

THE SPECIFIC HEAT OF GRAPHITE: AN EVALUATION OF MEASUREMENTS

A.T.D. BUTLAND and R.J. MADDISON

UKAEA, Atomic Energy Establishment, Winfrith, Dorchester, Dorset, UK

Received 27 June 1973

This paper reviews the measurements and evaluations of the specific heat at constant pressure for graphites in the temperature range 200 K to 3500 K. A polynomial fit to the data is made for use with nuclear graphite, valid over the range 250 K–3000 K. Some consideration is given to the difference between the specific heat at constant volume and at constant pressure. A measurement of the graphite phonon frequency spectrum at 1800 K is used to calculate the specific heat at constant volume, and then to modify slightly the polynomial fit to the constant pressure data.

Cet article passe en revue les mesures et les évaluations de la chaleur spécifique à pression constante pour les graphites entre 200 et 3500 K. Une représentation des résultats par un polynôme utile pour le graphite nucléaire, est valable entre 250 et 3000 K. Quelques considérations sont données sur la différence entre la chaleur spécifique à volume constant et à pression constante. Une mesure du spectre de fréquence des phonons du graphite à 1800 K est utilisée pour calculer la chaleur spécifique à volume constant et pour modifier légèrement l'ajustement d'un polynôme aux résultats à pression constante.

In dieser Arbeit werden die experimentellen und berechneten Werte der Wärmekapazität von Graphit bei konstantem Druck zwischen 200 und 3500 K zusammengestellt. Ein Polynom wird für Reaktorgraphit zwischen 250 und 3000 K angegeben. Einige Überlegungen zur Differenz zwischen der Wärmekapazität bei konstantem Volumen und konstantem Druck werden mitgeteilt. Mit Hilfe des gemessenen Phononenspektrums von Graphit bei 1800 K wird die Wärmekapazität bei konstantem Volumen berechnet, aus deren Ergebnis eine geringe Modifizierung des Polynoms für die Werte bei konstantem Druck folgt.

1. Introduction

Measurements of the specific heat of graphite are normally made on the artefact, i.e., a block of graphite crystals, at constant pressure, and this leads to some difficulties when we try to relate the specific heats at constant pressure and at constant volume, as will be seen in sect. 2.

Sect. 3 features a review of measurements and evaluations of constant pressure data, for the artefact, in the temperature range 200 K–3500 K. This is followed in sect. 4 by a polynomial fit to the data, valid over the range 250 K–3000 K.

Sect 5 attempts to derive a relation for the specific heat at constant volume, valid over the range 250 K–3000 K. This is followed in sect. 6 by a modification of the polynomial for C_p in the light of measured data on the phonon frequency spectrum for graphite.

2. The specific heats at constant pressure, and at constant volume

From the first and second laws of thermodynamics it may easily be shown that the specific heats at constant pressure, C_p , and at constant volume, C_v , are related by

$$C_p - C_v = -T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_T,$$

which may also be written as

$$C_p - C_v = \alpha_v^2 TV / \beta, \quad (1)$$

where $\alpha_v = V^{-1}(\partial V / \partial T)_P$, the volume expansion coefficient, and $\beta = -V^{-1}(\partial V / \partial P)_T$, the compressibility. Thus C_v may be calculated from measurements of C_p if α_v and β are known at the required tempera-

Table 1

Measurements in graphite of specific heat at constant pressure above 200 K.

No.	Reference	Type of graphite	Details of measurement	Symbol in figs. 1 and 2
1	Magnus (1915) [1] Magnus (1923) [2]	A form of artificial graphite	283 K–1103 K; measurement of heat content used to produce a polynomial expression for C_p	A
2	Worthing (1918) [3]	A form of artificial graphite	1173 K–2372 K	B
3	Von Schlapper and Debrunner (1924) [4]	Two forms of graphite; one appears to be for an electric arc, and the other is probably rather like coke	Data not available	—
4	Rossini et al. (1953) [5]	No information, probably prepared from petroleum	298 K–1500 K	—
5	Desorbo and Tyler (1953) [6]	High purity Acheson	13 K–300 K	O
6	Rasor and McClelland (1957) [7]	Four types of graphite were considered: (a) 3474D } –Speer Carbon Co. (b) 7087 } (c) GBH } –National Carbon Co. (d) GBE } GBH shows a lower thermal conductivity than AGOT, a nuclear graphite, indicating a lesser degree of graphitization than the latter, since heat is transferred predominantly by phonon vibrations	In each case the temperature range is from 1366 K to the destruction temperature (~ 4144 K). The results are presented in graphical form only. Type 7087 seems consistently to exhibit the highest specific heat, and type GBE the lowest, the differences being of order 9% at 1800 K. The experimental errors are, however, of this magnitude. Data, of a later vintage, are reported for 3474D graphite by Russell and McClelland [8] (see Item 7).	—
7	Russell and McClelland (1960) [8]	3474 D, described as very fine-grained and uniform.	1447 K–3905 K	F
8	Lucks et al. (1960) [9]	7087 and GBH graphite (see Item 5 above for discussion of GBH graphite)	366 K–1922 K. Total heat content determinations were used to produce an enthalpy plot, the slope of which was used to determine the specific heat. The two graphites show identical specific heat up to 1000 K, but diverge at higher temperatures, 7087 being about 5% higher at 1922 K	J (7087) K (GBH)
9	Fieldhouse et al. (1960) [10]	ATJ (Union Carbide Corp.). Used in fine grain moulds and dies for continuous metal casting, diamond core bit moulds, rocket motor nozzle inserts. Exhibits a lower thermal conductivity than nuclear graphite, probably not as highly graphitized as the latter (i.e. exhibiting a lesser degree of order)	700 K–1811 K. Measurement made in a helium atmosphere. Data vary smoothly and monotonically	M

Table 1 (Cont'd)

No.	Reference	Type of graphite	Details of measurement	Symbol in figs. 1 and 2
10	Fieldhouse and Lang (1962) [11]	ATJ	533 K–3033 K. Data exhibit a wide spread and lack a smooth monotonic temperature variation	L
11	Neel et al. (1962) [12]	CS. Used as rocket nozzle inserts and for constructing moulds and crucibles. Exhibits a somewhat lower electrical conductivity than nuclear graphite, and is therefore probably rather less well graphitized.	4 data points at 1644 K, 1922 K, 2200 K and 2478 K. The measurements indicate no temperature variation of specific heat	N
12	West and Ishihara (1965) [13]	Commercial graphite – no specification given	1200 K–2600 K. A consistent set of measurements featuring a monotonic temperature variation of specific heat.	H
13	Barriault et al. (1962) [14]	Commercial graphite – no specification given	1993 K–2483 K. Data features a wide spread and reported error of 5%. Impossible to decide temperature variation of specific heat	G
14	Kraftmakher and Shestopal (1965) [15]	Only details given are that the material was spectrally pure graphite of specific weight 1.61	1750 K–2850 K. Sample heated by an alternating current. Temperatures measured by the accurate technique of colour pyrometry. Results presented in a graphical manner only	D
15	McDonald (1965) [16]	SPK graphite, an extruded graphite of high purity used for electrodes	300 K–1800 K; measurements of heat content used to calculate enthalpy and specific heat	C
16	Perry (1950) [17]	Almost certainly an artificial graphite. The temperature range is large and the data above 3000 K quite different from other measurements, suggesting original work	100 K–5000 K	E
17	Reported in a compilation edited by Touloukian (1970) [18] Date of measurement 1962.	Reported as 'a graphite brick'	A single measurement at 729 K	I

tures. Since both α_v and β are positive for graphite, $C_p - C_v \geq 0$.

Eq. (1) may be rewritten as

$$C_p = C_v [1 + \gamma \alpha_v T], \quad (2)$$

where $\gamma = \alpha_v V / \beta C_v$. The parameter γ is called Grüneisen's constant; it may be assumed to be temperature-independent, and is dimensionless. Thus by calculating γ at some arbitrary temperature, C_v can be calculated from C_p at some other temperature

from a knowledge of α_v , thereby eliminating the necessity for a knowledge of the temperature dependence of β .

Strictly the specific heat measured for graphite at constant pressure is *not* that used in eqs. (1) and (2). The latter applies to a single graphite crystal, whereas the former applies to a block of graphite consisting of many crystals.

$$C_p \text{ for the artefact} = C_p \text{ for the crystal} + \begin{array}{l} \text{Contribution from relative crystal} \\ \text{movement, e.g. work done against} \\ \text{frictional forces} \\ \\ \text{Contribution from changes in crystal} \\ \text{surface energy, due to partial loss of} \\ \text{internal order at surfaces.} \end{array}$$

It is therefore clear that the measured C_p is an overestimate of the single crystal value, but by an amount which is difficult to quantify. This overestimation will be carried through to any values deduced for C_v , although the value of V used in eq. (1) or in calculating γ may be too large due to insufficient allowance for intercrystal voids in graphite blocks, with a consequent underestimate of C_v .

Owing to the great difficulty in quantifying the two additional contributions to the crystal C_p present in the measured C_p , no consideration has been given to them here: the measurements are taken as an estimate of the crystal C_p . Little error will result from this approximation since the graphite density changes with temperature are small, indicating that the amount of crystal movement and re-ordering must also be small; in addition, the amount of energy stored as surface energy must be small compared to that stored as internal energy, owing to the fact that the majority

Table 2
Evaluations of specific heat measurements.

Reference	Data used in evaluation	Details of evaluation
Wagman et al. (1945) [20]	Nernst (1911) [21] Worthing (1918) [3] Magnus (1915, 1923) [1, 2] Schlapfer and Debrunner (1924) [4] Jacobs and Parks (1934) [22]	Nernst (1911) [21] and Jacobs and Parks (1934) [22] provide low temperature data Data analysed graphically to yield selected 'best' values over the temperature range 0 K–1500 K
Spencer (1948) [23]	Petroleum Institute Publication (1947). Same data also seems to have been published by Rossini et al. (1953) [5]	Cubic fit to specific heat data produced by a least-squares analysis. Maximum % deviation of fit is recorded as 0.72%
Kelley (1949) [24]	Various references including Magnus (1915, 1923) [1, 2] Worthing (1918) [3] Wagman et al. (1945) [20]	Polynomial fit to enthalpy is made, and differentiated to produce a polynomial for C_p . The temperature range is 298 K–2300 K
Nightingale et al. (1962) [25]	Rossini et al. (1953) [5] Rasor and McClelland (1956) [7]	Tabulated data, 298 K–3500 K
Mantell (1968) [26]	Desorbo and Nichols (1958) [27] (for temps. below 300 K) Spence (1963) [28] Van der Hoeven and Keesom (1963) [29]	Recommends polynomials for C_p , valid over the temperature ranges 0 K–300 K, and 300 K–3200 K

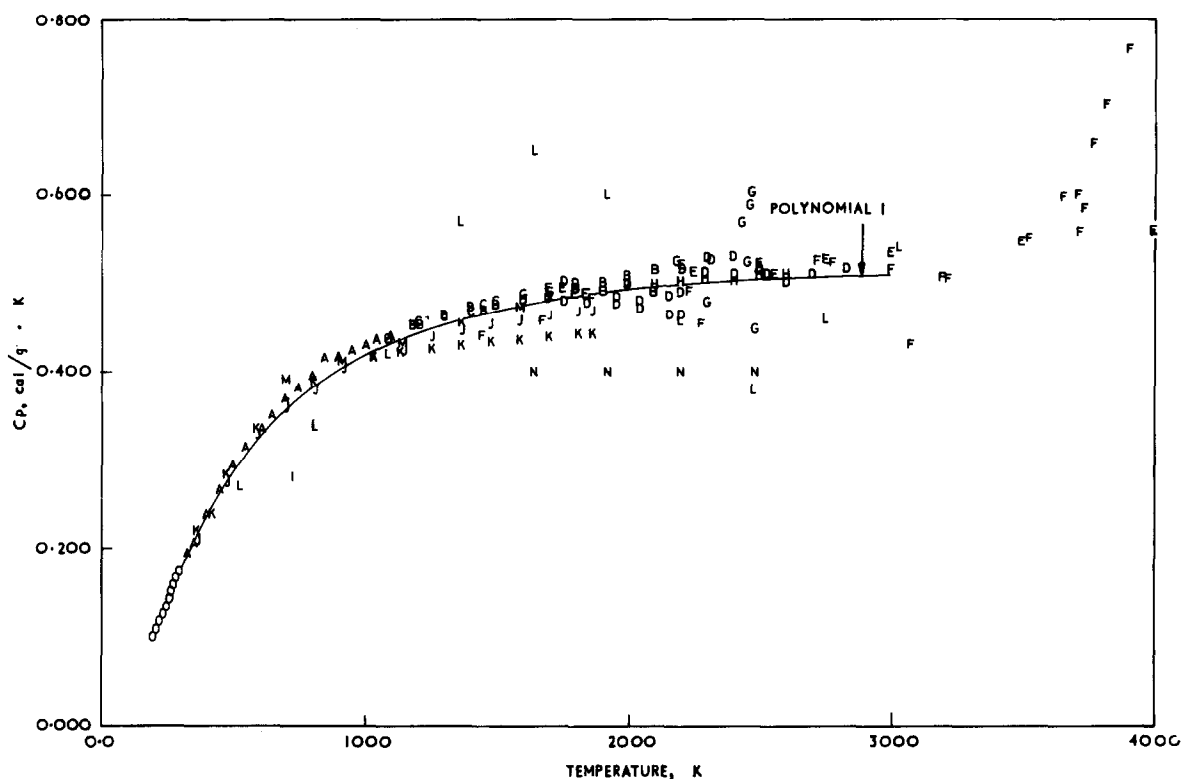


Fig. 1. Specific heat data for graphite over the temperature range 200 K–4000 K.

of carbon atoms are inside rather than on the surface of a crystal.

In conclusion it must be said that the values used for α_v , V and β should be crystal values and *not* bulk values, C_v being defined for the crystal.

3. Review of measurements and evaluations of C_p

Table 1 [1–18] summarises the main experimental determinations of C_p (or of enthalpy) at temperatures in the range 200 K–3500 K: from this summary we omit references which merely reproduce data originally published elsewhere. It will be noticed that none relate specifically to reactor grade graphite; some were made with natural graphites, and others with various other kinds of artificially produced graphites. The physical chemistry of carbon is so complex (see for example Cahn and Harris [19]), and the types of artificial graphite so numerous, as to make it difficult to determine whether any of the graphites used in the experiments bear any close affinity to reactor grade graphite.

Table 2 [1–5, 7, 20–29] features a list of evaluations of C_p , made using various combinations of data, some from table 1. Since none of these evaluations represented an effort to obtain a set of best data for use with nuclear graphite, and in view of the wide dispersion of the experimental data, especially above 1000 K, we found it necessary to make an independent assessment.

All the available data from table 1 are plotted in fig. 1. The symbols in fig. 1 refer to table 1. It is obvious that the data in the range 200 K to about 800 K are fairly consistent apart from two measurements due to Fieldhouse et al. [11] and the single measurement reported in the compilation by Touloukian [18]. At higher temperatures, however, the measurements diverge noticeably, with some experimenters, particularly Fieldhouse and Lang [11], reporting an extremely large scatter of data.

The general trend of the data in fig. 1 is for C_p to rise quickly between 200 K and about 1000 K, and then to flatten out, until another sharp rise occurs above 3400 K. The first rise and subsequent flattening off is typical of most solids and falls into the

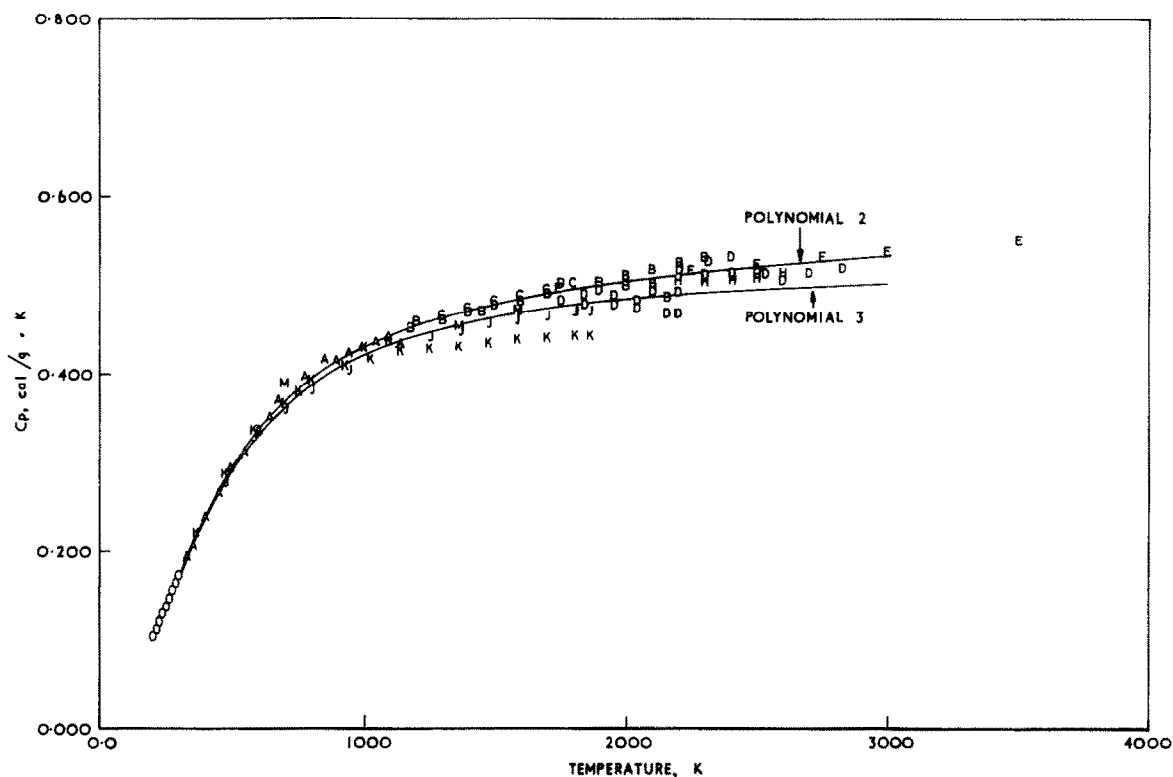


Fig. 2. The 'best' data for the graphite specific heat in the range 200 K–3500 K.

Debye pattern; the second rise is due to the formation of vacancies and interstitial carbon atoms.

4. Polynomial fit to data for C_p

The Debye theory of specific heat leads to an expression which has no exact analytic form. At temperatures high compared with the Debye temperature, θ_D (about 420 K (see Flubacher et al. [30]) or above for graphite) this expression may be approximated for one mole by

$$C_v/3R = 1 + D'/T^2 + E'/T^3 + F'/T^4,$$

where T is the temperature in deg K and R is the gas constant.

Since $C_p - C_v = \alpha_v^2 VT/\beta$, as discussed in sect. 2, and α_v , V and β exhibit little temperature dependence (see sect. 5), then

$$C_p/3R \sim 1 + D'/T^2 + E'/T^3 + F'/T^4 + B'T.$$

This polynomial form will not necessarily fit the experimental data for $T \sim \theta_D$, consequently the missing term in T^{-1} was added to attempt to allow for this; in addition the constant term was not fixed at unity.

The final polynomial form used in the least-squares fits to the experimental data was therefore

$$C_p = A + BT + C/T + D/T^2 + ET^3 + F/T^4.$$

An unweighted least-squares polynomial fit to all the available data gave polynomial 1:

$$\begin{aligned} C_p = & 0.630375 - 1.60535 \times 10^{-5} T \\ & - 225.861 T^{-1} + 3100.10 T^{-2} \\ & - 910737.0 T^{-3} - 9.64607 \times 10^7 T^{-4}, \end{aligned}$$

where T is in deg K and C_p in cal/g·K. This polynomial is plotted together with all the available data in fig. 1.

An attempt was then made to make a polynomial fit to the best sets of data available in table 1. Inspection of fig. 1 resulted in the following sets of data being rejected, because they were far removed from the main body of data, or because they showed such a large spread within the set as to render them valueless:

Russell and McClelland [8],

Barriault et al. [14],

Data from Touloukian [18],

Fieldhouse et al. [11],

Neel et al. [12].

The remaining data are plotted in fig. 2 over the temperature range 200 K–3500 K.

Since nuclear graphite is well graphitized (and of high purity), measurements made on poorly graphitized material were rejected, i.e.

Lucks et al. [9] – GBH graphite,

Fieldhouse et al. [10].

The data of Kraftmakher and Shestopal [15] and Lucks et al. [9] (7087 graphite) were also rejected, because they consistently exhibited a low specific heat above about 900 K, when compared with other measurements – the reasons for this are not known. These measurements *may* give some indication of the differences to be expected between the high-temperature specific heats of various types of artificial graphite.

An unweighted least-squares fit to the remaining data, i.e.

Magnus [1, 2],

Worthing [3],

Desorbo and Tyler [6],

Perry [17],

West and Isihara [13],

McDonald [16],

gave polynomial 2:

$$C_p = 0.538657 + 9.11129 \times 10^{-6}T - 90.2725T^{-1} - 43449.3T^{-2} + 1.59309 \times 10^7 T^{-3} - 1.43688 \times 10^9 T^{-4},$$

where T is in deg K and C_p in cal/g·K. This polynomial

Table 3
Calculated values for C_p .

Temperature (K)	Specific heat, C_p (cal/g·K)	
	Polynomial 1	Polynomial 2
300	0.17150	0.17035
700	0.35669	0.36786
1000	0.41845	0.42854
1500	0.46921	0.47727

is illustrated in fig. 2, where it is seen to pass smoothly through the data used in its production, but to be towards the higher end of the general spread of data.

No experimental errors were available for the data used in the above fits. It can however be said that the fitted polynomials agreed with the experimental data used to within their mean probable error.

Specific heats at specimen temperatures calculated using polynomials 1 and 2 are recorded in table 3.

It is obvious that polynomial 2 gives results which are everywhere higher than those given by polynomial 1, particularly at temperatures above 700 K, where the differences are up to 2%.

It should be noted that although data which span the temperature range 200 K–3500 K were used in the fitting procedure, the resultant polynomials may only be used with confidence over the range 250 K–3000 K. This is because as the polynomial draws towards either end of the fitted range less constraints are placed upon it, the bulk of the data now being ‘behind’ it; consequently errors in the fit, and at least in the slope, may be expected at these extremities.

5. Production of a relation for C_v

5.1. Measurements of the crystal volume expansion coefficient α_v

Kelly and Taylor [31] list a number of measurements of expansion coefficients for a graphite crystal; these are recorded in table 4, as coefficients in the basal plane (α_B), and perpendicular to it (α_z). There appear to have been only two measurements of α_B , that by Nelson and Riley giving some indication of

Table 4
Measurements of the expansion coefficients of crystalline graphite.

Reference	Temperature range (K)	α_z (K^{-1})	α_B (K^{-1})
Backhurst (1922) [32]	300 – 1073	28.7×10^{-6} a)	–
Nelson and Riley (1945) [33]	Ceylon nat. graphite, 288 – 1073	Polynomial fit b)	Average estimates b)
Walker et al. (1953) [34]	77 – 1283	28.6×10^{-6} a)	–
Matuyama (1955) [35]	1273 – 2073	28.09×10^{-6} a)	0.95×10^{-6} a)
Matuyama (1958) [36]	288 – 1073	27.0×10^{-6} a)	–
Baskin and Mayer (1955) [37]	Natural graphite, 78 – 296 Art. graphite, 78 – 296	22.0×10^{-6} a) 27.9×10^{-6} a)	– –
Steward and Cook (1960) [38]	Samples with different degrees of order	$(28.4 \pm 0.7) \times 10^{-6}$ a) $(29.2 \pm 0.7) \times 10^{-6}$ a)	– –
Steward et al. (1960) [39]	273 – 2873	26.4×10^{-6} a)	–

a) Average values over the temperature range.

b) $\alpha_z = 27.00 \times 10^{-6} + 3.05 \times 10^{-9} (T - 273)$; T in deg K,
 $\alpha_B = -1.5 \times 10^{-6}$; 273 – 523 K,
 $\alpha_B = 0.0$; 673 K,
 $\alpha_B = 0.9 \times 10^{-6}$; 873 – 1073 K.

temperature dependence. The measurements of average values for α_z are in good agreement, and consistent with the polynomial fit given by Nelson and Riley.

In establishing a relation for C_v over the range 250 K–3000 K it seems reasonable to take the polynomial expression for α_z due to Nelson and Riley as valid over the whole temperature range. In the case of α_B the work of Nelson and Riley, and Matuyama may be extended to give the smooth variation

$$\alpha_B = -1.5 \times 10^{-6} \text{ per deg K; } 250 \text{ K} - 523 \text{ K,}$$

$$\alpha_B = (1.0 \times 10^{-8} T - 6.73 \times 10^{-6}) \text{ per deg K; } 523 \text{ K} - 673 \text{ K,}$$

$$\alpha_B = (0.45 \times 10^{-8} T - 3.0285 \times 10^{-6}) \text{ per deg K; } 673 \text{ K} - 873 \text{ K,}$$

$$\alpha_B = 0.9 \times 10^{-6} \text{ per deg K; } 873 \text{ K} - 1073 \text{ K,}$$

$$\alpha_B = (2.5 \times 10^{-10} T + 0.63175 \times 10^{-6}) \text{ per deg K; } 1073 \text{ K} - 1273 \text{ K,}$$

$$\alpha_B = 0.95 \times 10^{-6} \text{ per deg K; } 1273 \text{ K} - 3000 \text{ K.}$$

$$\alpha_v \text{ may be found from } \alpha_v = \alpha_z + 2\alpha_B.$$

5.2. Measurements of the crystal compressibility

A number of compressibility measurements made on blocks of graphite exist, but only one appears to be recorded for a graphite crystal. This is by Bridgman [40] who gives

$$\beta = 2.92 \times 10^{-12} \text{ cm}^2/\text{dyne},$$

presumably at room temperature.

In their study of graphite thermal properties, Kelly and Taylor [31] quote no further values.

Table 5
Some calculated values for C_v .

Temperature (K)	C_p , (cal/g·K)	C_v (cal/g·K)	C_p/C_v
300	0.17035	0.170	1.004
700	0.36786	0.364	1.010
1000	0.42854	0.422	1.016
1500	0.47727	0.465	1.026
1800	0.49409	0.479	1.032

5.3. Estimation of Grüneisen's constant

Eq. (1) may be used at room temperature (293 K), together with polynomial 2 for C_p and the above information on α_v and β , to give

$$C_v (293 \text{ K}) = 0.16500 \text{ cal/g·K}.$$

The graphite crystal density was assumed to be 2.270 g/cm^3 (see O'Driscoll and Bell [41]). From this Grüneisen's constant, γ , for graphite is estimated to be 0.526.

5.4. Relation for C_v

Using polynomial 2 for C_p we may write

$$C_v = [0.538657 + 9.11129 \times 10^{-6}T - 90.2725T^{-1} - 43449.3 T^{-2} + 1.59309 \times 10^7 T^{-3} - 1.43688 \times 10^9 T^{-4}] [1 + \gamma\alpha_v T]^{-1},$$

where T is in deg K, C_v in cal/g·K, and γ and α_v are given above. This relation is valid for the temperature range 250 K–3000 K.

It is obvious that C_v will always be less than C_p , and by an amount which increases monotonically

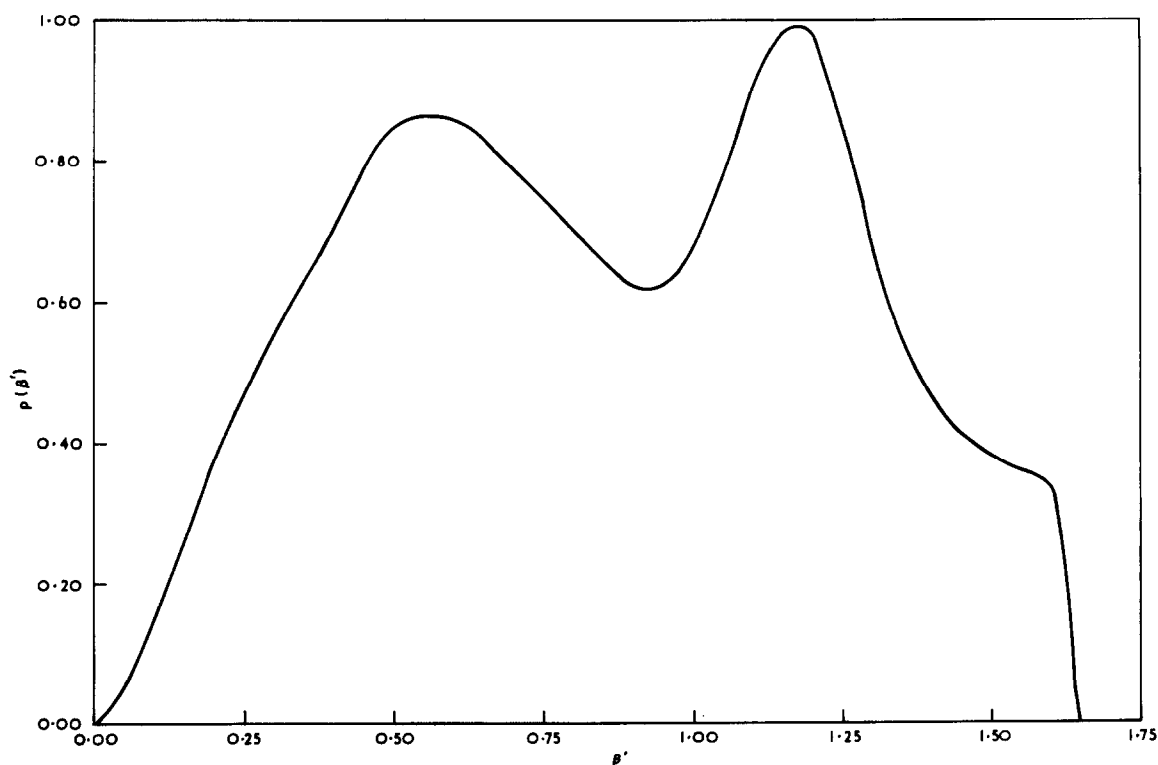


Fig. 3. The phonon frequency function for graphite at 1800 K (Page and Haywood [42]).

with temperature; the differences between the two specific heats are illustrated in table 5.

6. Evaluation of C_v from measurements of thermal neutron scatter; adjustment of polynomial for C_p

Page (see Page and Haywood [42], and Page [43]) developed a phonon frequency function, $\rho(\omega')$, illustrated in fig. 3, for 1800 K, from differential measurements of the graphite scattering cross section made at Chalk River, Canada.

The phonon frequency function is related to the specific heat at constant volume by

$$C_v/3R = \int_0^\infty \rho(\omega') \frac{\beta'^2 \exp(\beta')}{[\exp(\beta') - 1]^2} d\omega', \quad (3)$$

where

$$\int_0^\infty \rho(\omega') d\omega' = 1,$$

$$\beta' = \hbar\omega'/k_B T,$$

$$\omega' = \text{phonon frequency in radians/sec},$$

$$k_B = \text{Boltzmann's constant.}$$

$$\hbar = \text{Planck's constant divided by } 2\pi,$$

$$T = \text{temperature of scatterer in deg K.}$$

Therefore it is possible to use Page's frequency spectrum to calculate a value for C_v at 1800 K, and to incorporate this into the development of a temperature dependent relation for C_v , and some adjustment of the polynomial fit made to C_p . The prediction for C_v made from Page's model is given in table 6, 3.5% lower than that predicted by the evaluation in sect. 5

Table 6
 C_v predicted by Page's model.

Model temperature	C_v (cal/g·K)
1800 K	0.462

It is obvious from eq. (3) that C_v is not strongly dependent on any particular part of the phonon frequency spectrum. It is also true to say that drastic changes in $\rho(\omega')$ do *not* lead to correspondingly large changes in the calculated value for C_v . This observation may be illustrated by considering only those modes in the frequency spectrum for which $\beta' < 1.0$, their area being normalised to unity. This leads to an increase of only 2% in the calculated C_v .

We may therefore conclude that

- (a) the detailed form of the phonon frequency spectrum does not affect the precise value of C_v very significantly, and
- (b) that knowledge of the frequency spectrum provides a good estimate of C_v .

An increase of 116% in $\gamma\alpha_v T$ at 1800 K is necessary in order to bring the evaluation of sect. 5 into agreement with Page's prediction of C_v . Such an increase in α_v is not possible, and to assume a change in γ of this magnitude is difficult to justify without measurements of its temperature dependence. Instead, the difference between the evaluated and calculated value for C_v is thought to reflect an error in the polynomial derived for C_p , which results in a 3.5% overestimate at 1800 K. This may be justified, with reference to fig. 2, by noting that the second polynomial fit to C_p may be a little too high above about 800 K, where spreads in the measurements of up to 10% occur (see sects. 3 and 4).

The second polynomial fit to C_p has therefore been changed in a manner which grows more important with increasing temperature, by adjusting the constant and the coefficient of the term in T to give polynomial 3:

$$\begin{aligned} C_p = & 0.54212 - 2.42667 \times 10^{-6} T \\ & - 90.2725 T^{-1} - 43449.3 T^{-2} \\ & + 1.59309 \times 10^7 T^{-3} - 1.43688 \times 10^9 T^{-4}, \end{aligned}$$

where C_p is cal/g·K, and T in deg K.

This ensures that the value for C_v at 1800 K, evaluated in the manner prescribed in sect. 5, is in agreement with Page's prediction, whilst the estimate of C_p at 300 K is unchanged, the experimental data being relatively consistent in this region.

Values for C_p and C_v calculated using this poly-

nomial are compared with those predicted by the unadjusted polynomial, for sample temperatures, in table 7. It is obvious that the largest changes in C_p have been made at the higher temperatures, and that the calculated value for C_v is now in agreement with Page's prediction. All the changes made are within the spread of experimental data.

Table 7
Comparison of calculated values for C_p and C_v (cal/g·K).

Temperature (K)	Unadjusted polynomial		Adjusted polynomial	
	C_p	C_v	C_p	C_v
300	0.17035	0.170	0.17035	0.170
700	0.36786	0.364	0.36326	0.360
1000	0.42854	0.422	0.42047	0.414
1500	0.47727	0.465	0.46342	0.452
1800	0.49409	0.479	0.47678	0.462

7. Conclusions

A survey of specific heat measurements in the range 200 K–3500 K has been conducted, and attempts made to eliminate the worst data and to isolate measurements appropriate to nuclear graphite. The latter proved difficult in view of the dearth of data specifically for nuclear graphite. An unweighted least squares fit to the 'best' data gave the following polynomial expression for C_p , valid over the range 250 K–3000 K:

$$C_p = 0.538657 + 9.11129 \times 10^{-6}T - 90.2725T^{-1} - 43449.3T^{-2} + 1.59309 \times 10^7 T^{-3} - 1.43688 \times 10^9 T^{-4},$$

where C_p is in cal/g·K and T in K.

From a survey of data on the volume expansion coefficient α_v , and compressibility, the following relation for C_v is deduced:

$$C_v = C_p / [1 + \gamma \alpha_v T],$$

where C_p is given above, and $\gamma = 0.526$. α_v is to be

evaluated from the expressions given in subsect. 5.1.

After consideration of the graphite phonon frequency spectrum at 1800 K, measured by Page [43], which enables C_v to be calculated, a revised polynomial for C_p is deduced, i.e.

$$C_p = 0.54212 - 2.42667 \times 10^{-6}T - 90.2725T^{-1} - 43449.3T^{-2} + 1.59309 \times 10^7 T^{-3} - 1.43688 \times 10^9 T^{-4},$$

where C_p is in cal/g·K and T in deg K.

The relation recommended for C_v is changed correspondingly.

References

- [1] A. Magnus, *Ann. der Phys.* 48 (1915) 983.
- [2] A. Magnus, *Ann. der Phys.* 70 (1923) 303.
- [3] A.G. Worthing, *Phys. Rev.* 12 (1918) 199.
- [4] P. Von Schlappfer and P. Debrunner, *Helv. Chem. Acta* 7 (1924) 31.
- [5] F.D. Rossini, K.S. Pitzer, R.L. Arnott, R.M. Brown and G.C. Pimental, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons*, Pittsburgh Carnegie Institute (1953)
- [6] W. Desorbo and W.W. Tyler, *J. Chem. Phys.* 21 (1953) 1660.
- [7] N.A. Rasor and J.D. McClelland, *USAF Report WADC-TR-56-400* (1957).
- [8] N.S. Russell and J.D. McClelland, *J. Phys. Chem. Solids* 15 (1960) 17.
- [9] C.F. Lucks, H.W. Deem and W.D. Wood, *Am. Ceram. Soc. Bull.* 39 (1960) 313.
- [10] I.B. Fieldhouse, J.I. Lang and H.H. Blau, *USAF Report WADC-TR-59-744* (1960).
- [11] I.B. Fieldhouse and J.I. Lang, *USAF Report WADD-TR-60-904* (1962).
- [12] D.S. Neel, C.D. Pears and S. Oglesby Jr., *USAF Report WADD-TR-60-924* (1962).
- [13] E.D. West and S. Ishihara, *Third ASME Symp. on Thermophysical Properties*, Purdue Univ. USA (1965) p. 146.
- [14] R.J. Barriault et al., *USAF Report ASD-TR-61-260* (1962).
- [15] Ya. A. Kraftmakher and V.O. Shestopal, *J. Appl. Mech. and Tech. Phys. (USSR)* 4 (1965) 117.
- [16] R.A. McDonald, *J. Chem. Engng. Data* 10 (1965) 243.
- [17] J.H. Perry (editor), *Chemical engineering handbook* (McGraw Hill, New York, 1950).
- [18] Y.S. Touloukian (editor) *Thermophysical properties*

- of matter, vol. 5 (Thermophysical Properties Research Centre, Purdue University, USA, 1970).
- [19] R.W. Cahn and B. Harris, *Nature* 221 (1969) 5176.
 - [20] D.D. Wagman, J.E. Kilpatrick, W.J. Taylor, K.S. Pitzer and F.D. Rossini, *J. Res. Nat. Bur. Stds.* 34 (1945) 143.
 - [21] W. Nernst, *Ann. der Phys.* 36 (1911) 395.
 - [22] C.J. Jacobs and G.S. Parks *J. Amer. Chem. Soc.* 56 (1934) 1513.
 - [23] H.M. Spencer, *J. Ind. Engng. Chem.* 40 (1948) 2152.
 - [24] K.K. Kelley, *Bulletin U.S. Bureau of Mines*, (1949) p. 476.
 - [25] R.E. Nightingale, H.H. Yoshikawa and H.H.W. Losty *Nuclear Graphite* (Academic Press, New York, 1962).
 - [26] C.L. Mantell, *Carbon and Graphite Handbook*, (Interscience, New York, 1968).
 - [27] W. Desorbo and G.E. Nichols *J. Phys. Chem. Solids* 6 (1958) 352.
 - [28] G.B. Spence, *USAF Report WADD-TR-61-72* (1963).
 - [29] B.J.C. van der Hoeven Jr. and P.H. Keesom *Phys. Rev.* 130 (1963) 1318.
 - [30] P. Flubacher, A.J. Leadbetter and J.A. Morrison *Phys. Chem. Solids* 13 (1960) 160.
 - [31] B.T. Kelly and R. Taylor, *UKAEA Report: The Thermal Properties of Graphite*, TRG Report 1989 (C) (1971).
 - [32] I. Backhurst, *Proc. Roy. Soc. A* 102 (1922) 340.
 - [33] J.B. Nelson and D.P. Riley, *Proc. Phys. Soc.* 57 (1945) 477.
 - [34] P.L. Walker, H.A. McKinsty and C. Wright *Indust. Engng. Chem.* 45 (1953) 1711.
 - [35] E. Matuyama, *J. Sci. Instr.* 32 (1955) 229.
 - [36] E. Matuyama, *Tanso* 7 (1958) 12.
 - [37] Y. Baskin and L. Mayer, *Phys. Rev.* 100 (1955) 544.
 - [38] E.G. Steward and B.P. Cook, *Nature* 185 (1960) 78.
 - [39] E.G. Steward, B.P. Cook and E.A. Kellett, *Nature* 187 (1960) 1015.
 - [40] P.W. Bridgman, *Proc. Amer. Acad. Arts Sci.* 76 (1945) 9.
 - [41] W.G. O'Driscoll and J.C. Bell, *Nucl. Engng.* 3 (1958) 479.
 - [42] D.I. Page and B.C. Haywood, *AERE – R5778* (UKAEA Report). (1968).
 - [43] D.I. Page, *Symposium on Neutron Inelastic Scattering. IAEA Copenhagen Conf.* (1968) vol. 1, p.325.