Heat capacities of linear macromolecules containing chlorine and fluorine

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(Received 12 June 1985)

Heat capacities at constant pressure, C_p, and at constant volume, C_v are calculated from full and partially approximated normal mode frequency spectra and compared to experimental data for amorphous or semicrystalline poly(vinyl chloride), poly(vinylidene chloride) and poly(chlorotrifluoroethylene). A calculation scheme for all halogenated polyethylenes using a Tarasov-function for $2N$ skeletal vibrational modes and an approximation of the residual $7N$ normal modes of group vibrations is developed (N = number of backbone carbon atoms). Experimental data agree to ±3% with the calculations.

(Keywords: addition scheme; crystal; glass; heat capacity; poly(vinyl chloride); poly(vinylidene chloride); poly(chlorotrifluoroethylene); polyethylene, halogenated; vibration spectrum)

INTRODUCTION

In a previous paper[1] we have developed a prediction scheme for the heat capacities of solid, fluorinated polymers based on the knowledge or approximation of their normal modes of vibration. The Tarasov limiting frequencies θ_1 and θ_3 and the Lindemann constant A_0 were expressed as a function of fluorination ratio. Together with the appropriate group vibrations, it was then possible to compute the heat capacities at constant volume C_v and at constant pressure C_p for any degree of fluorination. Similar work was also carried out before for all polyoxides[2].

In this paper we want to report about chlorine-containing polymers. The results are compared with those on fluorinated polymers and some more general features of the heat capacity estimation from vibrational spectra are developed.

COMPUTATIONS

The computation procedure followed is similar to the previous work[3-7]. The heat capacities needed were taken from the prior established data bank[8]. First, the contributions of the group vibrations to heat capacity are calculated and subtracted from the experimental heat capacity after conversion to C_v. The remaining skeletal heat capacity is fitted to the Tarasov equation $T(\theta_1/T, \theta_3/T)$ to obtain the limiting three- and one-dimensional frequencies θ_3 and θ_1[3,6]. (Note that all frequencies are, for convenience, expressed in terms of Kelvin, $1\ \mathrm{cm}^{-1} = 1.439$ K). The computation method and the needed computer programs are described in detail elsewhere[3,5].

For the calculations involving poly(vinylidene chloride) a modified procedure was followed since there are no heat capacity data at sufficiently low temperatures to find a limiting Debye temperature. In this case we first fit our data to a one-dimensional Debye function $D_1(\theta_1/T)$ only, and find (at temperatures above 70 K) a θ_1 value. It was assumed that at these temperatures the vibrations up to θ_3 are practically excited (i.e. they contribute only a constant amount to the heat capacity) and the skeletal heat capacity can thus be described solely by a one-dimensional Debye function.

$$T(\theta_1/T,\theta_3/T)=D_1(\theta_1/T)-\frac{\theta_3}{\theta_1}[D_1(\theta_3/T)-D_3(\theta_3/T)] \quad (1)$$

$$D_1(\theta_3/T)\simeq D_3(\theta_3/T)\simeq 1 \qquad T\geqslant\theta_3 \quad (2)$$

$$T(\theta_1/T,\theta_3/T)\simeq D_1(\theta_1/T) \qquad T\geqslant\theta_3 \quad (3)$$

With a known θ_1, we are then able to find a suitable θ_3 at lower temperatures (see Appendix).

Poly(vinyl chloride) (PVC)

PVC is one of the most common polymers. Many investigations of its heat capacity were carried out. However, many of them do not meet the established standards of precision[8]. The PVC heat capacity has been measured over the temperature range from 5 K to 350 K[8]. Commonly, the polymer is essentially amorphous, but below the glass transition temperature T_g and above about 50 K amorphous and crystalline polymers have almost the same heat capacity. With the help of our computer programs[3,7] a Debye θ_D of 90 K was established. Actually θ_D decreases almost linearly below 20 K, at which θ_D is 144 K. We chose 90 K, which should be reached at about 3 K, as a reasonable compromise (±8 K). Since we are interested in an approximate value of θ_D only as a first approximation for the θ_3-calculation in the Tarasov function, a small error does not influence the results significantly.

The vibrational spectra of crystalline PVC were examined by Rubcic and Zerbi[9], and Opaskar and Krimm[10]. There are dispersion curves available for the

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following isolated chain configurations: all-*trans* syndiotactic, isotactic *TGTGTG*-conformation, and a syndiotactic so-called folded conformation (*TTGGTTGG*). Data also exist for a disordered chain which contains elements of all three cases. *Table 1* lists the group vibrations for the heat capacity calculation. None of these is fully appropriate to be compared with the experimental heat capacity data, since these are taken on samples essentially amorphous. Heat capacity due to group vibrations are, however, as indicated clearly by the data of *Figure 1*, not much affected by conformational or configurational changes at high temperatures. At lower temperatures, on the other hand, the magnitude of the heat capacity due to group vibrations is small and the contribution to the overall error is insignificant. Since there is little difference between the three spectra in the frequency range of interest, we decided to use the simpler syndiotactic all-*trans* spectrum for further calculations. (The syndiotactic configuration is also somewhat prevalent in the radical-polymerized PVC.)

Having found the Debye temperature θ_D and established the group vibrational spectrum of PVC, we are able to use a computer program[3] to calculate θ_1 and θ_3 from the Tarasov function fit. It resulted in reasonably

Table 1 Vibrations of the different configurations of poly(vinyl chloride) in Kelvin*

Syndiotactic		Isotactic		Folded		Assignment
ν	N	ν	N	ν	N	
4925	1	4925	1	4925	1	ν_s CH
4213	1	4213	1	4213	1	ν_{as} CH_2
4108	1	4111	1	4109	1	ν_s CH_2
2098	1	2098	1	2098	1	δ CH_2
2053	0.34	2035–2042	0.28	1958	0.17	δ CH+CH_2
2053–2039	0.16	1937–2035	0.72	2033–2052	0.50	
2039–1951	0.5			1958–1980	0.33	
1870–1908	0.5			1937	0.2	t CH_2
1863–1870	0.3	1880	1	1909–1937	0.3	
				1870–1898	0.3	
1863–1908	0.2			1860–1870	0.2	
1809	0.29					w CH_2+δ CH
1809–1784	0.21	1784–1790	0.47	1833–1838	0.5	
1735–1784	0.27	1784–1804	0.53	1761–1774	0.5	
1709–1735	0.23					
1682–1693	0.5	1665–1705	0.55	1708–1725	0.5	t CH
1670–1682	0.5	1705	0.45	1662	0.5	
1636	0.21	1624–1639	0.26	1636	0.21	ν_{as} CC
				1620–1636	0.29	
1590–1636	0.34	1568–1624	0.44	1587–1616	0.28	
1584–1636	0.45	1568–1607	0.30	1587–1603	0.22	
1554–1560	0.08					ν_s CC
1480–1554	0.25	1410–1426	0.16	1373–1480	0.5	
1452–1480	0.17	1426–1558	0.51	1550–1565	0.28	
1501–1506	0.08	1544–1558	0.33	1538–1565	0.22	
1452–1500	0.29					
1452	0.13					
1404–1415	0.11	1206–1296	0.44	1319	0.17	r CH_2
1286–1404	0.39	1206–1220	0.34	1319–1332	0.33	
1204–1217	0.17	1296–1318	0.22	1145–1226	0.50	
1217–1286	0.33					
896–918	0.5					ν_{C-Cl}
872–883	0.12	929–1007	0.67	1099–1104	0.5	
883–904	0.16	1007–1069	0.33	895– 942	0.5	
896–904	0.22					
504	0.21					δ_{C-Cl}
810–834	0.28	613	0.43	706–754	0.5	
819–834	0.12	613–719	0.32	624–653	0.5	
768–819	0.10	719–739	0.25			
504–768	0.29					
649–665	0.09					w_{C-Cl}
547–649	0.24	424–440	0.26	447	0.08	
518–547	0.17	424–550	0.21	447–516	0.42	
493–518	0.12	550–591	0.20	515–541	0.26	
456–493	0.09	591	0.33	529–541	0.24	
440–456	0.29					

* Data based on dispersion curves listed in refs. 9 and 10, 1 K = 0.695 cm^{-1}

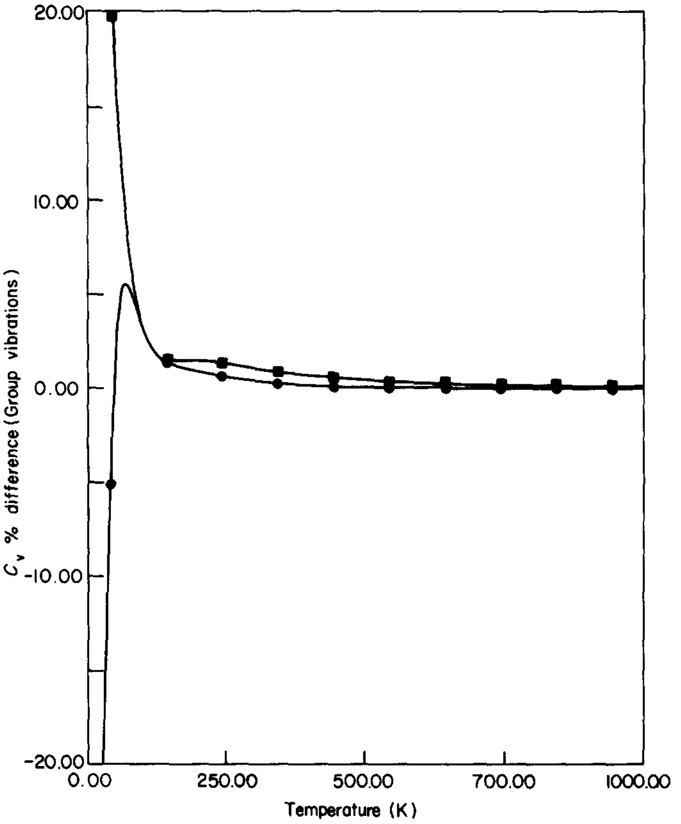

Figure 1 Group vibration contribution to the heat capacity of PVC. Comparison of the spectra of: (i) isotactic to syndiotactic (all *trans*) PVC (●); (ii) syndiotactic (folded) to syndiotactic (all *trans*) PVC (■). See *Table 1* for frequency distributions

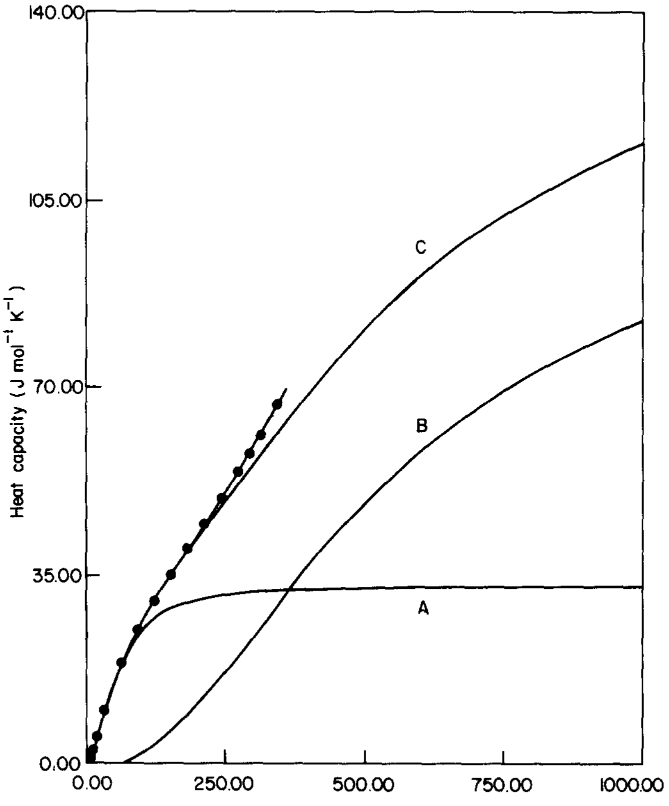

Figure 2 Heat capacity of PVC. Skeletal contribution to C_v (A), $\theta_1 = 353.5$, $\theta_3 = 45.4$; group vibrations contribution to C_v (B), (all-*trans* syndiotactic of *Table 1*); total C_v (C); experimental C_p (●)

constant parameters over the temperature range 80–160 K ($\theta_1 = 353.5 \pm 4.6$ K, $\theta_3 = 45.4 \pm 0.3$ K). Over the temperature range 18–180 K θ_1 and θ_3 are 343 ± 13 K and 46.1 ± 0.9 K, respectively. There is no significant difference between the two sets of parameters and the first set of θ-values was used for further calculation.

Next, the heat capacity C_v of the polymer was calculated from 0–1000 K. The results are shown in *Table 4* and plotted in *Figure 2*. Finally, using the Lindemann equation (Appendix, equation (A6)) with an A_0 per heavy atom (three heavy atoms per repeating unit) suggested earlier[11] ($T_m = 546$ K, $A_0 = 3.13 \times 10^{-3}$ K mol J^{-1}), we converted the heat capacity at constant volume (C_v) to the heat capacity at constant pressure (C_p). These results were compared with the experimental heat capacities. As can be seen in *Figure 3*, the agreement is excellent over the whole temperature range measured. Only below 10 K do the differences go above 5%; over most of the other temperature ranges the differences are within ±2%. At low temperatures the absolute value of heat capacity is small; their error thus causes little uncertainty in the integral thermodynamic functions. The deviations starting at about 300 K, although small, might be explained by the beginning of the glass transition. A very broad glass transition might be the reason for the increasing deviations already starting at about 200 K, but another explanation might be a poorly chosen value for A_0. It was found that $A_0 = 5.29 \times 10^{-3}$ K mol J^{-1} gives a better fit of the calculated C_p at temperatures above 200 K, reducing the deviations to within 1%. The data are shown in *Figure 4*. It is worth mentioning that this value is closer to the universal value suggested earlier[11] than the value used for

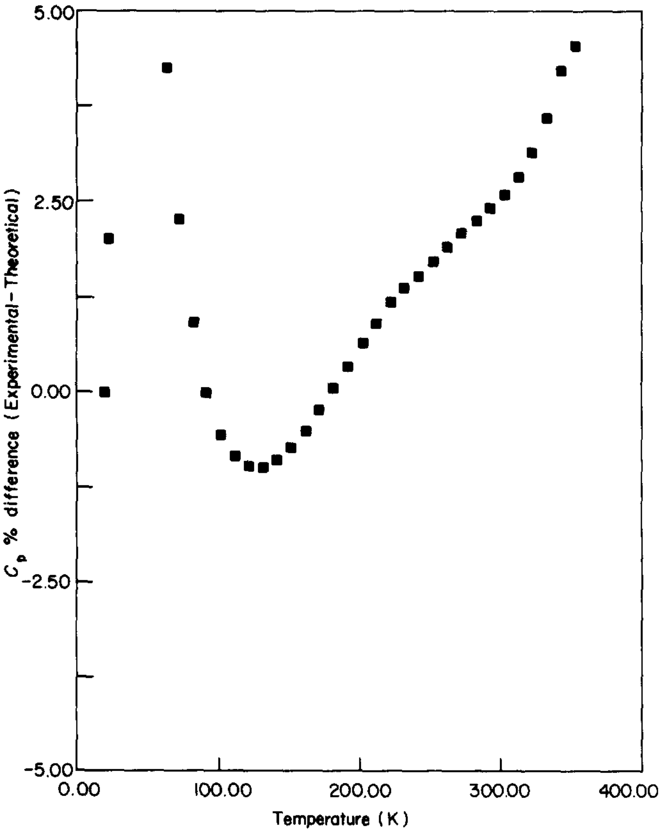

Figure 3 Comparison of experimental and calculated heat capacities C_p of PVC. (See calculation of *Figure 2*, C_p calculation equation (A6) with $A_0 = 3.13 \times 10^{-3}$ K mol J^{-1} and $T_m = 546$ K)

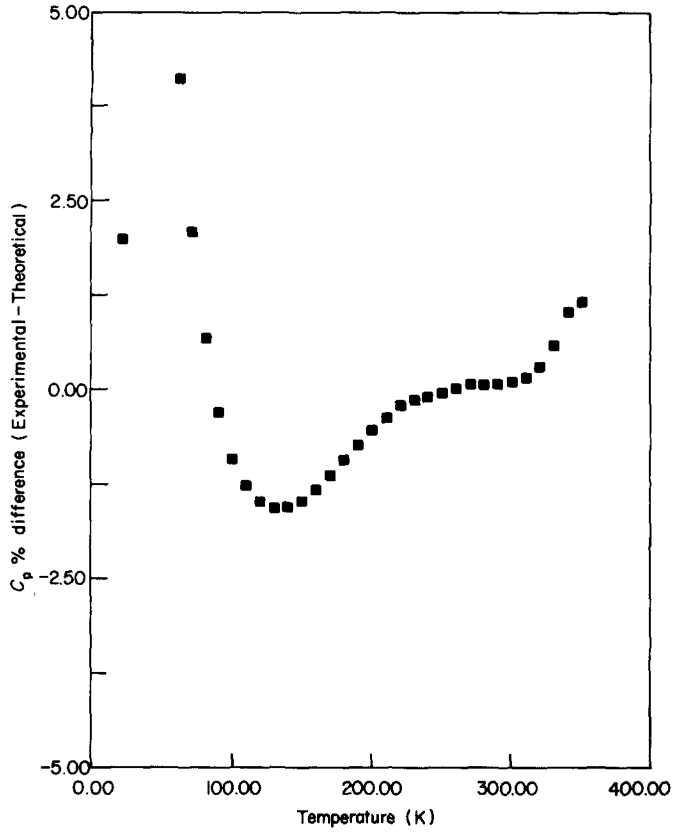

Figure 4 Comparison of experimental and calculated C_p as in *Figure 3*, but with $A_0 = 5.29 \times 10^{-3}$ K mol J^{-1}

Figure 3 which was based on limited experimental information on compressibility and expansivity at room temperature.

Poly(vinylidene chloride) (PVC2)

Although poly(vinylidene chloride) finds extensive industrial applications, neither its heat capacity at very low temperatures (below 60 K), nor a full vibrational spectrum is available.

There is one normal mode vibrational analysis of PVC2 in the literature[12], it lists, however, only the in- and out-of-phase vibrations of the various normal modes. Since there was not enough confidence in the chosen force field by the authors[12], no full dispersion curves were calculated. We used their in- and out-of-phase frequencies and approximated each single mode in the vibrational spectrum by a box distribution between these as a first approximation for the group vibrations.

In a second approximation we made use of the well known vibrational spectrum of poly(vinylidene fluoride)[1,13] and estimated the corresponding halogen bending and stretching frequencies by forming the ratio

$$\frac{\nu_{\mathrm{PVF2}}}{\nu_{\mathrm{PVC2}}} = \sqrt{\frac{f_{\mathrm{C-F}}}{f_{\mathrm{C-Cl}}} \frac{m_{\mathrm{CCl_2}}}{m_{\mathrm{CF_2}}}} \qquad (4)$$

where $m_{\mathrm{CCl_2}}/m_{\mathrm{CF_2}}$ is the ratio of reduced mass (1.35) and $f_{\mathrm{C-F}}/f_{\mathrm{C-Cl}}$ is the ratio of the force constants which we approximated by the ratio of bond energy to bond length (1.76). Equation (4) then becomes 1.54. A survey of 50 known CCl_2 and CF_2 frequencies from low molecular weight compounds[14] led to a similar ratio of 1.5 ± 0.4. Thus, all CCl_2 frequencies were shifted from their CF_2 values by dividing by 1.54. The CH_2 vibrations were left unchanged from the poly(vinylidene fluoride) values, and the two C–C stretching frequencies were shifted according to their corresponding reduced mass ratios (1.05). *Table 2* lists both vibrational frequency approximations and shows good correspondence.

In a third approximation an average vibrational spectrum was constructed using information on PVC[9]

Table 2 Vibrations of poly(vinylidene chloride) from normal mode analysis and comparison with poly(vinylidene fluoride) in Kelvin*

Normal mode[a]		From PVF2[b]		Assignment
v	*N*	*v*	*N*	
4200	1	4358	1	ν_{as} CH_2
4106	1	4288	1	ν_s CH_2
2001–2021	1	2047 2047–2114 2114 2003–2114 2003	0.12 0.25 0.13 0.25 0.25	δ CH_2
1978	1	2009 1986–2009 1986 1904–1986 1878–1904	0.48 0.11 0.11 0.20 0.10	w CH_2
1810–1899	1	1384–1414 1332–1384	0.67 0.33	t CH_2
1253–1515	1	1151–1187 1151 1151–1177	0.38 0.25 0.37	r CH_2
964–1006	1	1201–1284 1284–1290 1268–1290 1145–1268 1145–1327	0.40 0.15 0.10 0.25 0.10	ν_{as} CCl_2
752–842	1	1121–1231 1231–1252 1243–1252 1149–1243 1121–1142 1105–1121	0.25 0.10 0.13 0.32 0.10 0.10	ν_s CCl_2
386–407	1	475 475–501 501–758 758–785	0.06 0.16 0.65 0.13	δ CCl_2
242–558	1	439 439–466 466–506 506	0.09 0.44 0.37 0.10	w CCl_2
386–650	1	373–414 373	0.62 0.38	r CCl_2
213–564	1	245 245–281 281–373 373	0.21 0.29 0.41 0.09	t CCl_2
1617–1688	1	1458 1458–1515 1494–1514	0.13 0.44 0.43	ν_{as} CC
1324–1547	1	1159–1204 1204	0.90 0.10	ν_s CC

* 1 K = 0.695 cm^{-1}
[a] Data based on ref. 12
[b] Data based on the PVF2 analysis of ref. 1

and polyethylene, PE[15]. The difference 2PVC − 2PE is, however, more related to the vibrational spectrum of poly(1,2-dichloroethylene) than that of poly(vinylidene chloride). Larger differences arise from the data in *Table 2*. Similar differences were also observed in the analogous treatment of fluoro polymers[1], but because of the higher mass of chlorine, the differences in the PVC2 case are even larger.

A comparison of group vibration heat capacities of the second and third approximation frequency distributions from the computed heat capacity are shown in *Figure 5*. The first two spectra show good C_v agreement within ±10% below 200 K, and within ±5% at higher temperature. The agreement between the first and the third approximation is poorer.

As mentioned above, there are no experimental heat capacity data at low temperatures. Experimental data exists only above 50 K. Lebedev *et al.*[16], Sochava[17], and Warfield and Petree[18] proposed extrapolated data at lower temperatures using a Tarasov function[16] or a Debye function[17,18]. The results obtained are very different from ours (at 30 K discrepancies as high as 40% from Sochava's and 10% from Lebedev's). Lebedev *et al.*[16] considered six skeletal vibrations and disregarded the influence of the group vibrations. The influence of the latter is, however, significant at temperatures where he obtained the fit. Similarly, Sochava[17], and Warfield and Petree[18] used a three-dimensional Debye function. Above 50 K, however, heat capacities of polymers are never described by a Debye function. These previous treatments must thus be considered superseded by the present work.

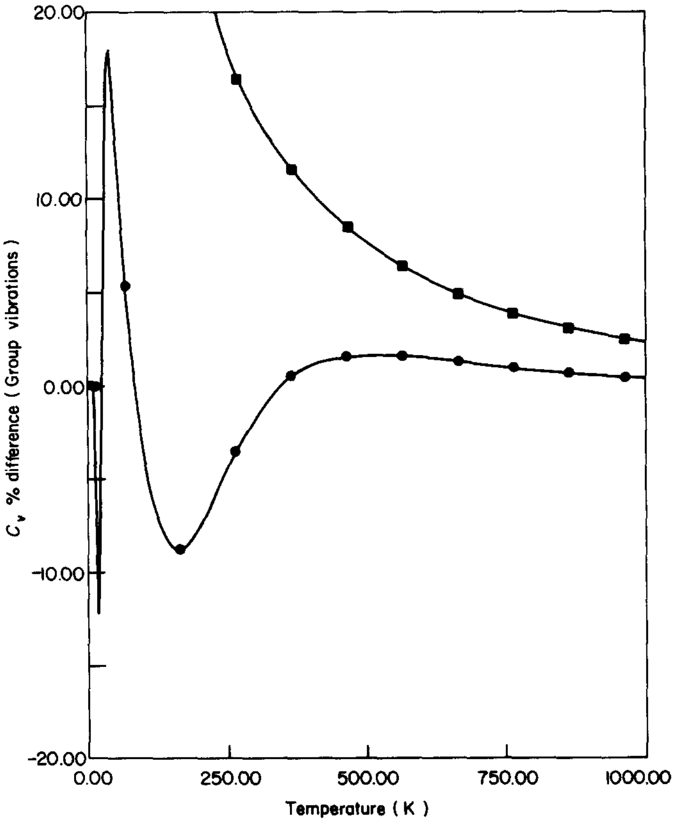

Figure 5 Group vibration contribution to the heat capacity of PVC2 Comparison of (i) spectrum of ref. 12 (first approximation) to the second approximation (mass adjusted PVF2) (●), (ii) average (third approximation) to the second approximation (■). (For second approximation spectrum see *Table 2*)

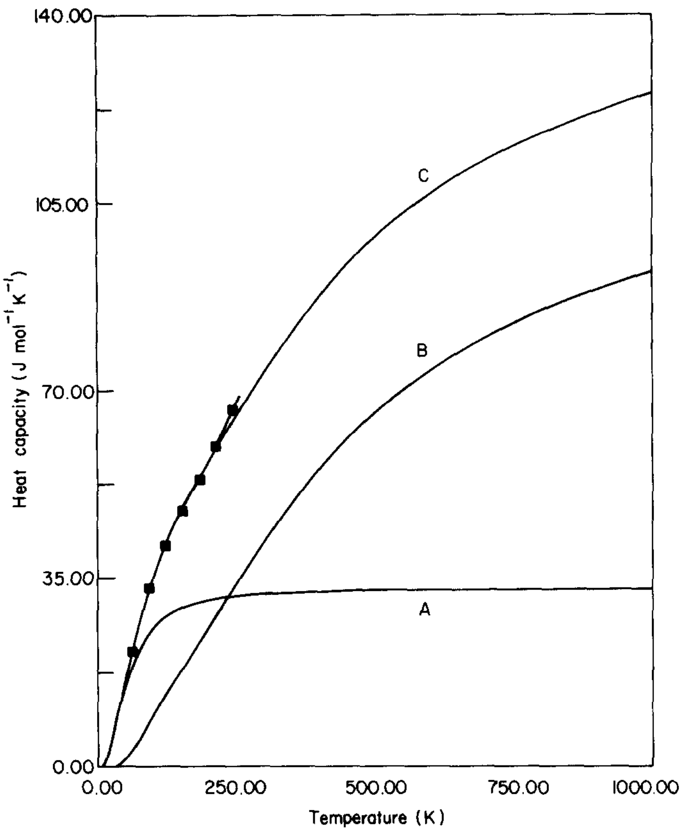

Figure 6 Heat capacity of PVC2. Skeletal contribution to C_v (A), group vibrations to C_v (B), total C_v (C), experimental C_p (■). $\theta_1 = 308$ K, $\theta_3 = 119$ K, group vibrations as listed in *Table 2*

Since no experimental heat capacity data at low temperatures exist, we used the inversion program outlined in the Appendix for the evaluation of θ_1 and θ_3. θ_1 is constant in the temperature range 70–100 K at $\theta_1 = 308 \pm 3$ K. Using this θ_1 we found that $\theta_3 = 119$ K at 60 K. We assumed that this is an appropriate θ_3 for poly(vinylidene chloride). For this and all later calculations the vibrational spectrum used for the group vibrations was that obtained by shifting the spectrum of PVF2 (approximation 2).

With these θ-values, heat capacities at constant volume C_v were calculated and are shown in *Table 4* and *Figure 6*. The heat capacities at constant volume were converted to heat capacities at constant pressure using the Lindemann equation. For A_0 the value of 4.86×10^{-3} K mol J^{-1} (ref. 11) was used per heavy atom (4 heavy atoms per repeating unit) and for the melting point 463 K was inserted into equation (A6) of the Appendix. The comparison between experimental and calculated heat capacities C_p is given in *Figure 7*. The agreement is better than ±4%.

Poly(chlorotrifluoroethylene) (PC3FE)

PC3FE was studied earlier by Choy *et al.*[19]. We used their heat capacity data, taken at temperatures higher than 80 K. At low temperatures (below 20 K), besides the data of Reese and Tucker[20] which were known at the time of Choy's investigation, new data are now available[21].

Our approach is somewhat different from that used in ref. 19. Instead of using an approximate spectrum of single Einstein frequencies constructed from i.r. and Raman data, we formed an average spectrum from the group

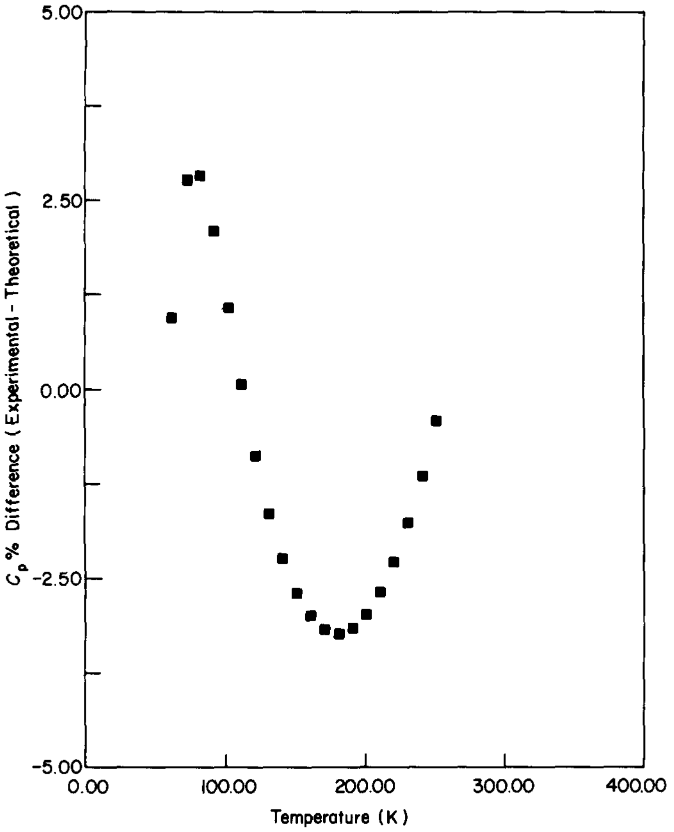

Figure 7 Comparison of calculated C_p of PVC2 based on calculations of *Figure 6* and experimental heat capacity. $A_0 = 4.86 \times 10^{-3}$ K mol J^{-1}, $T_m = 463$ K for equation (A6) of the Appendix

vibrations of PVC, poly(tetrafluoroethylene) (PTFE) and poly(vinyl fluoride) (PVF).

$$\mathrm{PC3F = 2PTFE + PVC{-}PVF} \qquad (5)$$

The additivity should be obeyed as similar normal modes of the group vibrations are added or subtracted. Similar manipulation proved successful earlier for the approximation of poly(vinyl fluoride) and poly(trifluoroethylene) spectra[1].

Using these approximated group vibrations leads to values of $\theta_1 = 215 \pm 28$ K and $\theta_3 = 42 \pm 3$ K when fitted over the temperature range of experimental data from 80 to 110 K. An initial θ_D of 72 K was derived using the low temperature heat capacity data of ref. 20 from 1 to 2 K. Using the data of ref. 21 from 3 to 9 K, a θ_D of 89 ± 6 K results. This would lead in the subsequent θ_1, θ_3 inversion to higher values of θ_3. Using the new inversion program detailed in the Appendix with a θ_1 value of 215 K, which describes heat capacity at higher temperatures well, we find that a $\theta_3 = 42$ K describes heat capacities of ref. 20 and a $\theta_3 = 55 \pm 3$ K those of ref. 21. Since poly(chlorotrifluoroethylene) is a polymer which can assume a wide range of crystallinities[22] and θ_3 is crystallinity dependent, the difference in θ_3 of the two measurements could be due to difference in crystallinity of the two samples. Unfortunately neither author lists any crystallinity, density, or heat of fusion data to check our speculation.

With $\theta_1 = 215$ K and $\theta_3 = 42$ K, heat capacities were calculated from 1–1000 K and are displayed in *Figure 8* and *Table 4*. Using the A_0 value suggested by Choy[23] of $A_0 = 1.2 \times 10^{-3}$ K mol repeating unit J^{-1} we converted C_v to C_p. To obtain A_0 per heavy atom, as listed before, one has to multiply with the number of heavy atoms in the repeat unit, 6 in this case. Calculated and experimental values for C_p were compared and the agreement is good, as shown in *Figure 9*.

There is a systematic deviation in the calculated C_p's that starts at 220 K and continues to increase up to the temperature where the glass transition (T_g) is expected. It should be emphasized that for this polymer T_g was not determined thermally. Dilatometometric studies give a T_g of about 325 K[24,25], while dynamic-mechanical tests[22,26,27] give a β-transition associated with T_g at about 330 K. Another relaxation (γ-relaxation) was observed at about 220 K. It was proposed[27] that this may be associated with the beginning of the glass transition, as may also be indicated by our analysis (see *Figure 9*).

Another explanation of the increasing discrepancy between calculated and measured C_p is, however, possible. It might be a poorly chosen value for A_0 (see equation (A6) of the Appendix). Changing A_0 to 10.2×10^{-3} leads to an agreement between experimental and calculated values within less than $\pm 0.5\%$, as is shown in *Figure 10*.

DISCUSSION

With the above analysis it is now possible to establish recommended heat capacities C_v of solid, chlorinated polyethylenes as was done before for the solid, fluorinated polymers. In *Table 4* the results of the analysis are collected.

In *Figures 3*, *4*, *7*, *9* and *10* the results are compared with the experimental data. It is seen that the analyses give results comparable with experimental accuracy since the overall accuracy of the measurements from different laboratories is usually within 3 to 5%[8].

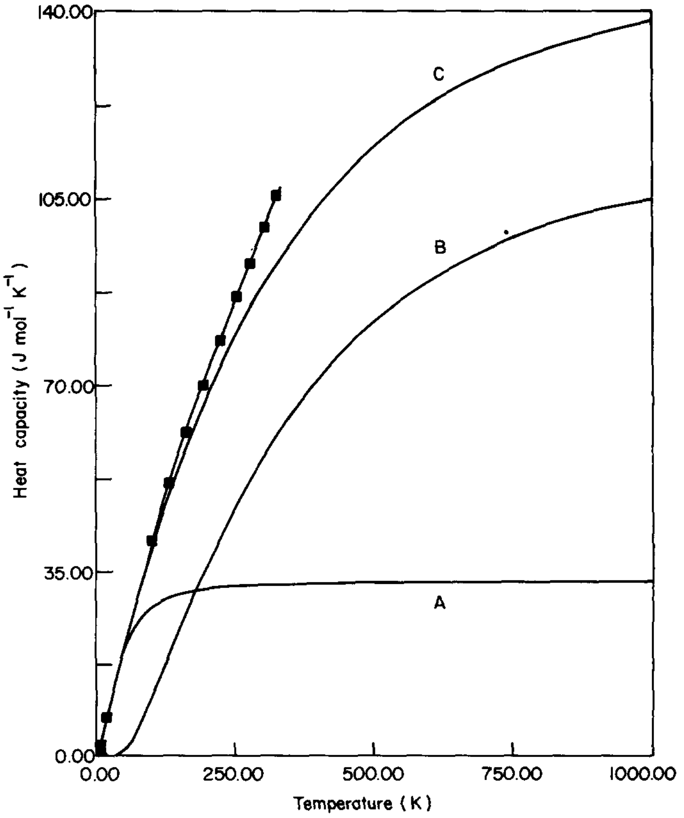

Figure 8 Heat capacity of PC3FE. Skeletal contribution to C_v (A), group vibrations to C_v (B), total C_v (C), experimental C_p (■). $\theta_1 = 215$ K, $\theta_3 = 42$ K, group vibrations as expressed by equation (5)

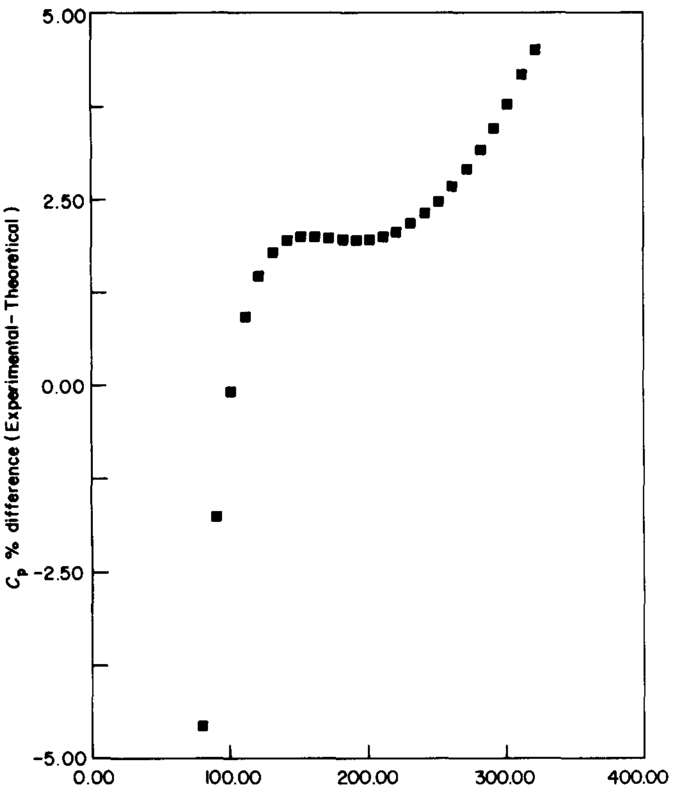

Figure 9 Comparison of calculated C_p of PC3FE based on calculation of *Figure 8* and experimental heat capacities. $A_0 = 7.2 \times 10^{-3}$ K mol J^{-1}, $T_m = 493$ K for equation (A6) of the Appendix

At higher temperatures, starting about 100 K below the glass transition, the deviations may become larger. This can be attributed either to a poorly chosen value for A_0, or to the beginning of a broad glass transition. Such a broad glass transition has earlier been documented for several macromolecules with small side-groups[2,28,29].

For PVC a poorly chosen A_0 seems more likely, since the experiment-based A_0 is significantly lower than that of similar polymers. In *Figure 4*, where the C_v to C_p conversion was made using an adjusted A_0 of 5.29×10^{-3} K mol J^{-1}, the agreement between experimental and calculated data is better and the glass transition appears to start sharply at about 300 K. For PVC_2 not enough precision is available to discuss the sharpness of T_g (see *Figure 7*). For PC3FE the beginning of a broad glass transition may be a likely reason for the increasing deviation between measured and calculated C_p values. The change in A_0 needed to achieve a match of experimental and measured data leads to an A_0 of about double that typical of macromolecules[11]. PC3FE would also have a relatively smaller side-group than PVC because of the replacement of H by F and would thus fit better into the series of linear macromolecules with broad glass transitions (polyethylene, polyoxides, selenium and poly(tetrafluoroethylene)).

Another systematic deviation of about 2% in the calculated heat capacities at temperatures from 100 K to 200 K of PC3FE can be seen in *Figures 9* and *10*. This deviation is independent of the various θ_1 and θ_3 and also cannot be removed by different choices of A_0. Since in this temperature range the vibrations described by θ_1 and θ_3 are already largely excited, the error must come from a contribution of some group vibrations to the heat capacity which has a lower frequency than assumed. Choy, who has also analysed PC3FE[19], found similar results to ours ($\theta_1 = 235$, $\theta_3 = 38$). The difference between calculated and experimental data may result from an error in measurements. It is worth mentioning that at higher temperatures Hoffman[30] found higher heat capacity data than Choy.

It is in this connection and it is also interecting to note that in both, PVC and PVC2 (*Figures 3, 4* and *7*) there are small, but clear systematic heat capacity deviations in the opposite (negative) direction. Similar negative deviations were observed before for poly(vinyl fluoride) and poly(trifluoroethylene)[1]. An explanation might rest with the nature of the particular polymers. All of them have alternating heavy and light chain segments. The C–C stretching vibrational mode should under such conditions separate into two branches, an acoustic and an optic one[6]. The optic one is of higher frequency and should not couple much with the skeletal vibrations. The acoustic one, however, should. In our present calculation of the vibrational spectra the contribution of the optical branch may be over-estimated and that of the acoustic one, neglected. An increase in the number of low frequency vibrations could remove the systematic deviation.

A similar explanation may apply to the higher θ_3 found for PVC2. Since we do not have low temperature heat capacity data, we used the data at higher temperatures to find θ_3. At these temperatures, however, the influence of the additional low frequency vibration becomes significant so that our program chooses a higher θ_3 in order to account for this additional vibration.

The earlier discussions of low temperature heat capacities from our laboratory[3] did not take the influence of the group vibrations into account and a poor fit was obtained. The same was true for the analyses of Lebedev[16] and Sochava[17].

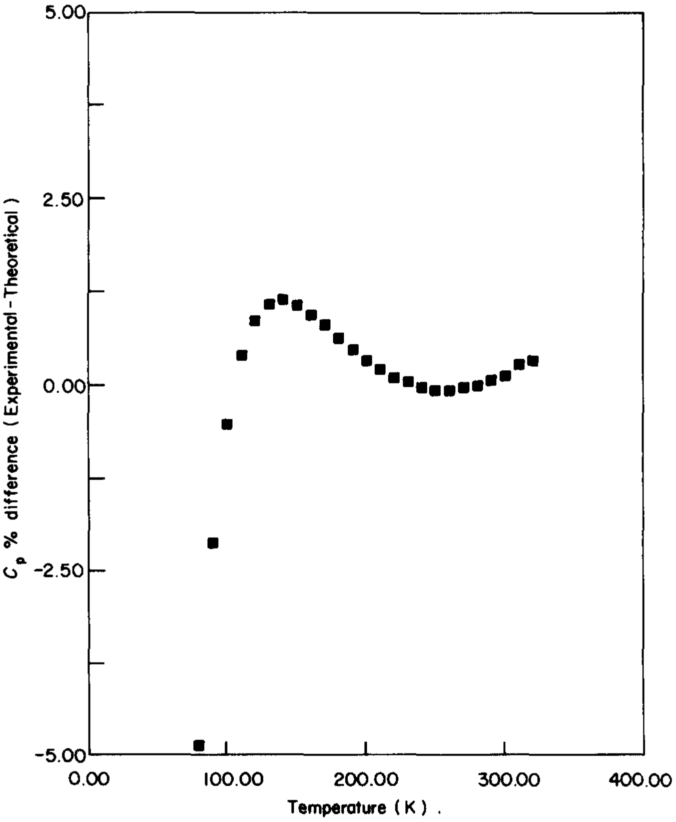

Figure 10 Comparison of experimental and calculated C_p values as in *Figure 9*, but with $A_0 = 10.2 \times 10^{-3}$ K mol J^{-1}

ADDITION SCHEME

In this and the previous work[1] it has been shown that heat capacity contributions from group vibrations are not significantly affected by crystal structure, conformational changes, stereo isomerism, positional isomerism, copolymerization and mixing. Structural isomerism may cause larger changes in group vibrations, as was illustrated in the heat capacity discussion of polystyrene and poly-*p*-xylylene[31], and can be expected in such isomers as poly-1-butene and polyisobutylene. Even for the poly(vinylidene chloride) and poly(1,2-dichloroethylene) discussed here special consideration of the group vibrations was necessary. In such cases only the group vibrations unaffected by the structure changes may be transferred from one polymer to the other.

Major differences in the dispersion curves of all different polymers arise from the low frequency region of intermolecularly coupled skeletal vibrations. They must, however, always be deduced by fitting to experimental heat capacities. Even in the cases where intermolecular force-fields were considered in computation attempts of the dispersion curves, an inversion to heat capacity led always to excessive errors[2,5].

For the higher-frequency intramolecular skeletal vibrations, a number of functional relationships between θ_1 and mass per repeating unit and measures of the force constants have been proposed[1,2,6]. In this section we will analyse to what degree addition schemes are possible for halogenated, linear polyethylenes.

To find the heat capacity for a polymer, one may try to find the contributions due to group vibrations just from the chemical formula of the polymer, subject to the restrictions posed by structural isomerism, as indicated above. For linear polyethylene-based halogenated polymers it is thus sufficient to know the full set of group vibrations (or their heat capacity contributions) of only a few polymers, namely, polyethylene, poly(vinyl fluoride), poly(vinylidene fluoride) or poly(tetrafluoroethylene), poly(vinyl chloride) and poly(vinylidene chloride). The proposed additivity of group vibrations was proven for poly(trifluoroethylene)[1], poly(vinylidene fluoride)[1] and poly(chlorotrifluoroethylene) (this paper). It is assumed, therefore, that the group vibrations of any halogenated polyethylene (homopolymer, copolymer or blend) may be approximated by an appropriate average of the group vibration of the above polymers. In *Table 5* and *Figures 11* and *12* the group vibration contributions to the heat capacity of these copolymers are listed. To use these, one has just to add the right proportions (mole fractions).

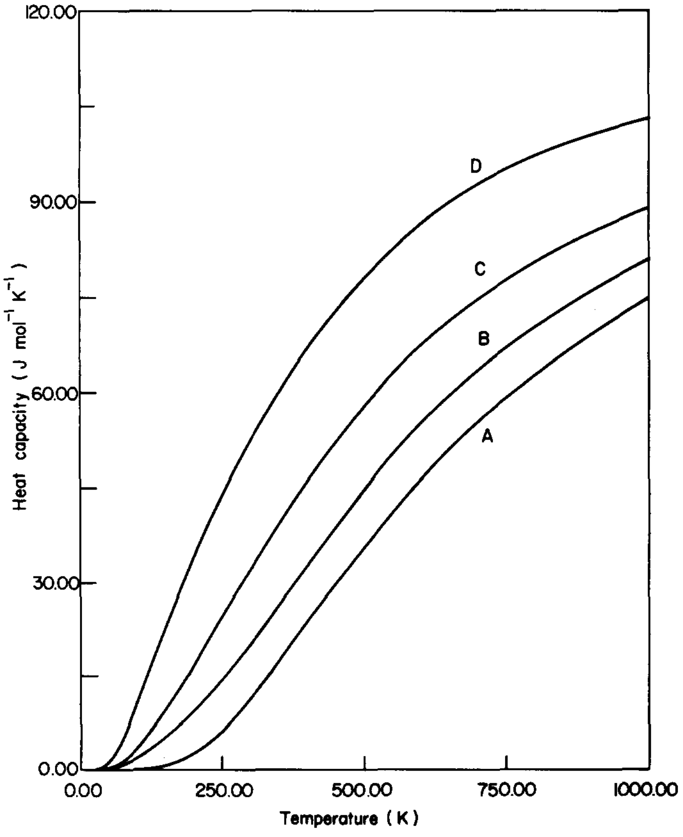

Figure 11 Heat capacity due to the group vibrations of fluorinated polyethylenes: (A) polyethylene, (B) poly(vinyl fluoride), (C) poly(vinylidene fluoride), (D) polytetrafluoroethylene (see *Table 5*)

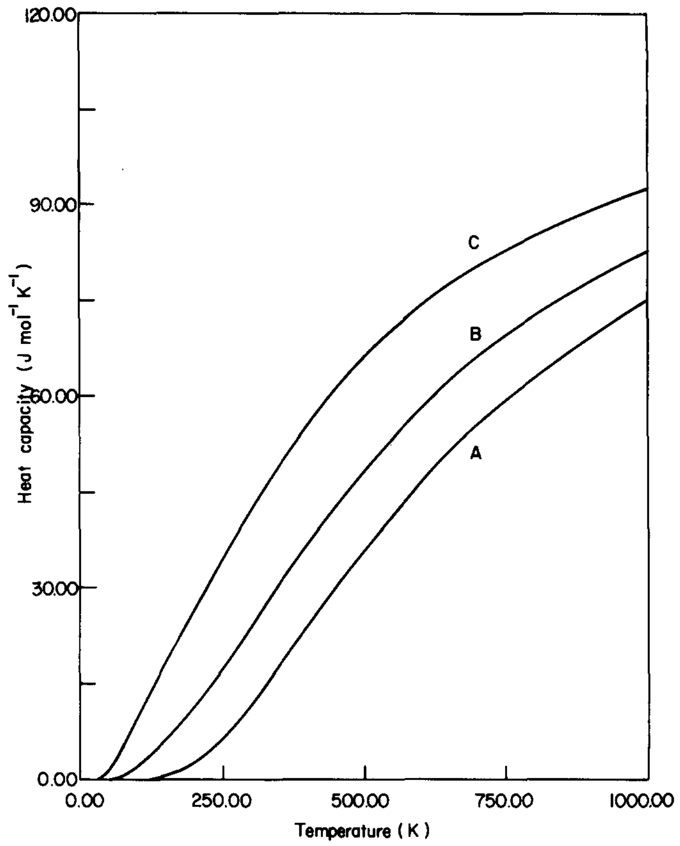

Figure 12 Heat capacity due to the group vibrations of chlorinated polyethylenes: (A) polyethylene, (B) poly(vinyl chloride), (C) poly(vinylidene chloride) (see *Table 5*)

The next step in deriving a prediction method for heat capacities must involve the evaluation of θ_1 and θ_3 for the variously halogenated polyethylenes. In our previous paper we gave θ_1 and θ_3 as empirical functions of degree of fluorination. It is difficult, however, to derive θ_1 and θ_3 as functions of degree of simultaneous fluorination and chlorination. We will try therefore to find θ_1 and θ_3 as functions of the mass of the average repeating unit.

In *Table 3*, θ_1 and θ_3 and the products of $\theta_1 \times \sqrt{M}$ and $\theta_3 \times \sqrt{M}$ are given, where M is the molecular weight of the two-chain-atom average polymer repeating unit. Because of the similarity in basic chain structure, N, the number of skeletal vibrations, is four for all the cases discussed. It can be seen from the Table that the product $\theta_1 \times \sqrt{M}$ is practically constant. From the constancy of $\theta_1 \times \sqrt{M}$ we conclude that changes in force constant of the polymers due to halogenation are not important for the purpose of calculation of intramolecular skeletal heat capacity contributions. The overall average of *Table 3* for $\theta_1 \times \sqrt{M}$ is 2790±160.

The estimation of θ_3 is more complicated since it is a measure of the frequencies of the skeletal vibrations largely governed by intermolecular interactions. Those vibrations should be both mass and force constant dependent: $\theta_3 = K \times \sqrt{f/m}$. The force constant is not readily predictable and in the past[5] we have tried to associate it with the cohesive energy density. It looks, however, that such treatment does not apply to the chlorinated polymers. The main reason may be the variation in crystallinity. It has been found that the heat capacity of PE, which has been studied extensively at low temperatures, depends strongly on the degree of crystallinity[32]. Its θ_3 changes from 80 K for amorphous samples to 158 K for crystalline samples[1,3].

Despite the many factors which influence *f*, one can see that the product $\theta_3 \times \sqrt{M}$ of *Table 3* shows relatively little variation where its mean value is 540±110. In addition, θ_3 is small, which means its value lies between about 40 and 160 K so that it does not influence the overall heat capacity at higher temperatures. Since at low temperatures the total heat capacity is small, the uncertainty introduced to the integral thermodynamic functions by less precise approximations of θ_3 is tolerable. We suggest thus as a first approximation in absence of low temperature heat capacity data to calculate θ_3 from the molecular weight of the polymer and the value of the product $\theta_3 \times \sqrt{M} = 540$.

Adding the skeletal and group vibration contributions leads to the total heat capacity at constant volume. Conversion to the heat capacity at constant pressure is possible through equation (A6) in the Appendix, using the universal value 5.11×10^{-3} K mol J^{-1} which applies to a single heavy atom (C, F or Cl in our case). To calculate A_0 per repeating unit, the universal value must be divided by the total number of heavy atoms. An approximation of the melting temperature, also needed in equation (A6), is usually available through the experimental melting temperature or one may use 3/2 of the glass transition temperature.

We use PC3FE to demonstrate the addition scheme, not only because it represents both series of fluorinated and chlorinated polyethylenes, but also because the deviations expected should be higher than from any other polymer in the series due to its rather high molecular weight and the way the group contribution of the CClF-group is to be derived. According to the just described prediction schemes, $\theta_1 = 258$ and $\theta_3 = 50$ K. The group vibration contributions are found using equation (5) and the results are shown in *Figure 13*. The deviations are within ±3%.

In our efforts to derive a method to predict heat capacity, a purely empirical addition scheme, based on the 1980 data bank has been derived[33]. In it the limited experimental heat capacities of a few polymers (PE, PVF, PTFE, PVC, PVC2) are used to derive the heat capacity of various groups (CH_2, CHF, CF_2, CHCl, CCl_2, respectively). Then the heat capacity of any polymer consisting of these groups can be calculated. This method also gives good predictions for the PC3FE heat capacity,

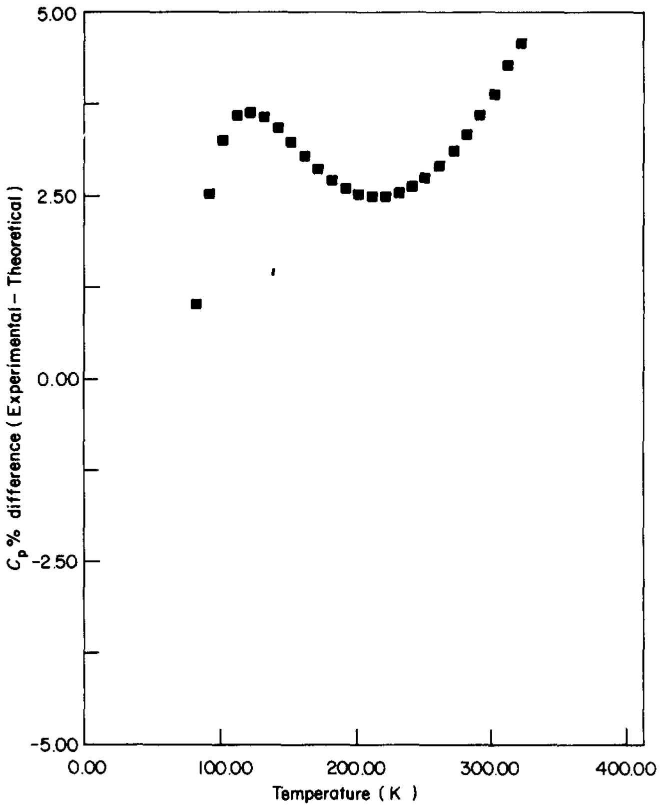

Figure 13 Comparison of calculated and experimental heat capacity of PC3FE. Making use of the addition scheme ($\theta_1 = 257$ K, $\theta_3 = 50$ K, $A_0 = 7.2 \times 10^{-3}$ K mol J^{-1}, $T_m = 493$ K) (compare with *Figures 9* and *10*)

Table 3 Summary of parameters needed for skeletal heat capacity calculations

Polymer	*MW*	θ_1 (K)	$\theta_1 \times \sqrt{M}$ [a]	θ_3 (K)	$\theta_3 \times \sqrt{M}$ [b]	$A_0 \times 10^3$ [c] (K mol J^{-1})
PE	28	520	2752	118[d]	624	4.86
PVF	46	440	2984	105	712	3.00
PVF2	64	346	2768	65	525	3.748
P3FE	82	315	2852	56	507	(4.86)
PTFE	100	250	2500	54	540	4.86
PVC	62.5	353.5	2795	45.4	359	3.13
PVC2	97	308	2905	(119)	(1172)	(4.86)
PC3FE	116.5	(215)	(2321)	48.5[e]	523	7.2

[a] Average $\theta_1 \times \sqrt{M} = 2970 \pm 160$ (excluding the questionable PC3FE data)

[b] Average $\theta_3 \times \sqrt{M} = 540 \pm 110$ (excluding the questionable PVC2 data)

[c] Per mole of heavy atom in the repeating unit, to convert to repeating unit: for PE divide by 2, for PTFE by 6, etc.

[d] 100% crystallinity (158 K) and amorphous (80 K) are averaged

[e] Average of the two θ_3 values described in the text

Table 4 Heat capacity at constant volume for chlorine containing polymers in J K^{-1} mol^{-1}*

Temperature	PVC	PVC2	PC3FE	Temperature	PVC	PVC2	PC3FE
1.0	0.004	0.000	0.007	440.0	74.4	93.0	109.3
1.2	0.006	0.001	0.012	450.0	75.6	94.0	110.4
1.4	0.010	0.001	0.019	460.0	76.8	95.1	111.4
1.6	0.015	0.002	0.028	470.0	77.9	96.1	112.5
1.8	0.021	0.002	0.040	480.0	79.1	97.1	113.4
2.0	0.028	0.003	0.055	490.0	80.2	98.0	114.4
3.0	0.096	0.010	0.184	500.0	81.3	99.0	115.3
4.0	0.226	0.024	0.431	510.0	82.3	99.9	116.2
5.0	0.429	0.047	0.81	520.0	83.4	100.8	117.1
6.0	0.70	0.081	1.30	530.0	84.4	101.6	117.9
7.0	1.02	0.129	1.86	540.0	85.4	102.5	118.7
8.0	1.38	0.193	2.47	550.0	86.4	103.3	119.5
9.0	1.76	0.275	3.10	560.0	87.3	104.1	120.3
10.0	2.14	0.377	3.74	570.0	88.3	104.8	121.0
15.0	4.03	1.26	6.80	580.0	89.2	105.6	121.7
20.0	5.79	2.80	9.64	590.0	90.1	106.3	122.4
25.0	7.46	4.89	12.30	600.0	91.0	107.0	123.0
30.0	9.08	7.28	14.80	610.0	91.9	107.7	123.7
40.0	12.22	12.35	19.27	620.0	92.7	108.4	124.3
50.0	15.19	17.25	23.18	630.0	93.6	109.1	124.9
60.0	17.94	21.78	26.79	640.0	94.4	109.7	125.5
70.0	20.46	25.93	30.28	650.0	95.2	110.3	126.1
80.0	22.76	29.70	33.72	660.0	96.0	110.9	126.6
90.0	24.88	33.13	37.11	670.0	96.7	111.5	127.2
100.0	26.83	36.24	40.45	680.0	97.5	112.1	127.7
110.0	28.66	39.07	43.70	690.0	98.2	112.7	128.2
120.0	30.37	41.64	46.88	700.0	99.0	113.3	128.6
130.0	32.00	44.01	49.96	710.0	99.7	113.8	129.1
140.0	33.55	46.22	52.9	720.0	100.4	114.3	129.6
150.0	35.05	48.30	55.8	730.0	101.1	114.9	130.0
160.0	36.50	50.3	58.6	740.0	101.8	115.4	130.4
170.0	37.92	52.2	61.4	750.0	102.4	115.9	130.9
180.0	39.31	54.0	64.0	760.0	103.1	116.4	131.3
190.0	40.69	55.9	66.5	770.0	103.7	116.9	131.7
200.0	42.05	57.7	69.0	780.0	104.4	117.3	132.0
210.0	43.42	59.4	71.4	790.0	105.0	117.8	132.4
220.0	44.78	61.2	73.7	800.0	105.6	118.2	132.8
230.0	46.15	62.9	75.9	810.0	106.2	118.7	133.1
240.0	47.5	64.6	78.1	820.0	106.8	119.1	133.5
250.0	48.9	66.3	80.1	830.0	107.3	119.5	133.8
260.0	50.3	68.0	82.2	840.0	107.9	120.0	134.1
270.0	51.7	69.6	84.1	850.0	108.5	120.4	134.4
280.0	53.1	71.2	86.0	860.0	109.0	120.8	134.7
290.0	54.5	72.8	87.9	870.0	109.6	121.2	135.0
300.0	55.9	74.4	89.6	880.0	110.1	121.5	135.3
310.0	57.3	76.0	91.4	890.0	110.6	121.9	135.6
320.0	58.7	77.5	93.0	900.0	111.1	122.3	135.9
330.0	60.1	78.9	94.6	910.0	111.6	122.7	136.1
340.0	61.5	80.4	96.2	920.0	112.1	123.0	136.4
350.0	62.8	81.8	97.7	930.0	112.6	123.4	136.6
360.0	64.2	83.2	99.2	940.0	113.1	123.7	136.9
370.0	65.5	84.5	100.6	950.0	113.5	124.1	137.1
380.0	66.9	85.8	102.0	960.0	114.0	124.4	137.3
390.0	68.2	87.1	103.2	970.0	114.5	124.7	137.6
400.0	69.5	88.3	104.6	980.0	114.9	125.0	137.8
410.0	70.7	89.5	105.8	990.0	115.3	125.4	138.0
420.0	72.0	90.7	107.0	1000.0	115.8	125.7	138.2
430.0	73.2	91.8	108.2				

* For calculation parameters see text

but is limited to the range of measured data and has larger deviations at temperatures close to the glass transition because of difficulties of experimentally separating T_g-effects. At low temperatures there are also differences between the predictions of the two schemes. Heat capacity is a function of θ_1 and θ_3, and therefore a function of the square root of M. The simple addition scheme, however, assumes θ_1 and θ_3 to be additive, i.e. functions of M.

CONCLUSIONS

(1) The heat capacities of solid, chlorinated polyethylenes were analysed based on experimental data below the glass transition temperature and information on the vibrational spectra. From this analysis heat capacities over the whole temperature range are derived (*Table 4*).

(2) A scheme for the prediction of the heat capacity of any solid, halogenated polyethylene is presented.

(3) Calculations and measurements agree within the limit of typical experimental error (3 to 5%).

ACKNOWLEDGEMENTS

This work has been supported by the Polymer Program of the National Science Foundation, Grant No. DMR-831709.

Table 5 Heat capacity contributions of group vibrations in J K^{-1} mol^{-1}*

Temperature	PE	PVF	PVF2	PTFE	PVC	PVC2	Temperature	PE	PVF	PVF2	PTFE	PVC	PVC2
20.0	0.000	0.000	0.000	0.000	0.000	0.002	510.0	37.03	46.00	59.34	79.62	49.51	66.93
25.0	0.000	0.000	0.000	0.006	0.000	0.019	520.0	38.13	47.08	60.35	80.52	50.54	67.80
30.0	0.000	0.000	0.002	0.032	0.000	0.007	530.0	39.22	48.14	61.32	81.40	51.54	68.65
40.0	0.000	0.007	0.026	0.261	0.077	0.434	540.0	40.29	49.18	62.28	82.26	52.53	69.48
50.0	0.000	0.050	0.131	0.921	0.050	1.22	550.0	41.35	50.20	63.21	83.08	53.50	70.28
60.0	0.000	0.177	0.380	2.13	0.177	2.45	560.0	42.39	51.20	64.12	83.89	54.45	71.06
70.0	0.001	0.422	0.811	3.85	0.426	4.02	570.0	43.41	52.18	65.00	84.66	55.38	71.82
80.0	0.003	0.796	1.44	5.96	0.810	5.80	580.0	44.42	53.14	65.87	85.42	56.29	72.56
90.0	0.011	1.29	2.25	8.34	1.32	7.67	590.0	45.41	54.08	66.72	86.15	57.18	73.29
100.0	0.031	1.87	3.21	10.88	1.95	9.55	600.0	46.38	55.01	67.54	86.86	58.06	73.99
110.0	0.069	2.52	4.31	13.47	2.67	11.40	610.0	47.34	55.92	68.35	87.55	58.92	74.68
120.0	0.135	3.21	5.51	16.08	3.47	13.20	620.0	48.29	56.81	69.14	88.22	59.76	75.35
130.0	0.238	3.94	6.79	18.65	4.33	14.93	630.0	49.22	57.69	69.90	88.87	60.59	76.00
140.0	0.386	4.68	8.13	21.17	5.24	16.62	640.0	50.13	58.55	70.66	89.50	61.40	76.64
150.0	0.588	5.44	9.51	23.63	6.19	18.27	650.0	51.03	59.39	71.39	90.11	62.20	77.26
160.0	0.852	6.21	10.94	26.02	7.18	19.89	660.0	51.92	60.22	72.11	90.70	62.98	77.87
170.0	1.18	7.00	12.39	28.33	8.20	21.49	670.0	52.79	61.03	72.81	91.28	63.74	78.47
180.0	1.58	7.82	13.87	30.57	9.25	23.09	680.0	53.64	61.83	73.49	91.83	64.49	79.05
190.0	2.05	8.66	15.36	32.75	10.33	24.69	690.0	54.49	62.61	74.16	92.38	65.23	79.61
200.0	2.60	9.52	16.88	34.86	11.44	26.28	700.0	55.32	63.38	74.82	92.90	65.96	80.17
210.0	3.22	10.43	18.41	36.92	12.58	27.88	710.0	56.14	64.13	75.46	93.41	66.66	80.71
220.0	3.92	11.38	19.95	38.91	13.74	29.48	720.0	56.94	64.87	76.09	93.91	67.36	81.24
230.0	4.68	12.36	21.50	40.86	14.94	31.08	730.0	57.73	65.59	76.70	94.39	68.05	81.76
240.0	5.51	13.38	23.06	42.75	16.16	32.68	740.0	58.51	66.30	77.30	94.85	68.72	82.27
250.0	6.40	14.44	24.62	44.60	17.40	34.27	750.0	59.28	67.00	77.89	95.31	69.38	82.76
260.0	7.35	15.54	26.18	46.41	18.66	35.86	760.0	60.03	67.69	78.46	95.75	70.03	83.25
270.0	8.36	16.67	27.73	48.18	19.94	37.42	770.0	60.77	68.37	79.03	96.18	70.66	83.73
280.0	9.41	17.83	29.28	49.90	21.24	38.98	780.0	61.50	69.03	79.58	96.59	71.29	84.20
290.0	10.50	19.02	30.82	51.58	22.55	40.51	790.0	62.22	69.68	80.12	97.00	71.90	84.65
300.0	11.64	20.24	32.36	53.23	23.87	42.02	800.0	62.93	70.32	80.65	97.39	72.50	85.10
310.0	12.80	21.48	33.87	54.84	25.19	43.51	810.0	63.62	70.94	81.17	97.77	73.10	85.54
320.0	13.99	22.74	35.37	56.41	26.52	44.97	820.0	64.31	71.56	81.68	98.14	73.68	85.97
330.0	15.20	24.01	36.86	57.94	27.84	46.40	830.0	64.98	72.17	82.18	98.51	74.26	86.39
340.0	16.42	25.29	38.32	59.44	29.16	47.80	840.0	65.65	72.76	82.66	98.86	74.82	86.81
350.0	17.66	26.58	39.76	60.90	30.48	49.18	850.0	66.30	73.35	83.14	99.20	75.37	87.21
360.0	18.91	27.86	41.18	62.32	31.79	50.51	860.0	66.95	73.92	83.61	99.53	75.91	87.61
370.0	20.17	29.15	42.58	63.71	33.09	51.83	870.0	67.58	74.49	84.07	99.86	76.45	88.00
380.0	21.43	30.44	43.95	65.06	34.38	53.10	880.0	68.20	75.04	84.52	100.17	76.97	88.39
390.0	22.68	31.72	45.30	66.38	35.65	54.35	890.0	68.82	75.59	84.97	100.48	77.49	88.76
400.0	23.94	32.99	46.61	67.66	36.91	55.56	900.0	69.42	76.12	85.40	100.78	78.00	89.13
410.0	25.18	34.25	47.91	68.91	38.15	56.74	910.0	70.02	76.65	85.83	101.07	78.50	89.50
420.0	26.42	35.49	49.17	70.13	39.37	57.89	920.0	70.61	77.17	86.25	101.35	78.99	89.85
430.0	27.65	36.73	50.41	71.31	40.58	59.01	930.0	71.18	77.68	86.66	101.63	79.47	90.20
440.0	28.87	37.95	51.62	72.45	41.76	60.10	940.0	71.75	78.18	87.06	101.90	79.94	90.54
450.0	30.08	39.15	52.80	73.57	42.93	61.16	950.0	72.31	78.67	87.46	102.16	80.41	90.88
460.0	31.28	40.34	53.96	74.65	44.08	62.19	960.0	72.86	79.16	87.84	102.41	80.87	91.21
470.0	32.46	41.51	55.09	75.70	45.21	63.19	970.0	73.40	79.64	88.22	102.66	81.32	91.54
480.0	33.62	42.66	56.19	76.73	46.31	64.17	980.0	73.94	80.10	88.60	102.91	81.77	91.86
490.0	34.77	43.80	57.27	77.72	47.40	65.11	990.0	74.46	80.56	88.97	103.14	82.20	92.17
500.0	35.91	44.91	58.32	78.68	48.46	66.03	1000.0	74.98	81.02	89.33	103.37	82.63	92.48

* PE = polyethylene, for vibrational spectrum see ref. 2. PVF, PVF2, PTFE = poly(vinyl fluoride), poly(vinylidene fluoride), poly(tetrafluoroethylene), for vibrational spectra (see ref. 1). PVC, PVC2 = poly(vinyl chloride), poly(vinylidene chloride), for vibrational spectra see *Table 1*, column 1 and *Table 2*, column 2, respectively. All are calculated for two chain-atom repeating units.

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APPENDIX

A new program was generated to calculate theta 3 for the Tarasov function $T(\theta_1/T, \theta_3/T)$ (see equation (1)). At high temperatures the influence of the θ_3 on heat capacity is small, so the heat capacity can be approximated by a θ_1 temperature only. At high temperature, θ_1 can be found by fitting to $D_1(\theta_1/T)$ (see equation (2)). At low temperatures the Tarasov equation becomes

$$C_v/NR = \frac{4\pi^4}{5}(T/\theta_3)^2(T/\theta_1) \qquad \text{(A1)}$$

$$\theta_3 = \sqrt{\frac{4\pi^4 T^3 NR}{5C_v\theta_1}} \qquad \text{(A2)}$$

By differentiation of equation (A2) we get

$$\frac{d\theta_3}{dC_v} = -\sqrt{\frac{\pi^4 NRT^3}{5\theta_1 C_v^3}} \qquad \text{(A3)}$$

It is also

$$\frac{\Delta\theta_3}{\Delta C_v} = \frac{d\theta_3}{dC_v} \qquad \text{(A4)}$$

From equations (A2)–(A4) we can take

$$\Delta\theta_3 = \frac{\theta_3}{2C_v}\Delta C_v \qquad \text{(A5)}$$

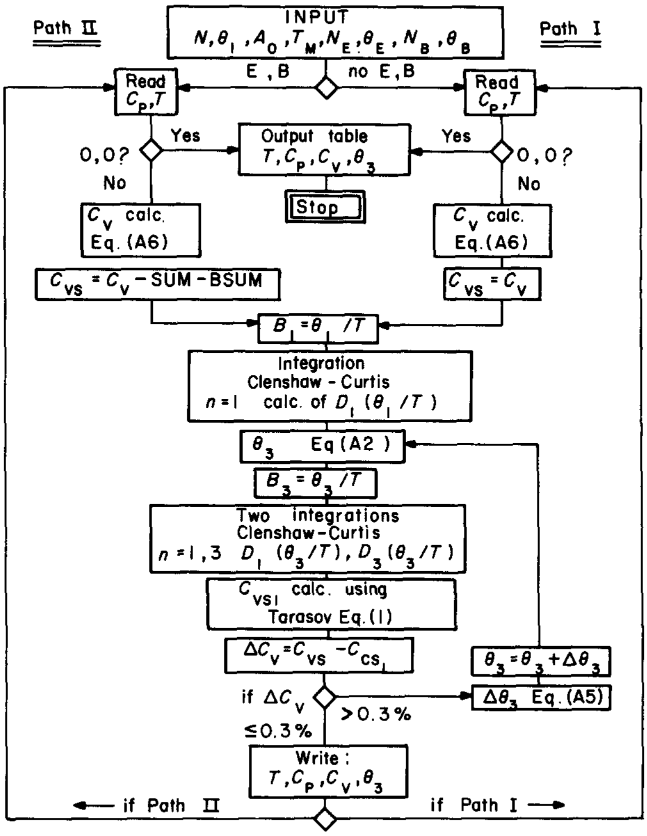

Figure A1 Flow chart of θ_{s} calculation, given θ_1

Using these equations, a program was generated to compute θ_3 from low temperature heat capacity and a known value of θ_1. From equation (A2) a first approximation of θ_3 is calculated. Then this is corrected through equation (A5). The Lindemann equation was first used to convert C_p to C_v:

$$C_v = C_p - \frac{A_0 C_p^2 T}{T_m} \qquad \text{(A6)}$$

A flow chart for the program is given in *Figure A1*.