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Temperature dependence of some thermodynamic functions for amorphous and semi-crystalline polymers

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The temperature dependence of some heat-capacity related functions is evaluated on the basis of experimental data, and a further elaboration is given for polyethylene.

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INTRODUCTION

The study of the thermal properties of polymers by calorimetric methods has become widespread especially in the past two decades. The main cause of this development was the increased availability of commercial differential calorimeters. As, in comparison with the calorimeters known of old, these instruments allow simple and rapid measurement, with reasonably accurate results, they are nowadays in routine use in many areas and for many purposes. By careful tuning and the use of well-elaborated measuring methods, a further increase in accuracy can be obtained, so that the instruments can be used also in fundamental research and, for instance, for establishing quantitative relations between molecular structure and properties of materials. An obvious application is in the kinetic determinancy of all types of processes, which is so characteristic of polymers. The recent availability of peripheral equipment for computerizing the measuring process, in combination with the possibilities of data manipulation and a further optimization of the various instrument components will, it is expected, lead to a further spread of application and potentialities of differential calorimeters.

This review is meant to provide a background to this development, in particular as regards the determination of the temperature dependence of the heat capacity, which is a paramount thermal property. Not only does this quantity provide direct experimental information on the possibilities of motion the molecules and parts thereof possess, also quantities that can be derived from the heat capacity, such as enthalpy, entropy and free enthalpy can give important information about the state of the material. The temperature dependence is important particularly in crystallization and melting processes of semi-crystalline polymers, as these often cover wide temperature ranges, and it is a factor also in the study of glass transition phenomena taking place in more or less amorphous polymers. As consequence of these recent developments, a large quantity of new data has become available, so that an evaluation such as given in this review is now useful. It is hoped that this article will incite specific experimental studies, as well as further evaluation,

and the development of empirical and theoretical methods of approach with improved applicability.

Some earlier approximations for the temperature dependence of the driving force for crystallization, and the consequences of this dependence for some other thermodynamic differential functions, is given initially. It is then shown that the temperature dependence of all these functions can be better estimated from direct experimental data on the heat capacity. The often abrupt change of the heat capacity in the glass transition range in polymers that are in the amorphous state is important. Various existing descriptions of this change are reviewed, and some indication of the usefulness of each of these methods of description is given.

Finally, there is an elaborate evaluation of literature data on polyethylene, a polymer about which much information is available. Extrapolation to 0% and 100% crystallinity of the heat capacity as a function of temperature gives the best possible estimate of the variation with temperature of each of the thermodynamic functions for the purely amorphous and purely crystalline states, and of the corresponding differential functions. These so-called reference states provide a useful frame for experimental work.

SOME APPROACHES TO THE DETERMINATION OF THE TEMPERATURE DEPENDENCE OF THERMODYNAMIC FUNCTIONS

The driving force and other differential functions for semi-crystalline polymers: some earlier approximations

To attain stability in the thermodynamic sense, all systems tend to minimize their free enthalpy (Gibbs free energy), g (specific and molar quantities will throughout be denoted by small letters). At temperatures below the equilibrium transition temperature, T_m , crystallizable systems will be in their stablest state when perfectly crystallized. When supercooled, such systems are in a metastable state, and there will be a force driving towards crystallization.

The driving 'force' for the crystallization of a segment of

an infinitely long polymer chain at temperature $T < T_m$ is defined as $-\Delta g(T)$, with:

$$\Delta g(T) \equiv g_a(T) - g_c(T), \text{ the driving 'force' for melting} \quad (1)$$

$$\Delta g(T_m) \equiv 0 \quad (2)$$

in which $g_c(T)$ is the smallest possible free enthalpy of the segment if it is in the crystalline state (index c) and $g_a(T)$ represents the free enthalpy of the segment if it is in a metastable, amorphous state (index a). It is assumed that in this amorphous state the entropy $s_a(T)$ is not reduced, for instance by orientation. It is further assumed that the enthalpy $h_a(T)$ is not lowered by intramolecular causes (e.g. a change of the *gauche/trans* ratio) or by intermolecular causes (e.g. better packing of juxtaposed segments)¹⁻³.

The difference in free enthalpy defined in this way relates to a segment of a thermodynamically macroscopic system. Every crystallization theory (cf., Flory⁴, Hoffman *et al.*⁵, Geil⁶, Mandelkern⁷, Schultz⁸, and Wunderlich⁹⁻¹¹), also those in which finite chains are regarded as small thermodynamic systems¹²⁻¹⁵, makes use of this free enthalpy differential function $\Delta g(T)$.

In principle, this function can be derived from the heat capacity differential function $\Delta c_p(T)$, via the analogously defined enthalpy differential function $\Delta h(T)$ and the entropy differential function $\Delta s(T)$:

$$\Delta g(T) = \Delta h(T) - T\Delta s(T) \quad (3)$$

$$= \frac{\Delta h(T_m)}{T_m} \Delta T - \int_T^{T_m} \Delta c_p(T) dT + T \int_T^{T_m} \frac{\Delta c_p(T)}{T} dT \quad (4)$$

with use being made of:

$$\Delta s(T_m) = \frac{\Delta h(T_m)}{T_m} \quad (5)$$

in view of equations (2) and (3) and

$$\Delta T \equiv T_m - T \quad (6)$$

which is called the supercooling.

As the first term in equation (4) represents the tangent to $\Delta g(T)$ in T_m , this expression is often used as an approximation at low ΔT values. Because the corresponding Δc_p function is zero, this approximation is indicated by CP 0:

$$\Delta g(T)_{CP0} \equiv \frac{\Delta h(T_m)}{T_m} \Delta T \quad (7)$$

Sanchez *et al.*¹⁶ showed that if

$$\Delta c_p(T) > 0 \text{ [see Figure 1a], then:} \quad (8)$$

$$\Delta g(T) < \Delta g(T)_{CP0}; \Delta h(T) < \Delta h(T_m); \Delta s(T) < \Delta s(T_m) \quad (9)$$

so that the CP 0 approximation gives a kind of upper limit for these three functions.

If, however, $\Delta c_p(T)$ is partly negative, which could be the case only at $\approx T_m$ [as $\Delta c_p(T_g)$ is always positive; see

later], the following holds for a specific temperature range:

$$\Delta g(T) > \Delta g(T)_{CP0}; \Delta h(T) > \Delta h(T_m); \Delta s(T) > \Delta s(T_m) \quad (10)$$

To illustrate this, Figure 1b presents a simulation of such a $\Delta c_p(T)$ and the consequences for the other differential functions. On account of Δc_p being positive at $\approx T_g$ and the consequent decrease of $\Delta h(T)$ [and $\Delta s(T)$] in that region when the temperature is lowered, $\Delta g(T)$ will intersect $\Delta g(T)_{CP0}$ at a certain degree of supercooling. This means that $\Delta g(T)_{CP0}$ will give a very good approximation to $\Delta g(T)$ in such a case (in this connection see also the later section concerning polyethylene).

As it is to be expected [especially with $\Delta c_p(T) > 0$] that the temperature dependence of the various differential functions will be of importance particularly at high degrees of supercooling^{5,17}, this is discussed first.

The temperature dependence of the differential functions was recognized at an early stage^{18,19}. A well-known approximation is the one given by Hoffman²⁰. For materials showing a glass transition when supercooled, he argued that, although $h_a(T)$ and $h_c(T)$ in general show a non-rectilinear decrease with increasing ΔT , the differential function $\Delta h(T)$ may be rectilinear in T :

$$\Delta h(T) = \Delta h(T_m) \frac{T - T_\infty}{T_m - T_\infty}, T_\infty \leq T_g \quad (11)$$

where, as is clear, T_∞ represents the point of intersection of $h_a(T)$ and $h_c(T)$. $\Delta c_p(T)$ is constant here:

$$\Delta c_p(T) = \frac{\Delta h(T_m)}{T_m - T_\infty} \quad (12)$$

The resulting approximation for the driving force for $T_g < T < T_m$ is:

$$\Delta g(T) = \frac{\Delta h(T_m)}{T_m} \frac{T_m T \ln \left(\frac{T_m}{T} \right) - T_\infty \Delta T}{T_m - T_\infty} \quad (13)$$

With the assumption:

$$T_\infty = \frac{T_g T_m}{T_g + T_m} \quad (14)$$

a set of differential functions has been defined which will be assigned the code HT_∞.

$\Delta h(T)$ is rectilinear in T :

$$\Delta h(T)_{HT_\infty} = \frac{\Delta h(T_m)}{T_m} \left(T - \frac{T_g \Delta T}{T_m} \right) \quad (15)$$

The use of:

$$\ln \frac{T_m}{T} \approx \frac{2\Delta T}{T_m + T} \quad (16)$$

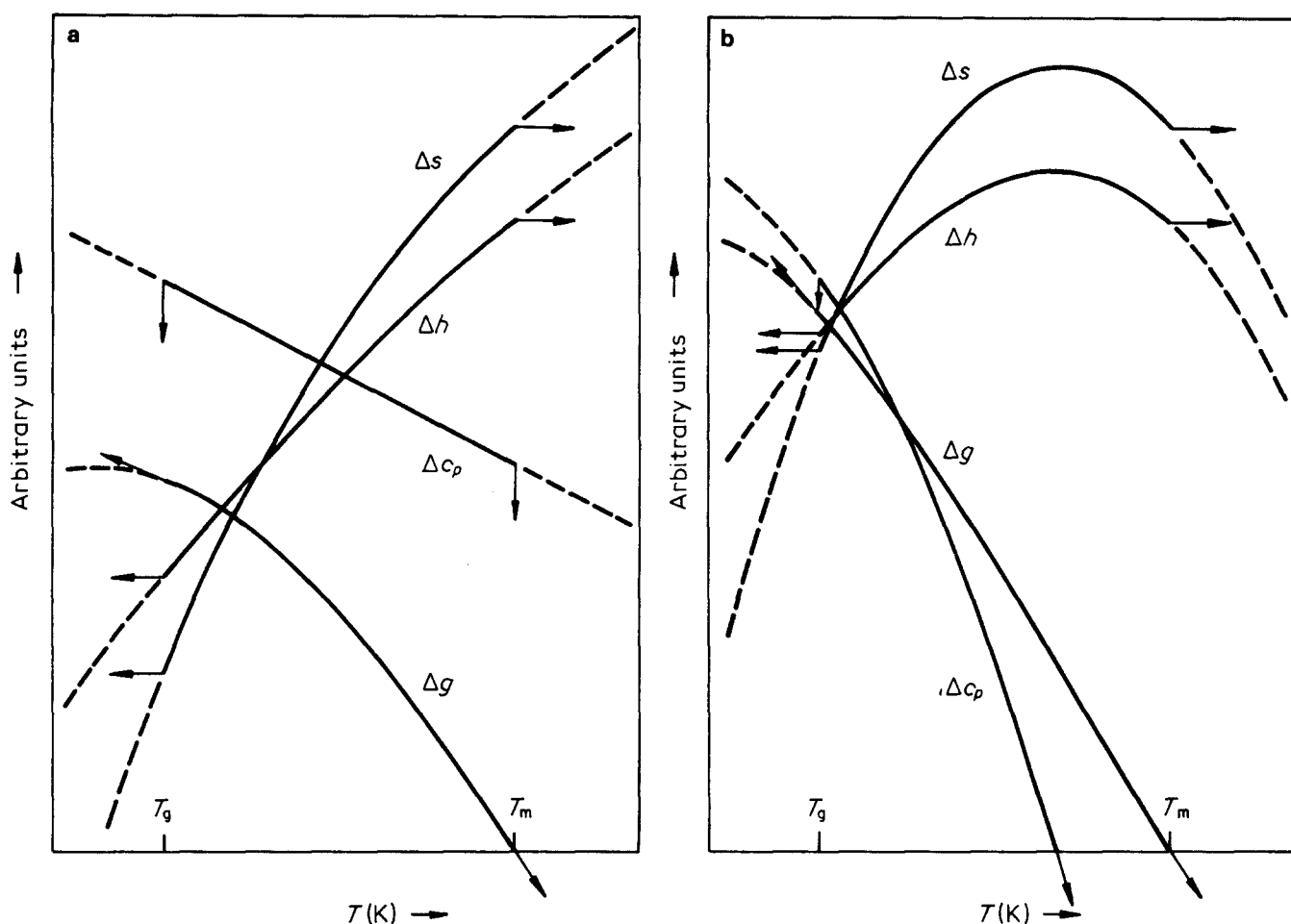


Figure 1 The differential functions $\Delta c_p(T)$, $\Delta h(T)$, $\Delta s(T)$ and $\Delta g(T)$ for the same values of T_m , T_g , $\Delta c_p(T_g)$ and $\Delta h(T_m)$ but different $\Delta c_p(T)$. In (a) and (b) the ordinates are arbitrary but equal. [(a) is, in fact, based on data for polyoxypropylene^{55,56}]. Arrows indicate the change in the functions if $\Delta c_p(T) = 0$, for $T < T_g$ and $T > T_m$. ---, extrapolations outside the temperature range (T_g , T_m)

leads to the well-known expression for the case of a high degree of supercooling (code HSC):

$$\Delta g(T)_{\text{HSC}} = \frac{\Delta h(T_m)}{T_m} \cdot \Delta T \cdot \frac{T}{T_m} \quad (17)$$

$$= \Delta g(T)_{\text{CP0}} \cdot \frac{T}{T_m} \quad (18)$$

Especially for high degrees of supercooling, this amounts to an appreciable correction of the CP 0 approximation. The question whether this approximation constitutes an improvement has no generally valid answer, as will be seen later. It depends on the specific change of Δc_p with T , as is illustrated by *Figure 1*.

If use is made of equation (16), the enthalpy differential function is no longer rectilinear in T , which it was originally:

$$\Delta h(T)_{\text{HSC}} = \frac{\Delta h(T_m)}{T_m} \cdot \frac{T^2}{T_m} \quad (19)$$

For $\Delta g(T)$, $\Delta h(T)$ and $\Delta s(T)$ the approximation of the HT_∞ functions by the HSC functions is very good, appreciable differences appearing only for $\Delta c_p(T)$.

For $T_\infty = 0$, equation (13) in combination with equation

(16) yields a set^{21,22} which will here be denoted by $\text{HT}_\infty = 0$. The following relation holds:

$$\Delta h(T)_{\text{HT}_\infty = 0} = \frac{\Delta h(T_m)}{T_m} \cdot T \quad (20)$$

Another approximation (code SDM) was given by Sanchez *et al.*¹⁶, who started from:

$$s_a(T) = k_1 T \text{ en } s_c(T) = k_2 T \quad (21)$$

$$\Delta s(T)_{\text{SDM}} = \frac{\Delta h(T_m)}{T_m} \cdot \frac{T}{T_m} \quad (22)$$

The SDM expressions are midway between the CP 0 and HSC expressions. The $\text{HT}_\infty = 0$ and SDM approximations were developed partly on the basis of the data then known for polyethylene, (see later).

Several authors²³⁻²⁶, finally, use the approximation:

$$\Delta c_p(T) = \frac{C}{T} \quad (23)$$

Since their introduction, the various approximations have not always been used in strict compliance with their starting points, which means that, in fact, their application amounts to a purely numerical use of the functions^{5,27}. Of

course, this is due also to experimental data being scarce, which, in view of the definition of the 'driving force', is not so surprising either. Here, these functions used by the earlier authors are used to establish whether, and to what extent, the various approximations are useful in a numerical sense.

Also of interest is a series of articles by Gutzow,²⁸⁻³³. Using a lattice hole model, this author calculates the temperature dependence of the thermodynamic functions for various glass types, allowing for free volume and for various mixing entropies and chain conformation possibilities. In addition to an exact calculation of some possible $\Delta c_p(T)$ functions, he uses other methods, notably the HSC approximation.

For the rest, it should here be observed that Tamman¹⁸, on the strength of experimental data, assumed $\Delta h(T)$ to be between $\Delta h(T)=\text{constant}$ (CP 0) and $\Delta h(T)/T = \text{constant}$ ($HT_\infty=0$) (ref.18, p.78; see also references therein).

Some approximations used for the differential functions are given later for polyethylene. In the plots the functions were calculated by means of the polynomial expressions in which the coefficients were determined by the Δc_p function. The use of polynomials naturally has no physical significance, but is purely a mathematical aid. It is advisable, however, to persist with a formula once chosen, as otherwise combination of equations may lead to possible discrepancies becoming surprisingly much greater (ref.34, p.73).

The heat capacity of some amorphous and semi-crystalline polymers

An approach to the determination of the temperature dependence of the various thermodynamic functions between T_g and T_m for semi-crystalline polymers that, more so than others, is based on experiments, is that which relies on heat capacity data.

In the first instance, it would seem reasonable to suppose that $c_{p_a}(T)$ and $c_{p_c}(T)$ for temperatures between T_g and T_m can be obtained by extrapolation using data on the melt (Index m) and the glass (Index g), respectively.

For $c_{p_a}(T)$ an extrapolation using melt data seems to give good results in some cases. The values for atactic polystyrene, for instance, correspond to values found by extrapolation for isotactic polystyrene³⁵; a correspondence with extrapolated values is seen also in the case of amorphous isotactic polystyrene^{35,36} and amorphous polyethylene terephthalate^{37,38} both obtained by quenching. Also, polypentene-1 shows analogous behaviour³⁹. In the case of polyethylene the value found by extrapolation corresponds to the $c_{p_m}(T)$ of low-molecular homologues (straight-chain alkanes^{40,41}). However, it is still uncertain in the case of polypropylene whether the differences between the atactic and the isotactic material measured by some investigators^{42,43} are due exclusively to a difference in tacticity or whether they are to be ascribed to a difference in molecular structure (other than tacticity), crystallinity of the atactic sample, or a similar factor^{44,45}. Recently, mention was made of attempts to describe $c_{p_a}(T)$ by means of additivity of group contributions⁴⁶. An evaluation method for $c_{p_a}(T)$ is given by Privalko *et al.*⁴⁷ whilst Eskin *et al.*⁴⁸ calculate $c_{r_a}(T)$ by means of the $c_{p_a}(T)$ of polymers in solution.

Extrapolation from glass data requires some explanation. As regards the heat capacity $c_{p_g}(T)$ for $T < T_g$, it is

known that from ≈ 60 K to the calorimetrically determined, glass transition this is practically independent of morphology, crystallinity, chain conformation and configuration, etc. An example is found in isotactic, atactic and syndiotactic polymethylmethacrylate (Figure 8 in O'Reilly *et al.*⁴⁹). It is even possible to estimate the c_p within 5% by summation of characteristic contributions of chemically different groups in the polymer molecule^{44,50-54}; for group contributions, see also Van Krevelen^{55,56}. Heating at $\approx T_g$ of amorphous samples produces an often step-shaped increase in $c_p(T)$ as compared with $c_{p_g}(T)$. This increase $\Delta c_p(T_g)$ is often seen also in semicrystalline samples, with, however, the step being smaller as crystallinity is higher. It might be expected, therefore, that extrapolation from glass data could result in a valid estimate of $c_{p_c}(T)$. The uncertainty in this estimate is, however, greater than that involved in extrapolating from melt data to estimate $c_{p_a}(T)$. The primary problem is from which section of the $c_{p_g}(T)$ curve the extrapolation should be made; this is the more uncertain because in semi-crystalline samples the position of the glass transition becomes unclear owing to crystallinity. Other than with extrapolation from melt data, there are hardly any further c_p data that could be used for testing the admissibility of the extrapolation. For polyethylene^{44,57}, and polyoxymethylene^{58,59} there are, however, $c_{p_c}(T)$ data. Extreme crystallinity was obtained for these polymers by means of high-pressure crystallization, by simultaneous polymerization and crystallization, and by solid-state polymerization. Comparison of these data with figures obtained by extrapolation from low-temperature data clearly shows that considerable deviations may occur, and that these deviations may, moreover, be significant in the determination of $\Delta c_p(T)$. Further, it is known that for non-polymeric substances c_{p_g} and c_p below the glass transition temperature can differ appreciably^{60,61}, which not only demonstrates clearly that an extrapolation as applied in the case of polymers is arbitrary here, but also makes it necessary to distinguish between $\Delta c_p(T_g)$ values determined from $c_{p_a}(T) - c_{p_g}(T)$ and from $c_{p_a}(T) - c_{p_c}(T)$. Nevertheless, extrapolation is the best approach to follow, for nearly all polymers. A clear illustration of this approach is given by the publication of Rabinovič *et al.*⁶² (see also references therein), which for 18 polymers gives a calculation of $h_g(0) - h_c(0)$, $s_g(0) - s_c(0)$, and $g_g(T) - g_c(T)$ for a few temperatures below T_g .

The heat capacity of liquid [index l; the term 'liquid' will here be used collectively for the amorphous phase (a) and the melt (m), as will be 'solid' (s) for glass (g) and crystal (c)] as well as glass is often approximated by a straight line, over a reasonably long temperature range. According to Dole⁶³, Van Krevelen^{55,56} and Bares *et al.*⁴³, this applies to the liquid, and according to van Krevelen also to the glass, for $T > 150$ K. Also Richardson³⁷ indicates that, certainly for amorphous homopolymers, the $c_p(T)$'s are rectilinear functions of T in the range 40-50 K below and above T_g . Illustrative examples are presented for PVC⁶⁴ and EP copolymers⁶⁵, for which $c_{p_s}(T)$ and $c_{p_l}(T)$, respectively, are rectilinear throughout a temperature range of > 200 K.

The c_p values based on data by Van Krevelen^{55,56}, for polymers for which:

$$\frac{1}{c_{p_l}(298)} \cdot \frac{dc_{p_l}(T)}{dT} \text{ en } \frac{1}{c_{p_s}(298)} \cdot \frac{dc_{p_s}(T)}{dT} \quad (24)$$

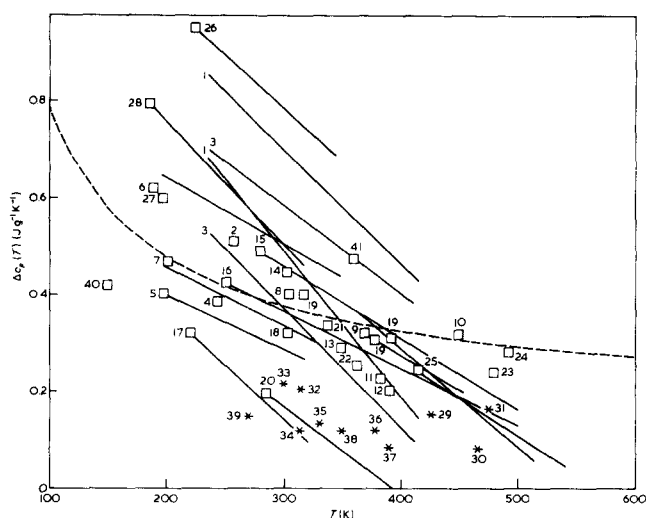


Figure 2 The specific heat capacity $\Delta c_p(T_g)$ plotted versus T_g according to Table 1. If there are several values for a polymer, use has been made of the averages (indicated by *a* in Table 1). The numbers correspond to those in the Table. \square , values for polymers containing no fluorine; *, fluorine-containing polymers; the lines indicate $\Delta c_p(T)$ according to Van Krevelen^{55,56}. The end points of the lines for PMA, PEA and PBMA are arbitrary here. The interrupted curve is according to equation (44)⁹⁰

are known, are in good agreement with the c_p values mentioned in the review by Wunderlich *et al.*⁴⁴, the deviations amounting at most to a few per cent.

In all cases $c_{p_s}(T)$ increases more rapidly with increasing temperature than $c_{p_l}(T)$, so that $\Delta c_p(T)$ is a decreasing function throughout (see also Figure 2). Also, the data presented by Bares *et al.*⁴³ show that $c_{p_l}(T)$ can be represented by a 1st degree polynomial over a reasonably wide temperature range. Over the entire temperature range a 2nd-order polynomial is sometimes suited best [isotactic polypropylene, polybutene-1, atactic (?) polystyrene], although in some cases a straight line suffices (polyethylene, polymethylmethacrylate). For a large section of the temperature range (the lower section) the straight line is very acceptable in the case of polybutene-1 and atactic (?) polystyrene. For polypropylene the situation is complicated, as mentioned previously. A comparison between the 1st degree polynomials from Bares and those from Van Krevelen shows the agreement to be reasonable, the maximum difference over the temperature range $T_g < T < T_{\text{end of fit-range}}$ being $\approx 10\%$.

In analogy to van Krevelen^{55,56}, it is evident that for $c_{p_l}(T)$ and $c_{p_s}(T)$ in the case of the polymers mentioned there (the stated percentages are standard deviations):

$$\frac{1}{c_{p_l}(298)} \cdot \frac{d c_{p_l}(T)}{dT} = (1.30 \pm 35\%) 10^{-3} (\text{K}^{-1}) \quad (17 \text{ polymers}) \quad (25)$$

$$\frac{1}{c_{p_s}(298)} \cdot \frac{d c_{p_s}(T)}{dT} = (2.96 \pm 7\%) 10^{-3} (\text{K}^{-1}) \quad (21 \text{ polymers}) \quad (26)$$

The good correlation in the latter expression is due to the $c_{p_s}(T)$ curves showing a convergence towards $T_0 = -40 \text{ K}$, so that:

$$\frac{1}{c_{p_s}(T_s)} \cdot \frac{d c_{p_s}(T)}{dT} = \frac{1}{T_s - T_0} \quad (27)$$

is reasonably constant at any value of T_s .

The equation following from equation (25):

$$c_{p_s}(T) = c_{p_s}(298) [0.118 + 2.96 10^{-3} T] \quad (28)$$

can, of course, also be written for other temperatures, e.g. 200 K [generally lower than T_g , so that $c_{p_s}(200)$ is in most cases experimentally accessible]:

$$c_{p_s}(T) = c_{p_s}(200) [0.166 + 4.17 10^{-3} T] \quad (29)$$

In these equations use can be made of the group contributions to c_{p_s} at 200 and 298 K as given by Satoh⁶⁶, Wunderlich *et al.*⁵⁰, and Van Krevelen^{55,56}.

By means of the $\tan^{-1} \left[\frac{d c_p(T)}{dT} (\text{J g}^{-1} \text{K}^{-2}) \right]$ values the following further derivations can be made:

$$\frac{d c_{p_l}(T)}{dT} = (2.60 \pm 30\%) 10^{-3} M (\text{J mol}^{-1} \text{K}^{-2}) \quad (15 \text{ polymers}) \quad (30)$$

$$\frac{d c_{p_s}(T)}{dT} = (4.16 \pm 23\%) 10^{-3} M (\text{J mol}^{-1} \text{K}^{-2}) \quad (19 \text{ polymers}) \quad (31)$$

in which M is the molar mass of the recurrent unit. It is clear, then, that equation (25) deserves distinct preference over equation (31).

These correlations should rather be seen as means for cataloguing the known experimental data than be used in predictions [except, possibly, for equation (25)].

The change in heat capacity in the glass transition range

Experimental data and semi-empirical description. From the foregoing it is clear that the heat capacity differential function $\Delta c_p(T)$ is best defined at T_g , so that it is clearly necessary to establish what is known about $\Delta c_p(T_g)$ for polymers.

Table 1 contains a compilation from various surveys published so far. The reader's attention is drawn to the fact that Gaur and Wunderlich are shortly to publish, in *J. Chem. Phys. Ref. Data*, a series of articles on the heat capacity and derived thermodynamic functions for linear macromolecules (see also Gaur *et al.*⁶⁷⁻⁶⁹ and Wunderlich *et al.*⁵⁴). The data of Kanig⁷⁰ are contained in Wrasidlo⁷¹. Avoidance of duplication has been attempted but was not always possible, as, for instance, Van Krevelen does not state sources, and the data of Wunderlich *et al.*⁵⁰ are themselves often averages⁴⁴. To render possible comparison between polymers, also the averages of T_g and $\Delta c_p(T_g)$ are included; they are, in addition, plotted in Figure 2.

Allowance being made for differences as regards origin and structure of samples, thermal history, crystallinity, measuring equipment, and interpretation, the agreement among the various laboratories is not disappointing. Presumably this may in part be ascribed to the fact that for amorphous polymers T_g and c_p are influenced by these effects only in the glass transition range itself, and not or hardly so, in principle, below and above this range (see, for example, Richardson *et al.*⁷²). For this reason the spread in $\Delta c_p(T_g)$ would be caused mainly by the differences in T_g , as the $\Delta c_p(T)$ function obtained by extrapolation from $c_{p_l}(T)$ and $c_{p_s}(T)$ should be the least sensitive to the effects

mentioned. In view of the fact that according to the experimental data now available the $\Delta c_p(T)$ determined in this way decreases as T increases (see later), it is reasonable to expect that a lower T_g will be accompanied by a higher $\Delta c_p(T_g)$. This is not confirmed by the data of Table 1, however, which will be due to the previously mentioned effects.

Also for other reasons it is advisable to consider the values in the Table with some caution and, if need be, consult the original publications. To give an example: where the Table gives values for polybutadiene it does not state whether what is referred to is the *cis* or the *trans* isomer, or a mixture of the two, which makes a significant difference⁴⁴.

Enough experimental material is available (in a literature search more than 400 publications containing data on c_p 's of polymers have been published since the review by Wunderlich *et al.*⁴⁴, i.e. from 1968) to allow the list to be extended and refined; however, this is outside the scope of this article.

Several authors have derived semi-empirical relations for $\Delta c_p(T_g)$. Probably the best known is 'the rule of constant Δc_p per bead', by Wunderlich⁷³. Collected data on 40 glass-forming substances, including various polymers, showed that:

$$\Delta c_p(T_g) = b \cdot (11.3 \pm 2.1) \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (32)$$

and, correspondingly, for 14 polymers⁵⁰:

$$\Delta c_p(T_g) = b \cdot 10.9 \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (33)$$

In these expressions b is the number of 'beads', i.e. 'the smallest molecular units whose movements may change the hole equilibrium'. It is seen that each bead contributes $\approx 11 \text{ J mol}^{-1} \text{ K}^{-1}$ towards $\Delta c_p(T_g)$. The major problem encountered in application is, of course, the determination of the number of beads. Table 1 shows that such groups in the main chain as $-\text{CH}_2-$, $-\text{CH}(\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{CH}=\text{CH}(\text{CH}_3)-$, *p*-phenylene, and groups in side-chains, such as phenyl in polystyrene, $-\text{COO}-$ in acrylates, should in general be regarded as beads. If this is done, agreement with the experimental values is good. For polyphenylphenylene ether and the fluorine-containing polymers with a phenyl side group the situation is less clear. As regards $\Delta c_p(T_g)$ values, they cannot be compared with the polystyrenes, although each of the numbers 29, 32, 33, 34, 35, 38 and 39 from Table 1 has its counterpart among the hydrocarbon polymers with the same $\Delta c_p(T_g)$ values, (but with different T_g values) so that there H and F are interchangeable. Also other authors^{46,74-78} noted deviations from the 'rule of constant Δc_p per bead'.

An interesting discussion is given by Brown *et al.*⁷⁹ for (not strictly proven) ring structures, such as no.37 in Table 1. With analogous polymers [not included in Table 1 because of the T_g and/or $\Delta c_p(T_g)$ values being less reliable] extension of one side of the ring, e.g. $-\text{[CF}_2\text{]}_2-$, $-\text{[CF}_2\text{]}_3-$, $-\text{CF}_2\text{CFCLCF}_2-$ and $-\text{[CF}_2\text{]}_4-$ instead of $-\text{CF}_2-$, leads to an increase in $\Delta c_p(T_g)$. The authors ascribe this to a gradual transition from one bead (the ring) to several beads (determined by the non-extended part of the ring), owing to a reduction of the restraint brought about by the extended part.

For 17 polymers [for which, however, not all $\Delta c_p(T_g)$ values were determined experimentally, some being

arrived at by estimating the number of beads] Becker^{80,81} finds a relation analogous to that of Wunderlich:

$$\Delta c_p(T_g) = z \cdot (8.04 \pm 0.89) \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (34)$$

in which z is the number of vibrating units ('selbständig schwingungsfähige Einheiten'). In part, these units are smaller than the beads; again, they are not exactly definable, so that assignment of z is empirical. For instance, groups such as $-\text{CH}_2-$, $-\text{CH}(\text{CH}_3)-$, $-\text{CH}=\text{O}-$, $-\text{CO}-$ en $-\text{COO}-$ (in the acrylates) have a z value of 1; $-\text{C}(\text{CH}_3)_2-$, $-\text{CHN}-$, the phenyl group in polystyrene have a z value of 2, and *p*-phenylene a z of 3-4. In general, the groups contained in side-chains are reckoned to give normal contributions, but with long side-chains, such as occur in polybutylacrylate and polybutylmethacrylate, this is no longer possible. In the case of polyoxides problems arise through the values calculated being too low. Also for the polymers containing fluorine the value of z will have to be adjusted, in view of the deviations mentioned previously.

Becker *et al.*⁸² and Becker⁸³ use z also in calculating T_g from group contributions:

$$T_g = \frac{\sum x_i z_i T_{gi}}{\sum x_i z_i} \quad (35)$$

where x_i is the number of structural elements i in the recurrent unit, and $z_i (z = \sum x_i z_i)$ the weighting factor for a structural element with a contribution T_{gi} . For the structural elements pure additivity is assumed. z_i is identified with the number of vibration units in the structural element, i , and for a number of structural elements z_i and T_{gi} are given. Analogous incremental methods are found in Weyland *et al.*⁸⁴ and Van Krevelen^{55,56}.

Hayes⁸⁵ relates the cohesive energy E_{coh} to T_g through an empirical number n determined by the structure of the polymer:

$$E_{\text{coh}} = n \cdot \frac{R}{2} \cdot T_g + c \quad (36)$$

with c being equal to $105n \text{ J mol}^{-1}$ for the polymers investigated by him, but being in general dependent of molecular mass and the experimental time scale (see also Kaelbe⁸⁶). R is the universal gas constant. For n the author draws up a number of empirical rules based on the capability of rotation for groups. He arrives, for example, at $n=8$ for $-\text{CH}_2-$, $-\text{CHCN}-$, $-\text{CH}=\text{CH}-$; $n=11$ for $-\text{CH}(\text{CH}_3)-$, $-\text{CH}=\text{C}(\text{CH}_3)-$; $n=15$ for the phenyl group in polystyrene, etc. Values of n as explicitly stated by Hayes⁸⁵ and Peiffer⁸⁷ are included in Table 1. Hayes also gives increment values for groups in respect of E_{coh} , so that:

$$E_{\text{coh}} = \sum_i E_{\text{coh } i} \text{ and } n = \sum_i n_i \quad (37)$$

For 9 polymers Peiffer⁸⁷ finds the following relation:

$$\Delta c_p(T_g) = 1.26n \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (38)$$

From Table 1 it follows that:

$$\Delta c_p(T_g) = 10.0 + 0.89n \pm 21\% \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (\text{for 18 polymers}) \quad (39)$$

Table 1 $\Delta C_p(T_g)$ and some other relevant quantities for amorphous and semi-crystalline polymers

No.	Polymer	Abbreviation	M	Ref.	T_g (K)	$\Delta C_p(T_g)$		b (From refs. 44 and 50)	n (From refs. 55 and 56 ^c)	z (From refs. 80 and 81)	E_{coh}	
						($J g^{-1} K^{-1}$)	($J mol^{-1} K^{-1}$)				($J mol^{-1}$)	($J mol^{-1}$)
I. P-olefins												
1	p-ethylene	PE	14					8	1	1	4200	2900
2	p-propylene	PP	42	a	257	0.512	21.5	22	2	2	14 300	13 800
				90	253	0.549	23.0					
				b	259	0.504	21.2					
				50	259	0.482	20.3					
3	p-butene-1	PB 1	56	a	—	—	—	—	—	—	18 400	—
				90	249	0.371	20.7					
				c	239	0.698	39.2					
				c	239	0.526	29.5					
4	p-pentene-1	PP 1	70	90	244	0.387	27.1	27			22 600	—
5	p-isobutylene	PIB	56	50 ^c	198	0.403	22.6	22	2	3	17 900	19 900
6	p-butadiene	PBD	54	90	190	0.620	33.5	33		4	18 600	20 900
7	p-isoprene	PIP	68	a	201	0.469	31.9	33	3	4	22 900	26 000
				110	200	0.449	30.5					
				90	210	0.502	34.2			27		
				50	196	0.460	31.3					
				c	196	0.464	31.6					
8	p-(4-me-1-pentene)	PMP	84	50	305	0.401	33.7	—	3	5	28 500	22 100
II. P-styrenes												
9	p-styrene	PS	104	a	369	0.321	33.4	32	3	4	35 600	30 600
				71	370	0.264	27.4					
				71	368	0.256	26.6					
				71	375	0.377	39.2					
				45	370	0.322	33.5					
				45	375	0.346	36.0					
				50	365	0.330	34.3					
				f	361	0.309	32.1					
				c	365	0.362	37.7					
10	p-(α -methyl styrene)	P α MS	118	90	450	0.318	37.5	38		4	39 300	44 800
11	p-(p-chlorostyrene)	PpCS	138.5	71	383	0.226	31.3	32		4	42 700	35 800
12	p-(p-bromostyrene)	PpBrS	183	71	391	0.201	36.7	38		4	45 300	38 900
III. P-vinylhalide												
13	p-vinylchloride	PVC	62.5	a	350	0.290	18.1	16	2	2	17 600	18 600
				118	353	0.285	17.8					
				110	350	0.294	18.4					
				71	343	0.277	17.3					
				71	352	0.297	18.6					
				50	350	0.297	18.6					

cont.

Table 1 - cont. . . .

No.	Polymer	Abbreviation	M	Ref.	T _g (K)	ΔC _p (T _g)		b (From refs. 44 and 50)	n (From refs. 55 and 56 ^c)	z (From refs. 80 and 81)	E _{coh}	
						(J g ⁻¹ K ⁻¹)	(J mol ⁻¹ K ⁻¹)				(J mol ⁻¹)	(J mol ⁻¹)
IV. P-esters												
14	p-vinylacetate	PVAc	86	a	303	0.447	38.5	41	31	4	27 700	26 900
				118	304	0.502	43.2					
				118	304	0.41	35.3					
				71	299	0.419	36.1					
				105	296	0.419	36.0					
				50	312	0.486	41.8					
15	p-(methyl acrylate)	PMA	86	c	281	0.491	42.2	41	31	4	27 700	
16	p-(ethyl acrylate)	PEA	100	c	251	0.426	42.6	41	39	5	31 900	
17	p-(butyl acrylate)	PBA	128	c	221	0.322	41.3	41	55	7	40 200	
18	p-(t-butyl acrylate)	PtBA	128	71	304	0.323	41.3	41		6	41 400	38 200
19	p-(methyl methacrylate) isotactic atactic	PMMA	100	113 ^d	318	0.40	40	-	34	4	31 300	32 700
				a	378	0.307	30.7					
				71	375	0.297	29.7					
				71	378	0.317	31.7					
				71	378	0.293	29.3					
				45	376	0.301	30.2					
				45	380	0.293	29.3					
				50	378	0.342	34.2					
				43	378	0.297	29.7					
				d	378	0.32	32					
				c	378	0.306	30.6					
				d	392	0.3 (?)	30 (?)					
20	syndiotactic p-(butyl methacrylate)	PBMA	142	c	286	0.198	28.2			7	43 900	
21	p-(ethylene terephthalate)	PET	192	a	338	0.337	64.8	64	45	9	60 300	49 800
				71	337	0.338	64.9					
				50	340	0.336	64.6					
V. Aromatic polymers												
22	p-(phenylene ether)	PPO	92	71	363	0.255	23.5	24			31 400	29 600
23	p-(dimethyl phenylene ether)	PDMPO	120	50	480	0.240	28.9	30			39 000	49 200
24	p-(phenyl phenylene ether)	PPPO	244	71	493	0.283	69.1	72			21 700	124 000
25	p-(biphenol-A carbonate)	PC-A	254	a	415	0.245	62.4	70	42		83 700	105 000
				50	415	0.250	63.6					
				c	415	0.240	60.9					
VI. P-oxides												
26	p-oxyethylene	POE	44	c	226	0.948	41.8	40			14 700	
27	p-oxypropylene	POP	58	a	198	0.600	34.9	40	25	3	20 500	
				50	198	0.551	32.0					
				c	198	0.649	37.7					
28	p-oxybutane	POB	72	a	187	0.794	56.5	56		5	23 100	
				50	187	0.79	55.4					
				c	187	0.797	57.5					

cont.

Table 1 — cont. . . .

No.	Polymer	Abbreviation	M	Ref.	T_g (K)	ΔC_p (T_g)		b (From refs. 44 and 50) ($J mol^{-1} K^{-1} g^{-1}$)	n (From refs. 85 and 87)	z (From refs. 80 and 81)	E_{coh}	
						($J g^{-1} K^{-1}$)	($J mol^{-1} K^{-1}$)				($J mol^{-1}$)	($J mol^{-1}$)
VII. Fluorine polymers												
29	$-CF_2CF(CF_3)-$		150	e	425	0.156	23.4	22	21		10 100 ⁱ	
30	$-CF_2CF(C_6F_5)-$		248	e	467	0.084	20.9	23			33 300 ⁱ	
31	$-CF_2CF(C_6H_5)-$		158	e	475	0.164	26.0	23			10 900 ⁱ	
32	$-CH_2CF(CF_3)-$		114	e	315	0.206	23.4	22	21		12 400	
33	$-CH_2CH(CF_3)-$		96	e	300	0.218	20.9	22			15 800	
34	$-CH_2CH(C_2F_5)-$		146	e	314	0.120	17.6				19 200	
35	$-CH_2CH(C_3F_7)-$		196	e	331	0.137	26.8	27				
36	$-CH_2CH(C_6F_5)-$		194	e	378	0.121	23.4	23				
37	$-CF_2CF-\begin{matrix} \diagup CF \\ \diagdown [CF_2]_2 \end{matrix}-$		262	e	390	0.086	22.6	24			11 900	
38	$-CFCl-$		66	e	350	0.120	8.0	8				
39	$-CF_2CF=CFCF(CF_3)-$		212	e	270	0.150	31.8	32				
VIII. Miscellaneous												
40	p-(dimethyl siloxane)	PDS	74	113	150	0.42	31.1	32	16	3	14 600 ^j	14 200
41	p-acrylonitrile	PAN	53	71	360	0.474	25.1	25	16	3	29 600	21 500

^a Averages of the values of T_g and ΔC_p (T_g) stated

^b Bares *et al.*⁴⁵ based on Passaglia *et al.*¹⁸⁰; Passaglia *et al.* themselves give ΔC_p (259) = 0.478

^c Van Krevelen^{55,56}, T_g from ref. 50 or from Table V, Van Krevelen⁵⁶, for PB and POE averages for T_g from that Table V; T_g for PBMA from Hoffman *et al.*¹⁸¹

^d O'Reilly *et al.*⁴⁹, from Figure 8. C_p^s (T_g) is practically independent of tacticity. The values for syndiotactic PMMA are uncertain

^e Selection from Table I by Brown *et al.*⁷⁹; T_g is defined as the starting point of the increase in c_p ; ΔC_p (T_g) given here holds for a mol of recurrent units, in contrast with the data in Table 179

^f Karasz *et al.*³⁵. Average of ΔC_p (360) = 0.304 (amorphous, isotactic) and ΔC_p (362) = 0.314 (amorphous, atactic)

^g From group contributions, Table 2

^h Van Krevelen⁵⁶, Tables 7.3 and VI1, E_{coh} (298 K)

ⁱ Calculated assuming $E_{coh} = -1110$ for $-C-$. Not included in correlative calculation

^j Average of 11723 and 17438

with a correlation coefficient of 0.81. It is clear that this relation is not very useful.

Peiffer relates n to the degrees of rotational freedom, and concludes that 'the smallest unit capable of independent torsional oscillation constitutes a bead'. Like Weyland *et al.*⁸⁴, he also finds a correlation between the increments of T_g and E_{coh} . Becker⁸⁰ finds a relation similar to that arrived at by Hayes:

$$E_{\text{coh}} = z(23.6 \pm 1.7)T_g \text{ (J mol}^{-1}\text{)} \quad (40)$$

Further analogous relations are given by Bondi⁸⁸ and Kaelbe⁸⁶.

From equations (34) and (40) an interesting relation follows⁸¹:

$$\Delta c_p(T_g) = (0.345 \pm 0.031) \frac{E_{\text{coh}}}{T_g} \text{ (J mol}^{-1}\text{ K}^{-1}\text{)} \quad (41)$$

Comparison with the relation given by Simha *et al.*⁸⁹:

$$\Delta c_p(T_g) = 105 \frac{M}{T_g} \text{ (J mol}^{-1}\text{ K}^{-1}\text{)} \\ \text{(polymers from Wunderlich}^{73}\text{)} \quad (42)$$

where M is the molar mass of the recurrent unit, or with the relation of Boyer⁹⁰ (see also *Figure 2*):

$$\Delta c_p(T_g) = \left(0.17 + \frac{63}{T_g}\right) M \text{ (J mol}^{-1}\text{ K}^{-1}\text{)} \\ \text{(30 values for 20 polymers and 6 copolymers),} \quad (43)$$

suggests the existence of a relation between E_{coh} and M , which, however, as Becker shows, is not very significant. The establishment of such a relation is, therefore, to be dissuaded, as actually equations (42) and (43) are not very useful. This is seen from the data in *Table 1* (excluding those for polyethylene and polybutene-1):

$$\Delta c_p(T_g) = \left(-0.04 + \frac{111}{T_g}\right) M \pm 42\% \text{ (J mol}^{-1}\text{ K}^{-1}\text{)} \\ \text{(41 values for 39 polymers)} \quad (44)$$

$$\simeq 111 \frac{M}{T_g} \quad (45)$$

Equation (41) deserves further study, although the fact that for polymers E_{coh} is not an experimental quantity is a disadvantage. *Table 1* includes E_{coh} values taken from two different sources so as to make allowance for a possible influence of variations in E_{coh} . One of these sources is Van Krevelen⁵⁶, Tables 7.3 and VII (group contributions), the other Wrasidlo⁷¹, whose figures are based on a method by Bunn⁹¹. As may be expected, the E_{coh} values from these two data sets differ widely, but in spite of this a 1st degree polynomial reveals hardly any difference. Van Krevelen's data set yields:

$$\Delta c_p(T_g) = 9.1 + 0.256 \frac{E_{\text{coh}}}{T_g} \pm 22\% \text{ (J mol}^{-1}\text{ K}^{-1}\text{)} \\ \text{(34 values for 32 polymers)} \quad (46)$$

with a correlation coefficient of 0.79. One may speculate that the deviations are caused in the first place by uncertainties in E_{coh} . In view of the low significance, it must be concluded that equation (46) is not particularly useful either. For the sake of completeness it was investigated whether a relation analogous to equation (46), with M instead of E_{coh} , could bring an improvement on equation (44). This proved not to be the case, there being no correlation whatever.

As long as the contributions to $\Delta c_p(T_g)$ of various structural units have to be determined empirically, as is the case in each of the concepts mentioned, it seems useful to establish whether use can be made of an incremental method for cataloguing these contributions. As such a method can in some cases be applied in different ways^{56,84} with little difference in result, a very simple method has been chosen here, i.e. simple additivity of group contributions according to:

$$\Delta c_p(T_g) = \sum_i \Delta c_p(T_g)_i \quad (47)$$

attempting to maintain if at all possible, the same contribution throughout for the same structural unit, regardless of the molecular surroundings.


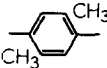
An initial attempt at cataloguing the polymers of *Table 1* is shown in *Table 2*. That it is not always possible to maintain the same contribution is evident, for example, in the case of the $-\text{O}-$ group in the polyesters, the aromatic polymers and the polyoxides. These differences are considered to be physically realistic, and are an indication that the simple additivity principle does not always apply. The contribution from $-\text{CH}_2-$ appears relatively good, if the various polymers are compared with simple recurrent units. This is indicated also by the difference between polyoxybutane and polyoxyethylene. However, it does not seem wise to draw conclusions from this with regard to polyethylene, or to make an estimate of T_g , for example in combination with E_{coh} (see also later). In the case of the polyoxides it proved impossible to obtain a relevant further subdivision. Comparison of the group contributions towards $\Delta c_p(T_g)$ with the n values given by Hayes⁸⁵ and the z values of Becker shows several correspondences. The $11 \text{ J mol}^{-1} \text{ K}^{-1}$ contributed by a bead to $\Delta c_p(T_g)$ according to Wunderlich could be viewed as an overall average. This is immediately apparent for combinations of groups with contributions of 8 and $14 \text{ J mol}^{-1} \text{ K}^{-1}$.

In view of the present availability of a large amount of experimental data on $\Delta c_p(T_g)$ (see, for example, Wrasidlo⁷⁵, Gaur *et al.*^{46,67} and Levita *et al.*⁹²) it is desirable to extend this catalogue of group contributions to $\Delta c_p(T_g)$ by including more polymers.

It is noteworthy that the values given in *Table 2* serve for cataloguing the polymers in *Table 1* but that this cataloguing is not unequivocal. Further, the data presented by Levita *et al.*⁹² show that there is no necessity for using the group contributions to make predictions about polymers not appearing in *Table 1*.

It is, further, interesting to know how far the approximations for semicrystalline polymers discussed previously correspond, numerically, with experimental data as regards $\Delta c_p(T_g)$. This has been established for a number of semi-crystalline polymers for which T_m and $\Delta h(T_m)$ are known with reasonable accuracy^{9,11}. In spite of the

Table 2 Group contributions to $\Delta c_p(T_g)$ in $\text{J mol}^{-1} \text{K}^{-1}$ according to $\Delta c_p(T_g) = \sum_i \Delta c_{p,i}(T_g)$; based on Table 1

Group	$\Delta c_p(T_g)_i$	Group	$\Delta c_p(T_g)_i$
-CH ₂ -	8		16
-CF ₂ -	8		
-CHF-	8		
-CHCl-	8		
-CFCl-	8		
$\begin{array}{c} \\ \text{[CH}_2\text{]}_2 \\ \end{array} \begin{array}{c} \\ \text{[CF}_2\text{]}_2 \\ \end{array}$	5		22
-CH(CH ₃)-	14	$\begin{array}{c} \text{CF}_2 \\ / \quad \backslash \\ -\text{CF}- \\ \quad \\ \text{[CF}_2\text{]}_2 \end{array}$	16
-CH(CF ₃)-	14		
-CF(CF ₃)-	14		
-C(CH ₃) ₂ -	14	-CH(COO[CH ₂] _{0,1,3} CH ₃)-	33
-Si(CH ₃) ₂ -	24	-CH(OCOCH ₃)-	33
-CH(CN)-	17	-CH(COOC(CH ₃) ₃)-	33
-CH=CH-	17	-CH(C ₆ H ₅)-	24
-CF=CF-	10	-CH(C ₆ H ₄ Cl)-	24
-CH=C(CH ₃)-	17	phenyl in	24
		phenyl-phenylene ether	
		-CH(C ₆ H ₄ Br)-	30
-O-	8	-C(CH ₃)(C ₆ H ₅)-	30
-CO-	8	-CH(C ₆ F ₅)-	15
-CH ₂ OCH ₂ -	40	-CF(C ₆ H ₅)-	15
-CH ₂ OCH(CH ₃)-	40	-CF(C ₆ F ₅)-	15

scarcity of data, it seems justifiable to conclude that the SDM approximation in general results in relatively low values, and that the other approximations may lead to non-negligible deviations. Of course, the CP 0 approximation cannot be used in the case of high supercooling, because the necessary increase at T_g is lacking.

Theory. Ever since c_p measurements first revealed the characteristics of the glass transition (selenium⁹³, natural rubber⁹⁴ and polyisobutylene⁹⁵), notably in combination with data on the thermal expansion coefficient, the isothermic compressibility, the volume, etc. $\Delta c_p(T_g)$ has been important in theories on the glass transition.

In addition to $c_p(T)$ itself, also the enthalpy calculated from it, $h(T)$, is of importance, not only because it gives information about enthalpy relaxation phenomena at the glass transition (see later), but also because it considerably clarifies and simplifies the interpretation of c_p data⁹⁶⁻⁹⁸. An interesting method for direct determination of $h(T)$, and some remarks on the use of integrated $c_p(T)$ curves have been presented by Filisko *et al.*⁹⁹ and Golba¹⁰⁰.

Also the cause of a change in c_p at T_g have for an appreciable time been a subject of study. Wunderlich⁷³ (see also Bares *et al.*⁴⁵) used the hole theory for liquids used by Hirai and Eyring^{101,102} (see also Smith¹⁰³) assuming $\Delta c_p(T_g)$ to be due to a change in hole concentration. An estimate of $\Delta c_p(T_g)$ by means of this theory showed reasonable agreement ($12.4 \text{ J mol}^{-1} \text{K}^{-1}$) with the experimental value per bead. It is noteworthy that Abdinov *et al.*¹⁰⁴ calculated a contribution to $\Delta c_p(T_g)$ of $15.5 \text{ J mol}^{-1} \text{K}^{-1}$ per bead as a result of changes in the capability of rotation in the glass transition range.

Other theories based on the hole theory are those by Nose¹⁰⁵ and Ishinabe¹⁰⁶. As causes of Δc_p , Nose distinguishes the changes in hole concentration and chain conformation, associated with intersegmental ($\Delta c_p^{\text{inter}}$) and intrasegmental ($\Delta c_p^{\text{intra}}$) interactions, respectively. Under certain conditions also in this case a constant $\Delta c_p^{\text{inter}}$ is arrived at. In a number of publications linking

up with this, the contributions were determined for polystyrene^{107,108} and poly(α -methylstyrene)¹⁰⁹.

Various authors have since indicated other causes for $\Delta c_p(T_g)$. Goldstein^{110,111}, for example, mentions changes in the 'lattice vibrational frequencies, anharmonicity, and the number of molecular groups participating in secondary relaxations'. With three of the polymers evaluated by him these factors contribute to between 21 and 85% towards $\Delta c_p(T_g)$, the balance coming from 'configurational' changes. Also Simha¹¹² concludes that the hole function, h , defined by him does not describe Δc_p fully. The non-applicability of hole theories to experiments carried out at constant volume led O'Reilly¹¹³ to hypothesize that for Δc_p the change in the conformational equilibrium (the number of *trans* and *gauche* states in the polymer backbone) has prime importance. He concludes that there is a certain correspondence between the number of conformational states and the number of beads as determined by Wunderlich and Jones. Interesting in this connection is a publication by Wunderlich¹¹⁴ in which he explains the results of c_p measurements on polyethylene at between 120 and 250 K from a gradual change in the *trans/gauche* equilibrium and a change in the hole equilibrium at 237 K.

DiMarzio *et al.*¹¹⁵ present an extension of the Gibbs-DiMarzio configurational entropy theory^{116,117}, taking into account not only the change in the number of flexible bonds and the number of holes, but also lattice vibrations. These causes contribute $\approx 6 \text{ J (flexible unit)}^{-1} \text{K}^{-1}$, $2 \text{ J (bead)}^{-1} \text{K}^{-1}$, and $1.25 \text{ J (bead)}^{-1} \text{K}^{-1}$, respectively, to the value of $\Delta c_p(T_g)$. The bead is here defined as the ratio of the volume of one monomer unit to the volume of one CH₂ unit; it should not be confused with Wunderlich's beads. The determination of the number of flexes per monomer unit is not straightforward, but is made via an estimate of the number of bonds a rotation around which can change the shape of the chain. This shows a certain correspondence with the determination of n according to Hayes.

Roe *et al.*^{118,119} and Tanaka¹²⁰ separate $\Delta c_p(T_g)$ into contributions from the free volume and the chain conformation, the balance being ascribed to changes in vibrational frequencies, in the mean nearest neighbour coordination number, and in other modes of thermal excitation.

Finally, the theories describing the changes in heat capacity and enthalpy occurring within the glass transition range are also of importance. The first was by Volkenshtein *et al.*¹²¹, while more recent examples can be found in Wolpert *et al.*¹²², Marshall *et al.*¹²³, Sasabe *et al.*¹²⁴, Choy *et al.*¹²⁵, Robertson³⁸, O'Reilly¹²⁶, and Kovacs¹²⁷, and in the references given by these authors.

The heat capacity differential function

If from the $c_p(T)$ and $c_p(T)$ functions, often obtained by extrapolation, the heat capacity differential functions between T_g and T_m are determined, these decrease with increasing temperature (Figure 2) and are positive so that equation (9) is applicable.

In this connection it is noteworthy that owing to use being made of extrapolation from $c_p(T_g)$, the value of $\Delta c_p(T)$ is uncertain especially for $T_g \ll T \leq T_m$, in which range it may also be negative in which case equation (10) is applicable. Examples of $\Delta c_p(T_m) < 0$ are to be found in Kelley¹²⁸ and Landolt-Börnstein¹²⁹ for non-polymers, and later for polyethylene. For metals, $\Delta c_p(T_m) \geq 0$ [Ubbelohde^{130,131} and Gorecki¹³²; Ubbelohde's¹³³ values are quoted wrongly in the latter reference, however: the quotation gives $c_p(T_m)/T_m \cdot 10^3$ instead of $c_p(T_m)$]. With reference to all these data it is noteworthy that pre-melting effects may have been significant. However, for non-polymers, in general, $\Delta c_p(T_m) > 0$ (see also Janaf¹³⁴).

As regards $\Delta c_p(T)$ it is of interest that according to the Gibbs-DiMarzio theory its value decreases as the temperature increases²⁶. Similarly, the extended Gibbs-DiMarzio theory¹¹⁵ gives a qualitative indication of c_p showing a weaker slope just above T_g than below. Calculations by Gutzow^{32,33} based on a lattice hole model indicate, in dependence on the type of the glass-forming substance, a decrease, constancy, or an increase of $\Delta c_p(T)$ with increasing T . The increase has, indeed, been reported for some non-polymers, although only in exceptional cases^{19,33,135}.

Based on Van Krevelen^{55,56}, the following relation holds, in analogy to equations (30) and (31):

$$\frac{d \Delta c_p(T)}{dT} = -(1.87 \pm 30\%) 10^{-3} M \text{ (J mol}^{-1} \text{ K}^{-2})$$

(14 polymers) (48)

For lack of a better expedient, the relation could be used again in combination with c_p values at 200, 298 K, or other more specific polymer temperatures, such as T_g and T_m . It is obvious to use the value at T_g for the $\Delta c_p(T)$ function:

$$\Delta c_p(T) = \Delta c_p(T_g) - 1.87 \cdot 10^{-3} M(T - T_g) \text{ J mol}^{-1} \text{ K}^{-1}$$

(49)

It is useful for the change in $\Delta c_p(T)$, which, as is clear, for most polymers is derived by extrapolation from data on melt and glass, whether or not extended with further experimental data, and compared with the $\Delta c_p(T)$ functions which implicitly are at the base of the approxi-

mations discussed previously. This is carried out later for polyethylene.

THE HEAT CAPACITY AND RELATED THERMODYNAMIC FUNCTIONS FOR POLYETHYLENE

Polyethylene has been the subject of frequent studies, for fundamental reasons as well as because of its importance in industry.

For linear polyethylene (LPE) and (short-chain) branched polyethylene (BPE) c_p measurements are available which, together, cover the temperature range from 0 to 630 K. The crystallinity of the samples concerned varies from $\approx 25\%$ to virtually 100%. The latter value, almost unique for polymers, can be attained by means of special techniques such as high-pressure crystallization⁵⁷. Conversely, it is almost impossible to prepare an amorphous polyethylene, although recently some progress has been made^{136,137}. Consequently, the heat capacity for the reference state of 0% crystallinity has not been determined experimentally.

Although it may be assumed that the two-phase model that is at the base of the crystallinity concept is a simplification of the actual situation, it may be asked how far it is possible by means of this parameter to give a valid description of the heat capacity, and if, in addition to an extrapolation to 100% crystallinity, also a meaningful extrapolation to 0% crystallinity can be made. Wunderlich^{138,139}, Wunderlich *et al.*⁴⁴, and Chang¹⁴⁰ carried out such extrapolations for a wide temperature range. The method has been used also for other semi-crystalline polymers¹⁴¹.

In the range from 0 K to the melting point at ≈ 415 –420 K, where a relation between crystallinity and c_p might be expected, experiments with polyethylene show that only between ≈ 80 and ≈ 120 K is a variation of c_p with crystallinity virtually non-existent.

Below 80 K a lower crystallinity value is found to correspond to a higher c_p (see, e.g., Tucker *et al.*¹⁴² for $T < 30$ K; Chang¹⁴⁰).

For the range between room temperature and T_m hardly any quantitative c_p data have been published. This is the range of interest in the majority of current studies in the field of calorimetry, and where c_p and degree of crystallinity are subject to sharp changes.

For the remaining range, ≥ 120 K, there has been controversy, especially with respect to the position of the glass transition of polyethylene. A factor also significant here is that until recently hardly any c_p data on polyethylenes of low crystallinity were available. With respect to the question of the glass transition two aspects are important: is it possible to conclude from the c_p data available that there is a calorimetrically observable glass transition, and, if so, what is the relation between this transition and the transitions which can be determined by means of other techniques? Here, only a brief survey of relevant data on the former aspect is given, partly because it is believed that the experimental data now available on the subject are decidedly insufficient as a basis for a full discussion. The interested reader can obtain further information from specific literature and the references mentioned therein^{143–145}.

Historical survey

Using c_p data for five LPEs and two BPEs, Wunderlich¹³⁸ carried out extrapolations of c_p to 0 and 100% crystallinity. In the range from 120 to 250 K these extrapolations were rectilinear (see also Wunderlich¹³⁹). The non-rectilinear behaviour of the BPEs at >250 K was attributed to premelting¹¹⁴. The resulting c_p curve for amorphous polyethylene at first changes in a rectilinear relation to T (from 120 to 190 K), after which there is a rapid increase until, from 250 K, values for the LPEs are attained that correspond to those obtained by extrapolation from the melt data. The whole range, covering 130 K, was interpreted^{114,146}, to represent an extensive glass transition range in which, when the temperature decreases, at ≈ 237 K the majority of the holes are frozen in, after which a slower freezing-in process affects the *gauche/trans* ratio and the rest of the holes. The *gauche/trans* ratio is not in equilibrium, for calculation predicts an increase in c_{p_a} in relation to c_{p_c} at decreasing temperature, which is contrary to the results obtained in the extrapolations. The failure to attain equilibrium would then be due to hindrance caused by the holes freezing in.

However, in his 1970 review, Wunderlich⁴⁴ could not but conclude, on the basis of a slightly more extensive set of data, that between 120 and 150 K the two c_p values do not differ by more than $\pm 2\%$, whilst between 160 and 210 K c_{p_a} is not uniformly higher than c_{p_c} . In the latter range c_{p_a} and c_{p_c} are, therefore, taken to be equal, and are determined from three LPEs.

Since Wunderlich's review there have been various publications which for linear polyethylenes of low crystalline content report a stepwise increase of c_p at ≈ 145 – 150 K^{147–153}, the step being greater if the crystallinity is lower and/or the molar mass is larger. The highest values^{148,153} are 1.1 – 1.8 J mol⁻¹ K⁻¹. Also the experiments by Chang *et al.*^{140,143,154,155} show an increasing difference between c_{p_a} and c_{p_c} from ≈ 100 K, both for linear and for branched polyethylenes.

The finding that in the area considered, samples showing a difference in crystallinity also have different c_p values leads to the conclusion that there are similarities with the results obtained by Wunderlich¹³⁸, except that in this case LPE is being considered.

In view of this, the following experimental calorimetric results are also of importance. In various publications Chang^{96,143,156} reported temperature drifts under adiabatic conditions. Depending on their history, amorphous non-polymers and amorphous selenium show endothermic and exothermic effects as a result of relaxation in the glass transition range leading to a more stable state. For LPE, analogous phenomena were found from ≈ 200 K, with maximum effects in the 240 ± 5 K interval, which were attributed to relaxation behaviour in the amorphous phase. In addition, at ≈ 160 K a weaker exothermic effect was found for quenched samples, which was ascribed to 'some stabilization process such as the relief of strain'. For BPE, analogous experiments resulted in a T_g value of 235 ± 5 K¹⁵⁴.

Sakaguchi *et al.*¹⁴⁴ interpreted these drift phenomena differently. After annealing of LPE at temperatures between 220 and 320 K, c_p measurements showed, especially for low-crystalline samples, the occurrence of an endothermic effect during heating, this effect starting above the annealing temperature and, depending on annealing temperature and time, covering >10 K. The

authors noted the possible occurrence of crystallization and melting processes to account for these effects and for Chang's drift phenomena.

It is clear that, depending on the time scale of the experiment, at >200 K, hence in a range easily attainable in experiments, thermal effects may occur.

Determination of $c_{p_a}(T)$ and $c_{p_c}(T)$ for linear polyethylene

With the new experimental material now available, an adaptation of the data found by Wunderlich *et al.*⁴⁴ has become possible, mainly the data for the range 120–290 K.

As noted previously, Chang¹⁴⁰ gives extrapolated data for 5–360 K. These were determined from Chang's own measurements on three LPEs having crystallinity values of 72, 89 and 96%. It was assumed that at >300 K premelting or melting of small crystallites occurs.

Beatty *et al.*¹⁴⁵ emphasize that LPE and BPE differ in several respects; these authors, also, consistently use an extensive selection of LPE's for an extrapolation to 0 and 100% crystallinity at 120 and 180 K.

Similarly, c_p data on LPE was collected here and are given in Table 3. Unfortunately, the data for an LPE with a degree of crystallinity of 20–25%¹⁵² were not available in tabulated form. In the range indicated in Table 3, data were available for 10 K intervals, except in the case of the values given by Beatty¹⁵⁰, which for the purpose here were fitted with a 10th degree polynomial. As all the other measurements could appropriately be described in a similar way, all measurements were described with the aid of 10th degree polynomials, see Figure 3. The highest curve fluctuates at higher temperatures, but because the fit was good (standard deviation 0.48%, correlation coefficient 0.9998), the values were still used in the calculations. The general shape of this curve differs slightly from that shown in Beatty¹⁵⁰ and Beatty *et al.*¹⁴⁵.

In the present analysis the detailed information available for the very lowest temperature range is neglected; for this information the reader is referred to the original publications and the various surveys^{44,140,157,158}.

Figure 3 shows that from ≈ 120 K the value of c_p in general increases more rapidly as the crystallinity decreases, which is in agreement with Chang¹⁴⁰ and Beatty *et al.*¹⁴⁵. Two measured results deviate markedly. The sample with $w^c = 45\%$ gives systematically lower results from 120 K than would be expected from the values shown by the rest of the samples. The sample of highest crystalline content gives relatively high results up to ≈ 210 K.

To determine $c_{p,c=0\%}$ and $c_{p,c=100\%}$ at every temperature, the data were fitted with a straight line, using the least squares technique. The resulting isothermal $c_p(w^c)$ plots systematically shifted to higher values with temperature increase. When the sample with $w^c = 45\%$ ¹⁴³ was omitted, the fit improved apparently without a qualitative difference. The $c_{p,c=0\%}$ values were shifted to a slightly higher level, whilst the $c_{p,c=100\%}$ values were hardly affected. From 10 to 170 K the standard deviations were almost all <1%, from 180 to 360 K they were between 1% and slightly over 3%. Half the number of curves obtained are shown in Figure 4, along with the points for $w^c = 45\%$, which were not included in the fit.

The deviations in the two measurements referred to previously are unsatisfactory, and should be studied further. Notably, it will be necessary to establish whether,

Table 3 Sources and further data for the extrapolation of $c_p(T)$ to 0 and 100% crystallinity for LPE

Reference	Polymer	Range (K)	d (g cm ⁻³) ^a	w^c (%) ^b	Standard dev. (%)
150	A-C-8X (run 1)	100–160	—	35 ^c	0.18
150	A-C-8X (run 2)	110–290	—	35	0.48
143	AC 8X	10–380	—	45 ^d	0.67
150	A-C-8X (run 3)	90–300	—	55 ^e	0.54
154	SRM 1475	10–360	0.964	72	0.26
182	Rigidex 50	30–310	0.964	78	0.20
182	Marlex 50	30–310	—	79 ^f	0.27
163	Marlex 50	90–380	0.968	81	0.21
142	Marlex 1 ^g	10, 20	0.973	84	—
155	Marlex 50	10–350	0.973	84	0.94
140	SRM 1475	10–360	0.981	89	0.10
140	SRM 1475	10–360	0.993	96	0.84
57	Marlex 50 ^h polymethylene	180–410	0.996	98	0.43

^a In many cases the density values were determined at room temperature

^b The weight percentage of crystalline material, w^c (%) at room temperature, was determined by means of $w^c/100 = (v_a - v)/(v_a - v_c)$, with $v_a = 1.17$ cm³ g⁻¹ and $v_c = 1.00$ cm³ g⁻¹, unless in the publications referred to a value calculated in an analogous way was mentioned

^c This value (from WAXS) was indicated in Beatty *et al.*¹⁴⁵ as 35 ± 5%; in the thesis, values of 35–40% and 35–45% are mentioned

^d Determined by d.s.c.

^e This value (from WAXS) was 55 ± 5% in Beatty *et al.*¹⁴⁵, 50–55% in the thesis

^f From X-ray analysis, 78% from infrared analysis

^g The Marlex 2 sample included in the measurements (often indicated as linear in literature) was disregarded, because ethyl branching had been induced in it so as to impede crystallization (see also Reese *et al.*¹⁸³)

^h Wunderlich combined two measurements, in analogy averages for d and w^c are given

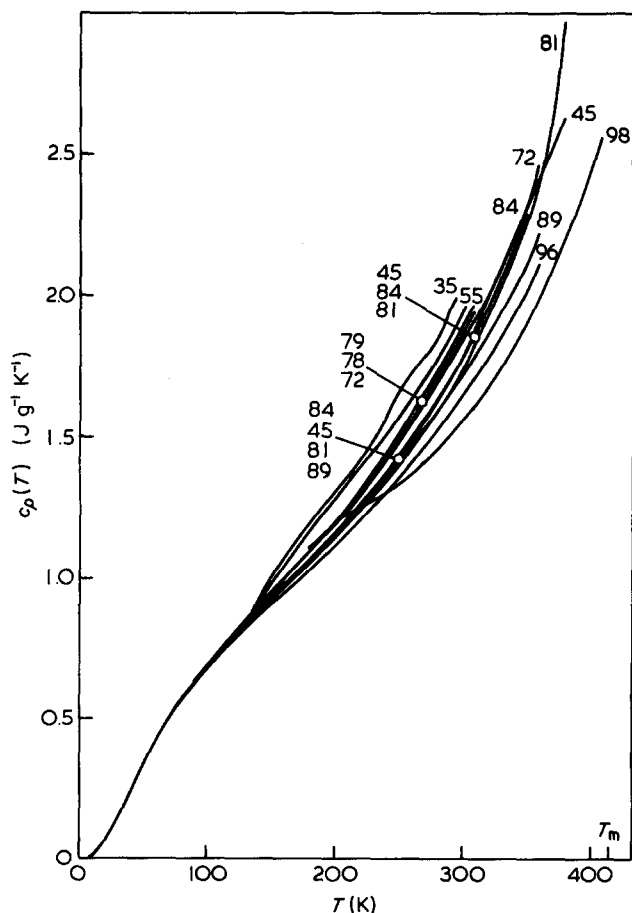


Figure 3 Specific heat capacity $c_p(T)$ relating to the LPE measurements of *Table 3*. The curves give a very good fit for the tabulated literature values referred to. The crystallinities are indicated to distinguish the samples

for example, LPEs showing the same crystallinity but differing in morphology should be considered to be alike, or whether a further refinement is needed. The results

obtained by Dushchenko *et al.*¹⁵³ also seem to indicate this.

The data of Illers¹⁴⁸ at ≈ 120 K are in reasonable agreement with the results here, if the sample with $w^c = 97\%$ is calibrated at the corresponding value from the fit in *Figure 4*. At higher temperatures, however, the increase in $c_p(w^c)$ with decreasing w^c is slightly less pronounced, which is due to $c_p(w^c) - c_p(w^c = 97\%)$ being constant throughout a temperature range of ≈ 70 K, as can be concluded from *Figure 8* in Illers' publication.

As appears from *Figure 4*, the data up to a value of 290 K can be reasonably fitted by means of straight lines, and there are no indications of curvature at low crystallinity, which was reported by Wunderlich^{138,139} and Wunderlich *et al.*⁴⁴. Possibly Wunderlich's finding is due to the inclusion of BPEs, which, as reported, at ≥ 230 K show c_p values increasing above the c_p average for LPE. The uncertainty in w^c in the low-crystallinity samples of *Table 3* may also be significant. According to Wunderlich, a rectilinear fit is no longer possible at > 260 K, and the values of $c_{p,c}$ [obtained from the almost 100% crystalline sample⁵⁷, see *Table 3*] are linked by a straight line with the values obtained by extrapolation from the melt data, which are taken as $c_{p,a}$ values⁴⁴. In *Figure 4* a rectilinear fit has been made at > 290 K also, but some curvature at lower crystallinity, in which range data are lacking, is possible.

The resulting $c_{p,c=0\%}(T)$ and $c_{p,c=100\%}(T)$ values for the 12 LPEs considered here are in very good agreement with what Chang¹⁴⁰ derived for three LPEs.

In analogy with Wunderlich, it is assumed that for $c_{p,a}(T)$ at ≥ 290 K the values obtained from extrapolation from the melt data, plus the melt data for paraffins, can be used. $c_{p,a}(T)$ is calculated with the aid of equation (10) in Wunderlich *et al.*⁴¹:

$$c_{p,a}(T) = 20.0 + 3.368 \cdot 10^{-2} T + 9.91 \cdot 10^{-6} T^2 \quad (\text{J mol}^{-1} \text{K}^{-1}) \quad (50)$$

which is a good fit for the paraffins from 230 K and for the

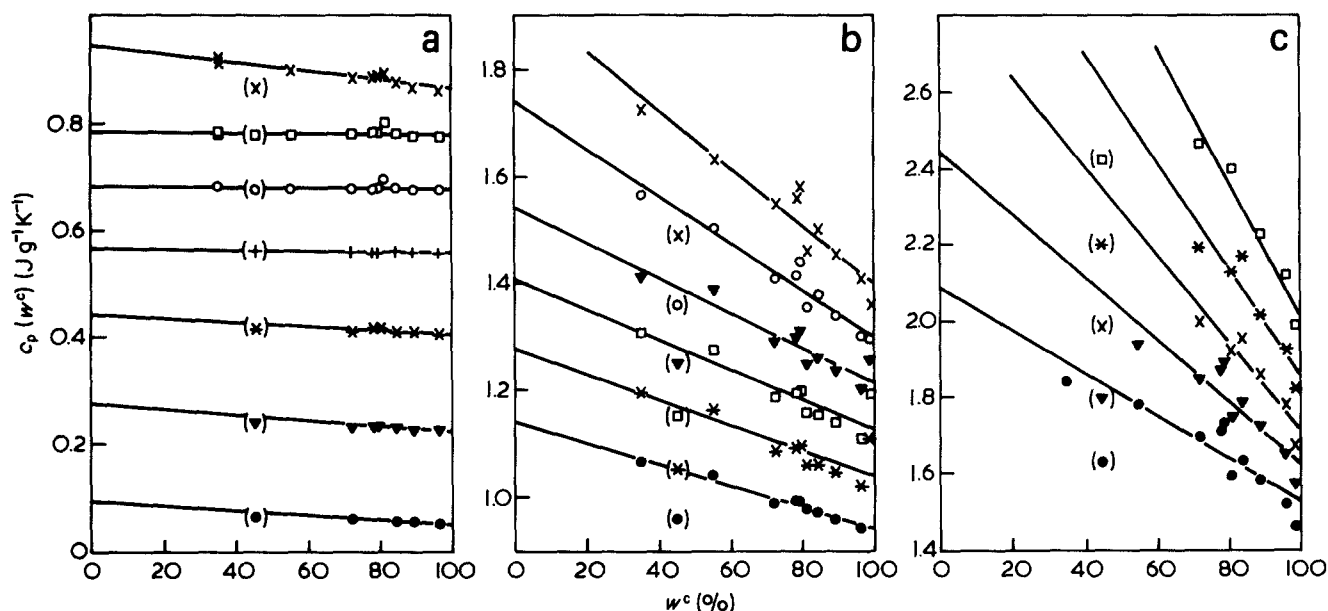


Figure 4 Specific heat capacity $c_p(w^c)$ fitted by means of straight lines at various temperatures, relating to the LPE measurements of Table 3. For the fit, the sample with $w^c=45\%$ was disregarded. (a): ●, 20; ▼, 40; *, 60; +, 80; ○, 100; □, 120; ×, 140 K. (b): ●, 160; *, 180; □, 200; ▼, 220; ○, 240; ×, 260 K. (c): ●, 280; ▼, 300; ×, 320; *, 340; □, 360 K

polyethylene data according to Bares *et al.*⁴³ between 413 and 633 K. Admittedly, this way of calculating $c_{p_a}(T)$ from a combination of $c_{p_c=0}(T)$ and equation (50) is rather artificial. For $c_{p_c}(T)$, from 240 K, the values according to Wunderlich⁵⁷ are used, which are identical with those stated by Wunderlich *et al.*⁴⁴. In this way $c_{p_a}(T)$ values have been determined from 10 to 630 K and $c_{p_c}(T)$ values from 10 to 410 K. Both functions are given in Table 4, and plotted in Figure 5.

From 120 to 290 K there is a gradually increasing difference between $c_{p_a}(T)$ and $c_{p_c}(T)$, which may again be due to the interpretation of Wunderlich¹¹⁴ and Wunderlich *et al.*¹⁴⁶ (see previously). If it is believed that the glass transition occurs at ≈ 145 K¹⁴⁵, it is necessary to establish what significance is to be attached to the discontinuity in $c_{p_a}(T)$ at ≈ 290 K, provided this artificially-induced discontinuity is accepted. If, however, T_g is assumed to be ≈ 240 K^{96,143,156}, and consequently, c_{p_a} could be used below this value instead of c_{p_a} , the difference between c_{p_a} and c_{p_c} appears relatively large, if compared with the T_g situation for low-molecular-mass materials and for other high-molecular-mass materials. A third possibility is that the capabilities of motion related to the various dynamic processes in the range 120–290 K (cf., e.g. Boyer¹⁵⁹) contribute collectively to c_{p_a} , and thus cause an almost continuous and very much extended transition. In this connection it is important that an analogous evaluation in regard of crystallinity should become possible for other polymers, so that it can be ascertained if the situation outlined here is unique for polyethylene or if it is of more general occurrence [a suggestion in favour of the latter possibility is to be found in Wunderlich *et al.*¹⁴⁶].

Without selecting one of the possibilities mentioned it is impossible to determine a $\Delta c_p(T_g)$ value, whilst the value depending on the group contribution mentioned in Table 2, which is ≈ 0.6 J g⁻¹ K⁻¹, can be inserted in Figure 5 in various ways. This certainly holds if use is made of the normally applied extrapolation of the c_{p_a} curve at > 290 K to lower temperatures (indicated by * in Figure 5).

Enthalpy, entropy and free-enthalpy functions for linear polyethylene

Figure 6 shows the $\Delta c_p(T) = c_{p_a}(T) - c_{p_c}(T)$ values, and also the values by Wunderlich *et al.*⁴⁴. The two-step representation between 120 and 290 K should not be given too much significance, in view of the manner of determination of c_{p_a} and c_{p_c} described previously. Numerical values for the enthalpy, entropy and free-enthalpy functions are given in Table 4 and plotted in Figure 7 showing that $s_a(T)$ is always greater than $s_c(T)$.

With respect to the details of the variation through the lowest temperature range some more information is available, as noted previously. The analysis here does not consider this temperature range but the marked influence of T in c_p/T in the determination of $s(T)$ by integration, indicates the possibility of a very rapid decrease in the value of the entropy functions in this range. This can be seen from the $\Delta s(T)$ function in Figure 7. Also of importance in this connection is the discussion relative to glycerin by Simon *et al.*¹⁶⁰ about the question of whether the difference in entropy between a crystal and the supercooled melt disappears at absolute zero.

The Kauzmann paradox

The Figures also show the values of the functions calculated according to the extrapolation in Figure 5 of the c_{p_a} curve by means of equation (50) (indicated by * in Figures 5 and 6, and by a dashed line in Figure 7). The link with the low-temperature c_{p_a} curve was obtained by taking, after the extrapolation to 160 K, the mean of c_{p_a} (160 K) and c_{p_c} (140 K) for the value at 150 K, and the c_{p_a} function for lower temperatures. Extrapolations of this type may lead to the well-known Kauzmann paradox¹⁹, i.e. the tendency of $\Delta h(T)$ and $\Delta s(T)$ functions when extrapolated from $T > T_g$ to pass through zero and become negative at temperatures between 0 K and T_g . In Figure 7 this is observed at ≈ 40 K.

It is emphasized here and by Smith¹⁰³ and Miller^{161,162}, that there are reasons for doubting the

Table 4 Specific heat capacity, enthalpy, entropy, and free-enthalpy functions (J, g, k) for amorphous and crystalline LPE, based on equation 51 and the measurements referred to in Table 3

T	Amorphous polyethylene				Crystalline polyethylene			
	$c_{p_a}(T)$	$h_a(T)$	$s'_a(T)$	$g'_a(T)$	$c_{p_c}(T)$	$h'_c(T)$	$s'_c(T)$	$g'_c(T)$
10	0.0249				0.00777			
20	0.0964	186	0.260	181.3	0.052	0.30	0.017	-0.04
30	0.195	188	0.317	178.5	0.129	1.20	0.051	-0.34
40	0.280	190	0.384	175.0	0.224	3.0	0.101	-1.1
50	0.370	193	0.456	170.8	0.319	5.7	0.161	-2.4
60	0.447	197	0.531	165.9	0.408	9.3	0.227	-4.3
70	0.509	202	0.604	160.2	0.489	13.8	0.296	-6.9
80	0.570	208	0.676	153.8	0.560	19	0.366	-10.2
90	0.628	214	0.747	146.7	0.626	25	0.435	-14.2
100	0.688	220	0.816	138.9	0.683	32	0.504	-18.9
110	0.733	227	0.834	130.3	0.736	39	0.572	-24.3
120	0.790	235	0.950	121.2	0.785	46	0.638	-30.3
130	0.857	243	1.016	111.3	0.829	54	0.703	-37.0
140	0.948	252	1.083	100.9	0.869	63	0.766	-44.4
150	1.053	262	1.152	89.7	0.905	72	0.827	-52.4
160	1.142	273	1.222	77.8	0.944	81	0.886	-60.9
170	1.23	285	1.294	65.2	0.981	91	0.945	-70.1
180	1.28	298	1.366	51.9	1.04	101	1.002	-79.8
190	1.35	311	1.437	37.9	1.08	111	1.060	-90.1
200	1.41	325	1.508	23.2	1.13	122	1.116	-101.0
210	1.47	339	1.578	7.8	1.17	134	1.173	-112.5
220	1.54	354	1.648	-8.4	1.21	146	1.228	-124.5
230	1.63	370	1.719	-25.2	1.26	158	1.283	-137.0
240	1.74	387	1.790	-42.7	1.30	171	1.337	-150.1
250	1.84	405	1.863	-61.0	1.34	184	1.391	-163.8
260	1.94	423	1.937	-80.0	1.36	198	1.444	-177.9
270	2.01	443	2.012	-99.7	1.40	211	1.496	-192.7
280	2.09	464	2.086	-120.2	1.47	226	1.548	-207.9
290	2.18	485	2.161	-141.5	1.51	241	1.601	-223.6
300	2.21	507	2.236	-163.4	1.57	256	1.653	-239.9
310	2.24	529	2.309	-186.2	1.61	272	1.705	-256.7
320	2.27	552	2.380	-209.6	1.68	288	1.757	-274.0
330	2.29	575	2.450	-233.8	1.76	306	1.810	-291.8
340	2.32	598	2.519	-258.6	1.82	323	1.864	-310.2
350	2.35	621	2.587	-284.2	1.91	342	1.918	-329.1
360	2.38	645	2.654	-310.4	1.99	362	1.973	-348.5
370	2.41	669	2.719	-337.2	2.09	382	2.028	-368.5
380	2.44	693	2.784	-364.8	2.20	403	2.086	-389.1
390	2.47	717	2.848	-392.9	2.30	426	2.144	-410.3
400	2.50	742	2.911	-421.7	2.43	450	2.204	-432.0
410	2.53	767	2.973	-451.1	2.58	475	2.266	-454.3
414.6		779	3.001	-465.0		486	2.294	-465.0
420	2.56	793	3.034	-481.2				
430	2.59	819	3.095	-511.8				
440	2.62	845	3.155	-543.1				
450	2.65	871	3.214	-574.9				
460	2.68	898	3.272	-607.3				
470	2.71	925	3.330	-640.4				
480	2.74	952	3.388	-673.9				
490	2.77	979	3.444	-708.1				
500	2.80	1007	3.501	-742.8				
510	2.83	1035	3.556	-778.1				
520	2.86	1064	3.612	-814.0				
530	2.90	1093	3.667	-850.4				
540	2.93	1122	3.721	-887.3				
550	2.96	1151	3.775	-924.8				
560	2.99	1181	3.829	-962.8				
570	3.02	1211	3.882	-1001				
580	3.06	1241	3.935	-1040				
590	3.09	1272	3.987	-1080				
600	3.12	1303	4.040	-1120				
610	3.15	1335	4.091	-1161				
620	3.19	1366	4.143	-1202				
630	3.22	1398	4.194	-1244				

$h'_c(T)$ was determined with the aid of $c_{p_c}(T)$ by cumulative addition from 10 K of the areas under the $c_{p_c}(T)$ curve. This curve was obtained by connecting the $c_{p_c}(T)$ values by straight lines. From the resulting values, $h'_c(414.6)$ was determined by extrapolation, after which $h'_a(414.6)$ was obtained by adding $\Delta h(414.6) = 293 \text{ J g}^{-1}$.

The $h_a(T)$ values determined by analogous integration were calibrated at 414.6 K at this value, as follows:

$$h'_c(T) \equiv \int_{10}^T c_{p_c}(T) dT; h'_a(T) \equiv \int_{10}^{T_m} c_{p_c}(T) dT + 293 - \int_{T_m}^T c_{p_a}(T) dT$$

The entropy functions were calculated by an analogous method from c_p/T , and the free-enthalpy functions were determined from $g'(T) = h'(T) - Ts'(T)$. The prime symbols added to the functions (not in the figures) denote that here the integration starts at 10 K. For the temperature range discussed here the c_p data now known for $T < 10$ K do not make any appreciable contribution

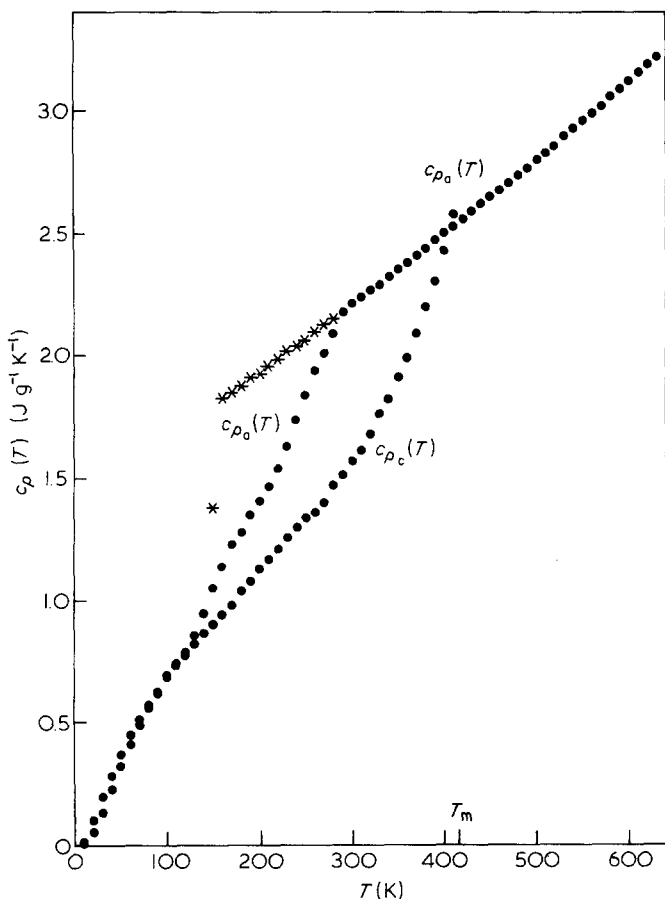


Figure 5 The specific heat capacities $c_{\rho_a}(T)$ and $c_{\rho_c}(T)$ for LPE as shown also in Table 4. $c_{\rho_a}(T)$ from $c_{\rho_{w,c}=0\%}(T)$ up to 290 K, supplemented with values obtained by extrapolation of polyethylene melt data and paraffin melt data by means of equation (51) at 290 K and above. $c_{\rho_c}(T)$ from $c_{\rho_{w,c}=100\%}(T)$ up to 240 K, supplemented with $c_{\rho_{w,c}=98.5\%}(T)$ according to Wunderlich⁵⁷ at 240 K and above. See text with reference to points indicated by *

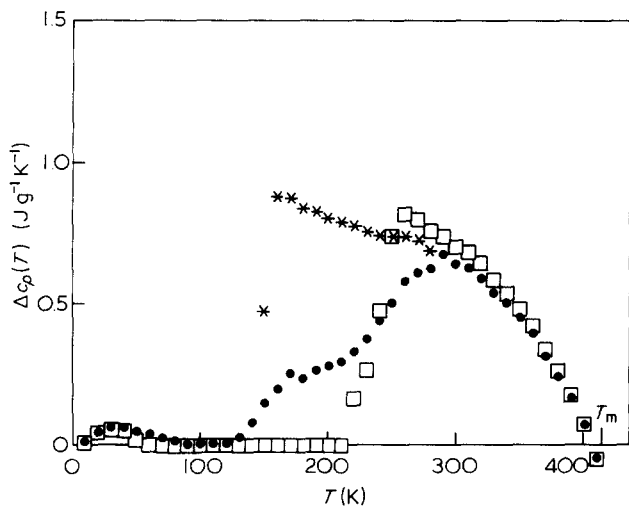


Figure 6 The specific heat capacity differential function $\Delta c_p(T)$. \square , Wunderlich *et al.*⁴⁴; \bullet , LPE from Table 4; *, as in Figure 5

existence of this paradox. For, whether this paradox does actually occur depends to a very high degree on the method of extrapolation applied. For example, if a link between the extrapolated c_{ρ_a} curve and the c_{ρ_a} curve below 150 K had not been made and the former curve had simply been extended to lower temperatures, then the Δs function would have become zero at ≈ 145 K (dotted line in Figure

7). Analogous extrapolations can be found in, for example, Kauzmann¹⁹, Passaglia *et al.*¹⁶³, Karasz *et al.*³⁵, Miller¹⁶⁴, Angell *et al.*^{23,24}, Lebedev *et al.*¹⁶⁵.

The arbitrariness of this method of extrapolation can also be illustrated in a simple manner with reference to Kauzmann's examples. He extrapolated the Δh , Δs , Δg and Δv functions in the range over T_g towards lower temperatures which, for example for Δs , as here for polyethylene, led to zero points at >0 K. For one of the substances involved, glycerin, in one of the original publications¹⁶⁶⁻¹⁶⁹ a different estimate for an 'equilibrium' continuation of c_{ρ_a} is evident, resulting in a Δs function becoming gradually zero as the temperature decreases. Also Smith¹⁰³ and Miller^{161,162} calculated a continuous decrease to zero of Δs and the conformational entropy, in the direction towards absolute zero.

Because different and in themselves plausible extrapolations of the thermodynamic functions for $T < T_g$ can be made, with widely different results, it must be concluded that it is currently impossible to decide whether or not the Kauzmann paradox actually exists. As Goldstein¹⁷⁰ noted, the paradox arises because of the aim to interpret the results of an extrapolation without knowing how this extrapolation should be made.

The temperature T_2 , which can be defined as $\Delta s(T_2) = 0$, is, therefore, completely uncertain. In the 'approximate' Gibbs-DiMarzio theory¹¹⁶ this temperature marks a sharp second-order (discontinuity in the slope of the Δs curve) transition, and T_2 is the lower limit of the range of T_g observed in experiments of infinite time. The possibility of an 'exact' theory leading to a diffuse transition is not

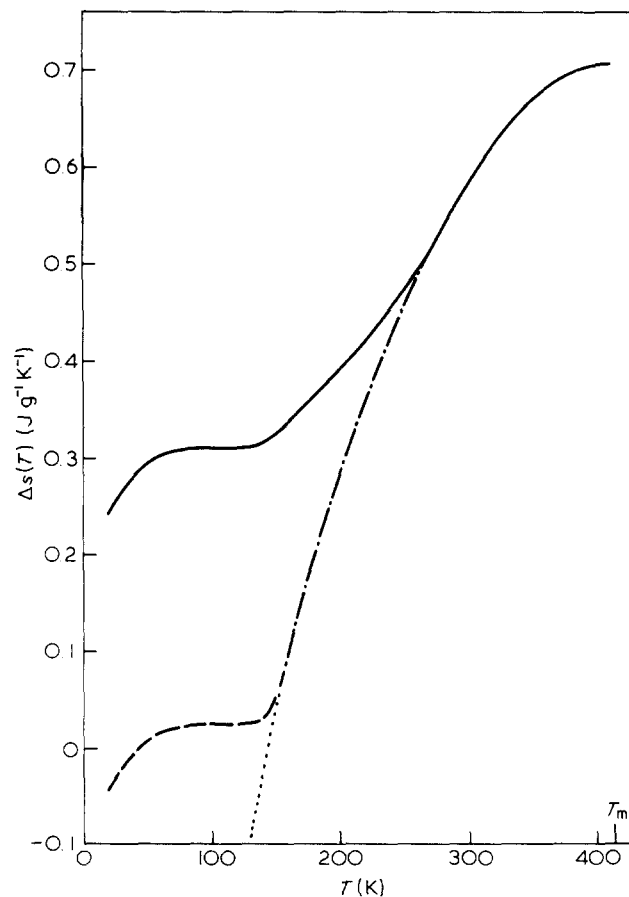


Figure 7 The specific entropy differential function $\Delta s(T)$ for LPE. Uninterrupted line from Table 4; see text for dashed line and dotted line

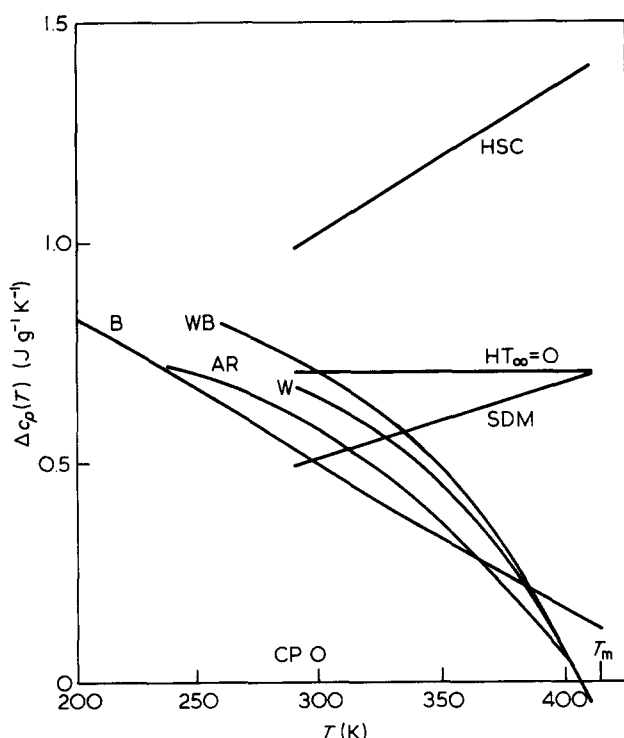


Figure 8 Various specific heat capacity differential functions for polyethylene. AR: Atkinson *et al.*¹⁷⁷, $T_m = 414.3$ K, $\Delta h(T_m) = 307$ J g⁻¹; B: Broadhurst¹⁷⁵, $T_m = 414.3$ K, $\Delta h(T_m) = 299$ J g⁻¹; WB, Wunderlich *et al.*⁴⁴, $T_m = 414.6$ K, $\Delta h(T_m) = 293$ J g⁻¹; W: from Table 4, $T_m = 414.6$ K, $\Delta h(T_m) = 293$ J g⁻¹; the approximations CP 0, HSC, $HT_\infty = 0$ and SDM are according to text, with $T_m = 414.6$ K and $\Delta h(T_m) = 293$ J g⁻¹

excluded by DiMarzio *et al.*¹⁷¹, and they cautiously represent T_2 as being a 'convenient reference point on the bend of a curve of at present undefined sharpness'¹⁷². However the conclusion¹⁷¹ that this bend cannot extend over a temperature range of arbitrary length, and that, consequently, T_2 must be reasonably sharply defined, is based on extrapolations such as the one represented in Figure 7 (dotted curve), and, consequently, has hardly any support (see also Gutzow³¹).

Of course, it may be agreed to determine or define T_2 by extrapolations as here. Such a pragmatic approach does not of course detract from the usefulness of, for instance, the Adam-Gibbs theory for $T \geq T_g$ ¹⁷¹. However, the results obtained by, for example, Bestul *et al.*¹⁷³ and Chang *et al.*⁷⁶, Adam *et al.*¹⁷⁴, Angell *et al.*^{23,24}, Gordon *et al.*²⁵, and many others, in respect of T_2 should be considered in this context.

The differential functions for polyethylene

The temperature range > 200 K is the area in which most of the experiments with polyethylene are carried out, and the differential functions in this range are now examined in detail.

A number of Δc_p functions are given in Figure 8. The functions based on experiments (codes AR, B, WB, W) decrease as the temperature increases and approaches zero close to T_m . It is possible to be reasonably sure of this because, as noted previously, the c_p values for almost 100% crystalline material at T_m are known from experimental evidence, which makes polyethylene an exception among the polymers. It is noteworthy that the decrease of the Δc_p function according to Broadhurst¹⁷⁵, is caused in part by a correction he applies to $c_p(T)$. The minimal

difference between the functions indicated by WB and W is caused by the difference in $c_p(T)$. The Figure also shows the approximations CP 0, HSC, $HT_\infty = 0$ and SDM, which do not have physical significance for polyethylene.

Figure 9 shows the resultant temperature dependence for the Δh function. Both Δh and Δs functions attain their maxima at $\approx T_m$, because $\Delta c_p(T_m) \approx 0$.

The Δg function is important in crystallization and melting theories. In accordance with that noted previously and indicated in Figure 1, $\Delta c_p(T_m) \approx 0$ also implies that the CP 0 approximation excellently represents the experimental Δg function over a wide temperature range, which has been concluded previously by Broadhurst¹⁷⁵. Actually, for $\Delta g(T)$ this simple approximation is better than the $HT_\infty = 0$ and SDM approximations, which were proposed partly on the strength of Broadhurst's results.

The experimental differential functions $\Delta h(T)$, $\Delta s(T)$ and $\Delta g(T)$ can be mathematically represented in a very simple way by making use of the parabolic character of $\Delta c_p(T)$. Considering a parabola drawn through 0 K, T_m , and a reference temperature T_r in the experimental measuring range, an experimental Δc_p function can be approximated by:

$$\Delta c_p(T)_M = f_r \Delta T T \quad (51)$$

where f_r is defined by taking the experimental Δc_p at the reference temperature:

$$f_r = \frac{\Delta c_p(T_r)}{\Delta T_r T_r} \quad (52)$$

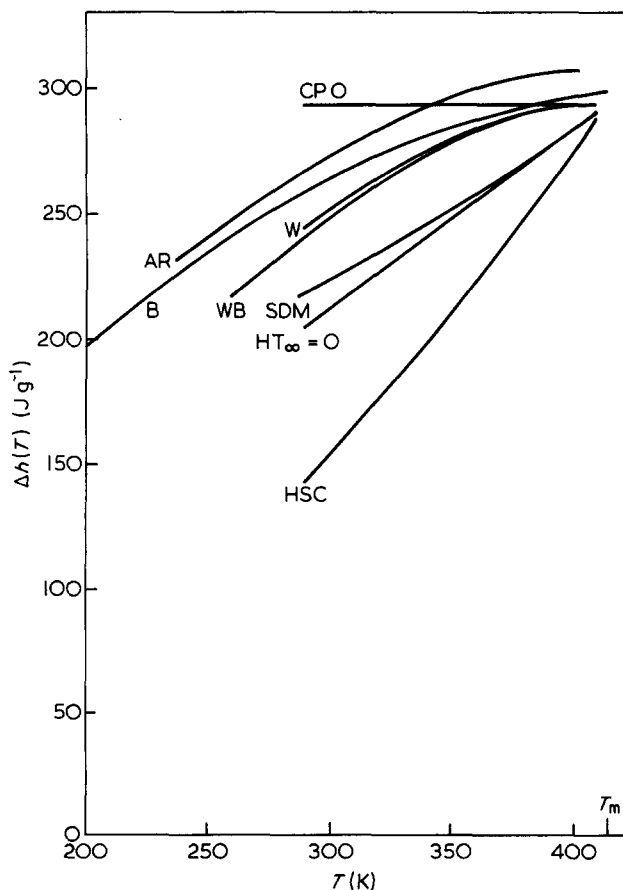


Figure 9 Specific enthalpy differential functions for polyethylene on the basis of the $\Delta c_p(T)$ functions shown in Figure 8

Table 5 Approximation formulae for various differential functions for polyethylene, and the literature-based numerical values required for a description of the differential functions, by application of these formulae

	CP 0 approximation	correction		
$\Delta c_p(T)_M = 0$		$+ f_r \cdot \Delta T \cdot T$		
$\Delta h(T)_M = \Delta h(T_m)$		$- \frac{1}{6} \cdot f_r \cdot \Delta T^2 \cdot (T_m + 2T)$		
$\Delta s(T)_M = \Delta s(T_m)$		$- \frac{1}{2} \cdot f_r \cdot \Delta T^2$		
$\Delta g(T)_M = \Delta s(T_m) \cdot \Delta T$		$- \frac{1}{6} \cdot f_r \cdot \Delta T^3$		
References	T_m (K)	$\Delta h(T_m)$ (J g ⁻¹)	$\Delta c_p(290)$ (J g ⁻¹ K ⁻¹)	$f_{290} \cdot 10^5$ (J g ⁻¹ K ⁻³)
177	414.3	307	0.6077 ^a	1.686
175	414.3	299	0.5332 ^b	1.479
44	414.6	293	0.7387 ^c	2.044
This work	414.6	293	0.6703 ^d	1.855
This work	419.7	293	0.6703 ^d	1.782

The $\Delta c_p(290)$ values were obtained by means of analytical expressions:

^a Using equation (7) of ref. 177

^b Using Table 3 of ref. 175 (in which the values 4.84, -0.00186 and +19.32 should be replaced by, respectively, 4.084, -0.00286, and -19.32)

^c 3rd degree polynomial fit of $\Delta c_p(T)$ using Table III. 8 of ref. 44 between 260 and 410 K, standard deviation 3.1%

^d 4th degree polynomial fit of $\Delta c_p(T)$ using Table 4, this work, between 290 and 410 K, standard deviation 3.6%

The last non-significant, digit in the $\Delta c_p(290)$ and f_{290} values has been included to avoid introduction of deviations through arithmetical causes

with:

$$\Delta T_r = T_m - T_r \quad (53)$$

The driving force now assumes a simple shape:

$$\Delta g(T)_M = \frac{\Delta h(T_m)}{T_m} \cdot \Delta T - \frac{1}{6} \cdot f_r \cdot \Delta T^3 \quad (54)$$

or:

$$\Delta g(T)_M = \Delta g(T)_{CP0} - \frac{1}{6} \cdot f_r \cdot \Delta T^3 \quad (55)$$

in which, as noted previously, the first term already gives a very good approximation of $\Delta g(T)$, whilst addition of the second term makes the description near-perfect. Also Broadhurst's $\Delta g(T)$ is very reasonably approximated, thus, there is an attractive simplification of the complicated function given by this author himself.

Table 5 gives a survey of the various expressions. In addition to $\Delta g(T)$ also $\Delta h(T)$ and $\Delta s(T)$ are adequately described. For example, the maximum deviation for these three functions between the approximation given here and the analytical descriptions of the experimental data in the measured range considered varies from 0.4% (present work, $T_m = 414.6$ K), 0.5%, 1% (present work, $T_m = 419.7$ K), 1% to 2% (Broadhurst, $T > 250$ K). These deviations are of the same order of magnitude as the differences between the values calculated from analytical expressions and values obtained by numerical integration. As an approximation $f_{290} = 1.8 \cdot 10^{-5}$ (J g⁻¹ K⁻³) [$2.5 \cdot 10^{-4}$ (J mol⁻¹ K⁻³) or 6.0 (cal mol⁻¹ K⁻³)], which leads to very simple shapes for the expressions in Table 5. The reference temperature of 290 K used in the Figure is not

critical: f_r (except in Broadhurst's case) and the error limits are only influenced slightly by a variation of T_r . Also, if there is some variation in melting temperature ($T_m = 419.7$ K, Hoffman *et al.*¹⁷⁶) or heat of fusion, still acceptable results are obtained, although the temperature dependence of the deviations changes markedly.

Recent publications

While completing this manuscript, the author received the thesis by Gaur⁶⁷, from which he learned that the latter had evaluated various polymers in a partly analogous way, and that publication would be made in *J. Chem. Phys. Ref. Data* (already published: Gaur *et al.*^{68,69}; see also Gaur *et al.*⁴⁶ and Wunderlich *et al.*^{54,178}). A note on the glass transition of PE has also appeared¹⁷⁹. The reader may be referred to the reviews yet to be published, which in several respects complement the present article. An application of the results given in this article is described in Mathot *et al.*¹⁸⁹.

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