $\bar{n}_1 = 0.13$, while m_1 values are in the range of 0.14–0.25 with $\bar{m}_1 = 0.17$ for the rare gas solids and 0.07–0.14 with $\bar{m}_1 = 0.099$ for polymers. The Grüneisen parameter γ_G defined by Slater is calculated from the equation of state in this work; $\gamma_G = 4.89$ for polymers and 2.78 for rare gas solids. The difference in γ_G for the rare gas solids and polymers is explained by taking into account the volume dependence of the heat capacity.

(Keywords: equation of state; rare gas solid; Grüneisen parameter; homogeneous function method; thermal expansion coefficient; isothermal compressibility)

INTRODUCTION

The equation of state for polymers and rare gas solids under an extremely low temperature and high pressure is very important for understanding thermodynamic properties of solids such as thermal expansion or the vibration of molecules. The Grüneisen equation of state is the most famous[1] and involves the Grüneisen parameter γ_G, which is a useful quantity for describing the volume dependence of vibrational frequencies in solids and is determined by various methods based on thermodynamic and spectroscopic data. For polymers *PVT* and heat capacity data are essential. Extensive experimental studies on the *PVT* properties of rare gas solids such as argon (Ar), krypton (Kr) and xenon (Xe) over a wide range of temperatures and pressures have been carried out[2–11]. Similar studies have been carried out for polymers[12–18]. The importance of intermolecular interactions in polymers in the evaluation of γ_G has been discussed previously[19–21] with the interchain heat capacity, $C_{V,\mathrm{inter}}$, being used instead of the heat capacity at constant volume, C_V. The volume or temperature dependence of γ_G has been discussed elsewhere[22–24].

One main purpose of this work is to establish a simple empirical equation for the temperature and pressure dependence of the specific volume at low temperatures and high pressures based on the experimental data available. An essential difference between γ_G for polymers and rare gas solids is discussed based on a general expression for γ_G derived from thermodynamic expressions.

DERIVATION OF THE EQUATION OF STATE BASED ON THE HOMOGENEOUS FUNCTION METHOD

A general procedure to derive a thermodynamic function such as $f(V, T)$, from a derivative, such as $(\partial f/\partial V)_T$, based on the homogeneous function method is presented. It is assumed that the function $f(V, T)$ is constant or zero at 0 K and expressed by:

$$f(V, T) = aV(\partial f/\partial V)_T\{[V - V(0)]/V\}^b + g(T) \qquad (1)$$

where a and b are constants, $g(T)$ is a function of temperature and $V(0)$ is a constant volume, such as V at 0 K. By differentiating equation (1) with respect to volume at constant temperature:

$$(\partial f/\partial V)_T = a(\partial f/\partial V)_T Z^b + aV[\partial(\partial f/\partial V)/\partial V]_T Z^b + aV(\partial f/\partial V)_T b Z^{b-1}(\partial Z/\partial V)_T \qquad (2)$$

where Z is defined by

$$Z = [V - V(0)]/V \qquad (3)$$

By dividing equation (2) by $aV(\partial f/\partial V)_T Z^b$, which is not zero if $V \neq V(0)$ and then integrating with respect to

0032-3861/91/173170-07

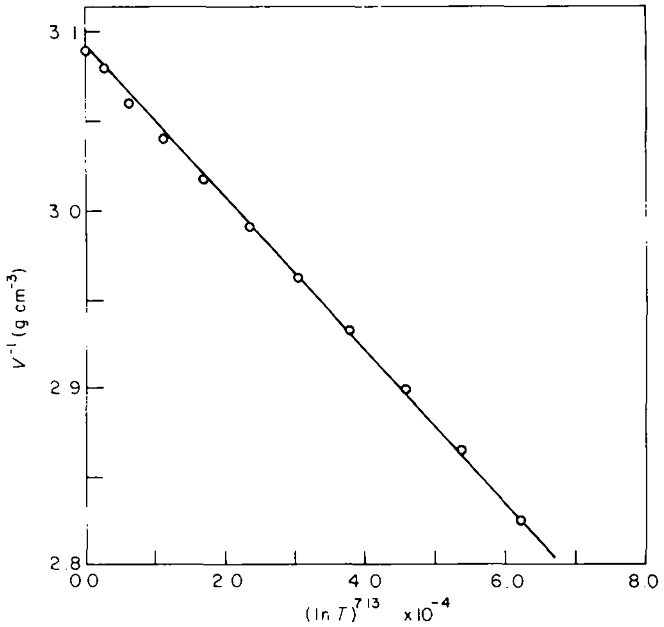

Figure 1 Plot of V^{-1} *versus* $(\ln T)^{7.13}$ for Kr at saturated vapour pressure[3]

volume at constant temperature, then:

$$(\partial f/\partial V)_{\mathrm{T}} = C(T)(VZ^{b})^{-1}\exp a^{-1}\int_{V(0)}^{V}(VZ^{b})^{-1}\,\mathrm{d}V \quad (4)$$

and from equations (1) and (4):

$$f(V, T) = C(T)a\exp a^{-1}\int_{V(0)}^{V}(VZ^{b})^{-1}\,\mathrm{d}V + g(T) \quad (5)$$

Also, from equations (4) and (5):

$$(\partial f/\partial V)_{\mathrm{T}} = \{f(V, T) - g(T)\}/\{a(VZ^{b})\}$$

In the case of $f = T$, from the definition of the thermal expansion coefficient α_{P}:

$$(\partial T/\partial V)_{\mathrm{P}} = (\alpha_{\mathrm{P}}V)^{-1} \quad (6)$$

By using equation (5) and assuming $g(P) = 0$, equation (6) leads to:

$$\alpha_{\mathrm{P}}T = A_0Z^{n_0} \quad (7)$$

where A_0 and n_0 are constants. In the case of isothermal compressibility, using the same procedure as for α_{P}:

$$(\partial P/\partial V)_{\mathrm{T}} = -(V\beta_{\mathrm{T}})^{-1} \quad (8)$$

and

$$(\partial P/\partial V)_{\mathrm{T}} = -C_1(T)(VZ^{b_1})^{-1} \times \exp\left\{-m_1^{-1}\int_{V_0}^{V}(VZ^{b_1})^{-1}\,\mathrm{d}V\right\} \quad (9)$$

Because $\beta_{\mathrm{T}} \neq 0$ at 0 K, it is determined that $b_1 = 0$ and therefore:

$$(\partial P/\partial V)_{\mathrm{T}} = -\{C_1(T)/V_0\}(V/V_0)^{-m_1^{-1}-1} \quad (10)$$

and P is given, using equation (10), by:

$$P = m_1C_1(T)(V/V_0)^{-m_1^{-1}} - P_{\mathrm{L}}(T) \quad (11)$$

where m_1 is a constant and $C_1(T)$ and $P_{\mathrm{L}}(T)$ are functions of temperature. It is useful to rewrite equation (11) as:

$$(V_0/V) = B_1(T)(P + P_{\mathrm{L}}(T))^{m_1} \quad (12)$$

where $B_1(T) = [m_1C_1(T)]^{-m_1}$. On the other hand, the temperature dependence of the specific volume V is derived from equation (7):

$$\ln T = \ln T_0 + A_0^{-1}\int_{V(0)}^{V}(VZ^{n_0})^{-1}\,\mathrm{d}V \quad (13)$$

and is given approximately by:

$$\ln T = A_1Z^{1-n_0} = A_1Z^{n_1} \qquad T \geqslant 1 \quad (14)$$

where $n_1 = 1 - n_0$, $A_1 = \{(1 - n_0)A_0\}^{-1}$ and $T_0 = 1$ K.

RESULTS

Typical plots based on equations (12) and (14) and experimental data available for polymers and rare gas solids are shown in *Figures 1–4*. The values of constants and indices determined by best fit are given in *Tables 1* and *2*. Values of n_1 for polymers and rare gas solids are in the range of 0.099–0.17 with $\bar{n}_1 = 0.13$, while m_1 values are in the range of 0.14–0.25 with $\bar{m}_1 = 0.17$ for the rare gas solids and 0.07–0.14 with $\bar{m}_1 = 0.099$ for polymers. The term γ_{G} defined by Slater[25] is expressed as:

$$\gamma_{\mathrm{G,s}} = -(1/6) + (1/2)(\partial\ln\beta_{\mathrm{T}}/\partial\ln V)_{\mathrm{T}} \quad (15)$$

The $\gamma_{\mathrm{G,s}}$ calculated using equations (10) and (15) is given by:

$$\gamma_{\mathrm{G,s}} = (2m_1)^{-1} - (1/6) \quad (16)$$

and $\bar{\gamma}_{\mathrm{G,s}} = 4.89$ for polymers and 2.78 for rare gas solids.

DISCUSSION

An original expression for γ_{G} is given by:

$$\gamma_{\mathrm{G}} = -(\mathrm{d}\log v_{i,j}/\mathrm{d}\log V) \quad (17)$$

where $v_{i,j}$ is the frequency of the normal mode and is reduced to a more useful expression by using the thermal

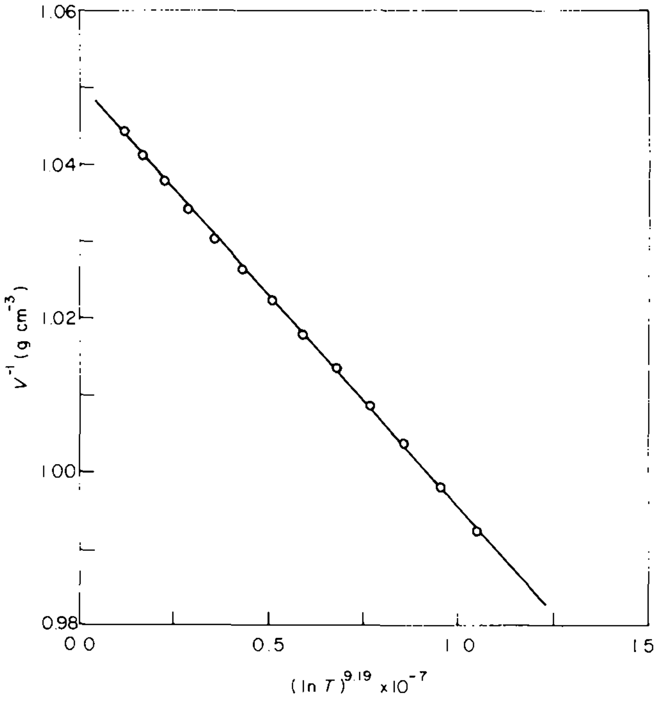

Figure 2 Plot of V^{-1} *versus* $(\ln T)^{9.19}$ for PE (32 days)[15]

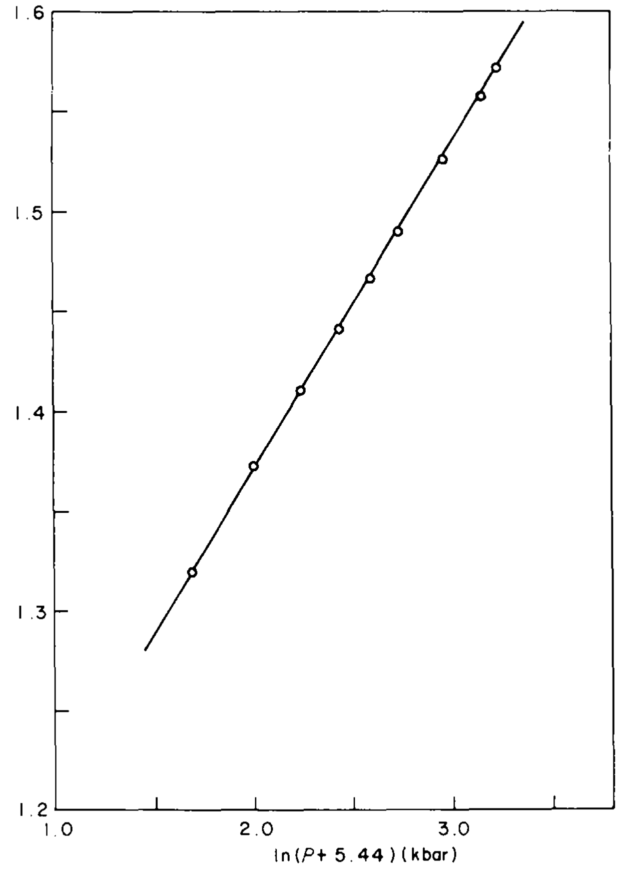

Figure 3 Plot of ln V^{-1} *versus* ln$(P + 5.44)$ for Xe at 30 K[9]

pressure coefficient γ_V;

$$\gamma_G = V\gamma_V/C_V \tag{18}$$

Wada *et al.*[19] proposed γ_G for a polymer crystal:

$$\gamma_G = V\gamma_V/C_{V,\text{inter}} \tag{19}$$

where $C_{V,\text{inter}}$ is the interchain heat capacity of the polymer. By using the thermodynamic relation $(\partial S/\partial V)_T = \gamma_V$ and a similar procedure as in equations (1)–(5), the following relation is derived:

$$\gamma_V = C_2(T)(Z^{\beta_1}/V)\exp\alpha_1^{-1}\int_{V(0)}^{V} Z^{\beta_1}/V\,dV \tag{20}$$

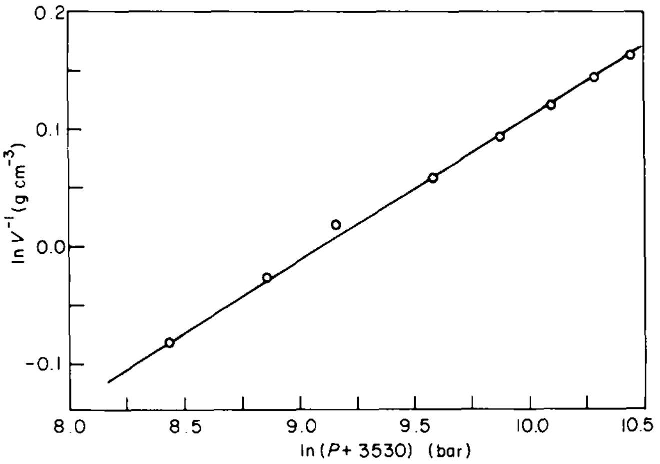

Figure 4 Plot of ln V^{-1} *versus* ln$(P + 3530)$ for PE at 296.2 K[14]

Table 1 The constants and indices in equation (14) for rare gas solids and polymers

	A_1	n_1	$V(0)$ (cm^3 g^{-1})	P (kbar)	Temperature range (K)	Ref.
Kr	6.63	0.140	0.3233	SVP	4–115	3
Ar	6.08	0.128	0.5646	SVP	4–83	2
Ne	4.57	0.116	0.6635	SVP	3–23.5	4
Xe	6.88	0.138	0.2645	SVP	0–75	28
	7.44	0.164	0.2643	0	0–150	9
	7.97	0.159	0.2526	2	0–150	9
	8.07	0.149	0.2435	4	0–150	9
	8.46	0.156	0.2361	6	0–150	9
	8.60	0.153	0.2300	8	0–150	9
	8.60	0.150	0.2247	10	0–150	9
PC5MA[a]	7.84	0.115	0.8388		10–140	16
PCHDMT[b]	8.94	0.135	0.7986		10–140	16
PE (32 days)[c]	7.97	0.109	0.9524		93–333	15
PE (2.5 h)	7.84	0.104	0.9538		93–333	15
PE(Quench)	7.81	0.103	0.9542		93–333	15
Oxidized PE	8.29	0.141	0.9662	0.001	296–424	29
	8.04	0.126	0.9599	0.72	296–424	29
	8.27	0.128	0.9469	2.10	296–424	29
	7.90	0.109	0.9422	2.79	296–424	29
PE(mono) (Å)		0.105			100–300	30
PE(*ortho*) (Å)		0.100			100–300	30

[a] PC5MA, poly(cyclopentyl methacrylate)
[b] PCHDMT, poly-1,4-cyclohexylene dimethylene
[c] Crystallization for 32 days at 402.9 K

Table 2 The constants and indices in equation (12) for rare gas solids and polymers

	T (K)	m_1	V_0 (cm^3 g^{-1})	P_1 (bar)	B_1	Maximum P (kbar)	Ref.
^{4}He	4.2	0.232	4.240	154	0.267	20.00	7
^{3}He	4.2	0.241	4.387	177	0.249	20.00	7
N_2	65.0	0.192	1.046	2708	0.219	18.64	6
H_2	4.0	0.228	11.240	579	0.233	19.62	6
D_2	4.0	0.231	4.851	922	0.206	19.62	6
Ne	4.0	0.166	0.694	1972	0.283	19.62	6
Xe	0.0	0.166	0.264	6330	0.235	20.00	9
	30.0	0.164	0.267	5440	0.244	20.00	9
	64.0	0.160	0.272	4690	0.259	20.00	9
	90.0	0.160	0.279	4030	0.265	20.00	9
	130.0	0.150	0.286	2820	0.301	20.00	9
	160.0	0.142	0.294	2170	0.336	20.00	9
Kr	4.0	0.158	0.323	5550	0.256	20.00	9
	20.0	0.154	0.325	5050	0.269	20.00	9
	40.0	0.149	0.329	4460	0.287	20.00	9
	77.0	0.148	0.341	3410	0.300	20.00	9
	90.0	0.145	0.346	2890	0.314	20.00	9
	110.0	0.145	0.355	2405	0.323	20.00	9
Ar	4.0	0.159	0.565	4800	0.260	20.00	9
	20.0	0.159	0.567	4615	0.261	20.00	9
	40.0	0.156	0.577	3880	0.276	20.00	9
	60.0	0.148	0.592	2970	0.307	20.00	9
	77.0	0.148	0.608	2450	0.315	20.00	9
PE	296.2	0.113	1.091	3530	0.3976	30.00	14
PE	298.7	0.123	1.087	4580	0.3550	30.00	12
PE	292.7	0.071	1.021	3180	0.5652	2.00	31
PE(high M_w)	291.9	0.088	1.078	2540	0.5105	2.00	31
PE(branched)	292.3	0.085	1.072	2540	0.5154	2.00	31
PE(branched)	341.7	0.082	1.112	1430	0.5512	2.00	31
PE(branched)	382.8	0.098	1.194	730	0.5261	2.00	31
PE(DA)[a]	293.0	0.087		4250	0.4834	2.94	18
PE(DA)	293.0	0.142		8970	0.2739	7.85	18
PE(DA)	293.0	0.088	–	3460	0.4900	3.90	17
PE(CEC)[b]	293.0	0.107	–	4080	0.4118	3.90	17
PE(MA)[c]	298.0	0.096	–	5960	0.4325	13.70	32
PE(CEC)	403.0	0.116	–	4080	0.3584	3.90	17
PE(oxidized)	296.2	0.097	1.036	4970	0.4381	4.00	29
	323.2	0.100	1.043	4720	0.4305	4.00	29
PCHMA[d]	291.8	0.089	0.908	3480	0.4829	2.00	31
PMMA[e]	290.4	0.103	0.844	3885	0.4287	2.00	31

[a] DA, drawn and annealed
[b] CEC, chain-extended crystal, isothermally crystallized at 5000 kg cm^{-2}
[c] MA, moulded and annealed (unoriented)
[d] PCHMA, poly(cyclohexyl methacrylate)
[e] PMMA, poly(methyl methacrylate)

The C_V is related to γ_V through:

$$(\partial C_V/\partial V)_T = T(\partial \gamma_V/\partial T)_V \tag{21}$$

A general expression for C_V as a function of temperature and volume is given by:

$$C_V = \int_{V(0)}^{V} (\partial C_V/\partial V)_T \, dV + \int_0^T (\partial C_V/\partial T)_V \, dT \tag{22}$$

By using the assumptions that $C_V = C_V(V, T) + C_V(T)$ and $\gamma_V = \gamma_V(T)\gamma_V(V)$ for equation (20), then:

$$\gamma_G^{-1} = 2[\mathrm{d}\ln \gamma_V(T)/\mathrm{d}\ln T]/[\mathrm{d}\ln S(V)/\mathrm{d}\ln V] + C_V(T)/V\gamma_V \tag{23}$$

where the entropy $S(V)$ is defined by $S(V) = \int_{V(0)}^{V} \gamma_V(V)\,dV$ and equation (21) is used. The first term in equation (23) is a contribution from $C_V(V, T)$ in C_V or $\int_{V(0)}^{V} (\partial C_V/\partial V)_T\,dV = T\int_{V(0)}^{V} (\partial \gamma_V/\partial T)_V\,dV$, while the second term is from $C_V(T)$ in $C_V = C_V(V, T) + C_V(T)$. In

Table 3 The constants and indices in equation (24)[a] for rare gas solids and PE at constant volume

	V (cm^3 mol^{-1})[b]	$A_2 \times 10^3$	B_2	k_0	Ref.
Ar	19.00	0.07	9.38	2.20	11
	20.00	0.49	5.39	1.79	11
	21.00	1.32	2.63	1.59	11
	22.00	2.08	0.72	1.51	11
Xe	29.00	4.90	13.00	1.23	11
	30.00	3.73	9.22	1.29	11
	31.00	3.70	6.33	1.29	11
	32.00	4.73	4.03	1.27	11
	33.00	4.85	2.19	1.25	11
	34.00	5.25	0.81	1.23	11
Kr	23.00	2.68	8.08	1.55	11
	24.00	2.68	6.31	1.41	11
	25.00	4.37	1.53	1.31	11
	26.00	5.90	1.53	1.25	11
	27.00	2.30	1.56	1.31	11
PE(linear)	1.02	111.6×10^{-7}	−1.03	2.84	31
	1.03	2.55×10^{-7}	−1.10	3.45	31
PE(high M_w)	1.07	65.5×10^{-7}	−0.87	3.34	31
PE(branched)	1.07	31.8×10^{-7}	−1.02	3.46	31
PE(high M_w)	1.09	2.95×10^{-7}	−1.04	3.83	31
	1.10	0.77×10^{-7}	−1.19	4.05	31
	1.11	0.166×10^{-7}	−1.22	4.29	31

[a] Unit of P in equation (24) is kbar

[b] Unit for PE is cm^3 g^{-1}

Table 4 The values of $C_V(V, T)$ calculated by using equation (26) and the ratio $C_V(V, T)/C_{V,\text{total}}$ for krypton and PE

	Temperature (K)	$C_V(V, T)$ (cal mol^{-1} K^{-1})[a]	$C_{V,\text{total}}$	$C_V(V, (\%)\, T)/C_{V,\text{total}}$	Ref.
Kr[b]	10	0.0009	1.4098	0.06	3
	20	0.0060	3.7115	0.16	
	40	0.0314	5.1537	0.609	
	60	0.0711	5.4487	1.31	
	80	0.1250	5.5060	2.27	
	100	0.1950	5.5320	3.52	
PE[c]	195	0.0070	0.2620	2.67	33
	303	0.0736	0.3820	19.30	

[a] Unit for PE is cal g^{-1} K^{-1}

[b] $k_0 = 1.31$, $A_2 = 2.30 \times 10^{-3}$, $V_0 = 27.093$ cm^3 mol^{-1} for $V = 27.0$ cm^3 mol^{-1}

[c] $k_0 = 3.34$, $A_2 = 6.55 \times 10^{-6}$, $V_0 = 0.947$ cm^3 g^{-1} (ref. 34) for $V = 1.07$ cm^3 g^{-1} and PE(high M_w)[31]

estimating two terms in equation (23), the temperature dependence of γ_V at constant volume is necessary. The experimental data of the P *versus* T line at constant volume are expressed approximately by:

$$P = A_2 T^{k_0} + B_2(V) \qquad V = \text{constant} \tag{24}$$

where A_2 and k_0 are constants and $B_2(V)$ is a function of volume. Values of A_2, k_0 and $B_2(V)$ are listed in *Table 3* where k_0 for rare gas solids is in the range of 1.2–2.2, while that for polyethylene (PE) is in the range of 2.8–4.3. Equation (23) may be expressed using equation (24):

$$\gamma_G^{-1} = 2\alpha_1(k_0 - 1)Z^{-\beta_1} + C_V(T)/V\gamma_V \tag{25}$$

where $S(V) = \alpha_1 \exp \alpha_1^{-1} \int_{V(0)}^{V} Z^{\beta_1}/V \, \mathrm{d}V$ is used. It is possible to evaluate $C_V(V, T)$ from the experimental data of P *versus* T at constant volume by using equations (21) and (24):

$$C_V(V, T) = A_2 k_0 (k_0 - 1) T^{k_0 - 1}\{V - V(0)\} \tag{26}$$

The typical values of $C_V(V, T)$ from equation (26) are shown in *Table 4* where the ratio $C_V(V, T)/C_{V,\text{total}} =$ 0.06–3.52% for Kr and 2.7–19.3% for PE, and both ratios increase with increasing temperature. Although the contribution of $C_V(V, T)$ to $C_{V,\text{total}}$ is small in both cases, the contribution of $C_V(V, T)$ to γ_G through equation (23) is not always negligible because γ_G relates to k_0 in equation (25) and not to $C_V(V, T)$ directly. It is interesting to point out that the ratio of $C_{V,\text{inter}}$ for the interchain contribution for $C_{V,\text{total}}$ reported by Warfield[20] for various polymers is in the range of 6–21%, which compares with that of $C_V(V, T)/C_{V,\text{total}}$ for PE. We cannot determine the first term in equation (25) because α_1 is unknown. However, the first term becomes negligible if k_0 is nearly equal to 1.0, which means $\gamma_V = f(V)$ and $C_V = g(T)$ and therefore $\gamma_G = \gamma_V V/C_V(T) = \gamma_V V/C_V$. On the other hand, if the first term in equation (25) is dominant, γ_G is given by $\gamma_G = Z^{\beta_1}/[2\alpha_1(k_0 - 1)]$ where $k_0 > 1.0$. It is suggested that the former case corresponds

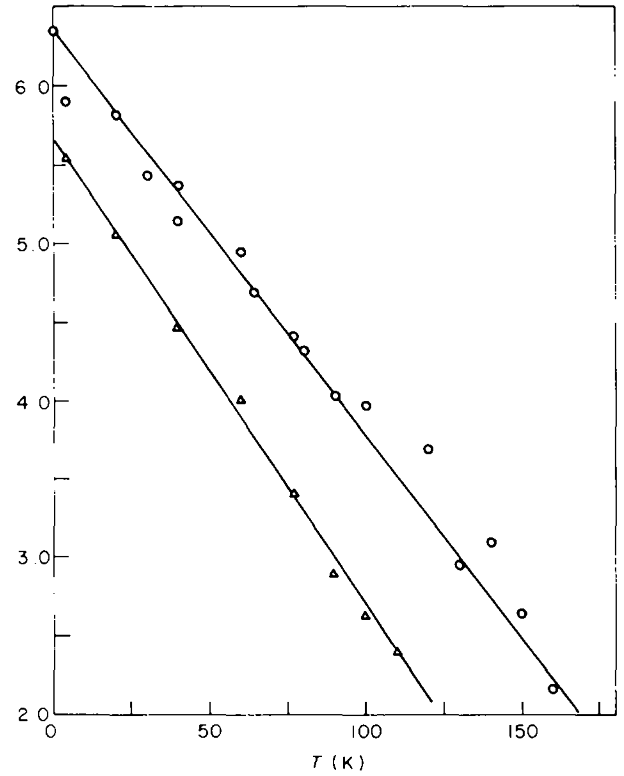

Figure 5 Plot of P_L *versus* T from equation (12) for Xe (○) and Kr (Δ). The empirical equation for P_L is $P_{L,Xe} = 6.34 - 2.57 \times 10^{-2}T$ for Xe and $P_{L,Kr} = 5.65\ 2.97 \times 10^{-2}T$ for Kr

to rare gas solids while the latter corresponds to polymers.

It is important to determine the functions such as $P_L(T)$ in equation (12) and $B_2(V)$ in equation (24). In *Figure 5* $P_L(T)$ is plotted against temperature and linearity is observed for Kr and Xe. The function $P_L(T)$ is given by:

$$P_L(T) = P_{L,0} - C_0T \tag{27}$$

The term $B_2(V)$ from equation (24) is given by:

$$B_2(V) = P(V)_{T-0} \tag{28}$$

where $P(V)_{T=0}$ is the $P(V)$ function at 0 K and using equations (12) and (27) is given by:

$$P(V)_{T=0} = [B_1^{-1}V(T=0, P=0)/V(0, P)]^{m_1^{-1}} - P_{L,0} \tag{29}$$

It is very interesting to refer to the equation of state derived by many authors. Gilvarry has given an isothermal equation of state, which can be expressed as[23]:

$$P = (n-m)^{-1}K_0[(V_0/V)^n - (V_0/V)^m] \tag{30}$$

where K_0 is the bulk modulus corresponding to the normal volume V_0, and n and m are constants. The bulk modulus $K = \beta_T^{-1}$ from equation (30) is:

$$K = (n-m)^{-1}K_0[n(V_0/V)^n - m(V_0/V)^m] \tag{31}$$

The Birch equation of state is obtained from equation (30) with $n = 7/3$ and $m = 5/3$, which was derived from Murnaghan's theory of finite strain[26]. Murnaghan[27] derived the equation of state such that:

$$P = n^{-1}K_0[(V_0/V)^n - 1] \tag{32}$$

Table 5 Comparison between the experimental values of specific volume for H_g and calculated values from equation (12)

P (kbar)	V at 21.9°C (exp.)	V^a (calc.)
1	1.000180	1.00001
2	0.996209	0.99618
4	0.988996	0.98891
6	0.982254	0.98210
8	0.975916	0.97569
10	0.969933	0.96965
12	0.964262	0.96393

[a] $V = 1.52496(P + 30.418)^{-0.1224}$ in P (kbar) where V(exp.)–P data is taken from the unrounded Davis–Gordon P *versus* V results[35] for H_g. The volume is not measured directly

which corresponds to equation (30) with $m = 0$. On the other hand, the usual Tait equation has been written in the form[22]:

$$V_0 - V = C\ln[(B+P)/(B+P_0)] \tag{33}$$

where B and C are constants with respect to pressure and P_0 is P at $V = V_0$.

Equation (12) in this work is similar to equation (32) if equation (32) is arranged to $(P + n^{-1}K_0) = n^{-1}K_0(V_0/V)^n$. Macdonald[22] has examined some experimental and analytical equations of state including four different polynomial equations and seven non-linear equations based on the recent water and mercury (Hg) isothermal data and stressed that certain polynomial equations were found to yield better fits with data than non-linear equations. In *Table 5*, it is demonstrated that values of V calculated using equation (12) give good agreement with the observed values for Hg (within 0.05%) over the pressure range 1–12 kbar.

REFERENCES

1 Grüneisen, E. 'Handbuch der Physik', Vol. 10, Springer, Berlin, 1926
2 Peterson, O. G., Batchelder, D. N. and Simmons, R. O. *Phys. Rev.* 1966, **150**, 703
3 Losee, D. L. and Simmons, R. O. *Phys. Rev.* 1968, **172**, 944
4 Batchelder, D. N., Losee, D. L. and Simmons, R. O. *Phys. Rev.* 1969, **162**, 767
5 Stewart, J. W. *Phys. Rev.* 1955, **97**, 578
6 Stewart, J. W. *J. Phys. Chem. Solid* 1956, **1**, 146
7 Stewart, J. W. *Phys. Rev.* 1963, **129**, 1950
8 Holste, J. C. and Swenson, C. A. *J. Low Temp. Phys.* 1975, **18**, 477
9 Packard, J. R. and Swenson, C. A. *J. Phys. Chem. Solid* 1963, **24**, 1405
10 Anderson, M. S. and Swenson, C. A. *Phys. Rev. B* 1974, **10**, 5184
11 Anderson, M. S. and Swenson, C. A. *J. Phys. Chem. Solid* 1975, **36**, 145
12 Bridgman, P. W. *Proc. Am. Acad. Arts Sci.* 1948, **76**, 71
13 Weir, C. E. *J. Res. Natl. Bur. Stand.* 1951, **46**, 207
14 Heydemann, P. L. M. and Houck, J. C. *J. Polym. Sci. A2* 1972, **10**, 1631
15 Davis, G. T., Eby, R. K. and Colson, J. P. *J. Appl. Phys.* 1970, **41**, 4316
16 Simha, R. and Roe, J. M. *J. Appl. Phys.* 1972, **43**, 4312
17 Nakafuku, C. *Polymer* 1978, **19**, 149
18 Ito, T. *Polymer* 1982, **23**, 1412
19 Wada, Y., Itani, A., Nishi, T. and Nagai, S. *J. Polym. Sci. A2* 1969, **7**, 201
20 Warfield, R. W. *Makromol. Chem.* 1974, **175**, 3285
21 Sharma, B. K. *Polymer* 1983, **24**, 314
22 Macdonald, J. R. *Rev. Modern Phys.* 1969, **41**, 316
23 Gilvarry, J. J. *J. Appl. Phys.* 1957, **28**, 1253
24 Pastine, D. J. *Phys. Rev.* 1965, **138**, A767
25 Slater, J. C. 'Introduction to Chemical Physics', McGraw-Hill, New York, 1939
26 Birch, F. *Phys. Rev.* 1947, **71**, 809
27 Murnaghan, F. D. 'Finite Deformation of an Elastic Solid', John Wiley and Sons, Inc., New York, 1951

28 Sears, D. R. and Klug, H. P. *J. Chem. Phys.* 1962, **37**, 3002
29 Sayre, J. A., Swanson, S. R. and Boyd, R. H. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 1739
30 Miyaji, H., Asahi, T., Miyamoto, Y. and Asai, K. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 159
31 Olabisi, O. and Simha, R. *Macromolecules* 1975, **8**, 206
32 Sham, T. P., Newman, B. A. and Pae, K. D. *J. Mater. Sci.* 1977, **12**, 771
33 Wunderlich, B. *J. Chem. Phys.* 1962, **37**, 1203
34 Shen, M., Hansen, W. N. and Romo, P. C. *J. Chem. Phys.* 1969, **51**, 425
35 Davis, L. A. and Gordon, R. B. *J. Chem. Phys.* 1967, **46**, 2650