# The Specific and Latent Heats of Fusion of Some Vegetable Fats and Oils

A. R. GUDHEIM

Lever Brothers Company

Today, many problems in oils and fats require a thorough understanding as to the changes taking place during heating and cooling, as well as their specific and latent heats of fusion. As the title indicates, this paper deals mainly with the latter aspects.

There are three main factors to be considered in this work, namely:

    a. Specific heat of the solid fat
    b. Latent heat of fusion
    c. Specific heat of the liquid oil.

The determination of latent heats of fusion of fats is much more complicated than this test on pure compounds, such as ice. At a uniform pressure, the latter group melts or changes from a complete solid to liquid at a constant temperature, whereas all commercial fats melt over a wide range. Thus, the latent heats of fusion of fats cannot be determined without knowing the specific heats of their liquid and solid phases, unless they happen to be the same, and this is not the case.

Because their liquid and solid phases have different specific heats, it is necessary to know or to closely approximate the equilibrium ratio of these two components at the temperature for which the latent heat of fusion is desired. An error as large as 5% in such a determination or approximation, nevertheless, would have only a slight influence on the latent heat values. It is also necessary to know the exact temperature at which complete melting occurs, that is, the temperature point where all the solid phase disappears under equilibrium conditions. This information, however, is not needed to determine the latent heats of pure compounds, and for this reason, their testing is much simpler.

A review of the literature for the past two or three decades reveals little information of importance other than the data published on this subject by the late David Wesson and Gaylord (1) about 25 years ago. This paper mentioned that a search through the oil and fat literature at the time had disclosed little information and that a study of the physical tables was equally barren of results.

Several specific heat results are given in the "International Critical Tables" (2), but they do not include any latent heat values. Rao and Jatkar (3) reported the following heats of crystallization for the gamma and beta forms of tristearine and the beta form of tripalmitin:

    Tristearine—
        Gamma Form: 44.2 Calories per Gram
        Beta Form: 61.6 Calories per Gram
    Tripalmitin—
        Beta Form: 62.3 Calories per Gram

A reference in a 1936 issue of "Food Manufacture" (4) states that the latent heat of solidification of fat varies from 18 to 54 B.T.U.'s per pound, depending on the amount of solids present. This is equivalent to 10-30 calories per gram, and the same article gives the specific heat as 0.50 B.T.U. per pound.

Jamieson mentions only two references in his book entitled "Vegetable Fats and Oils," (5) published in 1932. One of these is the aforementioned Wesson and Gaylord publication and the other, a short paper by Trevithick (6) published shortly thereafter, commenting on Wesson's procedure.

A study of Wesson's paper reveals two or three apparent procedure limitations and typographical errors. The latter will be commented on first.

The paragraph following the first table reads as follows: "In the column 'Total Heat Calories' is shown the number of calories required to raise the temperature of 1 gram of the fat or the oil 1°. By moving the decimal point two places to the left, we obtain the 'Apparent Specific Heat,' which is shown in the third column. This is the actual specific heat in the case of oils, but in the case of solid fats it includes the latent heat of fusion or crystallization, as the case may be."

It seems quite evident that the "Apparent Specific Heat" of 1 gram of fat or oil cannot be calculated by dividing by 100 the "Total Heat Calories" required to raise this amount 1°C., which is the same as moving the decimal point two places to the left. The method used would be correct for 100 grams and 1°C. or 1 gram and 100°C.

An analysis of the data, however, indicates that these results were calculated on the basis of 1 gram and 100°C. The sentence in question should probably have read: In the column "Total Heat Calories" is shown the number of calories required to raise the temperature of 1 gram of the fat or the oil 100°C.

The algebraic equation on solid fats is given as follows:

$$\text{``Specific + Latent Heat} = \frac{a \times c}{b \times d} = y\text{''}$$

This equation seems to be in error because the left hand side has two factors, both of which are in different units. For example, the specific heat depends upon the temperature change, whereas the latent heat is independent of this.

The equation following this reads:

$$\text{``Latent Heat} = x - y\text{''}$$

    Where x = Specific Heat
    and y = Specific Heat + Latent Heat

The x and y components appear to be reversed and the equation should probably have read:

$$\text{Latent Heat} = y - x$$

As just stated, Wesson's figures on "Total Heat Calories" appear to be based on the calculated amount of heat required to raise the temperature of 1 gram by 100°C. or probably from 0°-100°C., and the results on the "Latent Heat Calories" seem to have been arrived at by multiplying the "Apparent Specific Heat" of the kind of oil in question by 100 and then subtracting this product from the corresponding values for "Total Heat Calories." For example, the latent heat of the hydrogenized peanut oil seems to have been calculated as follows:

$$116.0^a - 100 \times 0.500^b = 66.0^c$$

    Where a = "Total Heat Calories" from first table
    b = "Apparent Specific Heat" of peanut oil
    c = "Latent Heat Calories"

There are a number of limitations involved in this procedure, at least as far as can be determined from the data. First, the assumption is made that the specific heat of that portion which is already solid is the same as that of the liquid component. This is not the case, as will be shown, and the tests were apparently not extensive enough to enable the specific heat of the solid phase to be determined.

As no latent heat is shown for the cottonseed oil sample, one would seem justified in assuming that its temperature just previous to dropping in the calorimeter was above 20°C. As is generally known, this stock begins to separate solid matter or to grain out at about this temperature, and if it had been below this temperature for any length of time, Wesson would certainly have recognized that a portion of its heat capacity was due to latent heat.

If one were to determine the amount of heat required to raise the temperature of cottonseed oil from 30° to 60°C., it cannot be assumed that the same amount would be needed to increase the temperature from, say, 0° to 30°C. The same reasoning also applies to the various hardened oils and stearines at temperatures below their melting points. It is perfectly correct to calculate the total heat actually needed to increase the temperature of a sample to a higher one, but this should then be reported as such and not modified to include a different temperature range.

Because of the limited value of the latent and specific heat data available in the literature and because of the need for such information to control Votator operations and to calculate, for example, the relative amount of heat work performed in each tube of such a machine, a series of determinations were carried out. Since then, the margarine-type Votator which cools the fat to a lower temperature has been introduced, and therefore, the experimental results may now be of more value to other investigators in this field than they would have been ten years ago when the work was undertaken, especially as no new data of importance have appeared in the literature.

### Theoretical Aspects

There is an inclination to believe that shortenings and stearines are composed principally of solid matter at room temperature. With the exception of moderately high titer stearines, this is not the case at all. In reality, most shortenings at household temperatures consist of two phases—a liquid component generally present in excess of 50% and a solid one finely dispersed or suspended throughout the liquid portion. Natural vegetable fats, for example, palm oil, also exist in the same condition, but their solid particles are usually larger and not as finely distributed.

The heat capacity of a fat at any one temperature with respect to another temperature above its melting point depends on the percentage of solid and/or liquid phases existing at the lower temperature. The possibility of the solid phase existing in more than one of its polymorphic forms with an accompanying variation in heat capacity is recognized, but this is not thought significant in fats of commerce at ordinary temperatures.

Fats derived from the same oil and having equal liquid-solid ratios at the same temperature will not necessarily have identical heat capacities with respect to a temperature above their melting points, say

100°C. As the specific heats of the solid and liquid phases are different, the total heat content will depend on the rate or change of the disappearance of the solid phase upon heating and this change, in turn, is a function of the character of the fat.

The ratio of solid to liquid phase below the melting point, however, is continually changing during either heating or cooling, and consequently, it follows that the total heat capacity is constantly varying. For this reason, such expressions as "Apparent Specific Heat" and "Heat Capacity" should be avoided when not specifying the temperature limitations. Even the term "Latent Heat of Fusion" should not be used without specifying the temperature unless it is understood that this refers to the heat capacity in the completely solid state.

### Experimental Procedure

A calorimeter, as pictured in Figure I, was used in making the determinations. Its heat or water equivalent was arrived at with lead and aluminum shot, and about the same volume of water as oil was used in the actual fat runs.
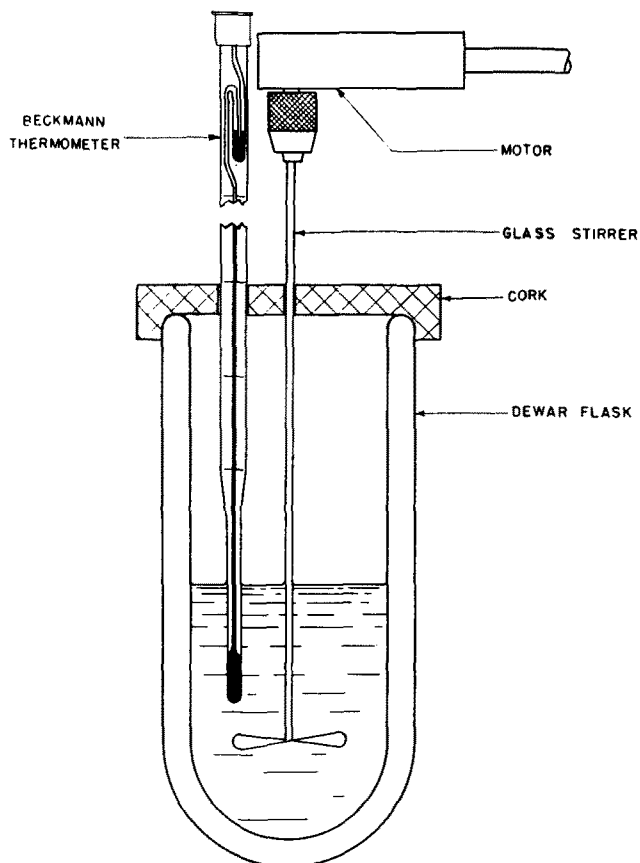


FIG. I. Apparatus used for the determination of specific and latent heats of fusion of vegetable fats and oils.

To determine the water equivalent value, the motor driven glass stirrer was operated at the same moderate speed as that employed in the fat experiments. In this way, it was felt that whatever mechanical energy the stirrer imparted to the liquid would be compensated for by the water equivalent of the calorimeter, since about the same time was required to make most of the tests.

The specific heats of the oils were determined first and the following procedure was used:

Approximately 1,200 grams of oil at a temperature slightly above the top graduation on the Beckmann thermometer were weighed into the Dewar flask. The cork cover plate, Beckmann thermometer, and glass stirrer were then placed in position. The stirrer was started and temperature readings taken every half minute for several minutes, or until the temperature change had become constant.

The stirrer was then stopped, the cork cover raised and a weighed amount of aluminum or lead shot which had been stored at a constant temperature quickly dropped into the calorimeter. The cover was replaced, moderate agitation resumed and temperature readings taken again every half minute for several minutes after the temperature drop had become uniform and equal to or less than that obtained before dropping the shot.

As the heat equivalent of the shot is known for the temperature range in question, the specific heat of the oil could be calculated readily, making due allowances for the water equivalent of the calorimeter, and thermometer and radiation corrections. Fortunately, repeated tests showed there was no temperature drop due to raising the cork cover.

Several somewhat complicated equations can be used for determining that portion of the temperature change due to radiation, but it was found that a rather simple graphical procedure gave results satisfactory for this work, and this method was used. Graph No. 1, which follows, shows a typical time-



GRAPH No. 1.    Temperature difference=5.49—2.85=
2.64°C.—Graphical
2.62°C.—Calculated.

True temperature drop

$$= T_1 - T_D = T_1 - (T_F + rt)$$

$$= T_1 - \left[ T_F + (t_r - t_s) \left( \frac{T_E - T_F}{t_r - t_e} \right) \right]$$

$$= 5.49 - \left[ 2.60 + 10 \left( \frac{2.72 - 2.60}{4.5} \right) \right]$$

$$= 5.49 - \left( 2.60 + \frac{1.2}{4.5} \right) = 5.49 - 2.87 = 2.62$$

temperature plot obtained with refined cottonseed oil, as well as a comparison between the graphical and formula methods for determining the radiation correction.

The same procedure was used in arriving at the apparent specific heats or heat capacities of the fat and stearine samples, except that these instead of the shot were dropped into the oil. The fat specimens were stored in light-weight aluminum cups and added to the calorimeter in this way, making allowance for the weight of aluminum. The term "fat" is used throughout this paper to denote any specimen exhibiting a solid phase at the testing temperatures.

None of the fat samples reported herein were accorded any special cooling treatment which might have resulted in their solid phase being in one of the more stable crystalline forms. They were, for the most part, completely melted on heating to 100°C., and were then placed directly in the constant temperature room where they were to be stored before dropping into the calorimeter.

## Results

Table No. 1 gives the specific heats of cottonseed, sesame and palm oils at various temperatures as well as the specific heats of cottonseed, sunflower and palm stearines in the completely solid phase. Note that the specific heat of the completely solid phase is approximately one-half that of the all-liquid phase.

TABLE 1

| Stock | Temperature Range °C. | Specific Heat* |
|---|---|---|
| Refined Cottonseed Oil | 45-50 | 0.524±0.010 |
| Refined Cottonseed Oil | 95-100 | 0.535±0.010 |
| Refined Sesame Oil | 95-100 | 0.544±0.010 |
| Refined and Bleached Palm Oil | 45-50 | 0.515±0.010 |
| Cottonseed Stearine, Iodine Value=0.5 | 0-21 | 0.276±0.010 |
| Sunflower Stearine, Iodine Value=0.5 | 0-21 | 0.285±0.010 |
| Palm Oil Stearine, Iodine Value=0.5 | 0-21 | 0.290±0.010 |

* Values on the low side of the average were obtained with lead shot and on the high side with aluminum shot.

Table No. 2 shows the apparent specific and latent heats of fusion of very low iodine value hardened cottonseed, sunflower and palm oils at different temperatures.
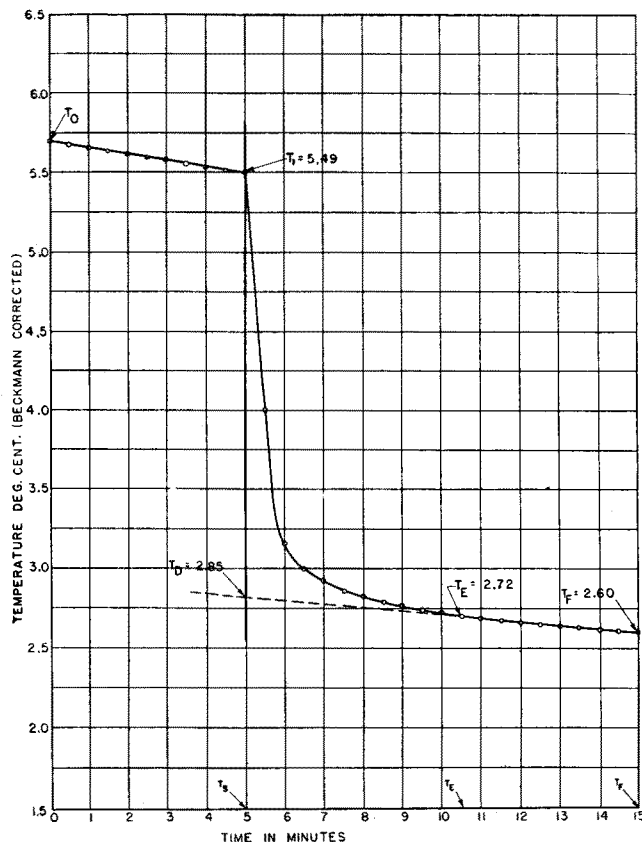
TABLE 2

Apparent Specific and Latent Heats of Fusion

| Stock | Temperature Range °C. | Apparent Specific Heat | Heat Change in Range Calories/Gram | Latent Heat of Fusion in Range Calories/Gram* |
|---|---|---|---|---|
| Cottonseed Stearine Iodine Value—0.5 Melting Range 50-65° | 21-48.0 | 0.557 | 15.0 | 7.55 |
| | 21-100.0 | 0.990 | 78.2 | 45.30 |
| | 0-100.0 | 0.840 | 84.0 | 45.30 |
| Sunflower Stearine Iodine Value—0.5 Melting Range 55-70° | 21-47.0 | 0.552 | 14.4 | 7.30 |
| | 21-100.0 | 1.065 | 84.0 | 51.95 |
| | 0-100.0 | 0.900 | 90.0 | 51.95 |
| Palm Oil Stearine Iodine Value—0.5 Melting Range 50-60° | 21-41.2 | 0.531 | 10.6 | 4.75 |
| | 21-46.1 | 0.697 | 17.6 | 10.00 |
| | 21-100.0 | 1.019 | 80.5 | 46.35 |
| | 0-100.0 | 0.866 | 86.6 | 46.35 |

*A minor portion of these values is thought due to a crystalline modification in the solid state. This is undoubtedly the reason why they exhibit some "latent heat" before beginning to melt.

Table No. 3 summarizes the apparent specific and latent heats of fusion obtained with a sample of cottonseed oil hardened to varying iodine values and the calculated percentage of solid phase present at 21.0°C. Graphs No. 2 and No. 3 depict the results shown in Table No. 3.

TABLE 3

Apparent Specific and Latent Heats of Fusion of Cottonseed Oil
Hardened to Varying Iodine Values and Calculated
Amounts of Solid Phase Present at 21.0°C.

| Iodine Value | Temperature Range °C. | Apparent Specific Heat | Heat Change in Range Calories/Gram | Latent Heat of Fusion in Range Calories/Gram | Calculated Per Cent Solid Phase Present at 21.0°C. |
|---|---|---|---|---|---|
| 69.2 | 21-100 | 0.565 | 44.6 | 2.7 | 9.8 |
| 56.5 | 21-100 | 0.637 | 50.3 | 9.9 | 36.0 |
| 41.0 | 21-100 | 0.729 | 57.6 | 17.3 | 62.9 |
| 24.8 | 21-100 | 0.840 | 66.4 | 30.4* | 100.0 |
| 11.9 | 21-100 | 0.950 | 75.1 | 40.7* | 100.0 |
| 0.5 | 21-100. | 0.990 | 78.2 | 45.3* | 100.0 |

*A minor portion of these values is thought due to a crystalline modification in the solid state.
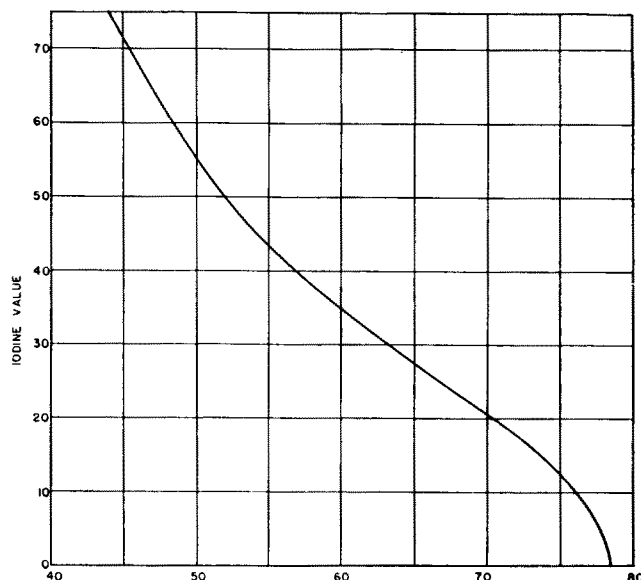


HEAT CONTENT (CALORIES PER GRAM)

GRAPH No. 2. Total heat (calories per gram) required to raise cottonseed oil hardened to varying iodine values from 21°C. to 100°C.
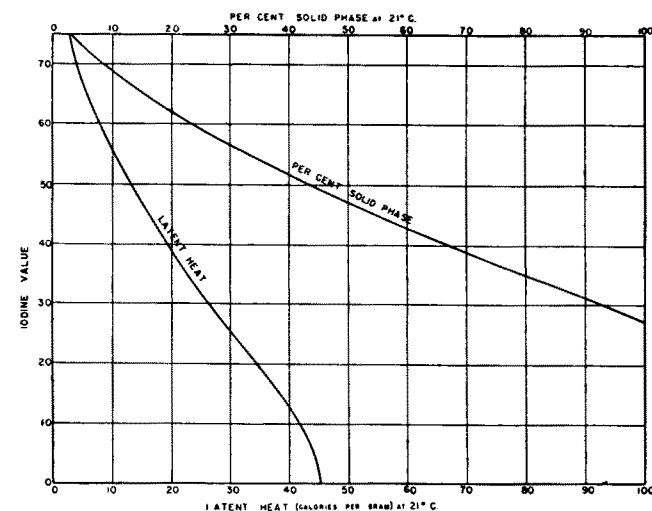


GRAPH No. 3. Latent heat at 21°C. and per cent solid phase at 21°C. of cottonseed oil hardened to varying iodine values.

## Discussion of Results

The determined specific heat values of the oils agree reasonably well with those reported by Wesson and Gaylord, that is, about 0.50. The latent heat results, however, vary a great deal from their data. Values from 45 to 52 calories per gram as compared to Wesson's results which are as high as 100 were obtained. It is not apparent from Wesson's data

whether the samples showing the higher values were completely hardened, but this would not appear to have been so, at least in the case of the cottonseed stearine. He included melting points, but it should be pointed out, though, that because of the different possible polymorphic forms, this determination is not necessarily an index of the degree of hardening. Furthermore, it is not an indication of the state of the stearine actually placed in the calorimeter. For example, melting point determinations may be made on one crystalline form, whereas specimens added to the calorimeter may exist in a different condition.

The factor which probably accounts for Wesson's high latent heat values is that his results were obtained over a range of, say, 25° to 50°C. and were then multiplied by four in order to report the results on a 0° to 100°C. basis. As has been pointed out, apparent specific heat and latent heat values are meaningless unless accompanied by temperature limits.

The determined latent heats of the cottonseed oils hardened to varying iodine values agree reasonably well with the values reported in the previously mentioned "Food Manufacture" reference.

As may have been noted, the average specific heat of the cottonseed stearine in the range 21° to 48°C. is approximately double that in the range 0° to 21°C., although it is known that the sample is still completely solid at the higher temperature. There is a good possibility that the stearine specimens existed in the gamma state before being dropped into the calorimeter due to the manner in which they were cooled. This increase in average specific heat may be the result of a partial change to the alpha and/or beta forms.

Also, it may have been observed that the average specific heat of the palm oil stearine varied considerably between the ranges 21.0° to 41.2°C. and 21.0° to 46.1°C., even though there is only a moderate temperature difference, and it is known that actual melting had not started in either range. This variation can be explained on the basis that a greater polymorphic change had taken place at the elevated temperature range. This theory can also account for the higher apparent specific heat values in either range as compared to that obtained at 0° to 21.0°C.

The latent heat of fusion results of the stearines in the range 21° to 48°C. and so on are all lower than the Rao and Jatkar value of 17.4 calories per gram for the crystallization heat value of tristearine from the gamma to the beta form as they should be if there is only a partial change to the latter state. No data seem to have been determined for the change from gamma to alpha, but this value is thought smaller than the gamma to beta result of 17.4.

If it is assumed that the crystalline modification of the substantially zero iodine value stearines is all from the gamma to the beta form, the following percentage transformations are obtained, using a value of 16.0 for complete change:

| Stearine | Range | % Change |
|---|---|---|
| Cottonseed | 21-48.0 | 47 |
| Sunflower | 21-47.0 | 46 |
| Palm | 21-41.2 | 29 |
| Palm | 21-46.1 | 62 |

Although it was indicated that the latent heat of fusion values for the different stearines in the ranges

21°-100°C. and 0°-100°C. probably included a small amount of energy due to a modification in the solid state, this is not necessarily so. For example, their temperatures were increased so rapidly to 100°C. (only two or three minutes), they may not have been converted to the alpha or beta form. Going on this assumption and also that the stearines were originally in the gamma form, the latent heat of fusion of cottonseed stearines agrees remarkably well with the 44.2 calories per gram value reported by Rao and Jatkar for the crystallization heat of tristearine in the gamma form.

Attention should be called to the agreement between the latent heat of fusion values for the different stearines in the range 21°-100°C. and 0°-100°C. This agreement is of especial interest when it is considered that detailed calculations were necessary to arrive at these results. It is also of interest to observe that the specific heats of the liquid oils and the completely solid stearines, as well as the latent heat of fusion, are a little more than one-half that of the corresponding states of water.

## Summary

The specific heats of several vegetable oils have been determined by a more exact procedure than those which seem to have been used heretofore. Values slightly higher than the literature figures were obtained, that is, an average value of 0.53 was determined as compared to reported results of 0.50. The specific heat of cottonseed oil with respect to temperature increases slightly with elevating tempera-

tures. The specific heats at different temperatures were not determined on the other oils, but likewise, these probably show no significant variation in specific heat with respect to temperature in the range 21° to 100°C.

The specific heats of completely solid vegetable fats are believed to be reported for the first time. These values are about the same for such different stocks as completely hardened palm and sunflower oils, and their values are approximately one-half that of the liquid, that is, 0.28 as compared to 0.53.

The latent heats of fusion of a number of fats have also been determined by what is thought to be a satisfactory procedure. Theoretical aspects and empirical results are given to show that the latent heat of fusion varies with the temperature when two phases are present, and that for this reason, any references to the latent heat of fusion should be accompanied by temperature limitations. This is not so important, however, when the specimen is completely solid at the temperature in question.

The data and graphs presented show the general variation in latent heat of hardened cottonseed oil at one temperature with respect to iodine value.

REFERENCES

1. Wesson, D., and Gaylord, H. P., Cotton Oil Press 2, No. 6, 40 (1918).
2. International Critical Tables, 2, 210 (1927), McGraw-Hill Book Company, New York.
3. Rao, M. M. R., and Jatkar, S. K. K., Jour. Indian Chem. Soc., 12, 5?? (1935).
4. Food Manufacture, 11, 452 (1936).
5. Jamieson, G. S., Vegetable Fats and Oils, p. 194 (1942), Chemical Catalog Company, New York.
6. Trevithick, H. P., Cotton Oil Press 3, No. 1, 40 (1919).

# Purification of Oleic Acid, Methyl Oleate, and Oleyl Alcohol for Use As Chemical Intermediates[1]

DANIEL SWERN, H. B. KNIGHT, and T. W. FINDLEY

Eastern Regional Research Laboratory
Philadelphia, Pennsylvania
Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration
United States Department of Agriculture

## Introduction

During research on the chemical modification of animal fats and oils, it was desirable to have readily available large quantities of oleic acid, methyl oleate, and oleyl alcohol of a relatively high degree of purity (90% or higher). None of the commercial samples examined contained more than 75% of the oleic constituent. As a rule, the oleic content was between 60 and 70%. It was impossible to purchase pure materials, and in the case of oleic acid high-priced preparations labelled to indicate a high degree of purity invariably contained high percentages of linoleic and saturated acids. For many commercial uses of these materials a high degree of purity was not essential, but it was felt that if purified products were available commercially new uses would develop.

The impurities present usually made reaction products more difficult to purify and necessitated handling

considerably more material for a smaller return of the desired product. Also, in many reactions the impurities were so altered that it was not possible to isolate any useful products from this portion of the starting material except with great difficulty. This was particularly true of the linoleic constituent, which in many reactions behaves essentially the same as the oleic constituent. As a result larger quantities of reagents were required to react with the impure starting materials in order to insure complete utilization of the oleic constituent, thereby increasing the cost of any reaction.

Laboratory procedures for the preparation of highly purified (96-100%) oleic acid (1) (6), methyl oleate (9), and oleyl alcohol (2) (4) are fairly well known, but these procedures are lengthy and tedious and often result in low yields. Low-temperature crystallization methods have been employed to prepare pure oleic acid and methyl oleate, but as far as we can ascertain, purified oleyl alcohol, other than its possible