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SPECIFIC HEAT OF CELLULOSE NITRATE*

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ABSTRACT

The specific heat of four military grade cellulose nitrates was measured from 298 to 390 K by use of differential scanning calorimetry. Over this temperature range the specific heat may be represented as follows: Grade B, $\bar{C}_p = (0.0184 \pm 0.764\theta)$ cal g^{-1} K^{-1}; Grade C (Type I), $\bar{C}_p = (0.0201 \pm 0.786\theta)$ cal g^{-1} K^{-1}; Grade C (Type II), $\bar{C}_p = (0.0241 \pm 0.791\theta)$ cal g^{-1} K^{-1}; Grade D (Pyroxylin), $\bar{C}_p = (0.0256 \pm 0.817\theta)$ cal g^{-1} K^{-1}; where $\theta = T/1000$ K.

INTRODUCTION

Specific heats of cellulose nitrates used in gun propellants are among the physical properties needed by those devising analytical models for ignition and combustion of these propellants. At present, estimates of the specific heats[1] must be relied upon, since experimentally determined values are unavailable. We have measured the specific heats of four military-grade cellulose nitrates by use of differential scanning calorimetry over the temperature range 298–390 K, in order to provide experimentally measured specific heats and to see how they compare with the presently used estimates.

EXPERIMENTAL

Four military-grade cellulose nitrates were obtained from Picatinny Arsenal and are listed in Table 1. The per cent nitration was determined at Picatinny Arsenal by the ferrous–titanous titrimetric method. The cellulose nitrate samples were dried at 105°C overnight to remove any residual traces of solvent. After this initial drying, the cellulose nitrate samples were stored under vacuum over anhydrous calcium sulphate.

Specific heats were measured with a thermal analyzer (DuPont Model 990) equipped with the differential scanning calorimeter (DSC) module. This DSC makes use of a constantan disc with two raised platforms for the sample pan and reference

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pan, respectively. The constantan disc serves as the primary means of heat transfer to the sample and reference pans and also serves as one element of a temperature-measuring thermoelectric junction. The DSC cell has a calorimetric sensitivity of 0.05 mcal sec^{-1} in^{-1}. Calorimeter precision is given as 1% for metal samples and as ± 5 % for polymeric materials[2]. Specific heats of polystyrene and natural rubber were measured to within 5% of the existing literature values[3].

TABLE I

CELLULOSE NITRATE SAMPLES USED FOR SPECIFIC HEAT MEASUREMENTS

Cellulose nitrate	*Empirical formula*	*Molecular weight (g mole^{-1})*
Grade D (Pyroxylin)	$C_6H_{7.68}N_{2.32}O_{9.64}$	267
Grade C (Type I)	$C_6H_{7.36}N_{2.67}O_{10.27}$	281
Grade C (Type II)	$C_6H_{7.33}N_{2.67}O_{10.34}$	282
Grade B (Guncotton)	$C_6H_{7.26}N_{2.74}O_{10.48}$	285

Specific heats were determined by comparing the thermal lag between the sample and reference systems under "sample" and "blank" conditions. The specific heat was calculated by measuring the difference in the Y-axis displacement between the "sample" and "blank" heating curves at a given temperature and substituting this difference into eqn. (1):

$$\bar{C}_p = \frac{60\,E\,\Delta qs}{Hr}\,\frac{\Delta Y}{m} \tag{1}$$

where $\bar{C}_p$ = specific heat (cal g^{-1} K^{-1}); E = cell calibration coefficient at temperature of interest (dimensionless); Δqs = Y-axis sensitivity (mcal sec^{-1} in^{-1}); Hr = heating rate (deg min^{-1}); ΔY = difference in the Y-axis deflection between sample and blank heating curves at the temperature of interest (in); m = sample weight (mg).

The cell calibration coefficient was determined from the heating curve deflection of a sample with known specific heat obtained under identical conditions as the sample. A sapphire (Al_2O_3) standard is provided in the DSC accessory kit for this purpose along with a table of specific heat vs. temperature for the standard sample.

Before any specific heat measurements could be taken, it was necessary to determine the interval between the starting temperature and the initial temperature at which eqn. (1) held for each heating rate. This interval was measured by observing that the deflection, ΔY, is proportional to the ratio $Hr/\Delta qs$ in eqn. (1). Heating curves of the sapphire standard were taken with heating rates of 2, 5, 10 and 20°C min^{-1}, but with the Y-axis sensitivity, Δqs, changed at each run to keep the ratio $Hr/\Delta qs$ constant for each run. The temperature at which the heating curve for each heating rate reached the 2°C min^{-1} heating curve defined the interval between the starting temperature and the initial temperature at which the specific heat could be computed by eqn. (1) for that heating rate. These temperature intervals for the 5, 10 and 20°C min^{-1} are 11,

20, and 30 °C, respectively. A heating rate of 20 °C min^{-1} was selected for these experiments with a Y-axis sensitivity of 1 mcal sec^{-1} in^{-1} in order to obtain deflections that were near full scale (8 in). The starting temperature was then set at −15 °C with a limiting temperature of 130 °C to insure that the cellulose nitrate would not begin decomposing. All of the DSC runs were made in air.

A typical run was performed as follows. The DSC cell was cooled to below −20 °C with liquid nitrogen, then heated to the starting temperature of −15 °C in the isothermal heating mode until steady-state conditions were reached. The thermal analyzer was then switched to the heating mode at the pre-selected rate of 20 °C min^{-1}. When the limiting temperature was reached, the thermal analyzer was switched to the stand-by mode which switched off the heater to conclude the run. At the end of runs with cellulose nitrate samples, the sample was weighed and the run repeated until the sample weight was constant. This usually took three runs. The change was attributed to residual solvent or moisture still adsorbed on the cellulose nitrate. After constant sample weight was reached, a final run was made which served as the heating curve used in the calculations. The cellulose nitrate was removed at the conclusion of this run and the empty aluminium pans were run to obtain the blank heating curve.

SPECIFIC HEAT OF CELLULOSE NITRATE SAMPLES

The cell calibration coefficient was determined as the mean of six runs with the sapphire standard provided in the accessory kit. The mean cell calibration coefficient E was calculated from eqn. (1) for each of ten temperatures as shown in Table 2.

TABLE 2

CELL CALIBRATION COEFFICIENT FOR CELLULOSE NITRATE DETERMINATIONS

Temp. (K)	$\bar{C}_p$[a] *(sapphire; cal* g^{-1} K^{-1}*)*	ΔY *(arr., in)*	E
298	0.1852	3.58	1.04
310	0.1911	3.71	1.04
320	0.1957	3.79	1.04
330	0.2002	3.85	1.05
340	0.2004	3.90	1.06
350	0.2083	3.94	1.07
360	0.2122	3.97	1.08
370	0.2158	4.00	1.09
380	0.2192	4.03	1.10
390	0.2224	4.04	1.11

[a] Ginnings and Furukawa, *J. Amer. Chem. Soc.*, 75 (1953) 522.

The specific heat of four or five samples of each grade of cellulose nitrate was determined at ten degree intervals over the temperature range 298–390 K. The results for each of the four cellulose nitrate samples are presented in Tables 3–6. The various

TABLE 3

SPECIFIC HEAT DETERMINATIONS OF 12.2% N CELLULOSE NITRATE[a]

Temp. (K)	$\bar{C}_p$[b]	$\bar{C}_p$[c]	$\bar{C}_p$[d]	$\bar{C}_p$[e]	$\bar{C}_p$[f]
298	0.244	0.253	0.298	0.291	0.253
310	0.255	0.261	0.313	0.302	0.263
320	0.264	0.266	0.323	0.310	0.273
330	0.275	0.271	0.331	0.318	0.281
340	0.289	0.278	0.337	0.326	0.291
350	0.297	0.285	0.343	0.334	0.301
360	0.305	0.291	0.350	0.343	0.312
370	0.310	0.298	0.357	0.352	0.324
380	0.315	0.305	0.364	0.363	0.334
390	0.317	0.313	0.370	0.374	0.340

[a] Specific heat in units of cal g^{-1} K^{-1}. [b] 29.95 mg sample. [c] 25.24 mg sample. [d] 36.80 mg sample. [e] 21.63 mg sample. [f] 42.14 mg sample.

TABLE 4

SPECIFIC HEAT DETERMINATIONS OF 13.1$_5$% N CELLULOSE NITRATE[a]

Temp. (K)	$\bar{C}_p$[b]	$\bar{C}_p$[c]	$\bar{C}_p$[d]	$\bar{C}_p$[e]
298	0.243	0.284	0.245	0.245
310	0.253	0.295	0.253	0.255
320	0.261	0.303	0.260	0.263
330	0.268	0.311	0.268	0.271
340	0.275	0.320	0.275	0.277
350	0.283	0.328	0.283	0.287
360	0.291	0.336	0.289	0.294
370	0.299	0.345	0.297	0.303
380	0.308	0.352	0.306	0.311
390	0.316	0.360	0.313	0.318

[a] Specific heat in units of cal g^{-1} K^{-1}. [b] 42.16 mg sample. [c] 32.03 mg sample. [d] 33.26 mg sample. [e] 25.13 mg sample.

TABLE 5

SPECIFIC HEAT DETERMINATIONS OF 13.2$_5$% N CELLULOSE NITRATE[a]

Temp. (K)	$\bar{C}_p$[b]	$\bar{C}_p$[c]	$\bar{C}_p$[d]	$\bar{C}_p$[e]
298	0.260	0.252	0.284	0.246
310	0.269	0.260	0.294	0.256
320	0.278	0.267	0.300	0.266
330	0.284	0.276	0.308	0.273
340	0.292	0.283	0.316	0.281
350	0.298	0.292	0.324	0.288
360	0.305	0.299	0.332	0.296
370	0.312	0.307	0.341	0.303
380	0.319	0.316	0.349	0.312
390	0.338	0.324	0.358	0.318

[a] Specific heat in units of cal g^{-1} K^{-1}. [b] 39.80 mg sample. [c] 27.74 mg sample. [d] 36.38 mg sample. [e] 37.84 mg sample.

TABLE 6

SPECIFIC HEAT DETERMINATIONS OF 13.4% N CELLULOSE NITRATE[a]

Temp. (K)	$\bar{C}_p$[b]	$\bar{C}_p$[c]	$\bar{C}_p$[d]	$\bar{C}_p$[e]	$\bar{C}_p$[f]
298	0.231	0.273	0.248	0.242	0.242
310	0.240	0.283	0.256	0.251	0.251
320	0.247	0.288	0.263	0.257	0.259
330	0.254	0.296	0.269	0.265	0.266
340	0.261	0.303	0.276	0.273	0.272
350	0.270	0.311	0.284	0.281	0.280
360	0.277	0.319	0.292	0.290	0.287
370	0.285	0.326	0.300	0.299	0.297
380	0.293	0.337	0.309	0.307	0.305
390	0.300	0.342	0.316	0.313	0.312

[a] Specific heat in units of cal g^{-1} K^{-1}. [b] 26.89 mg sample. [c] 30.36 mg sample. [d] 32.77 mg sample. [e] 39.40 mg sample. [f] 33.40 mg sample.

TABLE 7

MEAN $\bar{C}_p$[a] AND 95% CONFIDENCE INTERVAL FOR ALL CELLULOSE NITRATE SAMPLES

Temp. (K)	$\bar{C}_p$ (12.2% N)	$\bar{C}_p$ (13.1$_5$% N)	$\bar{C}_p$ (13.2$_5$% N)	$\bar{C}_p$ (13.4% N)
298	0.268 ±0.031	0.254 ±0.032	0.260$_5$ ±0.027	0.247 ±0.019
310	0.279 ±0.033	0.264 ±0.033	0.270 ±0.027	0.256 ±0.020
320	0.287 ±0.034	0.272 ±0.033	0.278 ±0.025	0.263 ±0.019
330	0.295 ±0.034	0.280 ±0.033	0.285 ±0.025	0.270 ±0.019
340	0.304 ±0.032	0.287 ±0.035	0.293 ±0.026	0.277 ±0.019
350	0.312 ±0.031	0.295 ±0.036	0.300$_5$ ±0.026	0.285 ±0.019
360	0.320 ±0.031	0.302$_5$ ±0.035	0.308 ±0.026	0.293 ±0.019
370	0.328 ±0.032	0.311 ±0.036	0.316 ±0.027	0.301 ±0.019
380	0.336 ±0.034	0.319 ±0.035	0.324 ±0.027	0.310 ±0.020
390	0.343 ±0.036	0.327 ±0.035	0.334$_5$ ±0.028	0.317 ±0.019

[a] $\bar{C}_p$ in units of cal g^{-1} K^{-1}.

grades of cellulose nitrate are identified by their per cent nitration. Mean values of the specific heat were then computed along with 95% confidence intervals calculated by standard techniques[4].

Maier and Kelley's[5] equation given below was used to represent the specific heats over the measured temperature range:

$$\bar{C}_p = a + bT - cT^{-2} \tag{2}$$

Since the specific heats appeared to vary linearly with temperature, the specific heats in Table 7 were fitted to eqn. (2) with c set equal to zero using a least-squares program[6] to obtain "best-fit" values of a and b. The "best-fit" values obtained for each grade of cellulose nitrate are listed in Table 8 followed by a comparison of the experimental

specific heats and the specific heats generated with the best-fit values of a and b for the 12.2% grade cellulose nitrate. Similar agreement was obtained for the other three grades.

TABLE 8

CONSTANTS FOR LINEAR REPRESENTATION[a] OF THE SPECIFIC HEAT OF CELLULOSE NITRATE AS A FUNCTION OF TEMPERATURE FROM 298 TO 390 K

Cellulose nitrate	$a \times 10^2$ (*cal* g^{-1} K^{-1})	$b \times 10$ (*cal* g^{-1} K^{-1})
12.2 % N	2.56	8.17
13.1$_5$% N	2.01	7.86
13.2$_5$% N	2.41	7.91
13.4 % N	1.84	7.64

[a] $\bar{C}_p = a + b\theta$, where $\theta = T'1000$ K.

TABLE 9

COMPARISON OF EXPERIMENTAL $\bar{C}_p$[a] WITH $\bar{C}_p$ CALCULATED FROM LINEAR REPRESENTATION FOR 12.2% N CELLULOSE NITRATE

Temp. (K)	$\bar{C}_p$ (*experimental*) × 10	$\bar{C}_p$ (*calculated*) × 10
298	2.68	2.69
310	2.79	2.79
320	2.87	2.87
330	2.95	2.95
340	3.04	3.03
350	3.12	3.11
360	3.20	3.20
370	3.28	3.28
380	3.36	3.36
390	3.43	3.44

[a] $\bar{C}_p$ in units of cal g^{-1} K^{-1}.

COMPARISON OF EXPERIMENTAL AND CALCULATED SPECIFIC HEATS

The presently-used specific heats for cellulose nitrates of military interest are calculated by means of zero-order additivity law for specific heats, which expresses the specific heat of a compound as the sum of atomic contributions only. According to Federoff and Sheffield[1] appropriate values for the contributions of carbon, hydrogen, oxygen, and nitrogen are 1.62, 3.265, 5.19, and 3.384, respectively (all in cal g-atom^{-1} K^{-1}). More recently, Cox and Pilcher[7] have recommended 1.8, 2.6, 4.0, and 6.3 for the same quantities. Specific heats calculated with these values are given below for the four cellulose nitrates examined in this report.

% N cellulose nitrate	C_p (ref. 1, cal g^{-1} K^{-1})	C_p (ref. 7, cal g^{-1} K^{-1})
12.2	0.348	0.314
13.1_5	0.342	0.313
13.2_5	0.342	0.312
13.4	0.340	0.312

Comparing these numbers with Table 7 shows that the values of Cox and Pilcher produce estimates close to the experimentally measured specific heats, although the additivity law cannot account for the linearly increasing specific heat with temperature. The decreasing specific heat with increasing nitrogen content as predicted by the additivity law is reflected in the experimentally measured specific heats.

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