

Ketelaar<sup>4</sup> calculated the average increase in potential energy of the crystal when a metal ion is moved from an ordered into a disordered position. He found 5660 cal./g. at. wt. at the transition temperature. This value corresponds to 0.245 electron volt and can be compared with the energy difference of 0.18 electron volt derived from the reflectance measurements. Since only part of the energy involved in the order-disorder transition would be expected to express itself in the absorption or reflectance characteristics in the visible range, the optical values are consistent with the results of Ketelaar's conductivity measurements on  $\text{Ag}_2\text{HgI}_4$ .

Since the energies corresponding to the shift of the reflectance edge between the  $\beta$ - and  $\alpha$ -forms have been found to be very nearly constant for all compositions, conductivity measurements on these materials might be expected to indicate approximately constant energy differences for their order-disorder transformations. It would therefore be

interesting to carry out such conductivity measurements. Also interesting would be a determination of specific heat of these materials over the entire composition range as a function of temperature.

It has been noted that the colors and transition temperatures of these materials are dependent to some extent upon the exact method of preparation employed. It therefore appears that very small quantities of impurities may be responsible for such slight variations superimposed upon the primary effect reported herein. Further study along these lines would be of interest.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

## Heat Capacity Standards for the Range 14 to 1200°K.

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In an effort to supply accurate heat capacity data on pure materials which will serve as standards in precision calorimetry, there are given the results of new heat capacity measurements at the National Bureau of Standards on *n*-heptane (25° to 523°K.) and on aluminum oxide (corundum), (14 to 1173°K.). These materials together with benzoic acid had been recommended by the Calorimetry Conference (U. S.) as standards for the intercomparison of calorimeters. Diphenyl ether is suggested as an additional standard to supplement the above three substances and water which is universally used as a standard. Tables of smoothed values of heat capacity and enthalpy are given for *n*-heptane, aluminum oxide, benzoic acid (up to 430°K.), diphenyl ether (up to 570°K.) and water (0 to 100°C.).

Since the beginning of calorimetry, water has been used as a standard for heat capacity measurements, partly because it is universally available in high purity. However, as heat measurements were extended below 0°, the large expansion of water on freezing made it impracticable to use in many calorimeters. Above 100°, the increasing vapor pressure of water is a serious drawback, both because of resulting constructional difficulties and also because of the necessity of accounting for the change with temperature of the relative amounts in the two phases. With these considerations, it is apparent that, in addition to water, other heat capacity standards are desirable. In 1949, the Fourth Conference on Calorimetry<sup>1</sup> recommended three substances to be used as standards for the intercomparison of heat capacity calorimeters, and the National Bureau of Standards undertook the task of preparation and distribution of these substances. It was the original purpose that samples of these substances be made available to those laboratories interested in very precise measurements of heat capacity. By having samples of any one substance taken from one source of very

high purity, it was hoped to have a means of comparing measurements made in different laboratories under different experimental conditions. The National Bureau of Standards has prepared the samples of benzoic acid, *n*-heptane and aluminum oxide for the Calorimetry Conference Program. These samples are not regarded as part of the Standard Sample series of the Bureau, but are available without charge to a limited number of laboratories. It is the main purpose of this report to give a summary of the results of our new heat capacity measurements on the Calorimetry Conference samples of *n*-heptane and aluminum oxide. In addition, the previously published heat capacity results on the Calorimetry Conference sample of benzoic acid are included, together with earlier results on diphenyl ether and water. All of the results given are derived entirely from measurements at the National Bureau of Standards. Other measurements (unpublished) on the Calorimetry Conference Sample of *n*-heptane have been made at the Bureau of Mines, Bartlesville, Oklahoma. It is hoped that other laboratories (including those outside the United States) will also make heat capacity measurements on these Calorimetry Conference Samples, and that after the comparison of results, agreement may be reached on heat capacity values for the standard materials.

(1) This conference consisted of an informal group of representatives from various U. S. Laboratories which were interested in precision calorimetric measurements (*Chem. Eng. News*, **27**, 2772 (1949)).

TABLE I  
HEAT CAPACITY AND ENTHALPY OF DIPHENYL ETHER, *n*-HEPTANE AND BENZOIC ACID AT SATURATION PRESSURES<sup>b</sup>

T, °K.	Diphenyl ether		<i>n</i> -Heptane		Benzoic acid	
	$C_{\text{satd.}}$ abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	$(H_T - H_0^{\circ}\text{K.})$ abs. j. mole <sup>-1</sup>	$C_{\text{satd.}}$ abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	$(H_T - H_0^{\circ}\text{K.})$ abs. j. mole <sup>-1</sup>	$C_{\text{satd.}}$ abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	$(H_T - H_0^{\circ}\text{K.})$ abs. j. mole <sup>-1</sup>
0	0.0	0.0	0.0	0.0	0.0	0.0
5	0.415	0.519	0.222	0.277	0.2426	0.3032
10	3.283	8.272	1.770	4.431	1.923	4.838
15	9.858	39.747	5.718	22.06	5.856	23.456
20	18.06	109.83	11.80	65.25	11.00	65.294
25	25.82	219.56	18.30	140.4	16.54	134.08
30	33.16	367.29	25.08	248.8	21.92	230.26
35	39.73	549.89	31.82	391.1	27.08	352.92
40	45.44	763.18	38.17	566.2	31.68	500.06
45	50.24	1002.7	44.17	772.2	35.77	668.86
50	54.53	1264.8	49.84	1007.3	39.50	857.20
55	58.41	1547.3	55.27	1270.2	42.81	1063.1
60	61.92	1848.2	60.48	1559.7	45.88	1284.9
65	65.14	2166.0	65.37	1874.4	48.65	1521.4
70	68.11	2499.2	69.83	2212.6	51.24	1771.2
75	70.97	2846.9	74.09	2572.4	53.52	2033.1
80	73.77	3208.8	78.28	2953.4	55.85	2306.5
85	76.52	3584.6	82.21	3354.7	58.13	2591.5
90	79.19	3973.8	86.03	3775.4	60.14	2887.3
95	81.80	4376.4	89.44	4214.2	62.04	3192.8
100	84.35	4791.8	92.77	4670.7	63.93	3507.7
110	89.49	5661.0	99.12	5629.4	67.69	4165.8
120	94.82	6582.5	105.20	6651.2	71.51	4861.8
130	100.26	7557.7	111.10	7732.8	75.27	5595.7
140	105.88	8588.3	116.83	8872.6	79.09	6367.5
150	111.72	9676.2	122.72	10070	82.90	7177.4
160	117.64	10823	129.03	11329	86.75	8025.6
170	123.70	12030	136.03	12653	90.70	8912.8
180	129.98	13298	145.13	14055	94.70	9839.7
182.56	...	.....	148.58	14430	....	.....
182.56	...	.....	203.15	28452	....	.....
190	136.45	14632	201.86	29958	98.75	10807
200	143.09	16028	201.31	31973	102.89	11815
210	149.88	17493	201.68	33987	107.11	12865
220	156.86	19027	202.74	36008	111.40	13958
230	164.00	20630	204.36	38043	115.78	15093
240	171.32	22306	206.47	40097	120.22	16273
250	178.83	24058	208.93	42174	124.71	17498
260	186.49	25884	211.73	44277	129.24	18768
270	194.25	27787	214.81	46410	133.81	20083
280	202.04	29770	218.23	48575	138.40	21444
290	209.94	31829	221.75	50775	143.03	22851
298.16	216.56	33569	224.74	52597	146.81	24033
300	218.06	33969	225.43	53011	147.66	24304
300.03	218.25	33975	...	.....	....	.....
300.03	268.42	51190	...	.....	....	.....
310	272.71	53884	229.26	55285	152.30	25804
320	277.17	56634	233.24	57598	156.96	27351
330	281.71	59428	237.37	59952	161.60	28943
340	286.25	62268	241.65	62349	166.22	30582
350	290.79	65153	246.07	64789	170.84	32268
360	295.35	68084	250.60	67276	175.52 <sup>a</sup>	34000 <sup>a</sup>
370	299.90	71060	255.26	69809	180.34 <sup>a</sup>	35779 <sup>a</sup>
380	304.39	74082	260.09	72386	185.25 <sup>a</sup>	37607 <sup>a</sup>
390	308.86	77148	265.04	75011	190.05 <sup>a</sup>	39483 <sup>a</sup>
395.52	...	.....	...	.....	192.74 <sup>a</sup>	40541 <sup>a</sup>
395.52	...	.....	...	.....	250.60 <sup>a</sup>	58547 <sup>a</sup>
400	313.33	80259	270.13	77687	253.33 <sup>a</sup>	59675 <sup>a</sup>
410	317.89	83415	275.36 <sup>a</sup>	80414 <sup>a</sup>	259.86 <sup>a</sup>	62241 <sup>a</sup>
420	322.36	86617	280.74 <sup>a</sup>	83195 <sup>a</sup>		
430	326.84	89863	286.29 <sup>a</sup>	86030 <sup>a</sup>		

TABLE I (Continued)

T, °K.	Diphenyl ether		<i>n</i> -Heptane		Benzoic acid	
	$C_{\text{satd.}}$ abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	( $H_T - H_0^{\circ\text{K.}}$ ) abs. j. mole <sup>-1</sup>	$C_{\text{satd.}}$ abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	( $H_T - H_0^{\circ\text{K.}}$ ) abs. j. mole <sup>-1</sup>	$C_{\text{satd.}}$ abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	( $H_T - H_0^{\circ\text{K.}}$ ) abs. j. mole <sup>-1</sup>
440	331.30	93155	292.02 <sup>a</sup>	88921 <sup>a</sup>		
450	335.77	96491	297.95 <sup>a</sup>	91871 <sup>a</sup>		
460	340.32	99872	304.14 <sup>a</sup>	94881 <sup>a</sup>		
470	344.71	103298	310.67 <sup>a</sup>	97955 <sup>a</sup>		
480	349.16	106769	317.85 <sup>a</sup>	101100 <sup>a</sup>		
490	353.60	110284	325.75 <sup>a</sup>	104310 <sup>a</sup>		
500	358.04	113845	335.68 <sup>a</sup>	107620 <sup>a</sup>		
510	362.48	117450	350.28 <sup>a</sup>	111040 <sup>a</sup>		
520	366.92	121100	379.45 <sup>a</sup>	114670 <sup>a</sup>		
530	371.35	124794				
540	375.78	128534				
550	380.19	132318				
560	384.63	136148				
570	389.05	140022				

<sup>a</sup> *n*-Heptane above 400°K. and benzoic acid above 350°K. are not recommended as heat capacity standards. <sup>b</sup> Molecular weights of diphenyl ether, *n*-heptane and benzoic acid are taken as 170.20, 100.20 and 122.12, respectively.

### Selection and Purification of Materials

In all the heat capacity measurements, the materials used were so pure that the effects of impurities were small in comparison with the accuracies claimed in the heat measurements. In the case of water in the range 0 to 100°, it is believed that the heat capacity measurements were generally accurate to 0.01–0.02%. With the other four materials, the measurements were accurate to 0.1–0.2%.

**Benzoic Acid.**—The benzoic acid was chosen as a solid substance for low-temperature calorimetry partly because it was already available in very pure form at the National Bureau of Standards as a thermometric standard.<sup>2</sup> The benzoic acid was purified by fractional crystallization<sup>1,3</sup> and the impurities in the sample selected for use in the Calorimetry Conference program were shown by freezing point studies to be about 0.003 mole per cent.

***n*-Heptane.**—The *n*-heptane was chosen as a standard substance for low temperature work where it is desirable to introduce the substance as a liquid, either directly or by distillation. It is a very stable compound with no undesirable solid–solid transitions. The sample was synthesized, fractionally distilled, fractionally crystallized and dried by silica gel. The impurities (liquid soluble–solid insoluble) in the final sample were shown by studies of the relation between fraction melted and equilibrium temperature to be about 0.003 mole per cent.

**Aluminum Oxide.**—The aluminum oxide in the form of synthetic sapphire (corundum) was chosen as a standard substance because of its chemical stability in air up to its melting point (about 2300°K.), its commercial availability in very high purity, its high heat capacity per unit volume, and the fact that it is non-volatile, non-hygroscopic and apparently has no solid–solid transitions. The synthetic sapphire was obtained in the form of boules from Linde Air Products Company, and processed to give pieces that passed a #10 and were retained by a #40 sieve. Spectrographic analysis indicated that the impurities of the material were between 0.01 and 0.02 weight per cent.

**Diphenyl Ether.**—Although this material was not among the substances selected by the Calorimetry Conference as a heat capacity standard, it is believed to be a useful standard because of its high chemical stability, its ease of purification and its relatively high boiling point (532°K.). It can be used conveniently to higher temperatures than *n*-heptane or water and its chemical inertness permits its use in some calorimeters which are attacked by liquid benzoic acid. However, it does dissolve enough water so that in precision calorimetry, either contact with water vapor must be avoided, or the water must be removed by pumping. The material was purified to about 99.999 mole per cent. by distillation and fractional crystallization.

**Water.**—The purity of the water used in the heat capacity experiments at this Bureau is believed to be better than that

of any of the other materials. The isotopic composition of the water is believed to be normal (source being river water) so that any uncertainty in its composition does not affect the accuracy of the heat capacity values.

### Experimental

Measurements have been made at the National Bureau of Standards of the heat capacities of all these substances, extending down to about 14°K. with benzoic acid, aluminum oxide and diphenyl ether, and to about 25°K. with *n*-heptane. The measurements extended up to 410°K. with benzoic acid, 523°K. with *n*-heptane, 573°K. with diphenyl ether, and 1173°K. with aluminum oxide. The new measurements on *n*-heptane and aluminum oxide will be described in detail in later publications<sup>4</sup> while the measurements on water,<sup>5</sup> benzoic acid<sup>6</sup> and diphenyl ether<sup>7</sup> have already been described.

The heat capacity measurements have been made with a variety of calorimeters, each being most suitable for a certain type of measurement. From 14 to about 400°K., adiabatic calorimeters were used, capable of accuracies of 0.1 to 0.2%.<sup>1,8</sup> From 273 to 1173°K., the "drop" method was used with a Bunsen ice calorimeter to measure the enthalpy of the material (referred to 273.16°K.), from which data, heat capacities were derived.<sup>9</sup> In the temperature range 273 to 400°K., measurements were made with both the adiabatic calorimeter and the ice calorimeter, thereby serving as a check on the two experimental methods. The measurements on water<sup>5</sup> were made with a large adiabatic calorimeter specially designed for these measurements to obtain the highest accuracy (0.01 to 0.02%). Some of the measurements on *n*-heptane were made with the same adiabatic calorimeter used for water, while other measurements were made with a smaller adiabatic calorimeter<sup>10</sup> designed primarily for measurements of heat of vaporization at 25° but also proved suitable for heat capacity measurements near this temperature.

### Summary of Results

The final smoothed results of the measurements are given in Tables I, II, and III. In Table I are given the values of  $C_{\text{satd}}$  (heat capacity at satura-

(4) *J. Research Natl. Bur. Standards* (1953).

(5) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *ibid.*, **23**, 197 (1939) (RP1228).

(6) G. T. Furukawa, R. E. McCoskey and G. J. King, *ibid.*, **47**, 256 (1951) (RP2251).

(7) G. T. Furukawa, D. C. Ginnings, R. E. McCoskey and R. A. Nelson, *ibid.*, **46**, 195 (1951) (RP2191).

(8) R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde and N. Bekkedahl, *ibid.*, **35**, 39 (1945) (RP1661).

(9) D. C. Ginnings, T. B. Douglas and Anne F. Ball, *ibid.*, **45**, 23 (1950) (RP2110).

(10) N. S. Osborne and D. C. Ginnings, *ibid.*, **39**, 453 (1947) (RP-1841).

(2) F. W. Schwab and E. Wichers, *J. Research Natl. Bur. Standards*, **34**, 333 (1945) (RP1647).

(3) F. W. Schwab and E. Wichers, *ibid.*, **32**, 253 (1944) (RP1588).

TABLE II  
HEAT CAPACITY AND ENTHALPY OF ALUMINUM OXIDE AT  
CONSTANT PRESSURE (1 ATMOSPHERE) (MOL. WT. 101.96)

T, °K.	$C_p$		T, °K.	$C_p$		$(H_T - H_0^\circ\text{K.}),$ abs. j. mole <sup>-1</sup>
	abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	$(H_T - H_0^\circ\text{K.})$ abs. j. mole <sup>-1</sup>		abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	$(H_T - H_0^\circ\text{K.}),$ abs. j. mole <sup>-1</sup>	
0	0.0	0.0	420	98.55	20965	
5	.0012	.0015	430	99.64	21956	
10	.0094	.0235	440	100.69	22958	
15	.0316	.1190	450	101.68	23970	
20	.0759	.3588	460	102.64	24992	
25	.1417	.8807	470	103.54	26022	
30	.2627	1.873	480	104.42	27062	
35	.4377	3.581	490	105.25	28111	
40	.6907	6.374	500	106.05	29167	
45	1.039	10.650	510	106.81	30232	
50	1.492	16.941	520	107.55	31303	
55	2.069	25.792	530	108.26	32381	
60	2.780	37.860	540	108.93	33468	
65	3.620	53.805	550	109.59	34561	
70	4.582	74.257	560	110.21	35660	
75	5.668	99.826	570	110.82	36765	
80	6.895	131.18	580	111.40	37876	
85	8.247	168.98	590	111.97	38994	
90	9.692	213.79	600	112.51	40116	
95	11.223	266.04	610	113.03	41243	
100	12.84	326.16	620	113.54	42376	
110	16.31	471.70	630	114.03	43515	
120	20.05	653.40	640	114.50	44658	
130	23.96	873.37	650	114.95	45804	
140	27.96	1132.9	660	115.40	46955	
150	31.99	1432.6	670	115.82	48111	
160	35.99	1772.4	680	116.24	49273	
170	39.94	2152.1	690	116.64	50437	
180	43.79	2570.9	700	117.03	51605	
190	47.53	3027.6	720	117.77	53953	
200	51.14	3521.1	740	118.46	56316	
210	54.60	4049.9	760	119.12	58691	
220	57.92	4612.7	780	119.74	61080	
230	61.09	5207.8	800	120.33	63480	
240	64.12	5834.1	820	120.88	65893	
250	67.01	6489.9	840	121.40	68316	
260	69.75	7173.9	860	121.90	70750	
270	72.36	7884.6	880	122.37	73192	
280	74.84	8620.8	900	122.82	75644	
290	77.19	9381.0	920	123.24	78104	
298.16	79.01	10018	940	123.65	80574	
300	79.41	10164	960	124.03	83051	
310	81.52	10969	980	124.40	85536	
320	83.50	11794	1000	124.74	88026	
330	85.39	12638	1020	125.08	90525	
340	87.18	13502	1040	125.39	93029	
350	88.88	14382	1060	125.69	95541	
360	90.52	15279	1080	125.98	98057	
370	92.06	16191	1100	126.26	100580	
380	93.51	17119	1120	126.52	103110	
390	94.88	18062	1140	126.77	105640	
400	96.18	19017	1160	127.01	108180	
410	97.40	19985	1180	127.24	110720	
420	98.55	20965	1200	127.47	113270	

tion pressure) for benzoic acid, *n*-heptane and diphenyl ether, together with values of  $H_T - H_0^\circ\text{K.}$  (enthalpy referred to the solid at absolute zero) at saturation pressure. In Table II are given values of  $C_p$  (heat capacity at one atmosphere)

for aluminum oxide, together with values of  $H_T - H_0^\circ\text{K.}$  at one atmosphere pressure. In both tables, the heat capacity values given below the experimental range were obtained by extrapolating a Debye equation fitted to the experimental values at the lowest temperature. In Table III are given values for water of  $C_{\text{satd.}}$ ,  $C_p$  (one atmosphere) and  $H_t - H_0^\circ\text{C.}$  (enthalpy referred to liquid at 0°) at both saturation and one atmosphere pressure. The estimated accuracies of the results given in the tables are given later under the discussion for each material. The results presented in all the tables are based on the International Temperature Scale of 1948, using 0°C. = 273.16°K.; 1 absolute joule = 0.239006 defined calorie = 0.999835 international joule; molecular weights of benzoic acid, *n*-heptane, aluminum oxide, diphenyl ether and water were taken as 122.12, 100.20, 101.96, 170.20 and 18.016, respectively. The smoothed molal heat capacity values of the four substances are plotted in Fig. 1 to show the shapes of the curves.

Figure 1 shows that benzoic acid has the lowest molal heat capacity of the three organic substances but higher than aluminum oxide or water. The experimental measurements with benzoic acid were made in the temperature range 14 to 410°K., using only the adiabatic calorimeter.<sup>6</sup> In view of the corrosiveness of benzoic acid at the higher temperatures, measurements below 320°K. were completed before proceeding to 410°K. The results are believed to be accurate to within about 0.2% between 60 and 395°K., but above the latter temperature, the results are less reliable (0.3%) due to the uncertainty arising from the chemical reaction of the benzoic acid with the container. Below 60°K., the inaccuracy increases to 1% at 14°K. because of the low absolute heat capacity and of the uncertainties in temperature measurements. The heat capacity results of the previous investigators are rather discordant except those of Jessup<sup>11</sup> and Parks, Huffman and Barmore,<sup>12</sup> who agree with the present results within about 1%. Above 350°K., benzoic acid is not suitable as a heat capacity standard due to its corrosive nature. This is particularly so in the liquid state. Furthermore, once melted, the problem of transfer of the sample becomes more difficult since it must be remelted to empty the sample container.

In the temperature range 273 to 373°K., the heat capacity values listed for *n*-heptane in Table I are based not only on the new results with the low temperature adiabatic calorimeter and the ice calorimeter, but also on previously published results<sup>10</sup> obtained with two other adiabatic calorimeters and two different samples of *n*-heptane at the National Bureau of Standards. In this temperature range, the maximum spread of all the results with the four different calorimeters is only 0.2%. Even though the earlier measurements were not made on the Calorimetry Conference Sample of *n*-heptane, greatest weight is given in this temperature range to the earlier values as

(11) R. S. Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942) (RP1499).

(12) G. S. Parks, H. M. Huffman and M. Barmore, *THIS JOURNAL*, **55**, 2733 (1933).

TABLE III  
HEAT CAPACITY AND ENTHALPY OF LIQUID WATER<sup>a</sup>  
(mol. wt. = 18.016)

<i>t</i> , °C.	<i>C<sub>p</sub></i>		<i>(H<sub>t</sub> - H<sub>0</sub>°C.)</i>		<i>t</i> , °C.	<i>C<sub>p</sub></i>		<i>(H<sub>t</sub> - H<sub>0</sub>°C.)</i>	
	<i>C<sub>satd</sub></i> abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	<i>p</i> = 1 atm. mole <sup>-1</sup>	Satd. pressure abs. j. mole <sup>-1</sup>	<i>p</i> = 1 atm. mole <sup>-1</sup>		<i>C<sub>satd</sub></i> abs. j. deg. <sup>-1</sup> mole <sup>-1</sup>	<i>p</i> = 1 atm. mole <sup>-1</sup>	Satd. pressure abs. j. mole <sup>-1</sup>	<i>p</i> = 1 atm. mole <sup>-1</sup>
0	75.993	75.985	000.000	000.000	50	75.320	75.318	3770.59	3770.12
5	75.714	75.706	379.22	379.18	55	75.350	75.348	4147.32	4146.78
10	75.532	75.525	757.31	757.24	60	75.385	75.385	4524.22	4523.61
15	75.417	75.410	1134.67	1134.53	65	75.428	75.428	4901.34	4900.64
20	75.345	75.339	1511.57	1511.39	70	75.476	75.478	5278.71	5277.91
25	75.303	75.298	1888.19	1887.97	75	75.532	75.536	5656.36	5655.44
30	75.282	75.278	2264.67	2264.41	80	75.594	75.601	6034.34	6033.27
35	75.277	75.273	2641.08	2640.78	85	75.667	75.675	6412.69	6411.46
40	75.283	75.280	3017.51	3017.16	90	75.746	75.757	6791.45	6790.04
45	75.298	75.295	3394.00	3393.59	95	75.835	75.850	7170.68	7169.05
50	75.320	75.318	3770.59	3770.12	100	75.934	75.954	7550.41	7548.56

<sup>a</sup> For international use in calorimetry, the International Committee on Weights and Measures has approved a heat capacity table (Procès-Verbaux of the International Committee on Weights and Measures, Session of 1950, p. 92) which differs from this table by less than 0.005 joule deg.<sup>-1</sup> mole<sup>-1</sup>.

they are considered to be slightly more reliable. It is believed that the purities of all the samples were sufficiently high so that they did not limit the accuracy of the measurements. For a considerable temperature range above the triple point, the heat capacity curve for *n*-heptane shows a negative slope. This behavior has been found to be not uncommon with many substances. It is interesting to note that the Bureau of Mines Laboratory at Bartlesville, Oklahoma, has recently completed heat capacity measurements on the Calorimetry Conference Sample of *n*-heptane and their results<sup>13</sup> agree with the heat capacity values in Table I to within 0.1% except below 50°K. It is believed that the listed values of heat capacity and enthalpy of *n*-heptane are accurate to about 0.1% except below 50°K. and above 450°K., where increasing tolerances must be allowed.

ture in the liquid region. This property should make it very useful as a heat capacity standard. Even in the solid region from 50 to 300°K., its heat is sufficiently linear with temperature so that linear interpolation between the tabulated values can be made. Smith and Andrews<sup>14</sup> also measured the heat capacity from 100° to 300°K. Their results are close to those from the present work,<sup>7</sup> agreeing for the most part to within 1%, which is the accuracy claimed by them. The accuracy of the present measurements is believed to be about 0.2% over most (50 to 500°K.) of the temperature range. The agreement of the two sets of NBS results using the two radically different methods and apparatus in the overlapping temperature range (300 to 360°K.) is better than 0.2%.

In Fig. 1, it is seen that aluminum oxide has a typical heat capacity curve for a hard crystalline

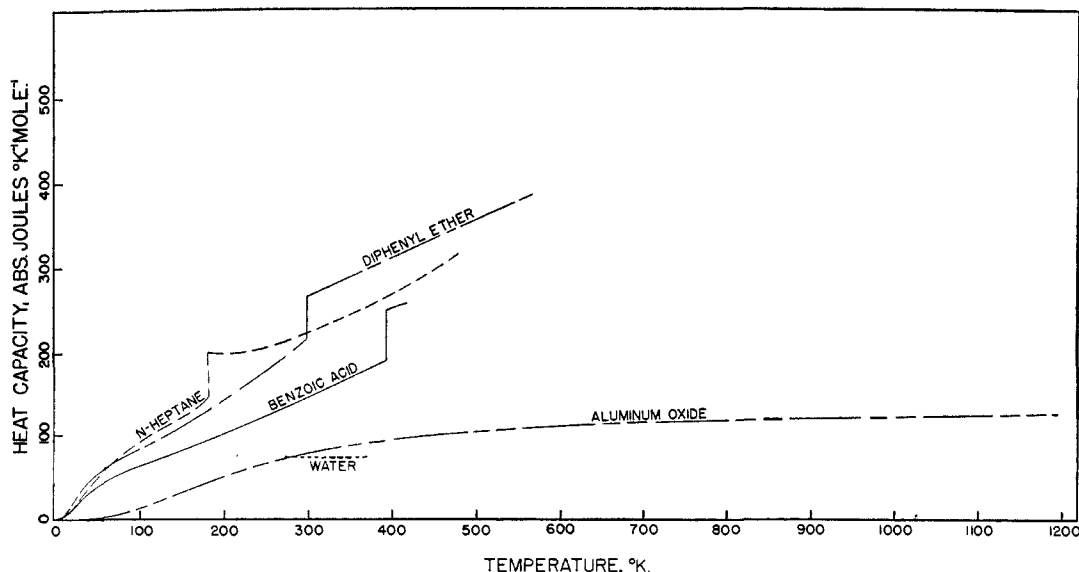


Fig. 1.—Comparison of molal heat capacities.

It is apparent in Fig. 1 that the heat capacity of diphenyl ether is essentially linear with tempera-

(13) Unpublished data, H. L. Finke, M. E. Gross and J. F. Messerly, Thermodynamics Laboratory, Bureau of Mines Experimental Station, Bartlesville, Oklahoma.

material with a high Debye temperature. As the aluminum oxide in the form of corundum ( $\alpha$ -alumina) is stable at all temperatures below its

(14) R. H. Smith and D. H. Andrews, THIS JOURNAL, 53, 3661 (1931).

melting point, there is no transition in the heat capacity curve to make troublesome its use as a heat capacity standard. In the higher temperature range, its heat capacity changes comparatively little, making it most useful in the range. It should be just as useful between 1200°K., the upper limit of the present measurements and its melting point (above 2300°K.). In the lower temperature range where its heat capacity is low, it may not be quite as useful as other materials having lower Debye temperatures.

A number of other investigators have reported the heat capacity (or enthalpy) of aluminum oxide. In the low temperature range, the most recent measurements are those of Kerr, Johnston and Hallett,<sup>15</sup> who have used an isothermal-jacket type of calorimeter in the range 19 to 300°K. Except at the ends of this temperature range, their agreement with the present results is within about 0.2%. Most of the high temperature measurements (including the present measurements) give enthalpy changes over large temperature intervals, from which heat capacities are derived. Ginnings and Corruccini<sup>16</sup> used a different apparatus and sample to obtain enthalpy values which agree with the present results to better than 0.1% over most of the higher temperature range. With the present measurements in the temperature range 0 to 100°, where the results with the adiabatic and ice calorimeters overlap, the agreement between the two sets of heat capacity values was about 0.2%, even though the ice calorimeter was at a disadvantage in this range. It is believed that the values of heat capacity and enthalpy listed in Table II are accurate to about 0.2% in the temperature range above 50°K. except in the region above 900°K. where somewhat increased tolerances on heat capacity are believed necessary.

In addition to the results given for the four materials, it is believed worthwhile to give a brief table showing the results of earlier accurate measurements at the National Bureau of Standards of heat capacity of liquid water in the range 0 to 100°<sup>5</sup> where it is most useful as a standard. The values of heat capacity and enthalpy given in Table III are believed to be accurate to about 0.01 to 0.02%.

With some calorimeters, the choice of a heat

(15) E. C. Kerr, H. L. Johnston and N. C. Hallett, *THIS JOURNAL*, **72**, 4740 (1950).

(16) D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 593 (1947) (RP1797).

capacity standard may be governed by its heat capacity per unit *volume*. In Fig. 2 are shown the heat capacities per unit volume for the five materials calculated using the density data at the different temperatures, where available. It is apparent that aluminum oxide at moderate temperatures has about twice the heat capacity per unit volume of the other materials except water. Below 120°K., however, the other materials have a much higher heat capacity. In the case of *n*-heptane below 180°K., the heat capacity curve is not given because no density data are available.

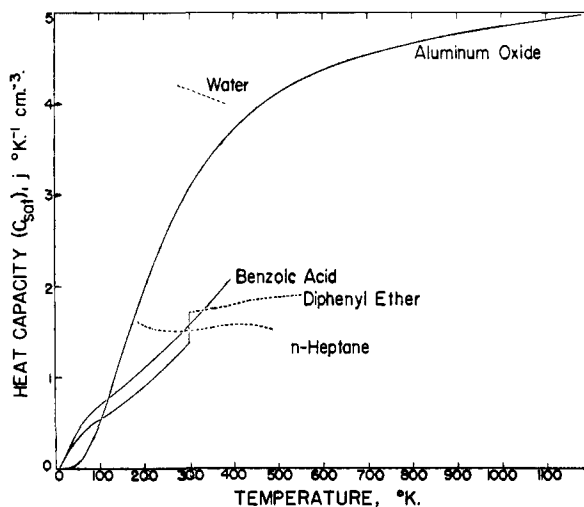


Fig. 2.—Comparison of volume heat capacities.

In summary, it is believed that the five materials whose heat capacities are given in the tables will answer most of the needs for heat capacity standards. In the range 0 to 100°, water will usually serve as the most useful material. In the range 14 to 350°K., benzoic acid will serve if a solid is needed, while *n*-heptane will serve up to 400°K. if a liquid is needed which can be distilled in and out of the calorimeter. In the range 300 to 570°K., diphenyl ether serves as liquid with relatively low vapor pressure. Although aluminum oxide is unique among these materials in that it can be used as a practical standard in the entire range 14 to 1200°K. (and probably even up to its melting point near 2300°K.), it will probably be used most in the high temperature range.

WASHINGTON, D. C.