Since temperature was more accurately known the uncertainties in the ΔH and log K_p values resulting from uncertainties in temperature are smaller than with the diphenyl-hydrogen system. The ΔH values cannot be directly compared with other data because accurate heat of combustion data are not available for the major components of the phenanthrene-hydrogen system. In general, the ΔH values are in satisfactory agreement with those calculated using the empirical procedure of Bondi (*3*). Because the heats of hydrogenation are equal for the reactions of phenanthrene and tetrahydrophenanthrene and of tetrahydro- to octahydrophenanthrene and both involve two moles of hydrogen, the ratio of their equilibrium constants is independent of hydrogen pressure and temperature. Experimentally, this ratio

$$\frac{\text{(phenanthrene) (sym. octahydrophenanthrene)}}{\text{tetrahydrophenanthrene)}^2}$$

varied from 0.78 to 1.03 and averaged 0.87.

Data on the minor components included in Table III show that the symmetrical compound accounts for about 70% of the total octahydrophenanthrenes, and the lowest boiling one accounts for 60 to 75% of the total perhydrophenanthrenes. In neither case are the data sufficiently accurate to determine heats of isomerization.

The experimental data show that Bondi's empirically calculated equilibrium constants (*3*) are significantly too low. For phenanthrene to sym. octahydrophenanthrene, for example, the calculated constant is less than a tenth of the actual equilibrium constant.

CONCLUSION

The experimentally determined equilibrium data for selected polycyclic aromatic provide a firmer base for interpreting hydrogenation data. They emphasize that empirical correlations can be seriously in error and show the need for similar experimental data for other polycyclic systems. The techniques used in the present work should serve in studying such systems.

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Specific Heat of Some High Temperature Materials

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DEMAND FOR materials capable of withstanding extreme temperatures has increased sharply in the past few years. This has resulted from an increased emphasis on space and reactor programs, which require high temperature materials with specific properties. Selection, application, and evaluation of new materials require a through knowledge of their physical and mechanical properties.

This laboratory has performed precise specific heat determinations from room temperature to 1000° C. on various materials such as synthetic sapphire and $MoSi_2$ (*15*), TiB_2 (*14*), and several organic liquids (*13*).

The present investigation involves similar specific heat determinations of 45 materials, which have potential high temperature applications. Heat capacities were derived from heat content measurements, performed over the temperature range 30° to 800° C., for BeO, Be, BeO-Be and BeO-Be-Mo cermet mixtures; beryllides of Ta, Zr, Mo, Ti, and Cb; BeO-beryllide mixtures; SiC, SiC-graphite mixtures; and BN, BN-graphite mixtures. Smoothed specific heat results are presented for all samples, and the effectiveness of the additive law in predicting specific heats is demonstrated.

EQUIPMENT

The apparatus has been previously described in some detail (*15*). Briefly, the calorimeter is a modified version of Southard's apparatus (*12*), and the drop method is employed. Samples are heated to a known temperature and then dropped into the calorimeter, which measures the heat evolved in cooling the sample from the furance temperature to the calorimeter operating temperature (30° C.). Heat capacities are then derived from the heat content measurements by the usual methods.

Type 304 stainless steel buckets, previously calibrated for heat content in the calorimeter system from 30° to 800° C., were used to contain the samples. Samples were obtained from several companies as hot-pressed solids, machined to fit the sample containers. Data on the composition of several samples are given in Table I. Those not listed are not known beyond the nominal compositions indicated in Table II.

EXPERIMENTAL RESULTS

Heat content measurements were obtained over the temperature range from 30° to 800° C. at 100° to 150° C. intervals for approximately 25 samples, and at 200° C. intervals for the remainder of the samples, which were duplicates or near-duplicates of eariler ones. Specific heats were then derived from the enthalpy data.

Smoothed experimental results were obtained graphically from precise plots of specific heat—temperature and are shown in Table II. The probable absolute error in this calorimetric system has been calculated to be less than $\pm 0.3\%$ for heat content measurements and less than $\pm 3\%$ for specific heat. Measurements on synthetic sapphire, a calorimetric standard, indicate that this calculated error

Table I. Composition of Materials (Weight per cent)

SiC	96.5 SiC, 2.5 Si, 0.4C, 0.4 Al, 0.2 Fe
80 SiC-20 C (low free carbon)	78.0 SiC, 1.0 Si, 20.0 C, 1.0 various metals
50 SiC-50 C (high free carbon)	50 SiC, 4 Si, 46 C
BN	97.4 BN, 2.4 B_2O_3, 0.2 Al and Si
58 BeO-42 Mo fiber	57.6 BeO, 42.4 Mo
Be	99.3 Be, 0.9 BeO, 0.1 Fe, 0.1 various metals
Be	98.4 Be, 2.1 BeO, 0.1 Fe, 0.1 various metals
Be	98.9 Be, 1.2 BeO, 0.1 Fe, 0.1 various metals
Be	98.6 Be, 1.4 BeO, 0.2 Fe, 0.2 various metals
Be	99.0 Be, 0.8 BeO, 0.2 Fe, 0.2 various metals

Table II. Smoothed Experimental Specific Heat Data

Sample, Wt. %	No. Measd.	C_p in Cal./G., ° C. at ° C. (1 Cal. = 4.184 abs. joules								
		30	100	200	300	400	500	600	700	800
BeO	2	0.248	0.298	0.354	0.384	0.408	0.426	0.443	0.460	0.476
Be	5	0.437	0.498	0.553	0.591	0.620	0.647	0.674	0.701	0.729
97BeO-3Be	1	0.254	0.305	0.360^5	0.392	0.414	0.434	0.451	0.468	0.485^5
94BeO-6Be	1	0.262	0.306	0.358	0.394	0.416	0.436	0.454	0.472	0.491
93BeO-7Be	1	0.261	0.303	0.349	0.384	0.408	0.430	0.450	0.468^5	0.486^5
91BeO-9Be	1	0.265	0.311	0.370^5	0.411	0.436	0.453^5	0.469	0.483	0.501
88BeO-12Be	2	0.275	0.313	0.362	0.395	0.420	0.441	0.457	0.473	0.490
86BeO-7Be-7Mo	2	0.248	0.297	0.356	0.387	0.407	0.423	0.438	0.454	0.470
58BeO-42Mo Fiber	2	0.168	0.188	0.223	0.242	0.255	0.263	0.270	0.278	0.285
$TaBe_{12}$	1	0.185	0.207	0.227	0.241	0.253^5	0.264	0.275	0.284^5	0.295^5
$MoBe_{12}$	1	0.261	0.293	0.322	0.346	0.364	0.381	0.398	0.413	0.428
$ZrBe_{13}$	1	0.276	0.307	0.338	0.363^5	0.385	0.403^5	0.420^5	0.437^5	0.454^5
$TiBe_{12}$	1	0.341	0.386^5	0.428	0.454^5	0.476	0.497	0.517	0.537	0.557
$NbBe_{12}$	1	0.265	0.294^5	0.327	0.350	0.365	0.376^5	0.387^5	0.400	0.411^5
94BeO-6$TaBe_{12}$	1	0.244	0.294	0.350	0.388	0.408	0.426	0.443	0.460	0.477
91BeO-9$TaBe_{12}$	1	0.242	0.302	0.355	0.388	0.410	0.428	0.444	0.459^5	0.474
82BeO-18$TaBe_{12}$	1	0.237	0.282	0.331	0.358	0.375	0.390	0.406	0.422	0.438
94BeO-6$MoBe_{12}$	1	0.249	0.300	0.360	0.399	0.417	0.434	0.451	0.468	0.484
91BeO-9$MoBe_{12}$	1	0.249	0.298	0.356	0.389	0.412	0.428	0.444	0.460	0.475
82BeO-18$MoBe_{12}$	1	0.250	0.299	0.362	0.392	0.407	0.423	0.438	0.454	0.470
94BeO-6$ZrBe_{13}$	1	0.249	0.300	0.354	0.395	0.419	0.436^5	0.454	0.471^5	0.489
91BeO-9$ZrBe_{13}$	1	0.250	0.300	0.357	0.394	0.417^5	0.435^5	0.452	0.469	0.486
82BeO-18$ZrBe_{13}$	1	0.253	0.300	0.351	0.381	0.403	0.423	0.440	0.456	0.473
94BeO-6$TiBe_{12}$	1	0.253	0.304	0.361	0.401	0.422	0.439	0.456	0.473	0.490
91BeO-9$TiBe_{12}$	1	0.256	0.309	0.366	0.401	0.423	0.441	0.459	0.475^5	0.493
82BeO-18$TiBe_{12}$	1	0.265	0.310	0.365	0.410	0.430	0.446	0.462	0.478	0.494
94BeO-6$NbBe_{12}$	1	0.249	0.299	0.352	0.383	0.404	0.424	0.441	0.456	0.474
91BeO-9$NbBe_{12}$	1	0.249	0.299	0.353	0.389	0.412	0.432	0.448	0.464	0.480
82BeO-18$NbBe_{12}$	1	0.251	0.298	0.352	0.387	0.403	0.419	0.434	0.449	0.466
SiC	1	0.163	0.196	0.224	0.242	0.255	0.267	0.277	0.287	0.295
80SiC-20C (low free carbon)	1	0.166	0.207	0.241	0.263	0.278	0.292	0.303	0.314	0.323
50SiC-50C (high free carbon)	1	0.171	0.207^5	0.255	0.292	0.314	0.332	0.347	0.360	0.373
43SiC-57C	1	0.170	0.206	0.249	0.280	0.305	0.325	0.341	0.355	0.365
28SiC-72C	1	0.173	0.215	0.263	0.299	0.326	0.347	0.360	0.373	0.383
23SiC-77C	1	0.173	0.230	0.274	0.304	0.328	0.349	0.367	0.384	0.398
BN	1	0.193	0.236	0.283	0.324	0.358	0.389	0.416	0.441	0.468
80BN-20C	1	0.190	0.250	0.300	0.336	0.362	0.387	0.411	...	...

may be high, since a mean deviation from National Bureau of Standards results on specific heat of less than ±0.5% was obtained (*15*).

Heat capacities of BeO, Be, SiC, and BN from this study are compared to those obtained by other investigators in Table III. These are the only materials for which previous data were available, and the close agreement of the results is evident. Specific heat—temperature plots for these materials conform to normal expectations; that is, a rapid rise of specific heat up to the Debye characteristic temperature, and then a leveling off to near linearity at high temperatures. A transition point at approximately 700° C. ($\Delta H_t = 0$) has been reported for beryllium (*4*). Since there is apparently little or no heat evolved in the transition (only a slight change in slope of the specific heat—temperature plot) and our measurements were only 100° C. beyond this point, no confirmation could be obtained.

GENERAL ADDITIVE LAW

Specific heat values for the beryllide compounds and various cermet mixtures were calculated by using the general additive law for specific heat. For a mixture or compound, composed of constituents *A*, *B*, and *C*, specific heats may be calculated directly from the following equation

$$C_{p_{ABC}} = X_A C_{p_A} + X_B C_{p_B} + X_C C_{p_C}$$

Table III. Comparison with Other Investigators

(Results corrected for impurities)

Material	C_p Reference	Temp. Range Compared, ° C.	Mean % Deviation NRL-Other
BeO	(*5, 9*)	30–800	±2.2
	(*6*)	30–800	±2.6
Be	(*5, 4*)	30–800	±1.7
	(*2*)	200–800	±2.8
	(*6*)	30–800	±4.1
SiC	(*6*)	30–800	±0.1
	(*8*)	300–800	±2.2
	(*5*)	30–800	±1.1
	(*2*)	500–800	±3.8
BN	(*3*)	30–800	±2.7
	(*5*)	30–800	±2.3

Table IV. Effectiveness of General Additive Specific Heat Law in Calculating C_p Values from Smoothed Results

Material, Wt. %	Source of C_p Values	Mean Deviation % Over 30° to 800° C., Obs.-Calc.
97BeO-3Be	BeO and Be[a]	±0.2
94BeO-6Be	BeO and Be[a]	±0.9
93BeO-7Be	BeO and Be[a]	±2.5
91BeO-9Be	BeO and Be[a]	±1.1
88BeO-12Be	BeO and Be[a]	±3.1
86BeO-7Be-7MO	BeO and Be[a]	±1.4
58BeO-42Mo Fiber	BeO[a]/, Mo (*11*)	±4.2
$TaBe_{12}$	Be[a]/, Ta (*11*)	±0.3
$MoBe_{12}$	Be[a]/, Mo (*11*)	±1.2
$ZrBe_{13}$	Be[a]/, Zr (*6*)	±0.8
$NbBe_{12}$	Be[a]/, Nb (*6*)	±1.2
$TiBe_{12}$	Be[a]/, Ti (*11*)	±0.4
94BeO-6$TaBe_{12}$	BeO and $TaBe_{12}$[a]	±1.9
91BeO-9$TaBe_{12}$	BeO and $TaBe_{12}$[a]	±3.3
82BeO-18$TaBe_{12}$	BeO and $TaBe_{12}$[a]	±0.8
94BeO-6$MoBe_{12}$	BeO and $MoBe_{12}$[a]	±2.2
91BeO-9$MoBe_{12}$	BeO and $MoBe_{12}$[a]	±1.1
82BeO-18$MoBe_{12}$	BeO and $MoBe_{12}$[a]	±1.2
94BeO-6$ZrBe_{13}$	BeO and $ZrBe_{13}$[a]	±2.0
91BeO-9$ZrBe_{13}$	BeO and $ZrBe_{13}$[a]	±2.0
82BeO-18$ZrBe_{13}$	BeO and $ZrBe_{13}$[a]	±0.2
94BeO-6$TiBe_{12}$	BeO and $TiBe_{12}$[a]	±1.6
91BeO-9$TiBe_{12}$	BeO and $TiBe_{12}$[a]	±1.7
82BeO-18$TiBe_{12}$	BeO and $TiBe_{12}$[a]	±1.6
94BeO-6$NbBe_{12}$	BeO and $NbBe_{12}$[a]	±0.1
91BeO-9$NbBe_{12}$	BeO and $NbBe_{12}$[a]	±1.4
82BeO-18$NbBe_{12}$	BeO and $NbBe_{12}$[a]	±0.6
78SiC-20C-2Si	SiC[a]/, C (graphite) (*7*)/, Si (*6*)	±1.7
50SiC-46C-Si	SiC[a]/, C (graphite) (*7*)/, Si (*6*)	±4.3
43SiC-57C	SiC[a]/, C (graphite) (*7*)	±1.8
28SiC-72C	SiC[a]/, C (graphite) (*7*)	±2.4
23SiC-77C	SiC[a]/, C (graphite) (*7*)	±2.2
80BN-20C (to 600° C.)	BN[a]/, C (graphite) (*7*)	±2.8
	Mean	±1.6

[a] Values from Naval Research Laboratory.

$C_{p_{ABC}}$ = specific heat of mixture *ABC* at a temperature t(° C.) in cal./g., ° C.
C_{p_A}, C_{p_B}, C_{p_C} = specific heat of constituents *A*, *B*, and *C* at a temperature t (° C.) in cal./g., ° C.
X_A, X_B, X_C = weight fraction of each component

Effectiveness of the general additive law is clearly shown in Table IV, which also identifies the sources of specific heat values used in the computations. The average of the mean deviations between observed and calculated values is less than ±1.6% for the 36 compounds and mixtures, and only two mixtures have mean deviations greater than ±4%.

This study extends the application of the additive law to cermets and ceramics and substantiates past use in other materials such as metal alloys (*10*), liquid metal alloys and liquid salt mixtures (*1*), and liquid organic mixtures (*13*).

The additive law is least accurate when the components of a substance are in different normal states. In BeO, for example, one component, Be, normally is in the solid state and the other, oxygen, is gaseous. In such cases, the additive law is not as effective due to heat differences resulting from bonding characteristics.

An empirical procedure has been used to predict specific heats for compounds of this type. For example, the specific heat of BeO can be calculated from data on beryllium, calcium oxide, and calcium. Using the known values (at some temperature, *t*) for CaO and Ca, we can calculate an empirical value for oxygen and then, using this oxygen value and the known value for beryllium, we can calculate the specific heat for BeO at this temperature.

This procedure was applied by the authors to approximately twenty oxide materials at several temperatures, and the predicted values were generally within 10% of the measured quantities. Inaccuracies in the measured results for the metals and oxides would account for a portion of this deviation; but, undoubtedly, the major part is influenced by physical state and bonding.

In view of the demonstrated accuracy of the general additive law, its use to predict specific heats of new compounds, mixtures, and alloys should be adequate for engineering and design considerations, unless important phase transitions are encountered. The general additive law for predicting specific heats should find wider application as more reliable specific heat data of the elements are obtained and the influences of physical state and bonding on the heat content of a compound are better understood.

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