solubility is approximately a linear function of the concentration of added substance. The dielectric constants of the solutions do not account for differences observed between the α-amino acids but permit the calculation of ionic radii for the salts which are of the right order of magnitude.

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Low Temperature Specific Heats. I. An Improved Calorimeter for Use from 14 to 300°K. The Heat Capacity and Entropy of Naphthalene[1]

BY J. C. SOUTHARD AND F. G. BRICKWEDDE

The calorimeter described in this paper has been constructed for the determination of the specific heats of liquids and solids of interest in fertilizer and nitrogen fixation investigations. Slow thermal changes anticipated in some of the substances to be investigated made it desirable to prevent as far as possible any transfer of heat between the substances and the surroundings.

Systematic and reliable low temperature specific heat determinations date from the design of the "vacuum" calorimeter first used by Eucken[2] in Nernst's laboratory, 1909. In principle the specific heat of a substance is determined by observing the rise in temperature produced when a measured amount of heat is added electrically to the substance suspended, for purposes of thermal insulation, in an evacuated space. The "vacuum" calorimeter was modified and improved by later investigators. The apparatus described here is a refinement of a "vacuum" calorimeter used by F. Lange[3] which was the first intended to operate "adiabatically," that is, so there should be no transfer of heat between the substance and its surroundings. This is accomplished by surrounding the substance, in a thin-walled container, with a "thermal" shield whose temperature can be

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(1) This paper is the first of a series communicating the results of two years of coöperative work by the Fixed Nitrogen Research Laboratory and the Bureau of Standards on the specific heats of compounds important in connection with fertilizer and fixed nitrogen investigations of the former laboratory. The experimental work was carried out in the Cryogenic Laboratory of the Bureau of Standards.

The series will include five papers, which with the exception of III will appear in THIS JOURNAL. Number III has already been published in the *Journal of Chemical Physics*, **1**, 95 (1933). The sub-titles of this series for which the principal title is "Low Temperature Specific Heats" are as follows: I. An Improved Calorimeter for use from 14 to 300°K. The Heat Capacity and Entropy of Naphthalene. II. The Calibration of the Thermometer and the Resistance of Pt, Pt-10% Rh and Constantan between −259 and −190°. III. Molecular Rotation in Crystalline Primary Normal Amylammonium Chloride. IV. The Heat Capacities of Potassium Chloride, Potassium Nitrate and Sodium Nitrate. V. The Heat Capacities of β- and α-Tricalcium Phosphate. Publication approved by Director of Bureau of Standards, Department of Commerce, and Chief, Bureau of Chemistry and Soils, Department of Agriculture.

(2) Eucken, *Physik. Z.*, **10**, 586 (1909).

(3) Lange, *Z. physik. Chem.*, **110A**, 343 (1924).

varied quickly and thus made to follow the temperature changes of the surface of the container. An adiabatic calorimeter with such a shield was used by Southard and Andrews for the determination of specific heats at low temperatures.[4] Under ideal conditions there would be no difference in temperature between the container and any part of the shield, and the substance in its container would neither lose heat to its surroundings nor gain heat from them.

Apparatus

The apparatus described here may be considered as being composed of four principal parts, (1) the inner container in which the material under investigation is placed, (2) the thermal shield surrounding the inner container, used to minimize heat leaks, (3) the jacket, inclosing the inner container and thermal shield, connected to a high vacuum system for evacuation to minimize gaseous conduction and convection of heat, and (4) the various electrical circuits for determining and controlling the temperature and for measuring the energy added to the inner container.

The inner container (Fig. 1A) is a cylindrical copper can (5 × 4 cm.) fitted with a reentrant tube (4.5 × 0.5 cm.) in which is soldered the platinum case of a specially constructed resistance thermometer which also serves as the heater. Around the tube are sixteen radial fins of 0.1 mm. copper foil. The top, which can be unsoldered and removed for loading, is pierced by a pin hole through which helium is admitted just before the final vacuum tight sealing. A small screw is soldered to the side of the container for attaching one junction of a difference thermocouple pressed into contact by a nut. The other junction is attached to the middle of the inside cylindrical surface of the thermal shield. The outside of the inner container is silver plated to reduce the transfer of heat to and from the container by radiation. The empty container has a weight of about 37 g., including the resistance thermometer, an inside volume of 54 cc., and a heat capacity of approximately 3 cal./degree at room temperature.

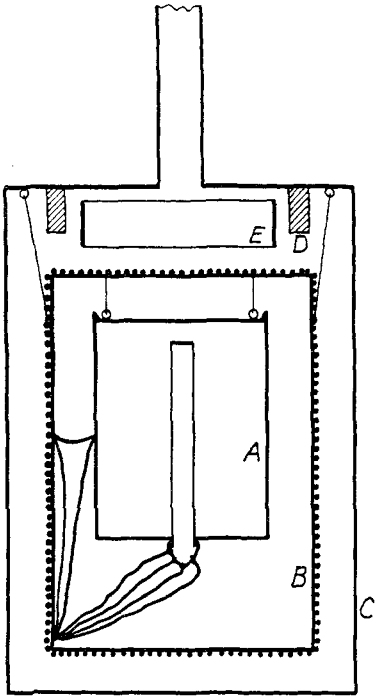

Fig. 1.—Calorimeter for low temperature specific heats: A, inner container; B, thermal shield; C, jacket; D, ring on top; E, floating ring.

The thermal shield (Fig. 1B) completely surrounds the inner container which is suspended inside of it on silk threads. The shield is a cylindrical brass shell (6 × 8.5 cm., wall thickness 0.8 mm.) fitted with a removable bottom. Its inside surface is gold plated and the outside completely covered by three separate heaters, one each on the top, side and bottom, made by covering the surface with a single layer of No. 32 constantan wire insulated with silk and bakelite lacquer. The electrical leads to the heater-thermometer and to three copper–constantan difference thermocouples are run under the

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[4] Southard and Andrews, *J. Franklin Inst.*, **209**, 349 (1930).

heater winding, in a spiral groove, 75 cm. long, cut in the side of the shield. One of the thermocouples is that previously referred to, between the inner container and side of the shield. The other two are between the inside top and side, and the inside bottom and side of the shield. Their e. m. f.'s, as indicated by a sensitive d'Arsonval type galvanometer, serve as a guide for the regulation of the shield heaters. In order to prevent a cold spot where the leads enter the groove, it was found necessary to wind the leads around a floating ring (E) whose temperature was kept within a few degrees of that of the shield by means of an auxiliary heater and difference thermocouple.

The jacket (Fig. 1C) is a brass case made in two separable parts, surrounding the shield. The lower part can be removed by unsoldering a slip joint at the outer edge of the top. The space inside the jacket is connected to a high vacuum system by a thin walled copper–nickel alloy tube (o. d. 1 cm.) through which the electrical leads pass. On the inside of the top is soldered a heavy copper ring (D) around which the leads, coming from warmer regions above, are wound in order to bring them to the temperature of the surrounding bath. Without the ring, the inner container could not be maintained at a temperature as low as that of the bath. The jacket is surrounded by a refrigerating bath in a Dewar flask, enclosed in a vacuum tight case connected to a high capacity mechanical vacuum pump. Using liquid air or liquid hydrogen, temperatures can be maintained with this pump corresponding to vapor pressures of 3 cm. A larger Dewar flask filled with liquid air is placed outside the case of the inner flask when the latter contains liquid hydrogen.

The combination thermometer-heater was made of an alloy, platinum–10% rhodium wire and has a resistance of about 53 ohms at 273°K. Its construction and its calibration below 90°K. against a gas thermometer are described in another paper[5] in which it is designated as K_4. Above 90°K. it was calibrated by comparison with a standard platinum resistance thermometer in a precision cryostat.[6] The equation $R/R_0 = 1 + at + bt^2 + ct^3$, in which the temperature is expressed in °C. (International) and $a = +0.00172075$, $b = -2.28297 \times 10^{-7}$, $c = -1.77572 \times 10^{-9}$ was found to represent the data with a maximum deviation of 0.006°. When the thermometer-heater was used as a thermometer its resistance was ascertained by determining the ratio of the potential drop across its ends to that across a standard 100-ohm coil connected in series, when a current of 1 ma. is flowing through them. When the thermometer was used as a heater the current and voltage were measured potentiometrically using a 1-ohm standard resistor and a 10,000-ohm volt box. The time of heating is controlled by an automatic switch operated by the standard time signals of the Bureau of Standards. Lead storage batteries of 120 volts are the source of heating current.

The three shield heaters each have a slide wire rheostat in series for independent regulation. In addition there is a master rheostat controlling all three circuits as a unit. The floating ring heater is independent of the shield. As an aid to regulation and for protection, a milliammeter and a 250 ma. fuse are connected in each of these circuits.

Two observers are needed. One makes a series of ten or more determinations at one-minute intervals of the thermometer resistance by comparing the potential across it with that across the standard resistance in series with it. After these measurements, during the following silent or fifty-ninth second of the time signals, the activating circuit of the automatic switch is closed so that the next time signal impulse throws the switch and begins the heating period. The current which flows through the heater in the inner container when the switch is thrown has previously been flowing through a steadying resistance so that the load on the batteries is constant. During the heating period of from five to ten minutes not less than four readings each on volt box and standard resistor are made. During these observations the other observer has been regulating the

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(5) Southard and Milner, THIS JOURNAL, **55**, 4384 (1933).

(6) Scott and Brickwedde, *B. of S. J. Res.*, **6**, 401 (1931).

shield heaters, top, side and bottom, so that the temperature of all parts of the shield as shown by the difference couples connected one after another to a galvanometer has closely followed that of the calorimeter. The automatic switch is reversed so that after the required number of minutes of heating the heating current is automatically switched to the steadying resistances by closing the activating switch as was done on starting. After a period of three or four minutes, when equilibrium is established, another series of thermometer resistance measurements is made and the procedure continued.

The temperature difference between shield and calorimeter is kept within 0.02°, with the exception of short intervals at the beginning and the end of the heating period, when it may rise to 0.05°. With a thermal head of 0.02° it was found that the temperature of the inner container did not change by as much as 0.001° during half an hour. This feature makes the calorimeter well suited for the investigation of slow thermal transitions since with such constancy a small amount of energy evolved or absorbed over a long period of time can be measured with accuracy.[7] Although in practice a liquid bath is used whose temperature does not differ much from that of the inner container, it was found that measurements made at 0° with a liquid air bath surrounding the jacket were as reliable as those made with a cool acetone bath at −10°. Measurements taken in the same temperature range on different days using refrigerating baths of widely differing temperatures were in agreement with each other within the limits of accuracy given in this paper.

Halving the rate of heating yields results which are in agreement with each other and with those found with the original rate of heating. Thus it is made apparent that the net transfer of heat to or from the inner container by radiation and by conduction along leads is negligibly small.

The principal source of error is in the measurement of the temperature rise. An error of 0.002° in the determination of a temperature rise of about five degrees makes for an error in heat capacity of 0.04%. The potentiometer with which the temperature and energy input determinations were made was periodically calibrated. Down to −190° temperatures are probably correct to within 0.01° on the International Temperature Scale and it is believed to within 0.05° on the thermodynamic scale between −190 and −250°, in which region the thermometer was calibrated against a gas thermometer. Temperature changes were determined with an accuracy of 0.002° down to −230°. Because of the uncertainty in the value of the thermodynamic temperature of the ice point, here taken as 273.16°, absolute temperatures may be in error by 0.05°K. Oscillograph measurements showed that the lag in the automatic heating circuit switch did not contribute errors exceeding 0.01 second. Irregularities in the time signals might account for an additional 0.02 second, which, however, in a heating period of three hundred seconds is negligible.

The correction for the irregularity in energy input while the heater resistance is rising to a steady state at the beginning of a run does not amount to more than 0.1% of the energy input. The actual error introduced, however, is only a fraction of this. The correction is calculated from a series of readings made at fifteen-second intervals during the first minute. It was found that such a series need only be taken occasionally and especially when the heating current was changed. Another correction of about 0.1% is required on account of the heat generated in the leads passing between the shield and the inner container. The heat generated is calculated from direct measurements of the lead resistance made during each heating period. On the assumption that this heat divides equally between the shield and the inner container, the error in applying the correction is very small. Measurements of electric power input are probably accurate to about 0.02%. The experimental error in determining the heat capacity of the

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(7) This calorimeter was used in the investigation of the slow thermal changes which take place in primary amylammonium chloride, *J. Chem. Physics*, **1**, 95 (1933).

empty calorimeter may introduce an error of 0.02 to 0.03% in the final results of a heat capacity determination.

The errors from all sources total about 0.1%. Plotting the data, the precision of measurement appears to be about this magnitude down as far as 40°K. Below this temperature the errors increase because of the decreasing sensitivity of the thermometer, and the increasing ratio of the heat capacity of the empty inner container to that of the sample. At the lower temperatures the thermal conductivity of the leads increases rapidly. At temperatures therefore for which the energy input is smallest there may be appreciable transfers of heat to or from the inner container. It is possible that at 14°K. the errors may in the worst cases exceed 1%.

Results

Naphthalene was selected for investigation for two reasons. (1) It is a good substance for testing the accuracy of the results obtainable with the calorimeter since it has been used by a number of other workers[8] and (2) because use has been made of it as a standard in calibrating other types of low temperature calorimeters.[9] It is obtainable from the Bureau of Standards as a standard sample[10] in a sufficient degree of purity to be used without further treatment.

In these measurements the international joule is used as the unit of energy, so that the specific heats are obtained in joules per gram degree. Except for the fact that the results of most of the other measurements have been expressed in calories, it would be desirable to give these results in international joules as they were obtained. For convenience of comparison with other results, the calorie has been used. The "I. C. T." defines the calorie as follows: 1 g. cal._{15} = 4.185 abs. joule. The factor relating the absolute joule and the Bureau of Standards international joule is, according to the latest information,[11] 1 int. joule = 1.0004 abs. joule, so that 1 g. cal._{15} = 4.185/1.0004 = 4.1833 int. joules. All weights are corrected to vacuum.

The results are presented in Table I and Fig. 2. The entropy at 298.16°K. was found to be 39.89 ± 0.12 e. u. by plotting C_p/T against T and measuring the area under the curve. This involved an extrapolation of 0.43 e. u. for the portion below 15°K. Six degrees of freedom for each of which θ_D was set equal to 133 were used to obtain this extrapolated value. Taking the entropy of C as 1.39 e. u. per mole[12] and H_2, 31.23 e. u.[13] at 298.16°K., and the heat of combustion of naphthalene as 1,231.6 kg. cal.[14] per mole, hydrogen 68.31 kg. cal.[15] and carbon 94.24 kg. cal.,[16]

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(8) Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1555 (1930); Andrews, Lynn and Johnston, *ibid.*, **48**, 1274 (1926); Taylor and Rinkenbach, *ibid.*, **46**, 1504 (1924); Dewar, *Proc. Roy. Soc.* (London), **76A**, 325 (1905).

(9) Smith, THIS JOURNAL, **53**, 3663 (1931).

(10) Standard sample 38b (naphthalene) is purified by two crystallizations from alcohol and sublimation in vacuum (see Bureau of Standards Circ. 25).

(11) Vinal, *Bur. Standards J. Research*, **8**, 448 (1932).

(12) "I. C. T.," Vol. V, p. 87.

(13) Giauque, THIS JOURNAL, **52**, 4816 (1930).

(14) "I. C. T.," Vol. V, p. 163.

(15) Rossini, *Bur. Stds. J. Res.*, **6**, 1 (1931).

(16) Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925).

TABLE I

MOLAL HEAT CAPACITY OF NAPHTHALENE

Mol. wt. 128.06. 273.16°K. = 0°C. Wt. sample (*in vacuo*), 37.121 g. C_p in 15° calories per mole.

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
15.14	1.411	62.32	10.52	140.33	18.46	218.13	27.86
17.73	2.035	62.52	10.54	145.61	19.04	223.10	28.52
21.45	2.964	67.86	11.10	150.80	19.67	226.90	29.09
22.25	3.283	73.36	11.69	151.99	19.77	228.01	29.25
25.54	4.058	78.58	12.26	155.93	20.20	232.92	29.87
26.66	4.337	83.57	12.92	161.02	20.79	232.95	29.84
29.79	5.074	88.38	13.29	163.48	21.03	237.78	30.45
31.74	5.507	89.86	13.44	166.00	21.34	238.94	30.66
34.35	6.068	93.06	13.72	168.52	21.54	242.54	31.28
36.47	6.513	95.39	13.86	173.49	22.16	244.83	31.57
39.34	7.038	100.77	14.46	178.39	22.74	250.68	32.39
41.32	7.395	106.04	14.86	183.23	23.36	256.42	33.23
44.64	7.916	111.18	15.38	187.99	23.94	262.09	34.11
46.53	8.222	116.21	15.85	192.69	24.65	267.70	34.98
50.23	8.730	121.11	16.35	197.62	25.17	273.21	35.86
51.95	9.071	125.94	16.93	202.85	25.84	278.69	36.76
56.22	9.709	130.68	17.43	208.00	26.52	284.09	37.65
57.37	9.878	135.35	17.93	213.10	27.19	289.42	38.54
						294.68	39.55

at the same temperature, the free energy of formation of naphthalene at 298.16°K. is found to be +48.5 kg. cal. per mole.

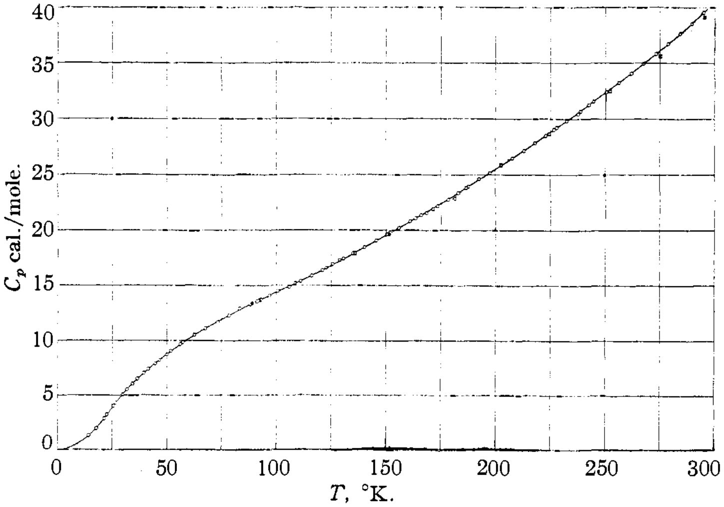

Fig. 2.—Molal heat capacity of naphthalene, $C_{10}H_8$: ○, S. and B.; □, H., P. and D.; ▽, T. and R.

The heat capacities of naphthalene reported in Table I, determined with the apparatus described, agree with the heat capacities determined by

Huffman, Parks and Daniels between 90 and 300°K. well within the limits of accuracy claimed by them (1%). Furthermore, there is no tendency for one curve to be consistently higher or lower than the other up to 250°K. It should be pointed out while Huffman, Parks and Daniels used a "vacuum" calorimeter, their method of operation was entirely different and it seems probable that their corrections for radiation lead to the divergence at the higher temperatures.

It is interesting to note that the value Huffman, Parks and Daniels obtained by extrapolation from 90 to 0°K. for the entropy at 90°K. was 12.69 e. u. while the value found here is 12.52 e. u. with an extrapolation of only 0.43 e. u. from 15 to 0°K.

Acknowledgment.—The authors are indebted to Dr. R. T. Milner for his helpful suggestions in the construction of the apparatus and for his assistance in measurements on the empty calorimeter. They are indebted to Mr. J. W. Cook for liquefying the hydrogen and to Mr. R. A. Nelson for assisting in the measurements and calculations on naphthalene.

Summary

1. An improved adiabatic calorimeter for the measurement of specific heats of liquids and solids between 14 and 300°K. has been constructed. It can be used with a precision of about 0.1% and is particularly suited to the study of slow transitions and thermal changes.

2. The molal heat capacity of naphthalene was determined between 14 and 300°K. and the entropy and free energy of formation at 298.16°K. calculated to be 39.89 ± 0.12 e. u. and +48.5 kg. cal., respectively.

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Low Temperature Specific Heats. II. The Calibration of the Thermometer and the Resistance of Platinum, Platinum–10% Rhodium and Constantan between –259 and –190°

By J. C. Southard and R. T. Milner

In the determination of a thermal property, the temperature scale and the thermometer that are used are of such fundamental importance that they deserve special consideration. The International Temperature Scale[1] was used for the specific heat measurements described in this series in the range over which it is defined, that is, above –190°. Below this temperature there is no accepted or established scale except that obtained by the use of a gas thermometer. This paper describes a helium constant volume thermometer that was used in a relatively simple manner to obtain

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(1) G. K. Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).