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ON THE C_p TO C_v CONVERSION OF SOLID LINEAR MACROMOLECULES II

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A modification is proposed for the Nernst–Lindemann equation that is used to convert calculated heat capacities at constant pressure (C_p) to heat capacities at constant volume (C_v) for solid, linear macromolecules. the constant A_0 per mole of repeating unit in this equation is derived by taking into account the variable number of vibrators excited at different temperatures. With the new equation it is possible to calculate C_p for solid polymers over a wider temperature range. The constant is calculated for solid polymers from experimental thermal expansivity, isothermal compressibility and heat capacity data obtained from the literature. An average value of $(3.9 \pm 2.4) \times 10^{-3}$(K mol)/J was obtained for A_0 (new) from data on 22 solid polymers. This average value may be used as a universal constant in case no experimental data on compressibility and expansivity are available for computation of A_0. The remaining variation of A_0 (new) with temperature is discussed and example calculations are shown for polyethylene. Effects of premelting and possibly large-amplitude motion are discovered for polyethylene in the temperature range 290 to 410 K.

Introduction and derivation of the new equation

The use of the Nernst–Lindemann equation to convert heat capacity at constant pressure (C_p) to heat capacity at constant volume (C_v) for solid, linear macromolecules was discussed earlier [1].

$$C_p - C_v = A_0 C_p^2 \, T/T_m^0 \tag{1}$$

It was suggested that in the usual absence of pVT data over a wide temperature range, it is permissible to convert C_v, calculated from an approximate vibrational spectrum, to C_p by using a universal constant A_0. An average value of 5.11×10^{-3} (k mol)/J (computed per mole of heavy atoms) was obtained for A_0 from pVT data of several polymeric crystals and glasses at a temperature of about

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298 K. This value of A_0 is numerically close to the original Nernst–Lindemann constant derived for metals and salts [2].

At ATHAS, our laboratory for *A*dvanced *TH*ermal *A*nalysi*S*, the linking of heat capacities of nearly 100 macromolecules to their vibrational spectra has recently been completed [3]. The heat capacity C_p obtained from calculated C_v was found to agree to better than $\pm 3\%$ with the experimental heat capacity C_p up to the glass or melting temperatures. Calculations carried out beyond these temperatures showed a rather sharp, unrealistic upturns in the calculated C_p. Since C_v showed only a moderate increase with temperature, the change in the calculated C_p was assumed to be in error and attributed to the limit of usefulness of the Nernst–Lindemann equation. Naturally such error at high temperature casts also doubt on the applicability of the equation at lower temperature.

It was, therefore, considered worthwhile to modify the assumptions made earlier in deriving A_0. The Nernst–Lindemann equation was derived originally for relatively heavy, monatomic solids [2] with T_m^0 representing the equilibrium melting temperature. In finding a suitable constant A_0 for solid, linear macromolecules it was assumed that only the vibrations associated with the heavy atoms (such as C, N and O) contribute to the heat capacity:

$$A_0 = A_0(\text{old})/(^{\#}\text{heavy atoms}) \tag{1a}$$

This can only be a first approximation since at higher temperatures vibrations, such as C—H, N—H or O—H stretching and bending, also contribute to the heat capacity. In fact, there is a simple measure of the number of vibrators excited at any given temperature, given by the heat capacity at constant volume itself:

$$C_v = 3nR, \tag{2}$$

where n is the average number of excited vibrators.

Based on Eq. (2) a better, temperature dependent value can be derived for A_0:

$$A_0 = A_0(\text{new})/n, \tag{3}$$

where A_0 is expressed per mole of repeating unit and A_0(new) represents the value for one mole of vibrationally excited atoms [1]. Substituting equations (2) and (3) into (1) one gets:

$$C_p - C_v = 3RA_0(\text{new})C_p^2T/(C_vT_m^0) \tag{4a}$$

and since in the original justification of Eq. (1) C_p was assumed to be equal to C_v one can also write

$$C_p - C_v = 3RA_0(\text{new})C_pT/T_m^0 \tag{4b}$$

or

$$C_p - C_v = 3RA_0(\text{new})C_vT/T_m^0 \tag{4c}$$

the differences between the three expressions are small at low temperature, typically 0.06% and 0.12% in A_0 for polyethylene at 298.15 K, much less than the changes in A_0 from sample to sample or with temperature. For computational reasons all further discussions will make use of Eq. (4a).

In this paper the results of C_v to C_p conversions of solid macromolecules are presented using this new equation. A value of the constant A_0(new) is proposed on the basis of experimental thermal expansivity (α) and isothermal compressibility (β) obtained from the literature for various polymers over wider ranges of temperature. The connection between A_0(new) and α and β is given by comparison of the thermodynamic relationship

$$C_p - C_v = TV\alpha^2/\beta$$

with Eq. (4a).

Data on pVT for macromolecules

Although many studies have been reported on pVT properties of various macromolecules, the dilatometry is often limited to semicrystalline and glassy states. Equations of state have been used to obtain crystal data from experimental information on semicrystalline materials [4, 5]. The combination of melt and crystal theories have shown good agreement between theoretically predicted and experimentally obtained specific volumes. A two-phase model of additivity of crystal and amorphous volumes was also used by Tsujita et al. [6] to obtain pVT data of crystalline regions from the information on semicrystalline solid and melt data on polyoxyethylene and polyoxytetramethylene. According to this model:

$$V = (1-x)V_a + xV_c \tag{5}$$

$$\alpha = (1-x)\alpha_a V_a/V + x\alpha_c V_c/V \tag{6}$$

$$\beta = (1-x)\beta_a Va/V + x\beta_c V_c/V \tag{7}$$

The degree of crystallinity, x, was assumed to be invariant with temperature and pressure, V is the molar volume of amorphous (a), crystalline (c) or the semicrystalline (no subscript) samples. The thermal expansivity (α) and isothermal compressibility (β) are defined similarly. For the amorphous regions in semicrystalline samples α_a and β_a were extrapolated from the melt. The glass transition temperature, T_g, was the lower limit of this extrapolation. Using these methods all literature data were reevaluated using either presented equations or newly derived best fits. The data were extracted using references [1, 6–20].

Results and discussion

For various polymers in the glassy, crystalline and semicrystalline states the resulting A_0(new) values are shown in Tables 1 and 2 and compared to values of A_0(old). Note that in all tables more significant figures than warranted by the precision of the experiments are listed. This is done for computational reasons so that the original data can be reproduced and proper error assessment made after further use of the data. Using the new Eq. (4a) an average value of $(3.9 \pm 2.4) \times 10^{-3}$ (K mol)/J is obtained. The old method using Eq. (1a) gave with the present data collection a value of $(5.4 \pm 3.3) \times 10^{-3}$ (k mol)/J. to obtain these averages, a weight of two was given to all A_0 values corresponding to a wider temperature range, while A_0 from a single temperature was given a weight of one. The average of A_0(new) glassy polymers is lower than that for crystalline and semicrystalline polymers. The variation from polymer to polymer does not seem to

Table 1 Calculated A_0 for various glassy polymers

Polymers*	Temp. range of experimental pVT data, K	Melting temp.,** K	Average $A_0 \times 10^3$, K mol J^{-1} (New)	$A_0 \times 10^3$, K mol J^{-1} (Old)
Poly(vinyl acetate) (6)	240–290	446	3.25 ± 0.66	5.18 ± 1.16
Poly(methyl methacrylate) (7)	340–370	450	1.78 ± 0.21	2.29 ± 0.34
Poly(4,4′-isopropylidene diphenyl carbonate) (19)	310–420	608.2	3.21 ± 0.57	4.93 ± 1.60
Polystyrene (8)	280–340	516.2	2.46 ± 0.33	3.88 ± 0.27
Poly(2,6-dimethyl-1,4-phenylene oxide) (9)	303	535	2.34	3.61
Poly(n-butyl methacrylate) (10)	290–370	439	2.63 ± 0.53	3.26 ± 0.49
Poly(vinyl chloride) (3)	220–320	546	2.64 ± 0.59	4.0 ± 1.67
Poly(vinyl fluoride) (3)	290–310	503.2	10.18 ± 0.51	15.67 ± 1.38
Poly(chloro trifluoro--ethylene) (6)	290–320	493	4.30 ± 0.23	6.88 ± 0.58
Poly(vinyl alcohol) (3)	280–300	521	3.73 ± 0.37	4.54 ± 0.68
Poly(ethylene terephthalate) (14)	300–330	553	0.81 ± 0.03	1.21 ± 0.10
Poly(oxy-1,4-phenylene--sulfonyl-1,4-phenylene oxy-1,4-phenylene(1-methylidene)-1,4-phenylene) (32)	300–450	687	3.15 ± 0.53	4.62 ± 1.19
			Average A_0(new) =	3.42 ± 2.31
			Average A_0(old) =	5.07 ± 3.64

* Number in parenthesis indicate the number of heavy atoms in repeating unit.

** Melting temperature used in A_0 calculation is our data's bank recommended data, see Ref. [3].

Table 2 Calculated A_0 for various crystalline and semicrystalline polymers

Polymers*	Temp. range of experimental pVt data, K	Melting temp.,** K	Average $A_0 \times 10^3$ K mol J^{-1} (new)	$A_0 \times 10^3$ K mol J^{-1} (old)
Polyethylene (1) (c)***	290–310	414.6	3.18 ±0.98	3.89 ±1.20
Polypropylene (3) (c)	300–370	460.7	5.93 ±0.51	6.59 ±1.12
Polyoxymethylene (2) (s)	293	457	2.54	3.52
Polyoxyethylene (3) (c)	230–330	342	0.74 ±0.36	1.04 ±0.46
Polyoxytetramethylene (5) (s)	240–270	330	3.92 ±0.28	3.94 ±0.27
Poly(1-butene) (4) (s)	300–320	411.2	8.80 ±1.15	10.20 ±2.11
Poly(4-methyl-1-pentene) (6) (s)	290–300	523	5.85 ±0.08	6.66 ±0.13
Polytetrafluoroethylene (3) (s)	300–390	605	4.578±0.63	7.557±1.49
	380–500	605	3.796	4.86
Poly(vinylidene fluoride) (4) (s)	293	483.2	2.55	3.76
Nylon 6 (8) (s)	293	533	8.01	11.02

Average A_0(new) = 4.56±2.33
Average A_0(old) = 5.67±2.84

* Number in parenthesis indicate the number of heavy atoms in the repeating unit. (c) indicates fully crystalline samples and (s) semicrystalline sample.

** Melting temperature used in A_0 calculation is our data bank's recommended data, see Ref. [3].

*** As can be seen from the discussion section, the A_0 values above 290 K have a contribution from premelting. A better A_0(new) value would be 2.05×10^{-3} (K mol)/J at 290 K.

Table 3 Calculated A_0 for glassy Poly(4,4-isopropylidene diphenylene carbonate)

Temp., K	$V_a \times 10^5$, m^3/mol	$\alpha_a \times 10^4$, K^{-1}	$\beta_a \times 10^{10}$, Pa^{-1}	C_p, J K^{+1} mol^{-1}	C_v, J K^{-1} mol^{-1}	$A_0 \times 10^3$ (new), K mol J^{-1}	$A_0 \times 10^3$ (old), K mol J^{-1}
310.00	21.310	2.624	2.538	316.900	298.976	4.197	7.704
320.00	21.366	2.617	2.605	327.100	309.121	3.958	7.026
330.00	21.422	2.611	2.674	337.400	319.384	3.735	6.417
340.00	21.478	2.604	2.745	347.700	329.663	3.527	5.871
350.00	21.533	2.597	2.817	358.100	340.058	3.333	5.379
360.00	21.589	2.590	2.892	368.500	350.467	3.152	4.936
370.00	21.645	2.584	2.968	379.100	361.090	2.982	4.532
380.00	21.701	2.577	3.047	389.700	371.726	2.823	4.167
390.00	21.757	2.570	3.127	400.300	382.374	2.674	3.838
400.00	21.813	2.564	3.210	411.100	393.234	2.534	3.536
410.00	21.869	2.557	3.295	421.900	404.105	2.403	3.263
420.00	21.925	2.551	3.382	480.300	462.585	2.062	2.446

be much different from the previous calculation [1], i.e. A_0(new) is also an approximate, but not a precise, universal constant. For polymers where data over a wider temperature range are available, it is possible to check into the variation of A_0 with temperature. For an exact fit of Eq. (4a), A_0 should be a constant. In case of glassy polymers, the improved, but still approximate nature of this equation was evident from a remaining, smaller change of A_0(new) than of A_0(old) with temperature. As an example the results of the calculations for poly(4,4-isopropylidene diphenylene carbonate) are depicted in Table 3 [14]. A decrease in A_0 with an increase in temperature was also observed for the other glassy polymers with exceptions of polystyrene [17], poly(methyl methacrylate) [7, 15] and poly(*n*-butyl methacrylate) [7] in which A_0 showed a slight increase with temperature. In addition to these changes, the conventional atactic PMMA showed a jump in A_0 between 330–340 K [the value of A_0(new) changed from 1.85×10^{-3} to 2.369×10^{-3} (K mol)/J]. A distinct break, as reported earlier, was also observed in molar volume and expansivity and linked prior to the presence of a sub-glass transition [15].

In an attempt to obtain A_0 beyond the range of actual pVT measurements, the molar volume, thermal expansivity and isothermal compressibility were extrapolated to lower temperatures using the well established equations of state [4, 5]. A_0(old) calculated, for example, for poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene) [20] at 40 K increased by a factor of 100. This increase is expected because of the simplifying assumptions of a constant number of vibrators in this calculation. The value of A_0(new) increased, however, also, but only tenfold. This abnormal increase in

Table 4 Calculated A_0 for a semicrystalline Polytetrafluoroethylene*

Temp., K	$V \times 10^5$, m³/mol	$\alpha \times 10^{10}$ K^{-1}	$\beta \times 10^{10}$ Pa^{-1}	C_p, J K^{-1} mol^{-1}	C_v J K^{-1} mol^{-1}	$A_0 \times 10^3$ (new), K mol J^{-1}	$A_0 \times 10^3$ (old) K mol J^{-1}
300.00	2.318	3.992	3.237	45.370	41.946	5.642	10.064
310.00	2.328	4.033	3.449	46.020	42.618	5.357	9.406
320.00	2.337	4.073	3.662	46.950	43.562	5.074	8.716
330.00	2.347	4.112	3.876	47.860	44.481	4.822	8.112
340.00	2.356	4.151	4.090	48.760	45.385	4.595	7.577
350.00	2.366	4.189	4.306	49.630	46.255	4.392	7.105
360.00	2.376	4.227	4.523	50.490	47.111	4.207	6.683
370.00	2.386	4.264	4.740	51.350	47.963	4.038	6.300
380.00	2.396	4.301	4.959	52.170	48.773	3.886	5.961
390.00	2.407	4.337	5.177	52.990	49.580	3.745	5.652

* Estimated crystallinity 51%.

A_0(new) may indicate that not only Eq. (1) but also the extrapolation of pVT data to lower temperatures (and the used equations of state) may need more extensive experimental checks. In this paper A_0(new) for glassy polymers was for this reason only calculated over the range of actual pVT measurements.

In semicrystalline and crystalline polymer, the difficulty of premelting is encountered, making data close to the melting temperature suspect. For the semicrystalline polymers listed in Table 2, the range of pVT measurement over which A_0 was calculated is thus limited to temperatures much below equilibrium melting. The results for semicrystalline polytetrafluoroethylene are depicted in Table 4. The equilibrium melting temperature of this polymer is about 605 K [13]. The A_0 obtained from 300–390 K originate from a comparison of Weir's [10] and Zoller's [12] data that agreed within about 2%. Beyond 390 K the A_0 values reported earlier were used [1]. For the temperature range of 300–500 K the average A_0(new) was 4.18×10^{-3} (K mol)/J compared to 6.2×10^{-3} (K mol)/J for A_0(old). Due to the wider temperature range the reported A_0(old) is about 9% higher than that reported earlier for the limited temperature range of 380–500 K [1]. As for the glassy polymers, this semicrystalline polymer shows more than 100 K below T_m (but above T_g) a similar, slow, decrease in A_0(new). The change of A_0(new) with temperature is much less than A_0(old). Using an average value over the 200 K wide temperature range leads to an error comparable to the fluctuations from polymer to polymer for the universal constant.

A_0 values for poly(1-butane) and nylon 6 were much higher than the other semicrystalline polymers. There seems to be no present explanation for these unusually high A_0 values. One can compare the data for poly(1-butene) to the more "normal" ones for poly(4-methyl-1-pentene). The expansion coefficients of these two polymers were within 6% of each other [8]. The higher A_0 must thus be largely

Table 5 Calculated A_0 for crystalline polyethylene

Temp., K	$V_c \times 10^5$, m³/mol	$\alpha_c \times 10^4$ K^{-1}	$\beta_c \times 10^4$, Pa^{-1}	C_p, J K^{-1} mol^{-1}	C_v, J K^{-1} mol^{-1}	$A_0 \times 10^3$ (new), K mol J^{-1}	$A_0 \times 10^3$ (old), K mol J^{-1}
290.00	1.396	1.669	1.432	21.210	20.422	2.050	2.504
300.00	1.399	2.206	1.509	21.800	20.447	3.225	3.934
310.00	1.402	2.739	1.600	22.380	20.342	4.437	5.441
320.00	1.406	3.267	1.709	22.950	20.139	5.583	6.915
330.00	1.411	3.791	1.835	23.560	19.913	6.590	8.254
340.00	1.417	4.308	1.987	24.300	19.800	7.376	9.293
350.00	1.423	4.819	2.170	25.250	19.919	7.910	9.905
360.00	1.431	5.322	2.393	26.510	20.414	8.176	9.990
370.00	1.439	5.817	2.666	28.130	21.374	8.189	9.567

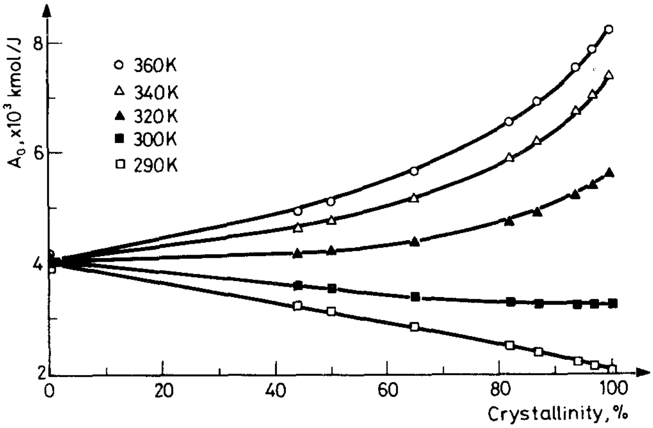

Fig. 1 Variation of A_0 as a function of crystallinity for polyethylene at several temperatures as derived from pVT data

attributed to the lower compressibility of poly(1-butene) when compared to poly(4-methyl-1-pentene).

Table 5 shows the results of calculations for crystalline polyethylene. They show a larger change with temperature and the opposite trend than those of polytetrafluoroethylene (Table 4). The equilibrium melting temperature of polyethylene is much closer to the temperature range of interest (416.4 K). The crystalline specific volume of polyethylene calculated from the two-phase model [Eqs (5–7)], was similar to that derived directly from X-ray data on crystals (V_c from X-ray data varies between 1.406×10^{-5} at 290 K to 1.440×10^{-5} m^3/mol at 370 K) [21], but the thermal expansivity of Table 5 shows a larger increase with temperature than the corresponding X-ray results, which change in expansivity from 2.752×10^{-4} to 3.375×10^{-4} K^{-1}, respectively. The expansivity of the amorphous polyethylene obtained by extrapolations of $V_a(0, T)$ from the melt showed only a moderate increase over this temperature range and could not be the reason for the disagreement (it changes from 5.068×10^{-4} K^{-1} at 290 K to 6.593×10^{-4} K^{-1} at 370 K). The high expansivity for crystalline polyethylene obtained by extrapolation of pVT data on semicrystalline polyethylene may perhaps result from some premelting. The two-phase model would then be inadequate if the crystallinity decreases at higher temperatures. In fact, a decrease in crystallinity with increasing temperature was already considered as the cause of the deviations observed between calculated and experimental isotherms reported for semicrystalline linear polyethylene using the two-phase model [4].

Assuming that the two-phase model holds, A_0(new) was also calculated using the experimental C_p data of linear polyethylene at several crystallinities, obtained from our ATHAS data bank. Figure 1 shows the variation of the so-calculated A_0 as a function of crystallinity at several temperatures. At 290 K A_0 shows the expected slight decrease with increase in crystallinity. This trend reverses at higher temperatures and the increase in A_0 with an increase in crystallinity can be clearly seen at higher crystallinities. Compared to the larger variation of A_0(new) for crystalline polyethylene, A_0(new) for liquid polyethylene extrapolated from measurements above the melting temperature to lower temperatures (290–370 K) varied much less (between 3.89×10^{-3} to 4.14×10^{-3} (K mol)/J). These observations further support the fact that the large variation in A_0 with temperature is associated with the crystalline regions in polyethylene.

Finally the A_0(new) was used for the computation of C_p from C_v obtained from the approximate vibrational spectrum using Eq. (4a). Figure 2 shows the results. An average and RMS deviation of (1.9 ± 3.0) % was obtained over the temperature range 4.0 to 410 K by using the new equation [Eq. (4a)] with A_0(new) of Table 2. The old equation [Eq. (1)] with the same A_0(new) gave superficially a slightly better fir [average and RMS deviation (1.06 ± 2.8)%]. It must be observed, however, that the erroneous upturn of A_0(old) at higher temperatures accidentally fits the observed increase in heat capacity due to premelting, discussed above. Both errors are within the experimental error limit considered usually to be ±3% [3]. The previously calculated values [22] showed the larger error (1.6 ± 4.9)% for the temperature range 4.0 to 450 K with Eq. (1) and an A_0 of 4.85×10^{-3} (K mol)/J. At low temperatures (below 200 K) the difference between C_v and C_p is small and all methods appear to be equally good. The erroneous, sharp upturn above the melting temperature, for the calculated C_p does not show-up when using Eq. (4a). In

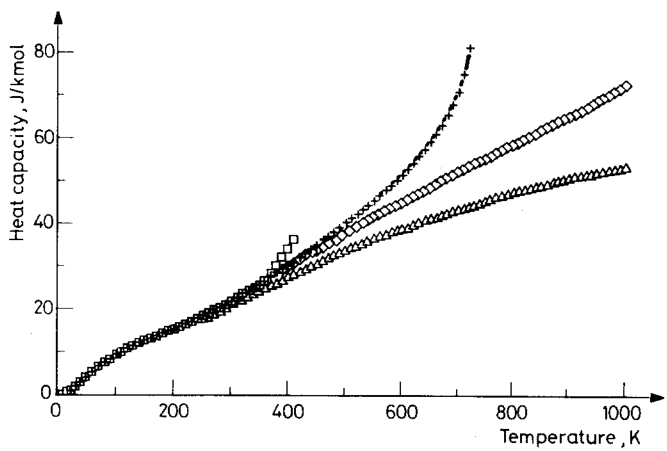

Fig. 2 Heat capacity C_p of crystalline polyethylene from C_v calculated using the approximate frequency spectrum and Eq. (4a) with an average A_0(new) of $3.18 \times 10^{+3}$ (K mol)/J

Table 6 Deviation of C_p calculated for crystalline polyethylene using different A_0(new) values, from C_p experimental

Temp., K	$C_p{}^a$ (experimental), J/K mol	$C_p{}^b$ (calculated), J/K mol	Deviation, %	$C_p{}^c$ (calculated), J/K mol	Deviation, %
290	21.200	21.206	0.038	21.206	0.03
300	21.811	21.910	0.45	22.461	2.98
310	22.380	22.629	1.11	23.904	6.80
320	22.947	23.347	1.74	25.511	11.17
330	23.564	24.074	2.16	27.272	15.73
340	24.302	24.813	2.10	29.116	19.80
350	25.253	25.559	1.21	30.935	22.5
360	26.508	26.315	− 0.73	32.582	22.91
370	28.132	27.069	− 3.77	33.917	20.56
380	30.125	27.820	− 7.65	—	—
390	32.357	28.560	−11.73	—	—
400	34.485	29.294	−15.05	—	—
410	35.830	30.026	−16.20	—	—

[a] Recommended experimental C_p, collected in the ATHAS data bank.
[b] C_p calculated from C_v using A_0(new) at 290 K.
[c] C_p calculated from C_v using A_0(new) values at the corresponding temperature.

addition, the computed C_p values remain within the limit of the Dulong Petit rule up to 1000 K when using A_0(new).

The data of Table 5 and Fig. 1 permit one further analysis of the cause of the abnormal increase in A_0(new). Assuming that A_0(new) changes little with temperature from 290 K to melting one can calculate a "vibration only" C_p based on the detailed analysis of heat capacity at lower temperature. These data are listed in column 3 of Table 6 and compared with the varying A_0(new) in column 5. Fit between experimental and calculated C_p is now good to 360 K instead to 290 K (column 3). Over the final 50 K the experimental C_p is however much larger. We expect the solution to these observations to be as follows: 1. The *pVT* data extrapolated from semicrystalline polyethylene contain, as discussed above, contributions from premelting, leading thus to erroneously high C_p. 2. The C_p (experimental) data were derived directly from close to 100% crystalline polymer and seemed to show little to no premelting and can thus not be represented by the A_0(new) above 290 K. 3. Making the reasonable assumption that A_0(new) is constant from 290–410 K, there is now a negative error, the calculated C_p is too low. This may be a first indication that even 100% crystalline polyethylene shows an increase beyond vibrational contributions in its heat capacities before melting. One expects this increase to be caused by introduction of defects and large amplitude

Table 7 Calculated A_0 for crystalline Polypropylene

Temp., K	$V_c \times 10^5$, m³/mol	$\alpha_c \times 10^4$, K⁻¹	$\beta_c \times 10^{10}$, Pa⁻¹	C_p, J K⁻¹ mol⁻¹	C_v, J K⁻¹ mol⁻¹	$A_0 \times 10^3$ (new), K mol J⁻¹	$A_0 \times 10^3$ (old), K mol J⁻¹
300.00	4.474	2.592	1.114	68.240	60.147	6.188	7.699
310.00	4.486	2.745	1.153	70.950	61.861	6.399	7.741
320.00	4.499	2.896	1.227	73.770	63.925	6.418	7.513
330.00	4.513	3.045	1.335	76.680	66.333	6.282	7.087
340.00	4.528	3.192	1.476	79.670	69.044	6.038	6.544
350.00	4.544	3.337	1.650	82.730	72.000	5.728	5.953
360.00	4.560	3.479	1.857	85.860	75.157	5.383	5.360
370.00	4.578	3.619	2.094	89.040	78.445	5.032	4.800

conformational motion of the molecules. 4. Recalculation of the error with A_0(new) from 4.0 up to 360 K taken to be constant at its 290 K value of 2.05×10^{-3} (K mol)/J leads to errors of (1.5 ± 1.411)%.

For crystalline polypropylene A_0(new) values were obtained over a range of temperature (300–370 K) that is again further away from the 460.7 K equilibrium melting temperature (Table 7). Variation in A_0 (both new and old) with temperature was less than that observed in crystalline polyethylene. This indicates that the contribution of premelting towards increasing the A_0 is significantly less in polypropylene. The data show furthermore that the A_0(new) varies less than A_0(old) i.e., Eq. (4a) is an improvement over Eq. (1). For semicrystalline polypropylene of 69.6% crystallinity an average A_0(new) value of $(5.2 \pm 0.4) \times 10^{-3}$ (K mol)/J was obtained over this temperature range with an A_0 of liquid polypropylene of $(5.7 \pm 0.5) \times 10^{-3}$ (k mol)/J.

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Zusammenfassung — Es wurde eine Abänderung der Nernst–Lindemann Gleichung vorgeschlagen, mit deren Hilfe für feste, lineare Makromoleküle errechnete Wärmekapazitäten bei konstantem Druck (C_p) in Wärmekapazitäten bei konstantem Volumen (C_v) umgerechnet werden können. Zur Ableitung der molaren Konstanten A_0 in dem sich wiederholenden Teil der Gleichung wurde die variable Anzahl der erregten Schwinger bei verschiedenen Temperaturen berücksichtigt. Mit der neuen Gleichung wird es möglich, die C_p fester Polymere für einen breiten Temperaturbereich zu errechnen. Die Konstante wurde für die festen Polymere auf Grund des ermittelten thermischen Ausdehnungsvermögens und der isothermen Kompressibilität sowie der der Literatur entnommenen Wärmekapazitätsangaben berechnet. Aus Angaben von 22 festen Polymeren wurde für A_0(neu) ein Durchschnittswert von $(3{,}9 \pm 2{,}4) \times 10^{-3}$ (K mol)/J erhalten. Verfügt man zur Berechnung von A_0 über keine experimentellen Werte für Kompressibilität und Ausdehnungsvermögen, so kann dieser durchscnittswert als universale Konstante angewendet werden. Die verbleibende Temperaturabhängigkeit von A_0(neu) wird besprochen und Beispielrechnungen für Polyäthylen gegeben. Für Polyäthylen wurden im Temperaturbereich 290 bis 410 K Effekte durch Vorschmelzen und Bewegungen mit großer Amplitude festgestellt.

Резюме — Предложена модификация уравнения Нернста–Линдеманна, используемого для превращения вычисленных теплоемкостей при постоянном давлении (C_p) в теплоемкости при постоянном объеме (C_v) для твердых, линейных макромолекул. В этом уравнении константа A_0 на моль повторяющегося звена выведена с учетом переменного числа вибраторов, возбужденных при различных температурах. С помощью нового уравнения представляется возможным вычислять C_p для твердых полимеров в более широком температурном интервале. Константа A_0 для твердых полимеров вычислена, исходя из литературных значений коэффициентов термического расширения, изотермической сжимаемости и теплоемкости. Исходя из данных для 22 твердых полимеров, было получено среднее значение константы A_0 (новая) равное $(3{,}9 \pm 2{,}4) \cdot 10^{-3}$ К·моль/дж. Такое среднее значение может быть использовано в качестве универсальной константы при вычислении A_0 в случае отсутствия экспериментальных данных по сжимаемости и расширению. Обсуждено изменение новой A_0 от температуры, а расчеты показаны на примере полиэтилена. Для полиэтилена в интервале температур 290–410 К обнаружены эффекты предплавления и возможное движение с большой амплитудой.