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ON THE C_v TO C_p CONVERSION FOR SOLID LINEAR MACROMOLECULES

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The C_v to C_p conversion for solid linear macromolecules via the Nernst–Lindemann equation $C_p - C_v = A_0 C_p^2 T/T_m$ is discussed on hand of data for 10 crystals and seven glasses. An average value of $A_0 = (5.11 \pm 2.41) \cdot 10^{-3}$ mol K J^{-1} was calculated if the mole is assumed to refer to heavy atoms only. This A_0 is numerically equal to the original Nernst–Lindemann constant.

All measurements of heat capacity are done at constant pressure, giving data on C_p. Heat capacities computed from vibrational spectra are, in contrast, always in terms of constant volume, C_v. Over the last years we established the ATHAS data bank [1] which contains critically evaluated heat capacities C_p for close to 100 macromolecules. As one tries to interpret these data in terms of their vibrational spectra [2, 3], it becomes obvious that there is rarely enough information available to use the thermodynamic relationship for C_p to C_v conversion:

$$C_p - C_v = -\frac{T\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T} \qquad (1)$$

For the comparison of measurement and calculation. Eq. (1) has thus central importance. The usual experimental evaluation of Eq. (1) makes use of isothermal compressibility

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad (2)$$

and isobaric expansivity data

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad (3)$$

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leading to

$$C_p - C_v = \frac{TV\alpha^2}{\beta} \tag{4}$$

The exact calculation of $C_p - C_v$ needs thus compressibility and expansivity data over the whole temperature range of the heat capacities of interest, which is usually between 0 and 700 K. Especially for the limiting amorphous and crystalline states, such complete data are not available for any macromolecule. The most frequent approximation used for the calculation of $C_p - C_v$ is that of Nernst and Lindemann [4] which will be discussed in this paper. Earlier work in this laboratory on the application of the Nernst–Lindemann equation dealt with polyethylene [5] and planar network crystals [6].

On the Nernst–Lindemann equation

The Nernst–Lindemann equation [4] is written as

$$C_p - C_v = \frac{A_0 C_p^2 T}{T_m} \tag{5}$$

where A_0, the Nernst–Lindemann constant is perhaps a universal constant, and T_m represents the crystalline melting temperature. The equation is based on the Grüneisen equation of state [7] which relates p, V and total energy through the Grüneisen constant γ.

$$\gamma = \frac{\alpha V}{\beta C_v} \approx \frac{\alpha V}{\beta C_p} \tag{6}$$

Furthermore, the ratio of α / C_p was shown for many metals to be practically constant [8]. This leads on insertion into Eq. (4) to

$$C_p - C_v = A C_p^2 T \tag{7}$$

where A is $V\alpha^2/(\beta C_p^2)$, a characteristic constant for every material, related to the Grüneisen constant. Adding the suggestion that V/β is proportional to the melting temperature T_m, which is based on suggestions of Einstein [9] and Lindemann [10] that the characteristic vibration frequency of a monatomic solid is related to volume, mass, compressibility and melting temperature, one can easily derive Eq. (5) with a value of A_0 of $5.12 \cdot 10^{-3}$ K mol/J or 0.0214 K mol/cal [4].

This far Eq. (5) looks like a well established, useful means to analyze and compare C_p and C_v. It must be pointed out, however, that all assumptions used in the derivation are, at best, semi-empirical. In addition, all equations are derived largely for monatomic solids. A comparison with experiment is thus necessary before applying Eq. (5) to linear macromolecules which have a much more complicated structure. First, it is necessary to refer the constant A_0 to the proper number of base moles.

Heat capacity is always quoted in terms of moles "repeating unit". In principle, A_0 should thus be divided by the number of atoms in the repeating units. It will be shown here, that better agreement with experimental data is achieved if one divides by the number of heavy atoms only, i.e. one neglects the number of H-atoms in the repeating unit. The reason lies with the rather high vibration frequencies of the O—H, N—H, or O—H stretching and bending vibrations, which are excited only to a small degree in the solid state [11, 12]. Furthermore, the basic Grüneisen constant should be constant with temperature only as long as a single vibration frequency can approximate the thermal properties (Einstein approximation). Particularly for macromolecules the Grüneisen "constant" is thus always based on an average frequency and it was shown [13] that this average, and with it the Grüneisen constant, varies with temperature as additional vibrations become excited. One expects thus that the range of extrapolation and the usefulness of an empirical A_0 is limited in temperature. Also, the connection of T_m with a characteristic vibrational frequency [10] is doubtful even for monatomic solids, and certainly could only be treated as an empirical observation for macromolecules. Overall, one must say that the usefulness of A_0 for macromolecules, which is documented below, is surprising. The relatively constant Grüneisen parameter at intermediate temperatures was also studied by thermal conductivity [14], bulk modulus pressure dependence [15], dynamic bulk modulus measurements [16], and thermoelastic effects [17].

A_0 values for macromolecules

A_0 — values for Eq. (5) were calculated for 10 polymeric crystals and seven glasses by equating Eqs (5) and (4) for temperatures close to 298 K. Table 1 displays the data used, results, and references. The average A_0 for the crystals per mole of heavy atom is $(5.4 \pm 2.7) \cdot 10^{-3}$ K mol/J, the average A_0 for the glasses is $(5.1 \pm 2.4) \cdot 10^{-3}$ K mol/J. To convert A_0 to the needed unit per mole of repeating unit these universal values must be divided by the number of heavy atoms in the repeating unit.

Discussion

A typical example of the use of Table 1 and Eq. (5) is that of the comparison of the heat capacities of a series of aliphatic polyoxides at constant volume, calculated from vibrational spectra, with measured heat capacities at constant pressure [18]. Table 1 contains four values for A_0 of the homologous polyoxide series which range from 4.86 (polyethylene) to 3.52 (polyoxymethylene). These data can be fitted with the equation

$$A_0(x) = 4.82 - 1.30\,x \qquad (8)$$

Table 1 Data for the computation of A_0

Polymer*	T_{exp}, K	$V \times 10^5$, $m^3\,mol^{-1}$	$\alpha \times 10^4$, K^{-1}	$\beta \times 10^{10}$, Pa^{-1}	C_p**, $J\,K^{-1}\,mol^{-1}$	T_m***, K	$A_0 \times 10^3$, $mol\,K\,J^{-1}$
				CRYSTALS			
Polyethylene (1)	293	1.40	2.64^a	1.82^a	21.39	414.6	4.86
Polypropylene (3)	290	4.45	3.16^b	1.85^b	65.64	460.7	7.68
	353	4.65	5.29^c	5.52^c	83.66	460.7	4.65
Polytetrafluoroethylene (3)	380–500	2.49	5.71	7.80	62.28	605	4.86^d
Poly(1-butene) (4)	290	5.89	4.13^b	1.85^b	97.96	411	9.28
Poly(4-methyl pentene-1) (6)	293	10.27	2.28^b	3.70^b	141.9	523	2.25
Nylon 6, α (8)	293	9.39	3.29^b	1.43^b	165.8	533	11.02
Poly(vinylidene fluoride)II (4)	293	3.39	1.89^b	1.25^b	70.65	483	3.76
Polyoxymethylene (2)	293	2.00	1.72^b	1.09^b	37.53	457	3.52
Polyoxyethylene (3)	293	3.57	1.97^b	1.17^b	53.61	342	4.22
Polyoxytetramethylene (5)	236	6.42	3.56^e	3.44^e	93.94	330	4.42

Average A_0 for crystals 5.44 ± 2.71

Table 1 (continued)

Polymer*	T_{exp}, K	$V \times 10^5$, $m^3\ mol^{-1}$	$\alpha \times 10^4$, K^{-1}	$\beta \times 10^{10}$, Pa^{-1}	C_p**, $J\ K^{-1}\ mol^{-1}$	T_m***, K	$A_0 \times 10^3$, $mol\ K\ J^{-1}$
				GLASSES			
Poly(vinyl acetate) (6)	298	9.23	2.98^a	2.60^a	101.2	456	8.42
Poly(methyl methacrylate) (7)	298	8.45	2.31^a	2.80^a	137.0	567	3.43
Poly(4,4'-isopropylidene diphenylene carbonate) (19)	298	21.26	2.37^a	2.80^a	304.9	568	4.94
Polystyrene (8)	298	9.88	2.24^a	3.00^a	126.5	516	4.24
	303	9.60	2.87^f	2.54^f	128.8	516	7.76
Poly(2,6-dimethyl-1,4-phenylene oxide) (9)	303	11.30	2.08^f	2.86^f	150.9	535	3.61
Poly(*n*-butylmethacrylate) (10)	280	13.42	4.36^g	3.81^g	222.6	439	6.00
Poly(vinyl chloride) (3)	298	4.56	1.95^h	2.53^h	59.03	531	3.13
					Average A_0 for glasses 5.08 ± 1.90		
					Averages A_0 for crystals and glasses 5.11 ± 2.41		

* Number in parenthasis indicates the number of heavy atoms in the repeating unit, ** data bank recommended data, see Ref. [1], *** for glasses 3/2 T_g was taken as an appropriate replacement for T_m. **References:** *a.* R. K. Arora, Ph. D. Thesis, University of Delhi, Delhi, India (1984). *b.* O. P. Pahuja, Ph. D. Thesis, University of Delhi, Delhi, India (1983). *c.* V.-H. Karl. F. A. Asmussen and K. Ueberreiter, Makromol. Chem., 178 (1977) 2649. *d.* S. F. Lau, H. Suzuki and B. Wunderlich, J. Polymer Sci., Polymer Phys. Ed. 22 (1984) 379, average over the whole temperature range. *e.* R. K. Jain and R. Simha, J. Polym. Sci., Polymer Phys. Ed., 17 (1979) 1929. *f.* P. Zoller and H. H. Hoehn, J. Polym. Sci., Polymer Phys. Ed., 20 (1982) 1385. *g.* O. Olabisi and R. Simha, Macromolecules, 8 (1975) 206. *h.* P. L. M. Heydemann and H. D. Guicking, Kolloid Z. Z. Polym., 193 (1964) 16.

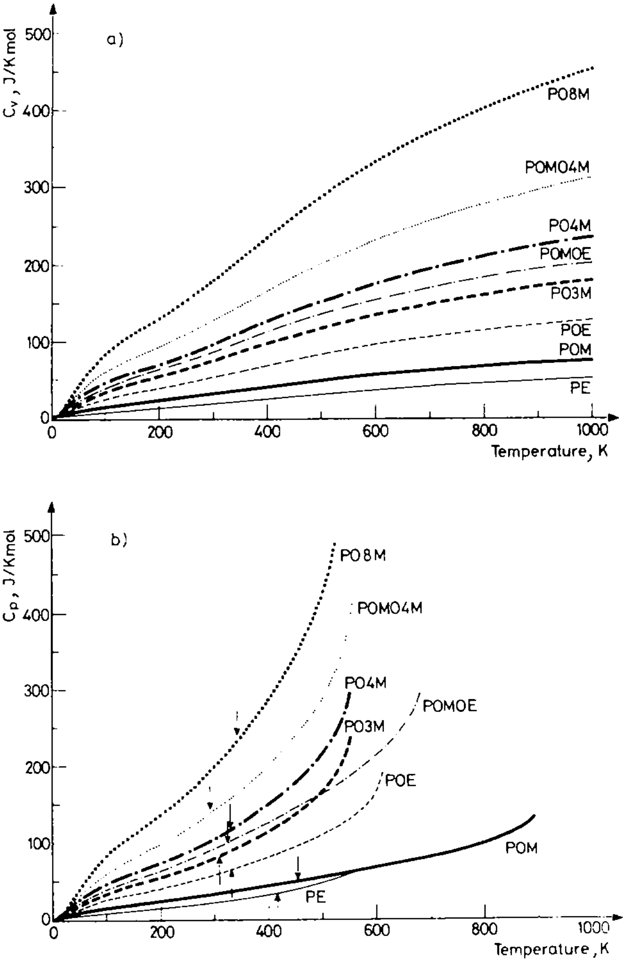

Fig. 1 Calculated heat capacities C_v (a) and C_p (b). PE: polyethylene, POM: polyoxymethylene, POE: polyoxyethylene, PO3M: polyoxytrimethylene, POMOE: polyoxymethyleneoxyethylene, PO4M: polyoxytetramethylene, POMO4M: polyoxymethyleneoxytetramethylene, PO8M: polyoxyoctamethylene. C_v was calculated from an approximate skeletal vibration spectrum (Tarasov) and group vibrations. The C_v to C_p conversion was carried out using Eq. (5) with values of $A_0(x)$ from Eq. (8) using the appropriate number of heavy atoms. For details see Ref. [18]. The arrows in Figure 1b indicate the melting temperatures of the respective polymers

where x is the oxygen to carbon atom ratio. Figure 1 shows the calculated C_v and C_p over a wide temperature range for crystalline polyoxides which have experimentally known heat capacities [1]. The melting temperatures which limit the practical application of the data are indicated by arrows in Fig. 1b. The average deviation of the calculated C_p from the experimental C_p is less than 5%, only slightly larger than the usual intrinsic agreement of data bank data from different laboratories (3%). Up to the melting temperature it seems thus empirically permissible to use a constant A_0-value fixed by an experimental set of data at one temperature only. In case even these limited data are not available it may even be sufficient to use the universal (average) A_0 values of Table 1 which, in turn, are similar to those derived for metals [4], salts [4], and layer crystals [6] if contributions from hydrogen atoms are ignored.

At temperature above melting a rather sharp upturn in C_p is noticed. Although this temperature range is far from realistic for actual experimentation, we feel that this upturn in the calculated C_p, which contrasts the more moderate increase in C_v, is an indication of the limit of usefulness of the Nernst—Lindemann equation at high temperature. A continuous decrease in A_0 is expected due to the increasing excitation of C—H bending frequencies. Similarly it was shown for many polymers that the Grüneisen 'constant' (Eq. 6) decreases slowly with increasing temperature [19, 20].

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Zusammenfassung — An Hand von sich auf 10 Kristalle und 7 Gläser beziehenden Daten wird die Umrechnung von C_V- in C_p-Werte für feste lineare Makromoleküle mittels der Nernst—Lindemann-

Gleichung $C_p - C_v = A_0 C_p^2 T/T_m$ diskutiert. Ein Durchschnittswert von $A_0 = (5.11 \pm 2.41) \cdot 10^{-3}$ mol K J^{-1} wurde unter der Annahme berechnet, daß sich das Mol nur auf schwere Atome bezieht. Dieser A_0-Wert ist numerisch gleich der ursprünglichen Nernst—Lindemann-Konstanten.

Резюме — На основе имеющихся данных для 10 кристаллов и нескольких стекол, обсуждено превращение C_v до C_p, исходя из уравнения Нернста—Линдеманна $C_p - C_v = A_0 C_p^2 T/T_m$. Предполагая, что моль относится только к тяжелым атомам, было вычислено среднее значение A_0 равным $(5.11 \pm 2.41) \cdot 10^{-3}$ моль • Кдж$^{-1}$. Это значение A_0 численно равно первоначальной константе уравнения Нернста—Линдеманна.