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Heat Capacity of Sodium Between 0° and 900° C, the Triple Point and Heat of Fusion

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Using an improved ice calorimeter and furnace, the enthalpy changes of two samples of pure sodium have been accurately measured by a drop method at a number of temperatures between 0° and 900° C. Equations are derived to fit the data, and values of enthalpy and entropy, based on zero values at 0° C, as well as the heat capacity are tabulated for both the solid and liquid. Sources of significant experimental error are examined critically, and some theoretical implications of the results are discussed qualitatively.

I. Introduction

The advantages of liquid sodium for heat transfer at high temperatures have been known for some time. Not only have experimental values of the heat capacity of sodium been limited to the temperature range below 300° C, but these values have been widely discordant at 200° to 300°. It was the purpose of this investigation to measure the heat capacity of pure liquid sodium with higher accuracy and at higher temperatures than had been done previously.

II. Samples

The measurements were made on two samples of sodium enclosed in stainless steel containers of the type shown in figure 1. The stainless steel used was chosen for its resistance to attack by sodium at high temperatures. The sodium had been distilled once in glass in vacuum at or below 300° C. The weights of the samples were 5.3404 and 6.0297 g, respectively, and each was admitted in vacuum to a stainless steel cylinder weighing 16.840 g and having a capacity of 9.7 cm^3. After admitting helium to a pressure of one-thirtieth atm, each cylinder was sealed by welding and subsequently tested for leakage by noting whether exposure to 850° C for 15 min in an evacuated vessel caused any change in weight. The welding process utilized pulsed inductive heating [1].[1] With this welding technique, it was possible to seal the container without changing its weight by more than a milligram.

The sodium sample used for most of the measurements was analyzed spectrochemically at this Bureau after the heat-capacity experiments. Of the 47 elements tested for, including all the common metals, only three were detected. Calcium and lithium were found in amounts estimated at between 0.0001 and 0.001 weight percent, whereas potassium was estimated to be between 0.001 and 0.01 percent. The sample was completely soluble in water.

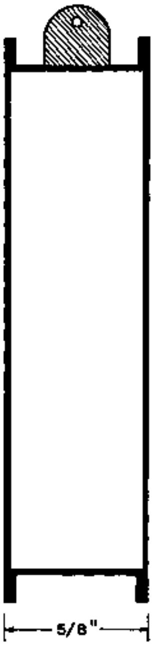

FIGURE 1. *Scale diagram of sample container.*

The spectrochemical analysis did not include a

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[1] Figures in brackets indicate the literature references at the end of this paper.

search for the common nonmetals. However, other samples from the same original source and distilled by the same procedure were reported to contain as much as 0.01 percent by weight of oxygen (as Na_2O). The typical content of hydrogen before distillation amounted to 0.006 percent by weight. A melting curve observed by the authors on the principal sample is described in this paper. This indicated that the impurity in solution in the liquid but not in the solid amounted to about 0.0016 mole percent at the triple point.

III. Method and Apparatus

The method as applied to an earlier apparatus has already been described [2, 3, 4]. In brief, the method is as follows. The sample, sealed in its container, is suspended in a furnace until it comes to constant temperature. It is then dropped into a Bunsen ice calorimeter, which measures the heat evolved by the sample plus container in cooling to 0° C. A similar experiment is made with the empty container at the same temperature. The difference of the two values of heat is a measure of the change in enthalpy of the sample between 0° C and the temperature in the furnace. From enthalpy values of the sample so determined for a series of temperatures, the heat capacity can be derived.

1. The Ice Calorimeter

The construction, calibration, and use of an earlier Bunsen ice calorimeter in this Bureau have been described [2]. The present model, shown together with the furnace in figure 2, incorporates several improvements. In the first place, the mercury-water interface is now located in the bottom of the inner glass calorimeter vessel. This has two advantages. First, the area of the interface is much larger than before, so that for a given influx of heat, the level of mercury in the calorimeter changes very little. The calorimeter and its contents are slightly compressible, so that a change in pressure in the calorimeter results in a change in volume that must be distinguished from the change in volume due to heat input. With the earlier calorimeter, the change in volume produced by the change in head of mercury affected the calibration factor by about 0.01 percent, but with the present

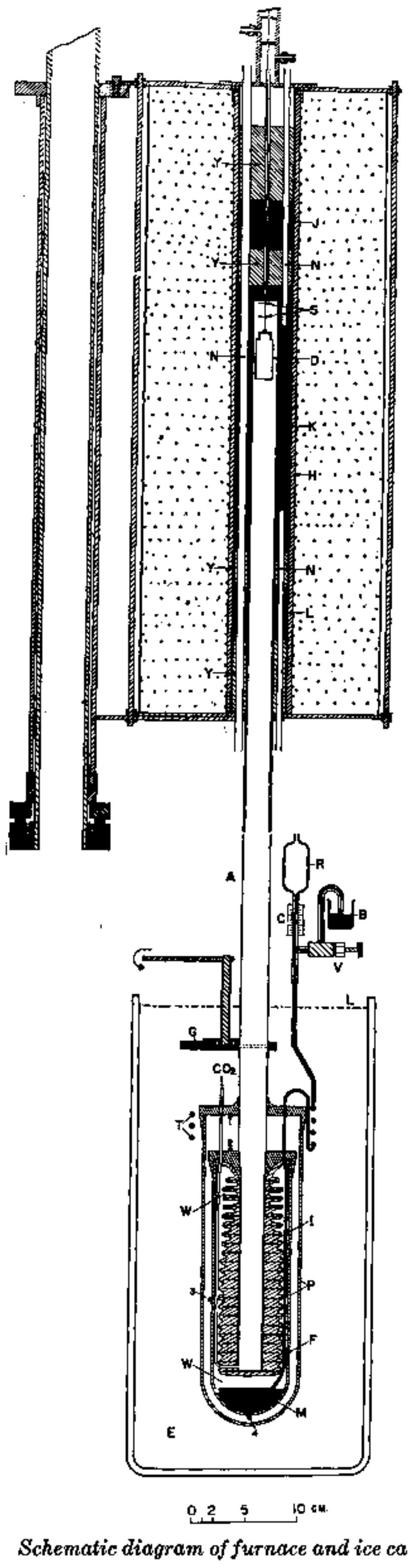

FIGURE 2. *Schematic diagram of furnace and ice calorimeter.*

A, Calorimeter well; *B*, beaker of mercury; *C*, glass capillary; *D*, sample container; *E*, ice bath; *F*, copper vanes; *G*, gate; *H*, platinum heater; *I*, ice mantel; *J*, *K*, *L*, silver cylinders; *M*, mercury; *N*, Inconel tubes; *P*, Pyrex containers; *R*, mercury reservoir; *S*, platinum shields; *T*, mercury "tempering" coil; *V*, needle valve; *W*, water; *Y*, porcelain spacers; 1, 2, 3, 4, thermocouple junctions.

calorimeter, the effect of the change in head is only about 0.004 percent. The electrical calibration experiments automatically compensate for this effect in heat measurements. However, reduction of the magnitude of the effect permits determination of the calibration factor of an "ideal" ice calorimeter (one that operates at constant head) with greater accuracy. A second reason for locating the mercury-water interface in the bottom of the calorimeter is to avoid danger of breaking the inner glass vessel. The inlet tube, now being filled with mercury rather than water, is not subject to blocking by freezing, an event that would burst the glass vessel. The present inlet tube includes a coil (*T*), for bringing the mercury to the temperature of 0° C before it enters the calorimeter.

The present calorimeter has been equipped with a tin-plated system of copper vanes, as pictured in figure 2. This results in more rapid distribution of heat from the well to the ice, so that the lag in reaching thermal equilibrium is now caused almost wholly by the thermal resistance between the heat source (sample in container) and the inner wall of the well. The latter lag has been considerably reduced by using a slow stream of dry helium gas up the well instead of carbon dioxide gas (as shown in fig. 1).

Unlike the earlier calorimeter, the new one has no built-in heater for electrical calibration. Calibrations were made with a removable heater provided with two zones of thermal contact with the calorimeter well for trapping the heat that would otherwise escape through the leads. This heater has a resistance of about 100 ohms instead of the 10 ohms in the earlier calorimeter. This reduces the uncertainty of accounting for the heat developed in the leads between the calorimeter and the jacket to a few thousandths of a percent of the total heat input to the calorimeter.

About one hundred electrical calibration experiments were made with the new calorimeter, with energies varying from 12,000 to 25,000 j. These experiments gave a calibration factor of 270.46 ± 0.03 abs j/g of mercury, which agrees with the value of 270.41 ± 0.06 obtained for the earlier calorimeter within the uncertainty assigned to the latter figure. About a hundred additional calibration experiments were made with low energies (about 100 j) in a search for small absolute errors that might not be detectable in high-energy experiments. These experiments indicated that the calorimeter failed to register about 0.4 j, an amount of heat that is negligible in most measurements.

2. The Furnace

The furnace is shown in position over the ice calorimeter in figure 2. It was mounted on a ball bearing so that it could be swung aside for access to the calorimeter. This furnace incorporated certain improvements that reduced temperature gradients in its central region and permitted more accurate temperature measurements over most of its temperature range.

In order to minimize end effects, the furnace was made 24 in. high, instead of 18 in. as with the earlier one [3]. The furnace was electrically heated by means of No. 26 platinum wire (*H*) wound on a grooved alundum tube having an inside diameter of 2 in. This heater was made in three separate sections corresponding in elevation to the three silver cylinders, which were located inside the alundum at *J*, *K*, and *L*. Silver was used because of its high thermal conductivity. By maintaining the silver cylinders *J* and *L* at the same temperature as the cylinder *K*, the temperature gradient in *K* could be made negligible. The silver cylinders were supported by porcelain spacers (*Y*). The silver and porcelain cylinders were lined with an Inconel tube (14% Cr, 80% Ni, 6% Fe) having an inside diameter of 1 in. in the central and lower parts of the furnace but with a diameter of one-eighth in. in the upper part. This tube served to enclose the sample container and its suspension wire (No. 32 Nichrome V), so that an inert atmosphere could be maintained at high temperatures where the stainless steel container would oxidize in air. Helium was used for the atmosphere in order to minimize the time necessary to hold the capsule in the furnace.

Figure 2 shows some of the vertical holes drilled through the silver and porcelain. These were placed 90 deg apart azimuthally. Three of them (one-fourth-in. in diameter) extended through the length of the furnace while two (three-sixteenth-in. in diameter) extended only to the top and bottom respectively of the center silver cylinder as shown in figure 2. These holes were fitted with thin-walled Inconel tubes, one of which served to hold the platinum-rhodium thermocouple sometimes used for temperature measurement of the central silver section (*K*). In the two $^{3}/_{16}$-in tubes were placed differential thermocouples used to keep the end silver sections (*J*, *L*) at the same temperature as the central section. All thermocouples were insulated in four-hole porcelain tubes, which fit snugly in the Inconel tubes. A platinum resistance thermometer was encased in a platinum-rhodium tube, which also fit snugly in one of the one-fourth-in. Inconel tubes.

In another one-fourth-in. tube were placed three small auxiliary heaters, located at the elevations of the three silver cylinders. It was possible with these heaters to add heat at a low rate to any silver cylinder for fine-temperature regulation. It was possible to maintain the central silver cylinder constant to 0.01 deg and the end silver cylinders within a few tenths of a degree of the central silver. These auxiliary heaters were very useful in fine-temperature regulation since their heat was mostly delivered to the silver in 30 sec, thus avoiding the larger and troublesome lag that would have been encountered had the fine regulation been dependent on adjusting the currents in the main heaters.

In addition to the thermocouple mentioned, several more were installed just outside the main heaters (*H*). These thermocouples served to measure the temperature of this region and were used in a safety device to turn off automatically all current in the furnace if its temperature approached 961° C (the melting point of silver).

The suspension of the container in the furnace and its drop into the calorimeter is similar to that described earlier [3]. The braking started after the container entered the calorimeter. The weight of the falling system was kept constant in all experiments. Two platinum shields were used above the container in the same manner as formerly except that the diameters of the shields were increased from five-eighths in. to three-fourths in. since the diameter of the calorimeter well was increased from three-fourths in. to seven-eighths in.

3. Measurement of the Temperature of the Capsule in the Furnace

Up to 600° C, a strain-free platinum resistance thermometer was used to measure the temperature of the central silver cylinder that surrounded the capsule. This thermometer was calibrated at this Bureau on the International Temperature Scale [5] at the ice, steam, and sulfur points, and its resistance was always checked at the ice point after experiments at 600° C. Between 600° and 900°, the resistance thermometer was removed from the furnace, and the platinum-rhodium thermocouple was used. This thermocouple also was calibrated at this Bureau and was checked against a standard thermocouple before and after the measurements. A comparison of the resistance thermometer with the thermocouple showed agreement within 0.2 deg C in the temperature range up to 600° C. Both the resistance thermometer and thermocouple were made to have good thermal contact with the silver, so that their indications would not be affected by heat conduction along their leads. Experimental verification of this was found in tests with varying depths of immersion. The resistance thermometer winding and the principal junction of the thermocouple were both located at approximately the height of the sample container in the furnace.

It has been assumed that the sample container attains the temperature of the central silver, which surrounds it except at the bottom. Although calculations showed this assumption to be justified, experiments were made to test this. These experiments consisted of first making regular drop experiments at 700° C with the end silver pieces (*J* and *L*) regulated in the normal manner within a few tenths of a degree of the central silver (*K*). Then another series of drops was made, regulating both end silver pieces about 50 deg colder than the center. In other words, the temperature difference between the ends and the central silver was exaggerated by a factor of over one hundred. Even under these extreme conditions, the experiments gave a result only 0.1 percent lower. This indicated two main facts. First, with the exaggerated temperature difference, either the temperature gradient in the central silver was small, or the thermocouple was so placed that it represented the temperature of the sample container in spite of the gradient. Actually calculations show that the gradient is negligible in normal use. Second, this also indicated that any lowering of the temperature of the sample container below that of the main silver cylinder *K* due to radiation loss from the sample container out the bottom of the furnace is negligible. Calculations considering the solid angle had already shown that this should be true.

Since the temperature of the sample container was not directly measured, it was necessary to allow sufficient time for the container to reach the temperature of the silver. Special tests have been made to determine this time, similar to those described in detail in an earlier publication [3]. In the present experiments using helium in the furnace, the container with sodium acquired the temperature of the furnace (within 0.01 deg) within 15 min, whereas the empty container took less time in proportion to its heat capacity. In the experiments with sodium just above its melting point, extra time was taken to allow for absorption of the heat of fusion.

It was also necessary to consider the possibility of azimuthal temperature gradients in the silver due to the periodic addition of small amounts of heat by means of the auxiliary heaters that are located in one of the vertical holes in the silver. Calculations showed that no significant temperature gradients resulted with the relatively small amounts of heat supplied in this way.

4. Errors Due to Cooling of the Sample Container During Its Drop into the Calorimeter

Some users of the "drop" method in the past have simply subtracted the calculated enthalpy of the sample container from the measured enthalpy of the container plus sample. Of course, this procedure does not make allowance for heat lost during the drop. By making drop experiments with the empty container, most of this heat lost is accounted for, since it is approximately the same in both types of experiments. However, for the most accurate measurements, it is desirable to test the validity of this assumption that the heat loss is essentially the same for both empty and filled containers. The heat loss during the drop is dependent on the temperature difference between the container surface and its surroundings. This temperature difference will be slightly greater for the filled container, since its total heat capacity is higher than that of the empty container. This difference between the amounts of heat lost by the empty and the filled containers has been estimated by the authors for a sample assumed to have infinite thermal conductivity and perfect contact with the container. This gives the maximum possible difference. The radiation loss was estimated on the basis of a container with an area of 35 cm^2 with an emissivity of approximately unity. The heat lost by radiation from a container at 900° C dropping through a region near room temperature for one-quarter sec is about 80 j. The convective heat loss is much more difficult to estimate. Using the formula given in the International Critical Tables [6] for horizontal cylinders as being somewhat analogous, the convective loss in helium was calculated as about 80 j. Using these figures with the known heat capacities of the empty and filled containers, it is estimated that there would be a maximum error of about 4 j in the value for the enthalpy of the sample at 900° C. This is equivalent to about 0.06 percent on enthalpy, and a somewhat greater error on heat capacity.

Due to the approximate nature of the calculations of this error, some experiments were made to test if the heat losses calculated in this way were reasonable. Eight experiments were made at 300° C, dropping another container having about the same emissivity. In these experiments, the time of fall of the container was varied by factors of two and four greater than the normal time of fall (almost free fall). Assuming that the heat loss is directly proportional to the time of fall, it was estimated that the total heat lost in a normal fall at 300° C was about 6 j. This figure is considerably less than the value of about 16 j calculated in the manner described above (12 j by convection and 4 j by radiation). This would indicate that the heat loss is less than the calculations indicate and that at 900° C, the error due to this loss may be 0.02 to 0.03 percent. Since this error is small and is not known accurately, no attempt was made to apply a correction.

IV. Results of Enthalpy Measurements

A total of 129 measurements of enthalpy was made, 67 with the two empty containers and 62 with the two containers containing sodium. The average deviation from the mean was ±0.02 percent with a given sample, and the difference between the values of enthalpy for the two samples did not exceed 0.3 j/g or 0.03 percent, whichever is larger. The detailed results of individual runs are given in table 1. Measurements were often repeated at lower temperatures after experiments at higher temperatures without disclosing any evidence that significant permanent changes had occurred in the samples meanwhile.

TABLE 1. *Corrected enthalpy values of individual experiments*

Temperature, t[a]	Measured heat		$(H_t - H_{0°C})$		
	Blank experiments	Experiments with sample	Observed	Calculated	Observed—Calculated
° C	*Abs j*	*Abs j*	*Abs j g⁻¹*	*Abs j g⁻¹*	
30.60	244.1	441.2	37.08	37.10	−0.02
	242.6	441.0			
	242.7	441.0			
	243.6	442.0			
59.00	474.1	862.4	72.64	72.61	+.03
	474.4	862.1			
	474.6	862.6			
	474.3	---------			
77.00	622.7	1,135.4	95.86	95.87	−.01
	623.3	1,135.2			
	623.7	1,134.9			
94.00	764.5	1,398.1	118.52	118.52	.00
	765.9	1,399.0			
	765.3	1,399.0			
	--------	[d] 1,479.2			
	--------	[d] 1,479.8			
	--------	[d] 1,479.1			
100.00	815.3	2,096.1	239.90	239.90	.00
	815.1	2,096.3			
	815.2	2,095.5			
	814.1	2,095.2			
	814.8	2,097.5			
	815.3	[d] 2,260.9			
	813.7	[d] 2,260.6			
	814.3	[d] 2,260.9			
	815.2	---------			
	[b] 814.0	---------			
	[b] 814.8	---------			
	[b] 814.6	---------			
150.00	1,241.2	2,889.0	308.48	308.47	+.01
	1,241.2	2,889.1			
	[c] 1,242.2	2,888.3			
200.00	1,676.8	3,682.2	375.84	375.95	−.11
	1,676.7	3,686.1			
	1,677.0	3,684.3			
	--------	3,683.1			
300.00	2,570.7	5,284.6	508.41	508.03	+.38
	2,570.2	5,285.5			
	2,571.7	5,285.2			
	-------	[d] 5,639.6			
	-------	[d] 5,636.7			
	-------	[d] 5,635.7			
	-------	[d] 5,636.3			
400.00	3,498.7	6,904.1	636.87	637.09	−.22
	3,496.1	6,897.2			
	[b] 3,496.9	6,901.3			
	[b] 3,507.4	6,900.0			
	[b] 3,499.0	--------			
	[b] 3,499.0	-------			
500.00	4,449.1	8,529.3	764.02	764.05	−.03
	4,449.1	8,529.2			
	4,448.3	8,528.4			
600.00	5,422.3	10,175.7	889.97	889.82	+.15
	5,423.3	10,173.3			
	5,422.2	[d] 10,791.6			
	-------	[d] 10,788.3			
	-------	[d] 10,788.8			
699.5	6,421	11,840	1,014.5	1,014.7	−.2
	6,418	11,836			
	6,420	11,837			
	-------	11,836			
796.8	7,417	13,496	1,137.2	1,137.5	−.3
	7,420	13,492			
	7,417	13,491			
	[b] 7,423	-------			
	[b] 7,420	-------			
	[b] 7,422	-------			
	[b] 7,420	-------			
896.6	8,455	15,211	1,265.2	1,264.9	+.3
	8,458	15,211			
	8,454	15,210			
	[b] 8,458	[d] 16,083			
	[b] 8,453	[d] 16,080			
	[b] 8,453	-------			
	[b] 8,448	-------			
	[b] 8,449	-------			
	[b] 8,449	-------			
	[b] 8,452	-------			

See footnotes at end of table.

[a] International Temperature Scale of 1948 [5].

[b] On alternate container of same mass.

[c] Weighted less because of unsteady heat leak.

[d] On alternate container, containing 6.0297 g of sodium. The other container had the same mass but contained 5.3404 g of sodium.

No corrections for impurities were made, since these were believed to be much smaller than the accidental error. All weights were reduced to an in-vacuum basis. Small corrections were made to bring the results to a common basis at the listed temperatures. The values of enthalpy $(H_t - H_0)$ given in table 1 are at the vapor pressure (saturation pressure). Small corrections were made for the thin oxide coatings that the containers acquired in the furnace, using published heat capacities of Fe and Fe_3O_4 [7]. In addition, in order to evaluate the heat capacity of the liquid alone, it was necessary to make small corrections at the highest temperatures for the heat given up in condensing the sodium vapor. These corrections, based on published vapor pressure data and the volumes of the vapor, amounted to about 0.03 percent of the enthalpy at the highest temperature. The total corrections of all kinds did not amount to more than 0.1 percent of the enthalpy.

The experimental values found for the enthalpy of sodium (at saturation pressure) in absolute joules per gram, are represented by the following empirical equations. H_0 is the enthalpy of the solid at 0°C, and t represents degrees C.

$$H_t\text{ (solid)}-H_0\text{ (solid)}=1.19926t+(3.247)\,(10^{-4})t^2$$

$$+(3.510)(10^{-6})t^3 \qquad (0^\circ \text{ to } 97.80^\circ\text{ C})$$

$$H_t\text{ (liquid)}-H_0\text{ (solid)}=98.973+1.436744t$$

$$-2.90244)\;(10^{-4})t^2+(1.54097)\;(10^{-7})t^3$$

$$+24000e^{-\frac{13600}{t+273}}\;(97.80^\circ \text{ to } 900^\circ\text{ C})$$

The last term of the latter equation (liquid) accounts for the difference between H_t-H_0 and the net heat measured. As shown by Osborne [10], this difference is equal to PV/m, where P is the vapor pressure of the sodium, V is the volume of the container, and m is the mass of sodium. In the temperature range investigated, this term reaches a maximum value of 0.02 percent at 900° C and is entirely negligible for the solid. These equations give 113.2 abs j/g as the heat of fusion at the triple point, 97.80° C.

After dropping the last term in the equation for the enthalpy of the liquid, the two preceding equations then give the measured heat differences along the saturation curve. Therefore their direct differentiation gives the heat capacities (C_s) under saturation temperature and pressure, as follows:

$$C_s\;\text{(solid)}=1.19926+(6.494)\;(10^{-4})t$$

$$+(1.0531)\,(10^{-5})t^2 \qquad (0^\circ \text{ to } 97.80^\circ\text{ C})$$

$$C_s\;\text{(liquid)}=1.43674-(5.8049)\;(10^{-4})t$$

$$+(4.6229)\;(10^{-7})t^2 \qquad (97.80^\circ \text{ to } 900^\circ\text{ C})$$

From these equations directly result the following equations for the entropy (also at saturation pressure), absolute joules g^{-1} deg K^{-1}, in excess of that at 0° C. T represents degrees Kelvin (taking 0° C=273.16° K).

$$S_T\text{ (solid)}-S_{273.16^\circ K}\text{ (solid)}=4.16241\log_{10}T$$

$$-(5.1036)\,(10^{-3})\,T+(5.2656)\,(10^{-6})\,T^2-9.14016$$

$$(0^\circ \text{ to } 97.80^\circ\text{ C})$$

$$S_T\text{ (liquid)}-S_{273.16^\circ K}\text{ (solid)}=3.75276\log_{10}T$$

$$-(8.3303)\;(10^{-4})T+(2.3112)\;(10^{-7})T^2-8.67398$$

$$(97.80^\circ \text{ to } 900^\circ\text{ C})$$

Values of enthalpy, heat capacity, and entropy calculated from these equations for rounded temperatures are listed in table 2.

TABLE 2. *Enthalpy, specific heat, and entropy of sodium*

Temperature, t	$H_t-H_{0^\circ C}$	C_s	$S_T-S_{273.16^\circ K}$
°C	*abs j g⁻¹*	*abs j g⁻¹ deg⁻¹*	*abs j g⁻¹ deg⁻¹*
0	0	1.1991	0
25	30.25	1.2221	.10590
50	61.21	1.2555	.20569
75	93.26	1.3071	.30116
97.80 (solid)	123.68	1.3636	.38581
[Melting	113.2	------	*.30510*]
97.80 (liquid)	236.86	1.3845	.69090
100	239.90	1.3832	.69906
200	375.95	1.3393	1.0222
300	508.03	1.3042	1.2757
400	637.09	1.2786	1.4832
500	764.05	1.2619	1.6590
600	889.82	1.2548	1.8121
700	1,015.3	1.2569	1.9481
800	1,141.6	1.2682	2.0715
900	1,269.4	1.2887	2.1853

V. Determination of the Triple Point and the Temperature Change During Melting

In order to measure the triple point and the amount of impurities (liquid-soluble, solid-insoluble) in the sodium, a resistance thermometer (60 ohms of No. 40 enameled copper wire) was wound directly around the lower half of the sample container used in most of the enthalpy measurements. This container was raised into the furnace, and the copper resistance thermometer was then calibrated at 94° and 100° C against the platinum resistance thermometer located in the silver cylinder (K). Starting with this container and the furnace at equilibrium at 94° C, the container was heated adiabatically using the copper resistance thermometer as an electric heater and raising the temperature of the furnace at about the same rate. After an appropriate time interval the electric power was turned off, and the container was allowed to come to a constant temperature, which was observed by the copper resistance thermometer. This cycle was repeated about 20 times, using electric power of one-fourth watt over a total heating period of 90 min. It was therefore possible to observe the relation between the temperature of the sodium and the fraction that had melted.

The temperature and fraction of the sample melted were consistent with Raoult's law within the precision of the measurements, and indicated the triple point of the sample to be 97.792° C and that of pure sodium to be 97.80°. This triple-point lowering corresponds to a liquid-soluble, solid-insoluble impurity of 0.000016 mole/gram-atom of sodium. The freezing point of pure sodium at 1-atm pressure is calculated to be 97.81° C.

VI. Effect of Mechanical State of the Solid

E. Griffiths [9] claimed that he found reproducible changes in the heat capacity of crystalline sodium amounting to as much as 1.5 percent, depending on whether in its previous heat treatment, the sample had been "quenched" or "annealed". Similar tests were made by the authors on the two sodium samples reported here, and with conditions of quenching and annealing somewhat more extreme than employed by Griffiths. The furnace temperatures used were chosen to cover the temperature range where he found the greatest difference. The results are summarized in chronological order in table 3.

The first set of experiments (Set 1) was made after freezing slowly over an interval of 1 hr and then cooling at the rate of about 5 deg/hr. Preceding the experiments in Set 2 and on the same day, the molten sample was quenched by putting its container into a tube immersed in ice. The treatments before Sets 3 and 4 were respectively similar, except that the annealing carried out on the day preceding Set 3 involved freezing the sample over a period of 3 hr and then cooling the solid to room temperature at a rate varying from 3 to 5 deg/hr. Before observing Set 5, the sample was remelted and requenched by immersing its container directly into a dry ice-acetone bath (−78° C). It was then kept at this temperature overnight until just before the experiments.

TABLE 3. *Experiments to determine the reproducibility of the mechanical state of solid sodium*

Set No.	Temperature t	Mass of Na in sample	Prior heat treatment	Measured heat (Na and container)	
				Individual experiment	Mean of set
	°C	*g*		*abs j*	*abs j*
1	59.00	5.3404	Annealed	860.7 861.7 863.4 862.2	862.0
2	59.00	5.3404	Quenched	864.5 862.7 863.2	863.5
3	39.90	6.0297	Annealed	619.2 615.8 616.0 616.7 617.9	617.1
4	39.90	6.0297	Quenched	616.3 616.8 616.0	616.4
5	39.90	6.0297	Requenched rapidly by dry ice	614.4 616.2 615.2 616.5	615.6

The results tabulated in table 3 indicate that the quenching and annealing treatments did not change the heat capacity of the sodium by more than 0.2 percent and that these changes seem to be accidental and within the precision of the measurements.

VII. Reliability

An index to the reproducibility, or "precision", of the enthalpy measurements is afforded by the deviations from the mean, as shown by the results of the individual measurements shown in table 1. Another index is provided by the deviations (also listed in table 1) from the smoothed values given by the empirical equations adopted. All the results for liquid sodium lead to a probable error of the mean of from 0.01 to 0.03 percent on enthalpy (depending on the temperature), and as much as 0.3 percent on the derived heat capacity values, with a somewhat increased uncertainty below 200° and above 800° C because of the difficulty of determining the derivative of an empirical function accurately near its ends. For solid sodium, the relative uncertainties become considerably greater at the low temperatures, owing to the inability to determine heats by the ice calorimeter with a precision of better than 0.4 j.

In addition, all factors suspected of contributing appreciable systematic errors were analyzed to determine their likely contributions. Direct comparisons between the platinum resistance thermometer and the platinum-rhodium thermocouple up to 600° indicated differences in temperature of from 0.0 to 0.2 deg. Calculations indicated that errors due to the very small temperature gradients inside the silver cylinder in the furnace were entirely negligible. As far as uncertainties in measuring the temperatures on the International Temperature Scale are involved, the resulting probable error [2] in the enthalpy is thought to be only about 0.02 percent between 100° and 600°, and perhaps three times this much at 900°, where it was necessary to resort to measurement using a thermocouple. As a consequence, the probable error in the heat capacity due to uncertainty in temperature measurement may be considered to lie within 0.03 percent from 100° to 600°, but may reach 0.2 percent at 900° C.

In case the sample contained 0.01 percent by weight of oxygen as sodium oxide, as discussed earlier in this report, the error in enthalpy or heat capacity due to its gradual deposition from solution as the temperature fell might be as much as 0.05 percent. A similar error would be present if the liquid sodium dissolved appreciable amounts of the steel container; but recent measurements on the solubility of iron in liquid sodium by L. F. Epstein [8], of the Knolls Atomic Power Laboratory, indicate a solubility at 900° C of 22 parts per million, which would lead to negligible error in the present measurements. The analysis of the difference between the heat lost, during the drop into the calorimeter, by the sample container and by the empty container, showed that this effect, greatest at the highest temperatures, might lead to errors of 0.03 percent on enthalpy and 0.1 percent on heat capacity at 900°. Taking due consideration of the sources of error mentioned and other less significant ones, the authors believe that the probable error of the enthalpy values of sodium reported here may be considered to be between 0.1 and 0.2 percent (except below 100°, as mentioned above), whereas the probable error of the heat capacity was similarly estimated to be between 0.3 and 0.4 percent.

One experimental check on the over-all accuracy of the apparatus in measuring enthalpy was made by measuring the heat delivered to the ice calorimeter by a Monel capsule containing water and dropping from 250° C. By thus determining in several measurements the difference in heats for two amounts of water differing by about 6 g, a value of 1042.05 abs j/g for $\alpha]_0^{250^\circ}$ of water, defined elsewhere [10], was obtained. This figure differs by only 0.02 percent from the value of 1041.85 published in the latest report [11] on the thermal properties of water as accurately measured earlier in this laboratory with an adiabatic calorimeter.

The value found for the triple point is considered to have a probable error of 0.03 deg, dependent mostly on the uncertainty in the calibration of the copper resistance thermometer used for the measurements. A probable error of 0.3 percent is assigned to the heat of fusion. This figure is based on the estimated reliability of the enthalpy values in the neighborhood of the triple point. If all the impurity indicated by the measured melting curve were actually in liquid solution at 94°, then 0.25 percent of the sample was liquid at this temperature. In that case, the value of the enthalpy of the solid given in table 1 would be 0.2 j/g too high due to this effect, making the calculated heat of fusion 0.3 j/g too low.

VIII. Comparison with Results of Other Investigations

A number of other investigators [9, 12, 13, 14, 15, 16, 17] have made measurements of the heat capacity of solid and liquid sodium above 0° C, and most of these are shown for comparison in figure 3, where the full-line curves represent the values of the present investigation as given by the equations presented earlier in this paper. Each experimental point (NBS) given for the liquid in figure 3 was calculated from two adjacent observed enthalpies given in table 1. Rengade's [12] measurements, which made use of an ice calorimeter, extended from 15° to 100°, and although he stated that his sample was not very pure, his precision amounted to about 0.2 percent. Griffiths [9] employed a dynamic method and covered the range 0° to 140°, claiming a

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[2] "Probable error" as used in the remainder of this paper includes the authors' estimate of certain systematic errors. To each factor subject to error, there was assigned a figure such that it was believed that the actual error was as likely greater as smaller than this figure. These figures were then combined statistically to yield an over-all probable error in the given experimental quantity.

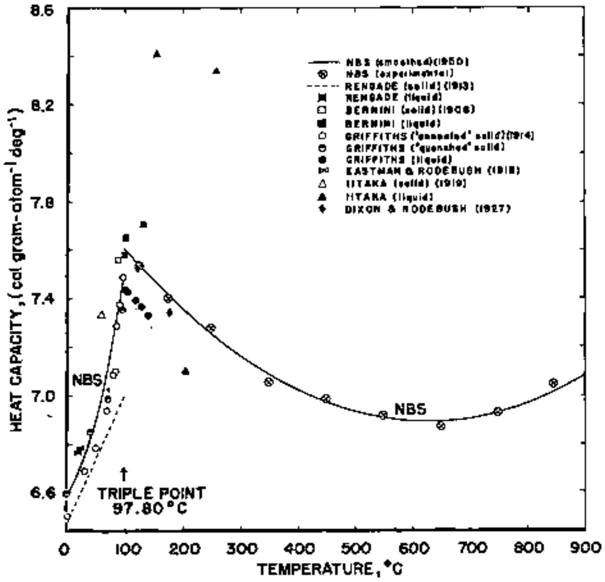

FIGURE 3. *Comparison of heat-capacity values.*

reproducibility of better than 0.1 percent, except for the variation of about 1.5 percent on the solid caused by varying the heat treatment, as mentioned above. Eastman and Rodebush's [13] measurements were mostly at low temperatures, but afford a comparison at 20° C. Iitaka [14] made determinations of the heat capacity of the liquid between 125° and 290°, the latter being the highest temperature attained prior to the present investigation. He dropped his samples from a furnace into his calorimeter and took due precaution to avoid certain systematic errors, but his precision was not better than several percent, and it will be noted from the graph that his values for heat capacity are considerably higher than those of the other investigators. Dixon and Rodebush [15] made measurements with a precision of about 1 percent, from 121° to 178°. Their method consisted in measuring the adiabatic temperature-pressure coefficient, and seems to have been subject to experimental difficulties due to the high thermal conductivity of the sodium.

TABLE 4. *Values for the melting point and heat of fusion of sodium*

Source	Melting point	Heat of fusion
	°C	*abs j g^{-1}*
This investigation	97.81±0.03	113.2
Ladenburg and Thiele [18]	97.8 ±0.1	----------
Edmondson and Egerton [19].	97.7	----------
Tammann [18]	97.8	----------
Griffiths [9]	97.61	115.35 (113.4, less accurate)
Bridgman [20]	97.63	125.5
Rengade [12]	97.90	----------
Bernini [11]	97.63	74.5
Iitaka [14]	----------	108.8
Joannis [16]	----------	132.6

The values reported for the melting point and heat of fusion of sodium are given in table 4. These melting point values in themselves are not, of course, a reliable criterion of the relative purity of the various samples used.

IX. Discussion of Results

The values of the heat capacity of sodium reported herein have practical importance, inasmuch as they cover the temperature range between 0° and 300° C with greater accuracy and precision than has been the case heretofore, and in addition extend the measurements to much higher temperatures, where experimental values for sodium have been entirely lacking until now. At the same time these values should be of considerable theoretical interest, since the extensive interest in the structure and properties of the liquid state in recent years has led to the theoretical calculation of the heat capacity of certain liquids, including sodium, whereas accurate experimental measurements on liquid metals have been relatively very meager.

The accuracy of the results given in this report is sufficient to show clearly the trends of the heat capacity curves of sodium with temperature, both below and above the triple point. The fall of the liquid curve to a minimum, a phenomenon in contrast to the steady rise with temperature for the great majority of liquids, is by no means unique in the case of metals, being paralleled by the heat capacity of mercury [21]. The entropy of fusion of sodium, 7.03 j deg^{-1} gram-atom^{-1}, is one of the lowest values for metals. According to current theories, the metal does not acquire complete randomness on melting, and the increased heat capacity of the liquid over what it displays at much higher temperatures is to be attributed to a further absorption of "communal" entropy above the melting point. Taking the values of the present investigation and extrapolating linearly to the melting point that part of the curve (fig. 3) above 700°, it was calculated that the excess heat capacity between the triple point and 600° is equivalent to an entropy increase of 1.3 j deg^{-1} $gram\text{-}atom^{-1}$, a figure of the right order of magnitude to be explained in this way.

It has been pointed out further that the increase of heat capacity of the solid alkali metals with increasing temperature is enhanced in the regions of temperature just below the respective melting points, and this has been attributed to an acquisition of a part of the randomness, most of which occurs in fusion. The equation which Rengade [12] gave for the heat capacity of solid sodium from 15° to the melting point, being linear with temperature, does not of course show this feature. The equation found for the solid in this investigation, however, does have the sign of curvature just referred to, and so in this respect is at variance with an unmodified Debye function above the characteristic temperature.

Aside from any theoretical explanation of its approximate values, the heat capacity of liquid sodium is, as is well known, one of the determinants of the curvature of the vapor-pressure curve. Ladenburg and Thiele [18], in a critical evaluation of numerous vapor-pressure data of sodium, were forced to assume an average heat capacity of the liquid. Although their calculations are based on an approximate partition function for the vapor which is not accurate at these temperatures, the effect of this on the vapor pressures is probably relatively small, and they were able to show that for the range 100° to 500° C an average heat capacity of liquid sodium of 1.326 j g^{-1}, deg^{-1}, based on the measurements of Dixon and Rodebush [15], have better agreement with the vapor-pressure data and theoretically calculated "chemical constant" than a value of 1.452, the latter being Iitaka's [14] mean value. The results of the present investigation lead to an average heat capacity of 1.310 in this temperature interval.

X. Summary

The enthalpy of sodium has been measured in the range 0° to 900° C and with an accuracy of 0.1 to 0.2 percent over most of the range. Values of heat capacity are derived from the enthalpy values with an accuracy of 0.3 to 0.4 percent over most of the range. The triple point of sodium was shown to be 97.80°±0.03° C, whereas the heat of fusion is 113.2±0.4 abs j/g.

This investigation was made possible by the splendid cooperation of the Knolls Atomic Power Laboratory, Schenectady, N. Y., in preparing the samples and developing techniques of handling and sealing the samples without changing the mass of the containers. For this assistance, the authors are particularly indebted to Clifford Mannal and William D. Davis, who planned and supervised the work; and to William A. Ruggles, who was responsible for filling, sealing, and testing the sample containers.

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