Thermal Properties of Fats and Oils

I. Apparatus and Techniques for Low Temperature Calorimetry[1]

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Introduction

THERE is at present a notable lack of accurate thermal data on pure triglycerides, fatty acids, and fatty acid derivatives, as well as on the triglyceride mixtures comprising the oils and fats of commerce.

In addition to their purely scientific interest, and their obvious utility in the design of processing equipment, thermal data on fatty substances are important in their relation to phase investigations of these materials. Calorimetry is a potentially useful tool for the investigation of transformations between the liquid and solid states, and between different polymorphic forms in the solid state, since all of these transformations are associated with definite heat effects. It should be remembered that the apparently solid materials commonly designated as fats are actually plastic mixtures of solids and liquids, at ordinary temperatures, and that many liquid oils also become partially solidified at only slightly reduced temperatures. The technology of fats and oils is in many respects closely related to the above-mentioned phase transformations.

This article will be confined to the description of apparatus and methods for calorimetry within the relatively low range of temperatures within which melting and polymorphic transformations of fatty materials take place, i.e. about 80° to 340° K., or —193° to 67° C.

The Method and Apparatus

A CALORIMETRIC technique highly suitable for the low temperature examination of fats consists of introducing successive small increments of heat into the weighed sample, and measuring the rise in temperature occasioned by each increment. The heat input must of course be accurately measured; this is accomplished by generating the heat electrically, by means of a suitable resistance element. In order to insure accuracy in the determinations, various precautions are taken to minimize heat transfer between the calorimeter and its surroundings, and corrections are introduced for the unavoidable transfer of small amounts of heat. Since the temperature intervals separately covered are small, this method has the advantage of yielding values for specific heat and derived properties which approach instantaneous values for the midpoint of each interval. In this respect it has an advantage over certain other methods which give only average values over extended temperature ranges.

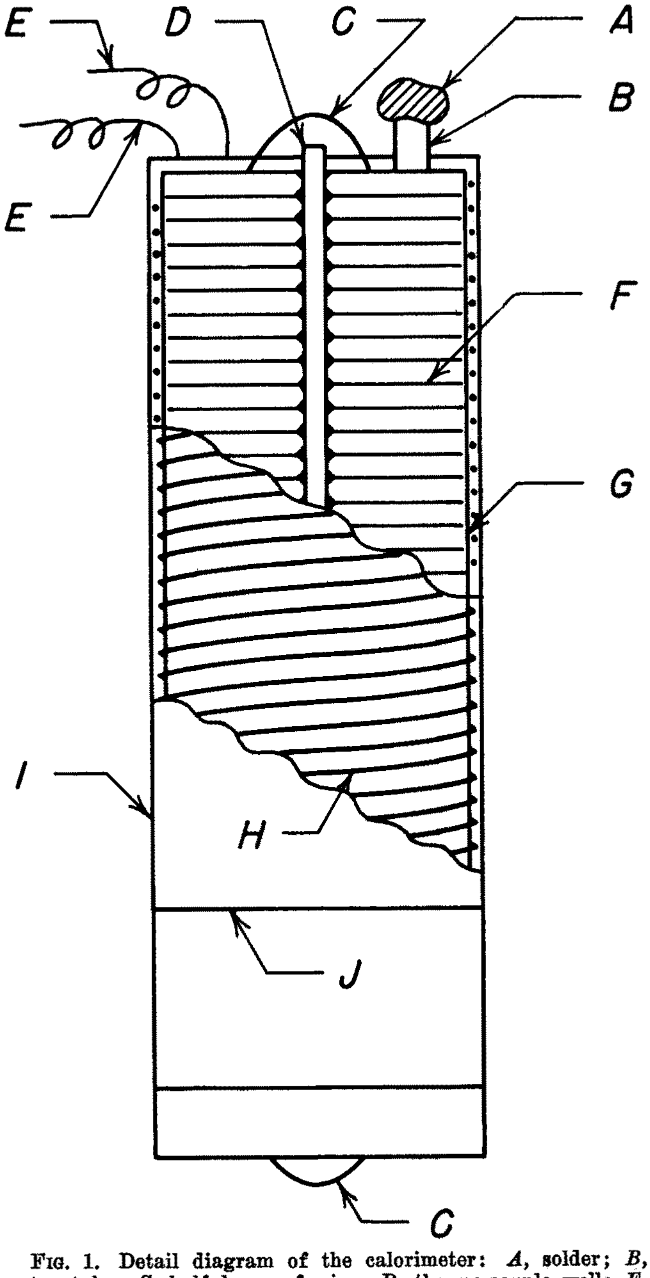

FIG. 1. Detail diagram of the calorimeter: *A*, solder; *B*, entry tube; *C*, half loops of wire; *D*, thermo-couple well; *E*, leads from heating coil; *F*, perforated discs; *G*, calorimeter wall; *H*, heating coil; *I*, platinum sheath; *J*, platinum ring.

A calorimeter designed for operation according to the above method was constructed for use in the present series of investigations. This calorimeter was of vacuum-enclosed aneroid type, as developed in principle by Eucken (2) and Nernst (6) and improved by Gibson, Latimer, and Parks (3) and Parks (7). The

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improved calorimeter of this type is considered to give results accurate to within about one percent. The calorimeter proper consisted of a gas-tight, closed copper cylinder 2.5 cm. in diameter and 9.0 cm. high, with soldered ends, which had a wall thickness of about 0.25 mm. Projecting slightly from one end of the cylinder was a 3 mm. copper filling tube. Projecting from the same end, and extending almost the length of the cylinder, was an axially-placed tube, closed at the lower end, in which was placed a single-element copper-constantan thermocouple. To this tube were soldered 42 copper discs of 0.002 inch thickness, each of which was perforated with 65 holes 1 mm. in diameter. The discs were of such diameter as to extend to, and make firm contact with the calorimeter walls. Since the discs were spaced but 2 mm. apart, it was impossible for any portion of the sample to be more than 1 mm. from a highly conducting copper surface. This arrangement insured rapid conduction of heat to and from the sample.

A heating-coil made from B&S No. 37, double-cotton-covered Advance wire, was around the outside of the cylinder and painted with a polystyrene-base coil dope. External leads of No. 40 copper wire were used to connect this heating-coil into the battery circuit. The entire calorimeter was wrapped tightly with a strip of onion skin paper and then with thin platinum foil, which was held in place with platinum wire rings. The platinum wrapping reduced heat losses through radiation, and provided a uniform, nonoxidizable radiating surface. The calorimeter had a capacity of 42.0 cc., and a total weight of 37.6 gms.

The calorimeter was filled with the aid of a small glass funnel, the stem of which was ground to seat in a large hypodermic needle extending into the filling tube. After each sample was introduced, the filling tube was closed with a drop of soft solder. In calculating the heat capacity of the calorimeter, allowances were made for the solder and for the air remaining in the head space of the calorimeter. The construction of the calorimeter is shown in detail in Figure 1.

Heat exchange between the calorimeter and its surroundings was held to a minimum by suspending the calorimeter by a cotton thread inside a cylindrical silvered copper jacket whose temperature could be closely regulated, and by maintaining a high vacuum in the space between the calorimeter and the jacket.

The general arrangement of the apparatus is evident from the photograph of Figure 2, which shows the various component parts, ready for assembly. In the photograph the calorimeter, *C*, is suspended from the cover for the jacket, *J*. In assembling the apparatus, the jacket, containing the suspended calorimeter, was placed in the external brass container, *B*, and the latter was soft-soldered vacuum-tight to its cover, B^1, and the attached Monel metal tube, *M*. The glass tube, *T*, containing charcoal, constitutes part of the evacuating system, as will be explained later.

The calorimeter jacket consisted of a heavy copper cylinder made from 2-inch copper pipe, silver-coated within and without, and provided with a fixed bottom and a tightly fitting, removable cover. The calorimeter was centrally suspended inside the jacket by means of cotton threads attached to wire loops soldered to the top and bottom of the calorimeter and passing through small holes in the top and bottom of the jacket. The temperature of the jacket was closely controlled by means of a 100-ohm heating-coil made of No. 33 Advance wire, and was measured with a single-element thermocouple imbedded in the side of the jacket.

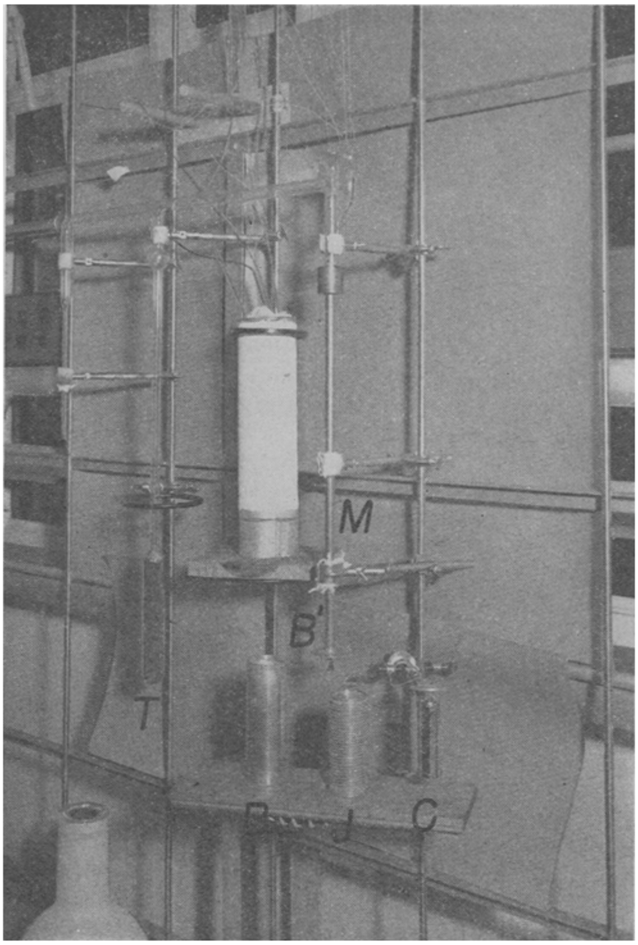

FIG. 2. The unassembled calorimetric apparatus.

THE vacuum-tight brass can containing the calorimeter jacket was 5 cm. in diameter and 15 cm. high, and was silver-coated within and without. Small wooden spacers were used to separate the jacket from the sides and bottom of the can. The Monel metal tube, 1 cm. in diameter and 51 cm. long, soldered into a hole in the cover of the brass container, served the threefold purpose of supporting the can and contents, connecting the can to the evacuating system, and providing an exit tube for the electrical connections. This tube was connected to the glass members of the evacuating system by a resin (9) seal. Resin was also used to seal the electrical connections into two small glass sidearms through which they were led outside the evacuated system.

It is important in an apparatus of this type to maintain a high vacuum around the calorimeter during the course of a run. To obtain a satisfactory vacuum, the system was first evacuated with a Megavac oil pump, and at the same time the charcoal in the side tube was activated by heating it to about 425° C. for 20 minutes with an external electric heater. While the charcoal was hot and the pump was running, the system was then sealed off at a constriction in the glass tube leading to the pump.

The high vacuum prevailing during operation of the calorimeter was finally reached after the charcoal bulb had been immersed in liquid nitrogen for about a day.

After the system had been evacuated, the calorimeter was cooled to any temperature desired for the measurements by means of appropriate constant-temperature cooling baths in Dewar flasks placed around the external brass container surrounding the jacket and calorimeter. The various baths consisted, in descending order of temperature, of solid and liquid tertiary butyl alcohol, ice and water, solid carbon dioxide, and liquid nitrogen. The maximum cooling rate obtainable depended upon the degree to which evacuation of the system had been carried when the cooling bath was applied. When desired, a very slow cooling rate could be obtained by heating the jacket during the cooling period.

All wires from the apparatus and batteries were brought to a control board located near a White double potentiometer, which was used for the energy and temperature measurements. This instrument, which had a range of 100,000 microvolts, was used in conjunction with a high-sensitivity galvanometer and the usual reflected scale and telescope arrangement. In making measurements, the galvanometer scale readings were recorded every minute at the signal of a buzzer operated by an electric clock.

The heat or electrical energy delivered to the jacket was supplied by one to four 6-volt batteries, and closely controlled with a rheostat. An 8-volt battery operating through a rheostat was used to supply heat to the calorimeter. In parallel with the heating circuit of the calorimeter was a resistance of 10,101 ohms made up of a 10,000-ohm resistance coil, a 100-ohm standard resistance, and connecting wires having one ohm resistance. The voltage drop across the 100-ohm standard resistance was measured with the potentiometer and from this drop the voltage applied to the calorimeter heating-coil was calculated. The voltage drop across a 0.1-ohm standard resistance in series with the calorimeter was measured with the potentiometer to determine the total current in the calorimeter circuit. The time of the energy input to the calorimeter was measured with an electric clock which was read to 0.01 second. In order to insure a steady energy input to the calorimeter, the battery used as an energy source was discharged through an auxiliary resistance of about 165 ohms for several hours prior to the start of each run.

The potentiometer, galvanometer, control board and other accessory parts of the apparatus are shown in the photograph of Figure 3.

Single-element copper-constantan thermocouples, constructed from B&S No. 40 copper wire and No. 30 constantan wire, were used to measure the temperatures of the jacket and calorimeter.

To convert microvolts to temperatures up to approximately 310° K., the Southard and Andrews (10) standard reference tables for copper-constantan thermocouples were used. For higher temperatures these tables were extended by extrapolation according to the data of the International Critical Tables (5). The thermocouples used were calibrated at the melting point of mercury and the transition point of sodium sulfate decahydrate to anhydrous sodium sulfate and checked at several other temperatures against a Bureau of Standards thermocouple.

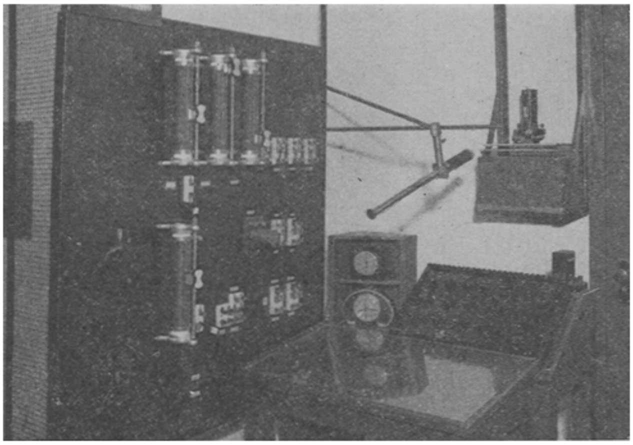

FIG. 3. The potentiometer, galvanometer, and accessory equipment.

Procedure for Heat Capacity Measurements

THE procedure for making heat capacity measurements is as follows: First the calorimeter is filled with the sample, as previously described, and the system is evacuated and sealed. After a suitable interval, the system is tested by determining the cooling rate of the calorimeter. If this rate is no greater than that known from previous experience to be normal, the system may be considered satisfactorily evacuated and free from leaks.

Actual determinations of heat capacity are carried out in a series of successive "runs," in each of which the temperature of the calorimeter and sample is raised through an interval of 3° to 6°. With the external brass container immersed in an appropriate constant-temperature bath somewhat below the lowest temperature of the run, the jacket is first heated to approximately the mean temperature of the interval. The heat input to the jacket is then adjusted to permit it to cool thereafter at a very small, and virtually constant rate. The calorimeter and sample are brought to the temperature at which it is desired to begin the run, and the initial heating rate (due principally to unavoidable radiation of heat from the jacket) is determined by temperature readings taken at 1-minute intervals for 10 to 20 minutes. Sufficient heat is then supplied to the calorimeter, over a period of about 8 to 16 minutes, to give the temperature rise desired. The heat input is accurately measured by making periodic readings of voltage and current, and accurately timing the heating interval. After the current is shut off, the cooling rate of the calorimeter is then recorded for 25 to 30 minutes. The last temperature reading is taken after the cooling rate has become steady; the true temperature at the end of the heating period is obtained by back extrapolation of the cooling curve.

Appropriate temperature corrections are made for all of the factors previously mentioned, including transfer of heat between calorimeter and jacket, heat loss through the leads to the calorimeter, and the heat capacities of the calorimeter, the solder used to seal it, and the air in the head space. The experimental data and calculations detailed in Table 1 serve to illustrate the method of computing specific heats. These particular data were obtained in the course of a run made with naphthalene, to check the over-all accuracy of the apparatus.

TABLE 1

Typical Experimental Data and Calculations of Specific Heat (From a test run on naphthalene)

(a)	Initial corrected potentiometer reading, microvolts	1033.75
(b)	Final corrected potentiometer reading, microvolts	859.90
(c)	Temperature corresponding to (a), °K.	245.091
(d)	Temperature corresponding to (b), °K.	249.950
(e)	Temperature rise of calorimeter, °K. (d-c)	4.859
(f)	Mean temperature of heat input, °K.($\frac{c+d}{2}$)	247.52
(g)	Voltage across terminals of heating coil	8.288
(h)	Current through heating coil, amperes	0.05085
(i)	Time of heat input, seconds	600.03
(j)	Total heat supplied to calorimeter and contents, calories (g) (h) (i) (1/4.1833)*	60.455....
(k)	Apparent heat capacity of calorimeter and contents at 247.52° K., calories per degree (j/e)	12.443
(l)	Heat lost in leads to calorimeter, calories per degree	.076
(m)	True heat capacity of calorimeter, etc., calories per degree (k-l)	12.367
(n)	Heat capacity of calorimeter, corrected for air and solder, at 247.52° K., calories per degree	2.680
(o)	Heat capacity of contents at 247.52° K., calories per degree	9.687
(p)	Weight of naphthalene (in vacuo), grams	38.896
(q)	Specific heat of naphthalene per degree at 247.52° K., calories per gram	0.2490

*The factor (1/4.1833) converts international joules to defined calories.

Procedure for Measuring Latent Heat

THE procedure for making a fusion run, to determine the latent heat of a material, is similar to that used for making specific heat runs, except that it requires considerably more time. The heat input is extended over a period of 1.5 to 4.5 hours, and the final cooling rate is determined over a period of about 45 minutes.

Since natural fats and oils are mixtures of many individual compounds of different melting points, the temperature range of a fusion run made on these materials must necessarily be quite extended. This circumstance makes it necessary to use a method for calculating heat losses which is somewhat different from that employed in specific heat runs. Actually, time-temperature curves for the calorimeter and jacket are plotted and the heat exchange between the two is estimated graphically. The electrical energy input is also determined graphically, by plotting the voltage and current used.

Obviously, latent heat measurements on a fat or oil must be preceded by determinations of the heat capacity of the material in both the solid and liquid phases, since the total heat effect over the melting range is a summation of the effects due to latent heat and the heat required for raising the temperature of the material in varying proportions of the two phases. A fusion run should overlap by about 10° the temperature ranges covered in specific heat runs made respectively on the completely solid and the completely liquid material. The latent heat necessarily represents an average value for the glycerides in the fat.

Since the specific heats of the solid and liquid phases are somewhat different, some slight uncertainty is introduced into the latent heat calculations by the lack of specific knowledge as to the relative proportions of the two phases at different temperatures. The basis for this uncertainty is indicated diagrammatically in Figure 4. The theoretical melting behaviour of a pure compound is represented in this figure by the partially solid, partially dotted line *OADFBC*. As heat is supplied to the solid compound, its temperature will rise as indicated along line *OE*, with the course of this line depending upon the specific heat of the solid. After the melting point is reached, at *D*, further input of heat will occasion no further rise in temperature until the substance is completely melted, as at *F*. Beyond *F*, the temperature will again rise along the line *FBC*, the course of this line being determined by the specific heat of the liquid. The latent heat of the substance is of course measured by the length of the line *DF*.

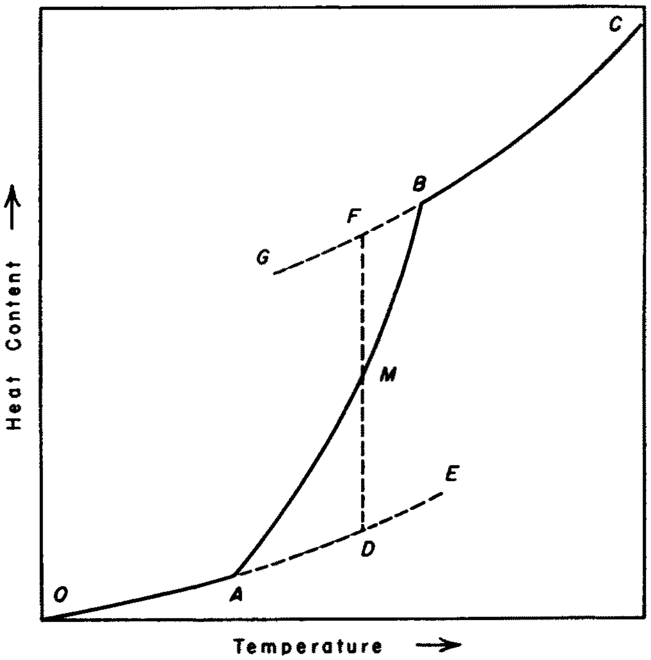

FIG. 4. Schematic representation of fusion in a pure compound and in a fat or similar mixture.

The melting behaviour of a fat or other mixture melting over a range of temperatures is represented by the solid line *OABC*. Obviously, the latent heat of the mixture is represented by some intercept between *OA* and *CB* projected, as for example, *DF*. However, owing to the difference in slopes of *OE* and *CG*, the length of this intercept will vary slightly according to the position of the point *M* through which it is drawn. The practice has been adopted of arbitrarily choosing the point *M* so that *MD* = *MF*. The point *M* is hereafter referred to as the point of "half-melting" or "half-fusion." It is easily located graphically. Extrapolation of lines *OA* and *CB*, to *D* and *F*, respectively, can be carried out with considerable exactness, since the specific heats of both solid and liquid are linear with temperature within the temperature ranges involved.

Calibration of the Apparatus and Test of Its Accuracy

THE heat capacity of the empty calorimeter was measured in a series of calibration runs under conditions corresponding to those obtaining in an actual run on a fatty material.

As a final test of the accuracy of the apparatus, a series of heat-capacity measurements was made on naphthalene, Bureau of Standards Sample No. 38b.

The data from these measurements are given in Table 2. They agree within the accuracy of the method (about one percent) with the data of Southard and Brickwedde (11), and those of Huffman, Parks, and Daniels (4) over a shorter temperature range.

TABLE 2

Experimentally Determined Values for the Heat Capacity of Naphthalene

Temp., °K.	Specific heat, cals. per gm.
182.1	.1797
196.6	.1950
215.2	.2141
230.9	.2327
247.5	.2490
263.4	.2665
278.4	.2848
286.2	.2985
295.6	.3074
300.6	.3156
306.9	.3239
313.7	.3337
320.1	.3463
329.4	.3622*
335.8	.3843*

* Value is high, due to premelting of sample.

Other Data Obtainable from the Calorimetric Examination of Fats

In the case of fats solidified in unstable crystal forms, calorimetric examination may yield information relative to the solid phases present, since each crystal form of a triglyceride has a characteristic heat of fusion, and polymorphic transformations are accompanied by definite heat effects. Thus, for example, Rao and Jatkar (8) found the latent heats of the gamma and beta forms of tristearin to be respectively 44.2 and 61.6 calories per gram.

Where polymorphism may occur in a fat, it may be desirable to provide a sample in which the solidified fat is known to be in the most stable crystal form. One method of obtaining the fat in such form is to chill the melted fat with extreme slowness. Another method makes use of the circumstance that a fat crystallizes from solvents only in the most stable and highest-melting form (1). If the heat capacity of the solvent and heat of solution of the fat in the solvent are known, calorimetric data on the oil-solvent mixture may be translated to data in terms of the fat alone.

The specific heat and latent heat data from the calorimetric examination of a plastic fat may provide the basis for a calculation of the proportions of solid and liquid glycerides in the fat at different temperatures. The accuracy of such calculations will, of course, depend upon the closeness with which the latent heats of the high- and low-melting glycerides correspond to the general average.

Particular mention should be made of the accuracy with which the beginning and end of the melting range of a fat can be determined. With the apparatus here described, it is possible to detect melting of as little as 0.01 to 0.02 percent of crystals, or the presence of a like amount of crystals in the nearly-melted fat.

Summary

1. A low-temperature calorimeter suitable for the examination of fatty materials with moderate accuracy is described and its method of use outlined.

2. The applications of calorimetry in the examination of fats and fatty materials are discussed.

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Thermal Properties of Fats and Oils. II. Heat Capacity and Latent Heat of Cottonseed Oil[1]

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THE present communication constitutes a report of the calorimetric examination of samples of both unhydrogenated and hydrogenated cottonseed oils over their complete range of melting. The temperature ranges covered were, in the case of the unhydrogenated oil, 174.5° to 326.0° K., (—98.6° to 52.9° C.), and in the case of the hydrogenated oil, 193.4° to 342.2° K. (—79.7° to 69.1° C.). Values were obtained for the specific heat of the oils in both the liquid and solid states, and also for the heats of fusion, or latent heats of the oils. The heat content of a mixture of the unhydrogenated oil with petroleum naphtha was also determined over approximately the same temperature interval as that of the oil alone.

The previous heat capacity data of Marden and Dover (4), Wesson and Gaylord (7), and Gudheim (3) are applicable only to liquid cottonseed oil within somewhat restricted ranges of temperature, and were obtained by techniques inherently less accurate than those employed in the present investigation. No values have been reported previously for the specific heat of completely solid oils or for the latent heat of cottonseed oil or partially hydrogenated cottonseed oil, although Gudheim has estimated the latent heat of some highly hydrogenated products.

The apparatus used and the general procedure followed in making the measurements and calculat-

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[1] Presented before the American Oil Chemists' Society Meeting, New Orleans, Louisiana, May 10 to 12, 1944.

[2] This is one of four regional research laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.