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.

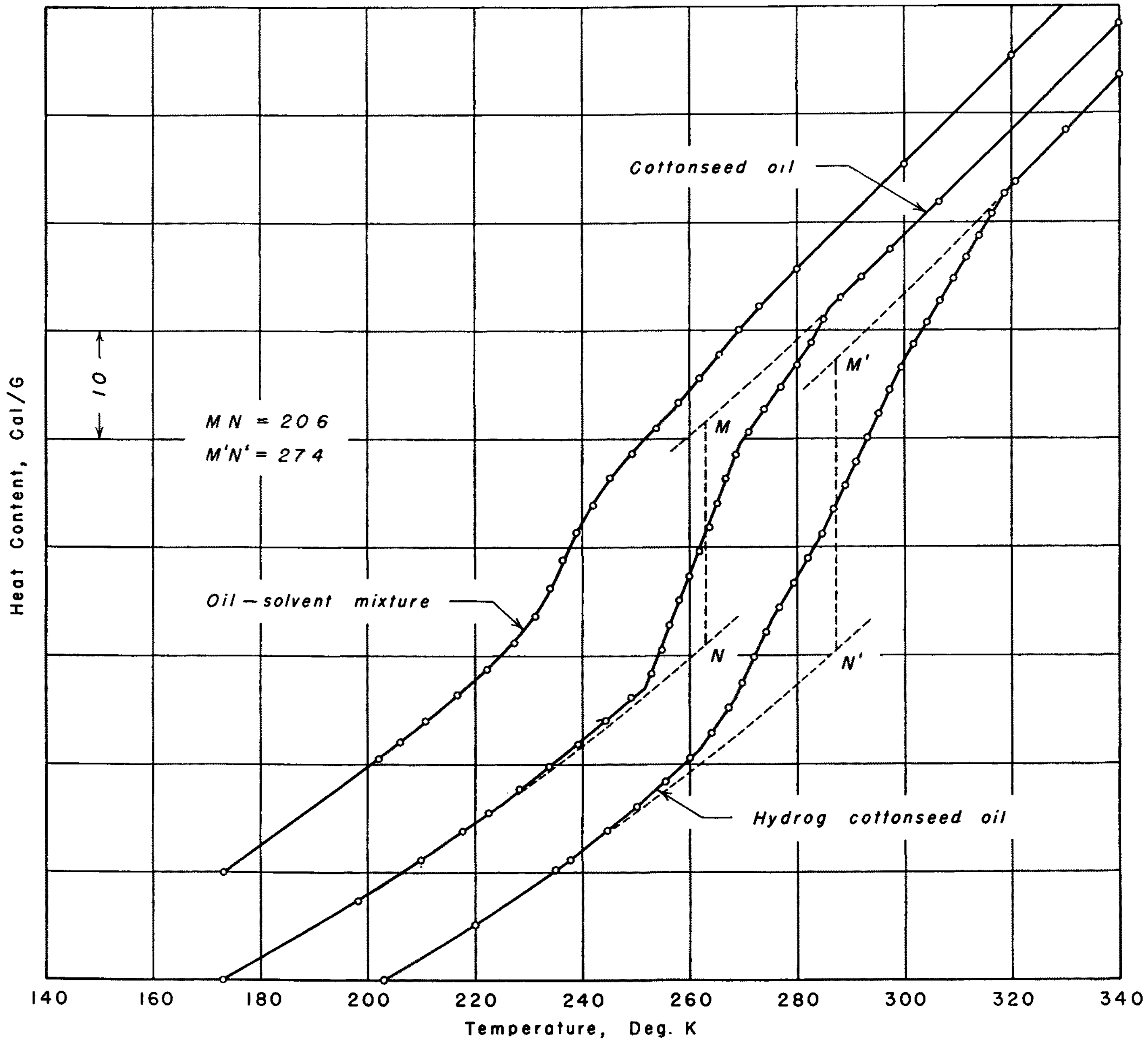

FIG. 1. Heat contents of cottonseed oil, hydrogenated cottonseed oil, and a mixture of cottonseed oil and petroleum naphtha, at different temperatures.

ing the results have been described in a previous publication (2).

### The Samples of Oil

THE cottonseed oil used in this investigation was commercially refined, bleached, and deodorized. Hydrogenation of the oil was carried out in the laboratory under selective conditions. The oils had the following characteristics, which were determined according to official methods of analysis of The American Oil Chemists' Society:

| | Unhydrogenated oil | Hydrogenated oil |
|---|---|---|
| Iodine value | 108.3 | 59.5 |
| Thiocyanogen value | 65.9 | 58.9 |
| Saponification value | 195.9 | ...... |
| Free fatty acids, percent as oleic | ...... | 0.08 |
| Composition of fatty acids, percent:[3] | | |
| Saturated | 27.1 | 30.2 |
| Oleic | 20.5 | 68.5 |
| Linoleic | 52.4 | 1.3 |

[3] The composition of the oil was calculated on the basis of thiocyanogen values of 89.3 for oleic acid and 96.7 for linoleic acid.

### Heat Contents of the Oil and an Oil-Petroleum Naphtha Mixture

The experimentally determined values for the change in heat content of the oils according to temperature, in terms of calories[4] per gram, are shown graphically in Figure 1. On the same graph are also shown corresponding values for the heat content of a mixture of 52.1 parts by weight of oil with 47.9 parts of commercial petroleum naphtha (Skellysolve B). Previous work in this Laboratory (1) has shown that this approximate ratio of solvent to oil is suitable for the solvent winterization of cottonseed oil.

Figure 1 may be used for estimating the heat or refrigeration input required for heating or cooling the oils or the oil-solvent mixture from one temperature to another. Within the range of temperatures in which melting occurs, each point on the curves represents the heat content at a state of equilibrium or

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[4] The factor 1/4.1833 was used in converting international joules to calories.

near-equilibrium between the liquid and solid phases, since this portion of the curves was defined by continuously heating the sample from the lowest temperature employed.

It is to be noted that the thermal data on the oil-solvent mixture include any heat effects attendant upon mixing of the oil and solvent. Investigations carried out in this Laboratory by other workers have shown that these effects are of considerable magnitude, amounting in some cases to several calories per gram of oil. Data on the heat of mixing of the oil and solvent in different proportions will be reported in a separate communication.

### Specific Heats of the Oil in the Liquid and Solid States

VALUES determined for the specific heat of the oils in the solid and liquid states at different temperatures are listed in Table 1. In this table are also corresponding values for the oil-solvent mixture.

From the calorimetric data the following equations have been derived for expressing the specific heat, $Cp$ (calories per gram), in terms of the temperature, $t$ (in degrees C.):

For the liquid oil, 15° to 60° C.,
$Cp = 0.462 + 0.00061t$ (1)
For the solid oil, —100° to —55° C.,
$Cp = 0.442 + 0.00172t$ (2)
For the liquid hydrogenated oil, 40° to 70° C.,
$Cp = 0.475 + 0.00055t$ (3)
For the solid hydrogenated oil, —80° to —35° C.,
$Cp = 0.406 + 0.00155t$ (4)
For the liquid oil-solvent mixture, 0° to 40° C.,
$Cp = 0.476 + 0.00065t$ (5)
For the solid oil-solvent mixture, —95° to —65° C.,
$Cp = 0.456 + 0.00108t$ (6)

The present data do not rigidly exclude the possibility of some slight melting occurring uniformly over the range of temperatures in which the oil is assumed to be completely solid. However, the data are so well correlated by typical heat capacity equations, and the method is so sensitive to heat of fusion effects, that this appears highly unlikely. Deviations of the observed specific heats from the values calculated by the means of the equations are shown in columns 3, 6, and 9 of Table 1.

The value for the specific heat of cottonseed oil reported by Marden and Dover (0.474 calories per gram at 20°-30° C.) is in very close agreement with the present data, but the values reported by Wesson and Gaylord and by Gudheim are somewhat higher than the values found in the present investigation.

### Heat of Fusion of the Oils

THE heat of fusion of the unhydrogenated oil was calculated to be 20.6 calories per gram. Melting of the solidified oil was first detected at a temperature of 198.3° K. (—74.8° C.), and crystals persisted up to a temperature of 306.5° K. (33.4° C.). The latter temperature is considerably higher than that at which all crystals disappear, according to visual observation of the oil. The amount of crystals which is detectable calorimetrically, about 0.02 percent, is apparently much less than can be seen in the oil. It appears possible that the last portions of oil melting may consist of crystalline aggregates of microscopic, or even sub-microscopic dimensions. In calculating the heat of fusion, the point of half-fusion of the oil was taken as 263.1° K. (—10° C.).

The heat of fusion of the hydrogenated oil was calculated to be 27.4 calories per gram. Melting began at 235.0° K. (—38.1° C.), and crystals persisted up to 318.5° K. (45.4° C.). The point of half-fusion was taken as 287.1° K. (14.0° C.).

Since the solidification of the oil was in each case carried out very slowly, over a period of about 5 days, it is believed that the solidified oil was entirely in the highest melting or most stable crystalline form.

The values of 20.6 and 27.4 calories per gram for the heats of fusion of the present oils are much below the respective values of 61.6 and 62.3 found by Rao and Jatkar (6) for tristearin and tripalmitin, and the values of 45 to 52 reported by Gudheim (3) for highly hydrogenated vegetable oils. However, in view of the fact that the *cis*-configuration in unsaturated acids introduces a considerable irregularity in the structure of mixed saturated-unsaturated triglycerides, it is not surprising that oils composed largely of such glycerides should have heats of fusion considerably lower than those of fats made up of completely saturated glycerides. Branched-chain hydrocarbons were observed by Parks and Huffman (5) to have much lower heats of fusion than the corresponding more compact straight-chain hydrocarbons. The difference in molecular structure between mixed tri-

TABLE 1

Heat Capacities of Cottonseed Oil, Hydrogenated Cottonseed Oil, and a Mixture of 52.1 Parts by Weight of Cottonseed Oil and 47.9 Parts Petroleum Naphtha. (Specific Heat, $Cp$, in terms of calories per gram of substance.)

| Cottonseed Oil | | | Hydrogenated Cottonseed Oil | | | Cottonseed Oil and Petroleum Naphtha | | |
|---|---|---|---|---|---|---|---|---|
| Temp., °K. | Cp | Deviation of obs. from calc. values | Temp., °K. | Cp | Deviation of obs. from calc. values | Temp., °K. | Cp | Deviation of obs. from calc. values |
| Solid Oil | | | Solid Oil | | | Solid Oil plus Solvent | | |
| 177.4 | 0.276 | —0.001 | 196.2 | 0.288 | +0.001 | 180.0 | 0.356 | +0.001 |
| 182.9 | 0.288 | +0.001 | 201.7 | 0.295 | 0 | 184.3 | 0.359 | —0.001 |
| 188.1 | 0.295 | —0.001 | 207.2 | 0.304 | 0 | 188.9 | 0.365 | 0 |
| 193.3 | 0.304 | —0.001 | 212.4 | 0.312 | 0 | 194.2 | 0.369 | —0.002 |
| 195.9 | 0.309 | 0 | 217.5 | 0.320 | 0 | 198.6 | 0.376 | 0 |
| 201.1 | 0.316 | —0.001 | 222.5 | 0.329 | 0 | 204.2 | 0.383 | +0.002 |
| 206.1 | 0.327 | 0 | 226.9 | 0.333 | —0.001 | | | |
| 210.9 | 0.335 | 0 | 231.6 | 0.342 | 0 | | | |
| 215.8 | 0.344 | +0.001 | | | | | | |
| Liquid Oil | | | Liquid Oil | | | Liquid Oil plus Solvent | | |
| | | | | | | 276.0 | 0.478 | 0 |
| | | | 316.5 | 0.499 | 0 | 276.7 | 0.476 | —0.002 |
| 292.4 | 0.475 | +0.001 | 321.6 | 0.501 | —0.001 | 281.3 | 0.481 | 0 |
| 296.7 | 0.476 | 0 | 325.9 | 0.506 | +0.001 | 285.9 | 0.485 | +0.001 |
| 301.1 | 0.480 | +0.001 | 330.5 | 0.507 | 0 | 290.4 | 0.490 | +0.003 |
| 304.6 | 0.481 | 0 | 335.4 | 0.509 | —0.001 | 294.2 | 0.488 | —0.002 |
| 308.7 | 0.484 | 0 | 340.0 | 0.513 | +0.001 | 298.7 | 0.492 | —0.001 |
| 313.2 | 0.485 | —0.001 | | | | 303.4 | 0.496 | 0 |
| 319.1 | 0.491 | +0.001 | | | | 307.9 | 0.501 | +0.002 |
| 323.8 | 0.495 | +0.002 | | | | | | |

glycerides and completely saturated triglycerides is roughly comparable to that existing between the branched-chain and straight-chain hydrocarbons.

### Summary

1. The heat contents of cottonseed oil, a hydrogenated cottonseed oil, and a mixture of cottonseed oil and petroleum naphtha have been measured over ranges of temperature within which there is transformation of the glycerides of the oils from a completely solid to a completely liquid form.

2. From the heat content data determinations have been made of the heats of fusion of the oils and of the specific heats of the oils in both solid and liquid states.

3. Equations have been derived for expressing the heat capacities of the oils and the oil-solvent mixture, with the oil in either the liquid or solid form.

4. Values found for the specific heat of the liquid oils are in general agreement with values found by previous investigators. The values calculated for the heat of fusion of the oils are much lower than values reported by other workers for highly saturated glycerides. However, a low value for mixed glycerides of saturated and unsaturated fatty acids is to be expected, from considerations of molecular structure.

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# Thermal Properties of Fats and Oils

## III. Calorimetric Estimation of Solid and Liquid Glycerides in Cottonseed Oil and Hydrogenated Cottonseed Oil[1]

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IT has previously been pointed out (1) that plastic fats, such as lard, shortenings, butter, and margarine are at ordinary temperatures multi-phase, liquid-solid systems, and that the consistency of such fats depends upon the relative proportions of solid crystals and liquid oil, as determined by the temperature of the material.

From the calorimetric data reported in a previous communication (4), it has been possible to estimate the proportions of solids and liquid over the entire melting range of both cottonseed oil (iodine value, 108.3) and a hydrogenated cottonseed oil (iodine value, 59.5). In addition, from micropenetration measurements made upon the hydrogenated oil and similar measurements made previously on other fats (1), estimates have been made of the probable proportions of solids and liquid in typical commercial products, and some information has been obtained relative to the effect of hydrogenation on the proportions of the two at different temperatures.

It should be pointed out that the amounts of solids and liquids can be accurately estimated only if the calorimetric examination is extended to a sufficiently low temperature to insure that the specific heat and heat of fusion data are based upon the initial existence of the fat in a completely solid state. In general, plastic fats require rather low temperatures for complete solidification; the hydrogenated cottonseed oil chosen for the present investigation was not wholly solidified except at temperatures below —38° C.

Straub and Malotaux (5) have published "consistency curves" for a number of plastic fats, in which melting (in terms of heat content) is represented as a function of temperature, and recently Jack and Brunner (3) have reported similar data on butterfat. It is apparent, however, that in neither case did these workers achieve complete solidification of their materials, hence ther data cannot be considered adequate for a quantitative analysis of the fats in terms of solids and liquids.

### Method of Making the Calculations

CALCULATIONS of the amount of solid glycerides melting in the oil in a specific temperature interval were made by distributing the increment in heat content during the interval to heat of fusion and sensible or specific heat, and then translating the heat of fusion to percent glycerides melting, upon the basis of the previously determined average heat of fusion of all the glycerides in the sample. The individually calculated percentages were accumulated at successive temperatures through the melting range, and the accumulated percentages were uniformly adjusted to make the final accumulated value equal to exactly 100 percent.

In estimating the sensible heat, it was necessary to make an arbitrary assumption regarding the changing proportions of solids and liquids over the interval. If it is assumed that all melting occurs at the temperature corresponding to the end of the interval, a maximum value will be obtained for the amount of solids melting, since the heat capacity of the liquid was found to be greater than that of the solid. If all melting is assumed to occur at the beginning of the interval, a minimum value will be obtained. Actually, there was in any case but a slight difference between the maximum and minimum values, and for

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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 the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.