"BOIL-OFF CALORIMETRY"
FOR DETERMINING FOOD ENTHALPY

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
CHARLES WELLINGTON GROESBECK
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ABSTRACT

"BOIL-OFF CALORIMETRY"
FOR DETERMINING FOOD ENTHALPY

By

Charles W. Groesbeck

This study describes a calorimetric method designed for the specific purpose of providing enthalpy measurements of food substances. The procedure utilizes the heat evolved in lowering the temperature of an immersed food to vaporize liquid nitrogen which is in equilibrium with its own vapor at its boiling point. The energy removed from the food is directly proportional to the amount of liquid nitrogen evaporated. The enthalpy change in going from a reference temperature to the temperature of liquid nitrogen $-320^{o}F$ ($-195.8^{o}C$) is calculated from the amount of liquid evaporated and its heat of vaporization. The term boil-off calorimetry thus refers to the measurement of the mentioned liquid nitrogen vaporization (or boil-off) as a means of determining enthalpy changes.

The purpose of this study is to establish feasibility of this calorimetric method for determinining food enthalpies. The author believes this method can be used as a useful tool in the food industry, as several advantages over previous calorimetric methods are possible:

(a) liquid nitrogen vaporization calorimetry is based on removal of heat from the food system as is the freezing

process. Many calorimetric studies measure the enthalpy during a very slow thawing rate;

(b) duration of the test is twenty minutes which is considerably less than most conventional calorimetry;

(c) no complicated electrical or mechanical devices are necessary for temperature control or measurement;

(d) very few manipulations or adjustments are required between experiments, allowing for consecutive runs to be made quickly;

(e) the apparatus is made up of readily available and relatively inexpensive components compared to commercially available calorimeters;

(f) measurements and calculations are few and simple;

(g) sample size is limited only by the dewar opening and overall dewar size. This permits measurements of whole intact food substances eliminating concern for homogeneity in sampling from dried or ground preparations.

Accuracy and limitations of the liquid nitrogen vaporization calorimetric method is shown and compared with water of known thermal behavior. The accuracy of the method was also indicated by comparing the experimental results obtained for potatoes with the model formula of Riedel (1951) whose results are regarded as the most reliable of those available in the literature.

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by

Charles Wellington Groesbeck

A THESIS

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in partial fulfillment of the requirements
for the degree of

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and Human Nutrition

1972

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Professor Alvin

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INTRODUCTION

Understanding the thermal properties of foods is necessary for accurately predicting heating and cooling requirements and for designing heat transfer equipment. Reliable information concerning thermal properties for food substances is not always available or utilized due to lack of uniformity in reported values, disagreement between theoretical calculations and actual thermal requirements, and inadequate tabulations.

Values for specific and latent heats of frozen foods can be found in the literature but their usage can lead to significant errors since water in a food does not all freeze at the food's initial freezing point. In the freezing range of a food both specific and latent heat is involved over a fairly wide temperature range. In the freezing range, there is no way to separate and measure the energy change in latent or sensible heats. When the sensible and latent heat values are mathematically derived, the values are used to determine the change in enthalpy or total heat transfer requirement. Change in enthalpy or change in heat content refers to the total amount of heat to be added or removed from a food substance. The thermal property enthalpy, as a function of temperature, is becoming a useful measurement from which to predict heat transfer requirements and equipment design

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A method of measuring the thermal property enthalpy of foods was investigated. A liquid nitrogen vaporization calorimeter was used to measure the amount of liquid nitrogen vaporized by a food sample. The enthalpy measurement was that amount of energy removed from the food substance from a known temperature to the temperature of liquid nitrogen, -320 F (-195.803 C), bringing it to equilibrium with the calorimeter. The quantity of heat removed from the sample is proportional to the amount of liquid nitrogen vaporized.

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GENERAL CLASSIFICATION OF CALORIMETERS

Calorimetry can be defined as the process of measuring quantities of heat energy absorbed or evolved by a substance. The device for measuring this heat energy is a calorimeter, defined by Wilhoit (1967) as an instrument used to measure the change in internal energy or enthalpy which occurs when a system changes from an initial state to a final state.

The different types of calorimeters that have been used are numerous. Because of this, a complete review of calorimetry would be lengthly and somewhat irrelevant to this discussion. The general classification of calorimeters will be outlined with emphasis on those parts of particular concern to this study.

A calorimeter is designed to reduce as much as possible thermal leakage or heat transfer that is not related to changes in heat absorbed or evolved by the substance being measured. Temperature and quantity of heat transferred by the calorimeter chamber and/or its contents to the surroundings are the principal calorimetric measurements. All other sources of heat transfer must be minimized and compensated for to ensure a reliable measurement. Heat energy transferred by conduction, convection, and radiation to or from the calorimeter must be limited whenever possible. An example of minimized heat transfer can best be explained by describing

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describing a vacuum dewar. Heat conduction through the dewar can be reduced by placing insulating materials such as low heat conducting powders between the double walls of the vessel. A vacuum between the vessel walls minimizes convection heat transfer. The inner surfaces of the double walled vacuum vessel are polished or coated with a high reflecting metal such as silver to avoid heat exchange due to radiation. Calorimeter design requirements are also influenced by sample type and the measurement desired.

The numerous calorimeter designs can be grouped, according to Wilhoit (1967), into three categories: isothermal, adiabatic, and conduction. The groupings are made in respect to the interaction between the calorimeter and its immediate surroundings and/or protecting shield. An isothermal calorimeter is kept at a constant temperature during the test measurement usually by a substance undergoing an isothermal phase change at a constant temperature. Minimizing conduction, convection, and radiation loss from the calorimeter by adjusting the temperature of the surroundings to equal the calorimeter temperature is accomplished by the adiabatic method. Usually a protective shield is electrically regulated. The shield is maintained as near as possible to the temperature of the calorimeter vessel, reducing thermal leakage to or from the calorimeter proper. This technique is particularly favored for experiments with long duration periods but has less advantage when used for shorter periods covering a wide temperature range. Heat energies absorbed or evolved in a conduction calorimeter are

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transferred by conduction through the calorimeter vessel to the surroundings.

Brief mention of a drop calorimeter, so named for its method of sample delivery, is pertinent to the apparatus used in this study. Drop calorimeters are designed to measure enthalpy of substances in which the energy of the sample is changed rapidly over a large temperature range. The substance's temperature is measured and quickly dropped into the calorimeter which may contain a liquid heat exchange medium at equilibrium. Enthalpy can be determined by knowing the initial and final temperature of the sample and calorimeter, the sample weight, and the latent heat of transition when a phase change occurs in the heat exchange medium.

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REVIEW OF CALORIMETRIC METHODS

As there are several types of calorimeters; there are several methods of calorimetry each with distinguishing principles. A brief review of general calorimetry methods will be made here. There are basically two major types of calorimetry; thermometric (nonisothermal) and latent heat of transition (isothermal) (Allen _et al_. 1948 and Tomezako _et al_., 1964). In thermometric calorimetry, the temperature varies (during the determination) with the quantity of heat being measured, as a change in temperature measured by a thermometer. Latent heat calorimetry determines heat quantities by the amount of calorimetric material that undergoes an isothermal phase change produced by the heat quantity.

A. Thermometric Calorimetry

Worthing _et al_. (1948) and Allen _et al_. (1948) each provided excellent historical and literary reviews of the methods of thermometric calorimetry in their texts. A summary of information from their review is presented in Table I.

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Principle:

Method:

Measurement:

Example:

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Principle:

Method:

TABLE I

Methods of Thermometric Calorimetry[a,b]

Method of Mixture

Principle:	Exchange of thermal energy without having a change of phase.
Method:	Two substances are placed in thermal contact; the substances are of known mass and temperature.
Measurement:	$m_1c_p(T_1 - T_3) = m_2c_{p'}(T_3 - T_2)$ (1) Two substances of known mass: m_1, m_2 One substance has a known specific heat of $c_{p'}$ Known initial temperatures: T_1, T_2 Final common temperature: T_3
Example:	Combustion bomb calorimeter

Method Involving Differential Rates of Cooling and Heating

Principle:	Differential rates of cooling or heating due to thermal leakage to the surroundings.
Method:	A substance of mass (m) is heated to a temperature (T) in a container with thermal capacity (C). Time required for the heated substance and container to cool is $\Delta_1 t$; through a small temperature range (ΔT).

Measure

Example

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TABLE I (cont)

Time required for the container alone to cool through the same temperature range (ΔT) is $\Delta_2 t$; within the same surrounding conditions.

Measurement: $$(mc_p + C) \frac{\Delta T}{\Delta_1 t} = C \frac{\Delta T}{\Delta_2 t} \qquad (2)$$

$$\therefore c_p = \frac{C}{m}\left(\frac{\Delta_1 t}{\Delta_2 t} - 1\right) \qquad (3)$$

An assumption is made that the rate of cooling is the same in both experiments, as heat transferred to the cooler surroundings in both experiments was under identical conditions.

Example: Conduction Calorimeter: The method of heating is conducted in the same way described with heat being absorbed by the cooler calorimeter and its contents.

Method Involving the Supply of Heat Electrically

(A) Solids and liquids

Principle: Electrical energy added is accurately measured and controlled to induce a temperature change in a substance.

Method: An electric heating coil is used to heat the substance on which specific heat (c_p) is desired; the coil can also serve as a resistance thermometer.

Measurement: Volts (V) and resistance (R) are measured by a potentiometer and the current (I)

TABLE I (cont)

determined by Ohm's law,

$$(R)\ \text{ohm} = \frac{(V)\ \text{volt}}{(I)\ \text{amp}}. \qquad (4)$$

Energy added to the sample is:

$$IVt = mc_p\Delta T + h. \qquad (5)$$

The specific heat then can be derived from,

$$c_p = \frac{IVt - h}{m\Delta T}. \qquad (6)$$

(h) represents the thermal leakage of the calorimeter system.

Example: Conduction calorimeter with the substance caused to change the temperature by heat energy added electrically.

(B) Differential continuous flow of a liquid or gas

Principle: Control of induced exchange of energy supplied by electricity is accurately regulated and measured.

Method: A liquid or gas of unknown c_p is made to flow at a constant rate $\frac{m}{t}$ through a narrow tube.

The rate of electrical energy added IV through a heating coil is found by Ohm's law $R = \frac{V}{I}$.

Volts (V) are measured by a potentiometer as V the potential differnce between two pieces of copper and R (ohms) the potential across a 1-ohm resistor: I (amps) being calculated.

TABLE I (cont)

	The quantity of electrical energy added per unit time would be IV. The difference between the substances inlet and exit temperature is ΔT.
Measurement:	Two experiments are conducted at the same temperature difference (ΔT) but with different rates of electrical energy supplied and different rates of substance flow. Both experiments will have the same thermal leakage loss (h) as this depends on the difference between the test substance and surroundings thus (h) will drop from both equations: $(IV)_1 = \left(\frac{m}{t}\right)_1 c_p\Delta T + h$ and (7) $(IV)_2 = \left(\frac{m}{t}\right)_2 c_p\Delta T + h$ Subtracting the two equations: $c_p = \frac{(IV)_1 - (IV)_2}{[(m/t)_1 - (m/t)_2]\Delta T}$. (8)
Example:	Continuous flow calorimeter used for liquid and gas.

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[a] Allen, H. S. and R. S. Maxwell. 1948. "A Text-Book of Heat, Part 1". 3rd Ed. MacMillan and Co., London, England.

[b] Worthing, A. C. and D. Holliday. 1948. "Heat". John Wiley and Sons, Inc., New York.

B. Isothermal Calorimetry (Phase Change Calorimetry)

Calorimetric methods involving an exchange of the quantity of heat with a phase change of the calorimetric heat exchange material are different than the thermometric methods in which the heat quantities are measured by changes in temperature of the system being studied. Isothermal calorimetry is essentially different in that the temperature remains constant as the calorimeter exchanges thermal energy with its surroundings. The quantity of heat is measured by the quantity of heat exchange material that changes phase resulting from the heat quantity exchanged with the substance being studied. The actual measurement is made of the amount of calorimetric material melted, vaporized, or condensed.

(1) Ice Calorimetry

The Bunsen ice calorimeter is perhaps one of the more familiar isothermal calorimeters. However, earlier work by Joseph Black, Antoine Lavoisier and Pierre Laplace utilized the principles of phase change calorimetry. Joseph Black in about 1760 showed the latent heat of ice to be about 80 calories. His calorimeter was a large block of ice with a hole carved out in which a heated ball was placed and the cavity was then covered with a sheet of ice. By knowing the mass of the ball (m_1), specific heat of the ball (c_p) and, the amount of ice melted (m_2) in cooling the ball to 0°C from initial temperature (T); the latent heat of fusion for ice (L) may be calculated by the equation:

$$m_1 c_p \, (T - 0^\circ C) = m_2 L. \qquad (9)$$

Equation 9 can also be applied to calculate specific heat of a substance when the latent heat of transition of the other material is known. As the heated solids were completely surrounded by the large block of ice; heat transfer to the calorimetric chamber (hole) was restricted. Possibility of error was introduced into the system when making the measurement of the melted ice. Melted ice was removed by a pipette; the remaining water was absorbed onto cotton. It would be difficult to be certain all the melted ice had been completely removed and that the use of the pipette and cotton would not cause additional heat exchange resulting in further melting of the ice (Allen *et al.*, 1948 and Worthing *et al.*, 1948).

Lavoisier and Laplace in 1789 investigated the specific heat of heated solids using a calorimeter built of two chambers, each containing ice and a spout to collect the melted ice. Some allowance was made to protect the calorimeter from external heat transfer. The outer chamber filled with ice insulated the inner calorimeter chamber. The inner chamber contained a wire basket surrounded by ice which held the heated sample. They termed their apparatus a "calorimeter" (Figure 1). Calculating the unknown heat capacity or average specific heat (c_p) can be done using equation 9 knowing the latent heat of fusion of ice (L), mass of water collected (m_2), mass of sample (m_1) and initial temperature of the heated sample (T). The fundamental calorimeters of Black, and Lavoisier and Laplace contain possible errors due to heat transfer by conduction, convection and radiation.

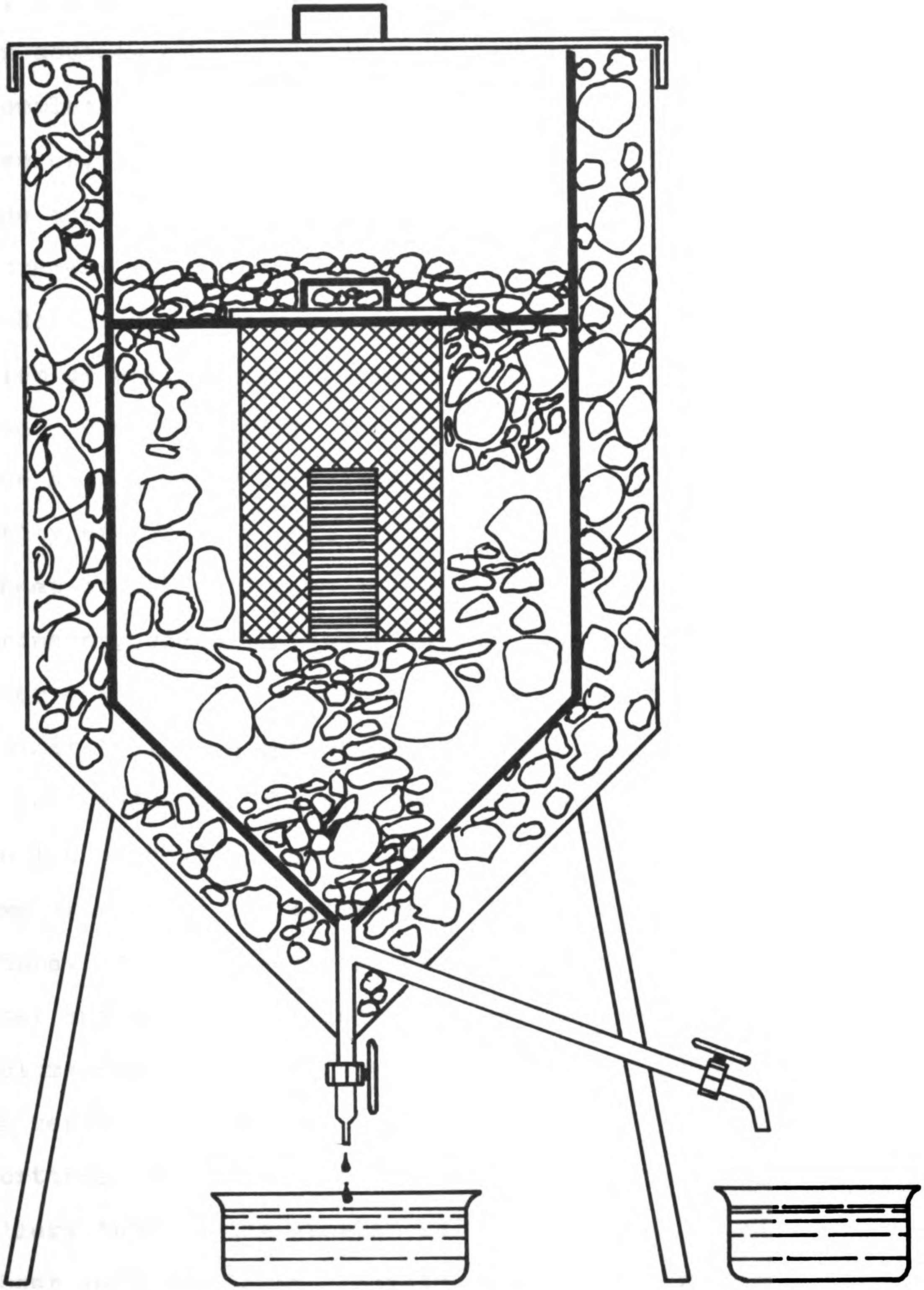

Figure 1. Ice calorimeter of Lavoisier and Laplace (Allen <u>et</u> <u>al</u>., 1948)

Also, the collection and measuring the melted ice introduced other sources of error such as the melted ice not being free to completely drain around the other pieces of ice in the system or, in Lavoisier's apparatus, water may have remained in the collecting spout and not been included in the final measurement (Allen _et al_., 1948 and Worthing _et al_., 1948).

Robert Bunsen's ice calorimeter reduced some of the problem of collecting and measuring the actual amount of ice melted. Bunsen, knowing the volume of a specific quantity of ice at 0°C was 0.0907 greater than the volume of the same quantity of water at 0°C, built a calorimeter which measured the heat of transition by its resulting volume change. The calorimeter, shown in Figure 2, consisted of a glass calorimeter vessel (A) surrounded and attached to another glass container (B). The remaining space of container B was filled with purified water and mercury. The calorimeter was immersed in an ice bath and permitted to equilibrate to 0°C. Some ice (C) was formed in the calorimeter by bubbling ether inside the tube. The sample to be observed was placed in the calorimeter and its heat melted the formed ice producing a change in volume (decrease). The mercury capillary connected to the glass vessel (B) registered the change in volume which was proportional to the volume of ice melted. Calibration of the capillary tube, using substances of well established specific heat values allowed recording mercury movement as a definite quantity of heat (Q) absorbed from the sample in the form of latent heat required to melt a specific quantity of ice at 0°C to liquid at 0°C. The specific heat of the sample

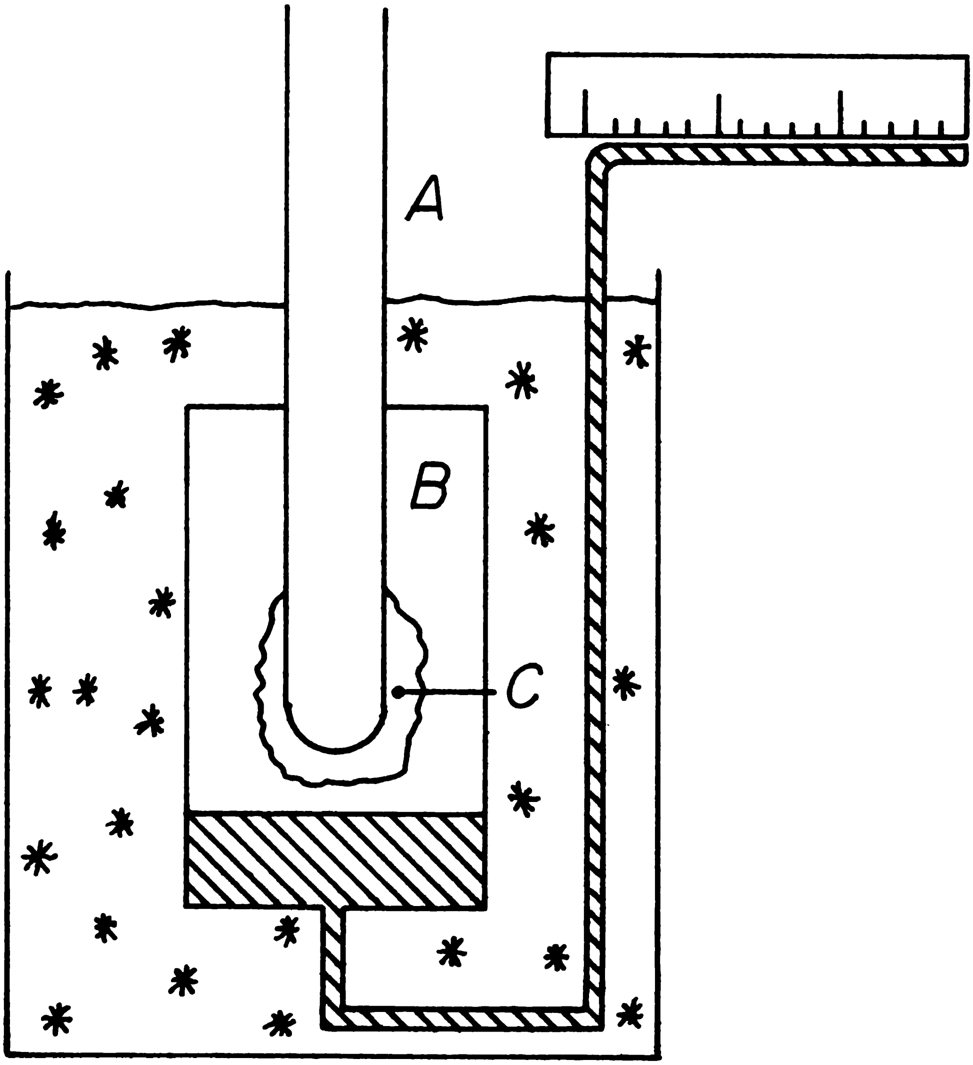

Figure 2. Bunsen's ice calorimeter (Worthing, 1948)

(c_p) can then be determined having found the heat absorbed (Q) from the sample at an initial temperature (T) to 0°C for the specific sample mass (m) in the equation of

$$Q = mc_p \text{ (T to } 0^{\circ}\text{C)} \qquad (10)$$

(Allen <u>et</u> <u>al</u>., 1948 and Worthing <u>et</u> <u>al</u>., 1948).

(2) <u>Steam Calorimetry</u>

Work done by John Joly in the late 1800's utilized the latent heat of condensation for water in developing a steam calorimeter which was used to measure the specific heat of gems and different gases at constant volume. The amount of steam condensed to raise the sample temperature was determined and its specific heat calculated. The apparatus (Figure 3) consisted of a chamber secured in place in which a balance pan was suspended from a balance beam by a wire. The balance pan held both the sample and the collected steam condensate. Steam was injected rapidly through an opening (A) into the chamber reducing radiation losses to the cold air and walls of the chamber. To maintain atmospheric pressure of the steam in the chamber an opening (B) was provided for steam exit. The quantity of steam condensed in raising the sample and balance pan temperatures was directly measured by the balance. Precautions were taken to eliminate error caused by collection of condensate around the opening of the wire which would affect the weighing. A platinum wire was placed around the opening and heated by an electrical current to prevent such condensation. A correction, k (thermal capacity of the pan), for the energy

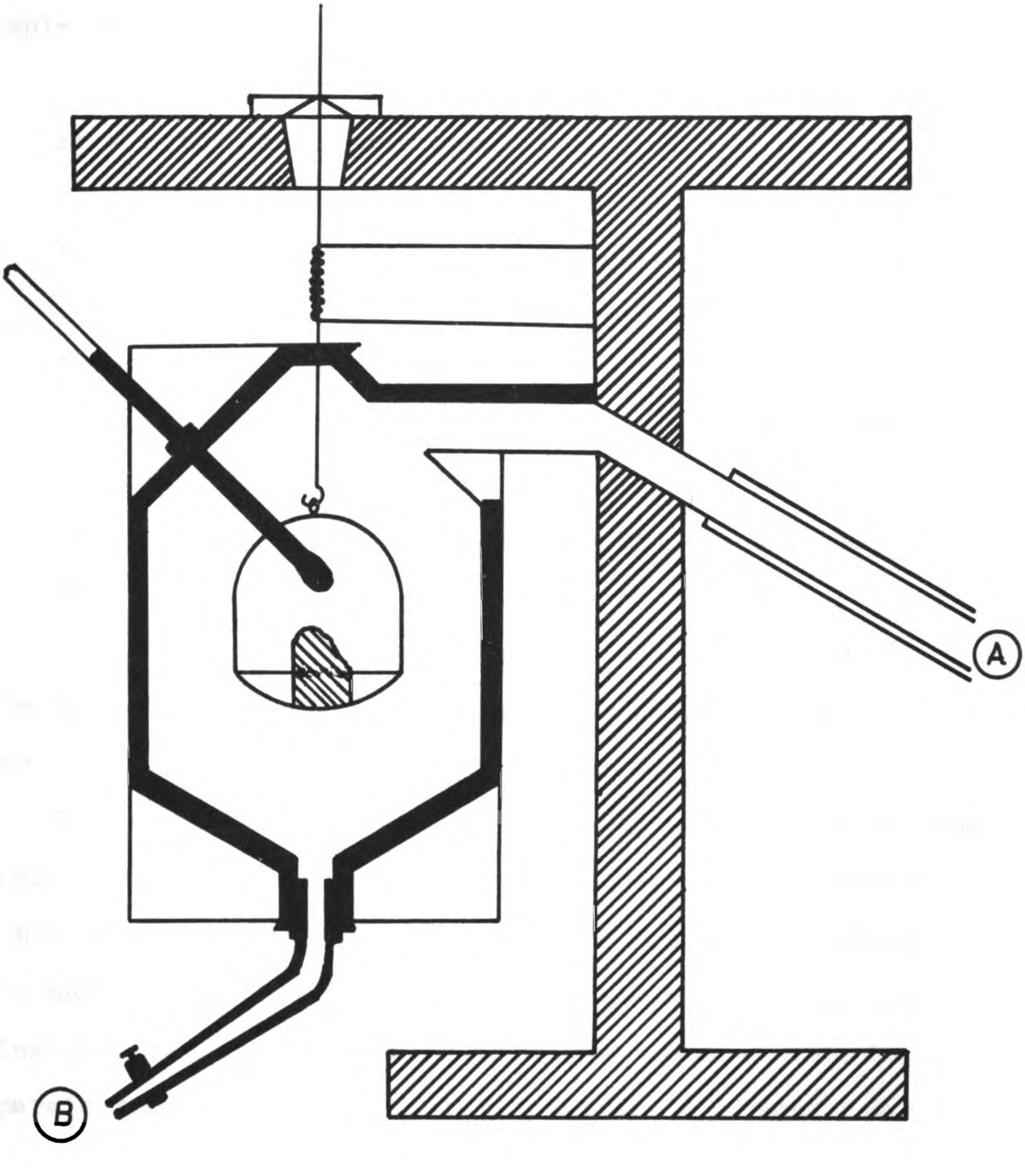

Figure 3. Steam calorimeter used by Joly to determine specific heats of solids (Allen _et_ _al_., 1948)

absorbed by the balance pan was determined prior to the sample experiment. The equation used to calculate the sample specific heat was:

$$m_1c_p\ (T_2 - T_1) + k(T_2 - T_3) = m_2L \qquad (11)$$

m_1 = being the sample mass

c_p = unknown specific heat of the sample

T_2 = final temperature of the sample and balance pan (steam temp.)

T_1 = initial sample temperature

T_3 = initial temperature of the weighing pan (same as T_1)

k = thermal capacity of balance pan and accessories

m_2 = condensate mass

L = known latent heat of vaporization for water.

Joly used this method to determine the specific heat of gems.

In Joly's later investigations, the possible error from steam condensation on the balance pan was better overcome in his development of the differential steam calorimeter. Joly made use of identical weighing pans and accessories being enclosed in the same steam chamber each hooked to separate ends of the same swing balance. The sample was placed in one pan, with the other pan being empty. It functioned as a control for the amount of steam condensation due to the weighing pan itself. This directly corrected for the k value in equation 11, reducing the equation to

$$m_1c_p(T_2 - T_1) = m_2L. \qquad (12)$$

This type of apparatus was used by Joly to calculate the

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specific heats of gases at constant volume. Two hollow copper spheres were placed on the balance pans; one containing a gas which was under the 30 to 40 atmospheres of pressure that was to be determined. This latter apparatus was more accurate as the error introduced by the weighing pan and accessories is directly compensated for by the side that did not contain the test sample. The quantity of condensate due to the sample was read as the differential between the two sides and no heat loss correction was required (Allen et al., 1948 and Worthing et al., 1948).

(3) Latent Heat of Vaporization Calorimetry

James Dewar, in the 1890's, measured the specific heat of more than 50 substances using latent heat of vaporization calorimetry at very low temperatures. In principle, a weighed sample (liquid or solid) at a known temperature will vaporize a quantity of liquid oxygen, hydrogen or air proportional to the amount of energy removed in reducing the sample temperature to the normal boiling point of the liquid heat exchange medium. The quantity of gas vaporized was measured, from which the amount of heat absorbed could be calculated and the specific heat of the substance determined.

Dewar's apparatus, shown in Figure 4, was a larger vacuum flask (A) of about 2 to 3 liters capacity and a smaller, 25 to 55cc, vacuum flask (B) which was suspended in the larger vessel. Both flask A and B were filled with the liquid heat exchange medium (liquid oxygen, hydrogen or

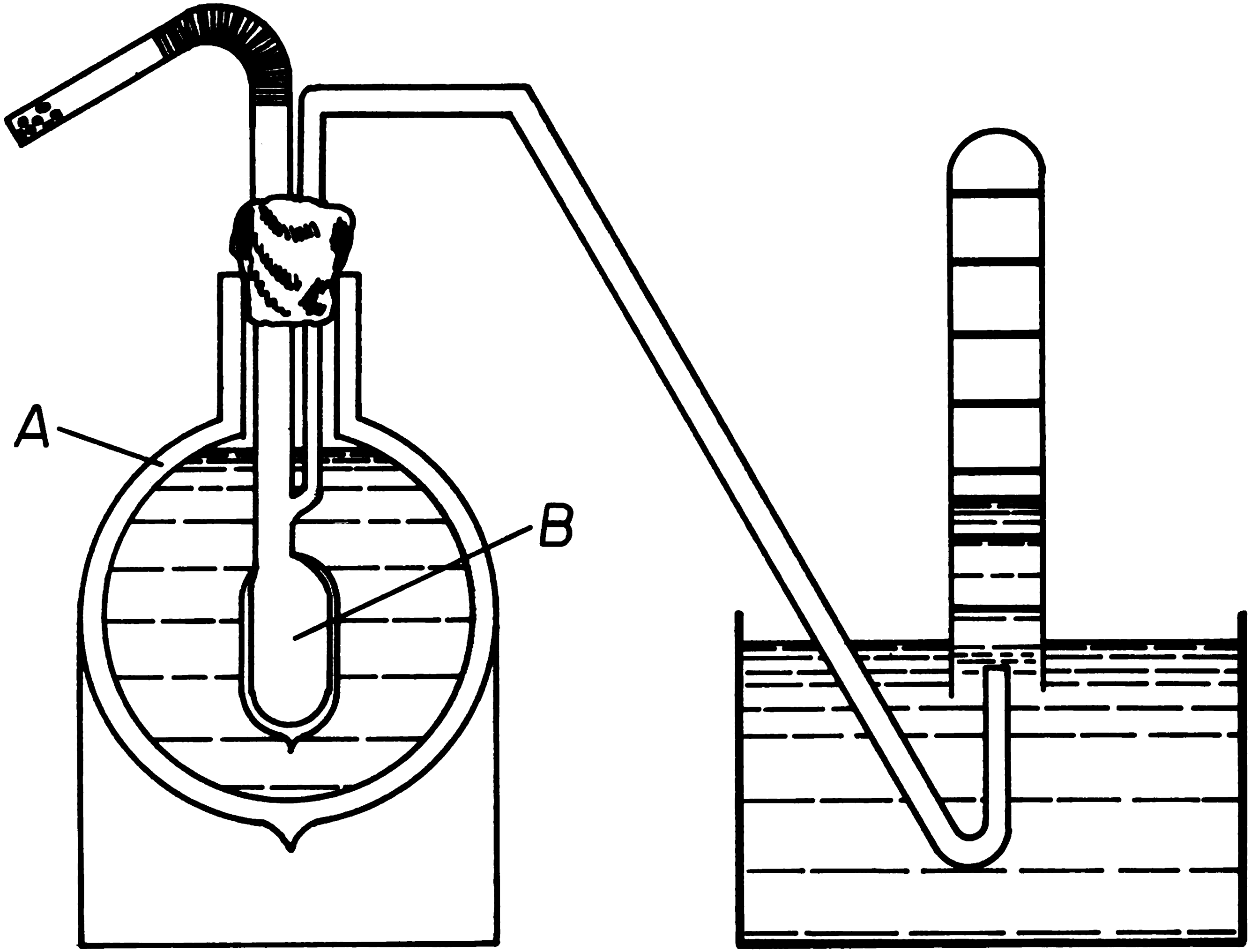

Figure 4. Dewar's liquid oxygen calorimeter (Allen *et al.*, 1948)

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air). Most any low boiling point substance could be used. A small test tube held the sample. Flexible rubber tubing connected the test tube to the calorimeter flask in a manner to permit the delivery of the sample into the inner calorimetric chamber. A sample inserted into the chamber resulted in vaporization of the calorimeter fluid which was collected by fluid displacement in a calibrated tube. Dewar collected the vapor over water or oil. He validated his experiment and calibrations by determining the specific heat for lead which was accurately known at low temperatures (Allen <u>et al</u>., 1948).

Kraus and Ridderhof (1934) studied the heat of solution of electrolytes and heats of reaction in liquid ammonia. They developed a unique calorimeter "that by determining the ammonia vaporized as a result of the heat effect, the heat effect itself might be determined from the known heat of vaporization of liquid ammonia" (Kraus and Ridderhof, 1934). The apparatus (Figure 5) consisted of a dewar vessel calorimeter (A) which was surrounded by another dewar vessel (B) providing a boiling ammonia bath at -33.4°C. Liquid ammonia was dried through sodium and condensed in the measuring chamber (D) having an exact capacity of 20 gm at -33.4°C for ammonia. The system was flushed with ammonia vapors to remove air from the connecting tubing before the experiment was started.

The calibrated amount of ammonia in (D) was vaporized and recondensed in the calorimeter vessel (A). Absorption flask (E) was weighed and attached to the system. A stirrer

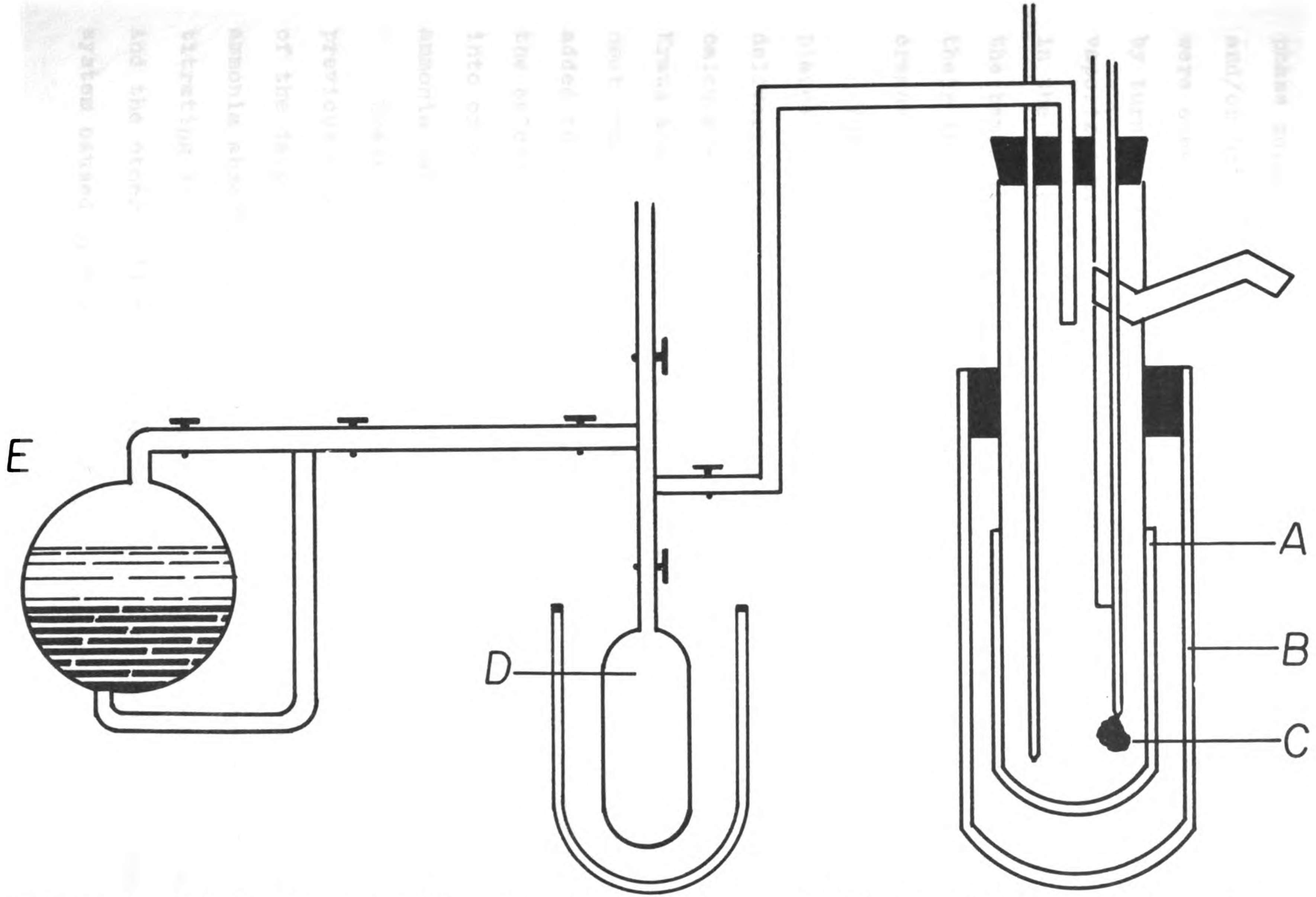

Figure 5. Liquid ammonia calorimeter used by Kraus and Ridderhof (1934) in determining heats of reaction and solution

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(C) established equilibrium between the liquid and vapor phase permitting a constant temperature to be maintained and/or boiling point. When the pressure and temperature were constant over a 10 minute period, the sample was added by turning the delivery tube (F) a half turn. Ammonia vaporized by the reaction energy was absorbed by the water in the collection flask. The experiment was terminated when the temperature and pressure of the calorimeter returned to their initial conditions. The absorption flask weight increase was measured and the quantity of heat determined.

When determining heats of reaction, one substance was placed in the calorimeter vessel and the other in the delivery tube (F). Several corrections and constants were calculated to compensate for thermal leakage. As listed by Kraus and Ridderhof, they were: 1) temperature change of the heat transfer medium; 2) temperature change of the substance added to the calorimeteric liquid; 3) temperature change of the calorimeter, thermocouple, and stirrer; 4) heat transfer into or out of the calorimeter; 5) heat absorbed by the ammonia vapor.

Kraus and Prescott (1934), in conjunction with the previous study, modified the system to increase the precision of the data. Two principal changes were made. The amount of ammonia absorbed in the collection flask was determined by titrating an aliquot of the solution rather than by weighing. And the other modification was regulating the pressure in the system caused by the ammonia vapors. This was accompanied by regulating a mercury pool at the bottom of the collection flask by a column leveling innovation. The maximum pressure rise in the system was only a few millimeters. The apparatus and techniques remained principally the same as those discussed above.

Tong et al. (1945 and 1946) designed an isothermal calorimeter to measure heats of reaction. Their method utilized heats of reaction to evaporate a liquid heat exchange medium. The heat of the reaction being derived from the mass of liquid vaporized and the latent heat of vaporization.

Figure 6 shows the apparatus used. The inner jacket (B) had a hole in it permitting vapors from the refluxing liquid in flask (C) to maintain the inner vessel (A) at a constant equilibrium temperature at the boiling point of the calorimeter fluid. The heat exchange medium and refluxing liquid were the same, and prior to beginning the reaction, a siphon was used to fill the inner vessel from the refluxing liquid supply. A reaction tube (D) held the reactants (methyl methacrylate and benzoyl peroxide). The reaction tube was immersed in the vessel and the heat of reaction recorded as a weight loss of the calorimetric liquid vaporized. A wire connecting the calorimeter vessel to a balance made a weight loss determination possible. The heat of reaction was calibrated from the amount of liquid heat exchange medium evaporated and its heat of vaporization. In their experiments with methyl methacrylate, the heat of polymerization was measured at three different temperatures using different heat

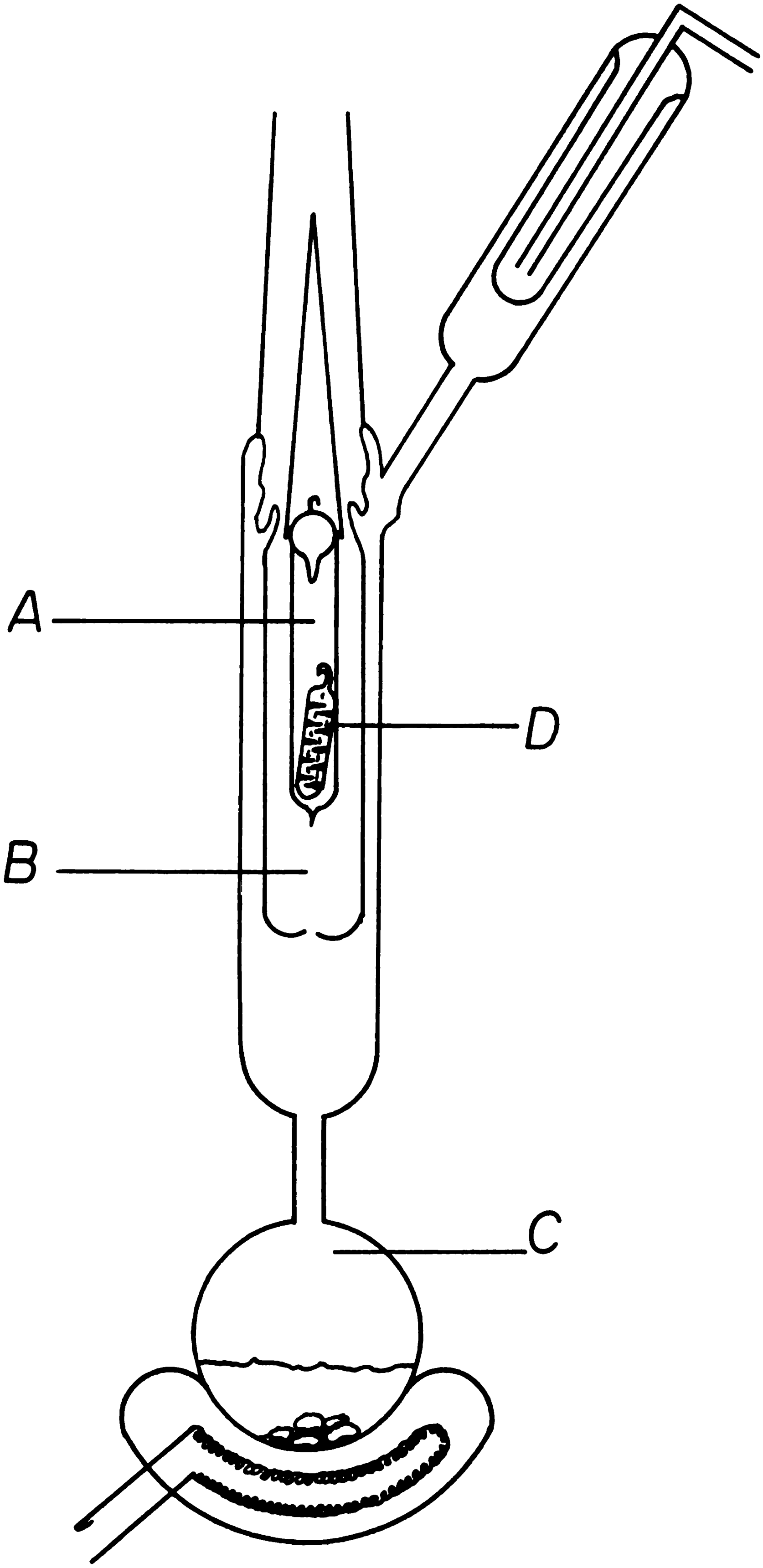

Figure 6. Refluxing isothermal calorimeter (Tong *et al.*, 1945)

exchange liquids, toluene, benzene, and carbon tetrachloride. An advantage of this method would be that the reactants and the reaction are not in a solution mixture with the calorimetric fluid as were the reactions conducted by Kraus et al.

Another form of isothermal phase change calorimetry is thermal boil-off calorimetry. Boil-off calorimetry is used in evaluating the rate of heat transfer for cryogenic insulations. Such information is critical in the transport and storage of cryogenic fluids. The measurement is made from the heat transfer rate to the cryogen from the warmer outer surface of the container to the cooler inner surface by recording the rate of cryogenic fluid vaporized (Jacobs, 1964). The determination of the rate is made by a flowmeter with the thermal leakage (q) being:

$$q = \frac{mL}{t} (\rho\text{liquid}/\rho\text{liquid} - \rho\text{vapor}). \qquad (13)$$

where:

m = mass of cryogenic fluid vaporized

L = latent heat of vaporization of the cryogenic fluid

t = time

ρliquid = density of liquid at specific temperature (T)

ρvapor = density of vapor at specifc temperature (T).

The correction ρliquid/ρliquid - ρvapor was made for the amount of vapor that remains in the vessel occupying the space left by the vaporized liquid (Fulk, 1959).

Fulk (1959) used this technique to evaluate the properties of several insulating powders evacuated between the walls of a dewar type vessel. His results indicated that certain evacuated powders made a more efficient insulation for the dewar vessel than either high vacuum or gas filled powders alone. The instrument used was in essence a dewar vessel design with modifications to meter the vapor flow rate, means to add the insulation powder to be studied between the vessel's walls, and connection for drawing a vacuum. Jacobs (1964) later pointed out that the neglect of the sensible heat effects would cause a significant error in calculation using equation 13. It was assumed that all heat that flowed to the calorimeter vessel was used to vaporize the liquid, with no allowance for absorbtion of sensible heat by the vapor present in the chamber.

Isothermal calorimetric methods of measuring heat quantities are accurate and precise within certain innate limits of the method. Heat of transition methods discussed are limited by the particular equilibrium temperature of the calorimetric material at which the isothermal phase change occurs. Tong et al. (1945) were able to extend the temperature ranges in their study by using different substances, each having particular thermal properties, as heat exchange media. Steam temperature was varied in the Joly steam calorimeter to provide a wider working temperature range, from which enthalpy measurements were made. The enthalpy determined is usually over a wide temperature range ΔT, enabling measurement of the average heat capacity, $\Delta H/\Delta T$. Measurement precision is made possible because of the excellent thermal contact between the substance being studied and the calorimetric medium, as the substance and/or calorimeter are completely immersed in the heat exchange medium. Accuracy is directly limited by the accuracy of the predetermined values selected or knowledge of the phase change thermal characteristics. Another important consideration is the purity of the calorimetric material. For instance, only pure water melts at 0° C. Further corrections are required for methods in which the vapor is collected. In Dewar's cryogenic calorimeter, there is a possible error from the solubility of the vaporized material in the substance being displaced. In Kraus et al.'s method, the pressure increase of the closed system will increase the point at which phase equilibrium occurs. Each calorimeter apparatus has certain corrections to be determined and minimized to reduce the transfer of heat to or from the system not indigenous to the substance being measured.

Phase change calorimetry relies on the principle that the calorimetric heat exchange medium undergoes an isothermal phase change. The temperature of the calorimetric system remains constant and the substance being studied exchanges heat with the calorimeter heat exchange medium. Quantities of heat are measured volumetrically or gravimetrically, but not by temperature change. The heat quantity absorbed or evolved is directly proportional to the amount of phase transition of the calorimetric material. The heat quantity is calculated from the heat of transition value and the

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measured amount of isothermal change induced by the heat energy transferred. The measurement of the amount of transition was previously discussed with Bunsen's ice and Dewar's cryogenic calorimetric methods measuring the volume change, while Tong and Kraus measured the weight loss of the calorimetric medium. Kraus also measured the amount of phase transition by titrating the ammonia absorbed in the water collector; this being a unique technique for ammonia. The steam calorimeter by Joly measured the energy provided to the system in the form of steam by measuring the weight of condensate collected.

REVIEW OF METHODS FOR DETERMINING LATENT AND SPECIFIC HEATS OF FOODS

A. Siebel's Equation

The specific and latent heats of food substances were investigated first by Siebel (1892). The purpose of his study was to establish a method for calculating approximate values for specific and latent heats utilized for refrigerated food storage.

This early work established that a direct relationship existed between moisture content and specific and latent heats. Siebel derived the following formulas for calculating specific and latent heats from his work:

specific heat above the freezing point

$$S = .008a + .20. \tag{14}$$

specific heat below the freezing point

$$S = .003a + .20. \tag{15}$$

Latent heat of fusion was calculated by multiplying the latent heat of fusion for water (143.4 BTU) by percent moisture divided by 100.

where:

S = the specific heat of a substance

a = percent moisture

.20 = empirical constant representing the specific heat of the solid constituents.

With these equations the sensible heats above and below freezing were derived, and with addition of the latent heat of fusion provides a means of estimating enthalpy value.

Siebel's calculations assumed that the water and solid constituents existed as a simple mixture, also that the solids did not influence the water phase change but remained in their "original condition". He knew that the measured specific heat value for salt solutions was comparable to the calculated value found by adding the sums of the products from the specific heat of the constituents and its weighted percentage. It was then proposed by Siebel that the specific heat of a food was the sum of its constituents, principally water combined with a smaller solids fraction.

B. Thermometric Method of Mixtures

Several years elapsed before active studies were resumed at the University of Tennessee by Cooper, Smith and Woolrich, all contributing their investigations between 1929 and 1933[7,36,50]. Their work credited Siebel's assumption that latent heat was directly related to the water content of the food. They also pointed out that most of the heat energy removed from a food during freezing was the latent heat of fusion of the water content, the sensible heats contributing substantially less. Because of its predominant influence, a reliable method for calculating latent heat was desired to better predict refrigeration requirements and design.

Woolrich (1933) pursued the study with increased interest after realizing the few, then-established latent heat of fusion values for foods showed a linear relationship when plotted against the foods' moisture contents. The line plot passed through zero and 143.4, the latent heat of water. Woolrich, using a calorimetric measurement, determined the latent heats for 27 different foods and found their plot relation also fell on this line. "No value was found that did not fall on this line within the limits of experimental error " (Woolrich, 1933).

He measured the quantities of heat absorbed to raise the temperature of a frozen food sample by the thermometric method of mixtures. Water was used as the heat exchange medium. The frozen food sample was added to the calorimetric fluid and the change in temperatures recorded. The calorimeter used in the study consisted of a two walled vacuum bottle, stirrer, and thermometer (Figure 7). A measured amount of water was put into the calorimeter and allowed to equilibrate at room temperature. A frozen sample, after its temperature was recorded, was quickly added with its weight being determined at the end of the test as the weight increase of the previously weighed calorimeter and water. Temperature recordings were made at 30 second intervals until the food sample and water reached constant temperature. The experimental latent heat value was calculated from the equations:

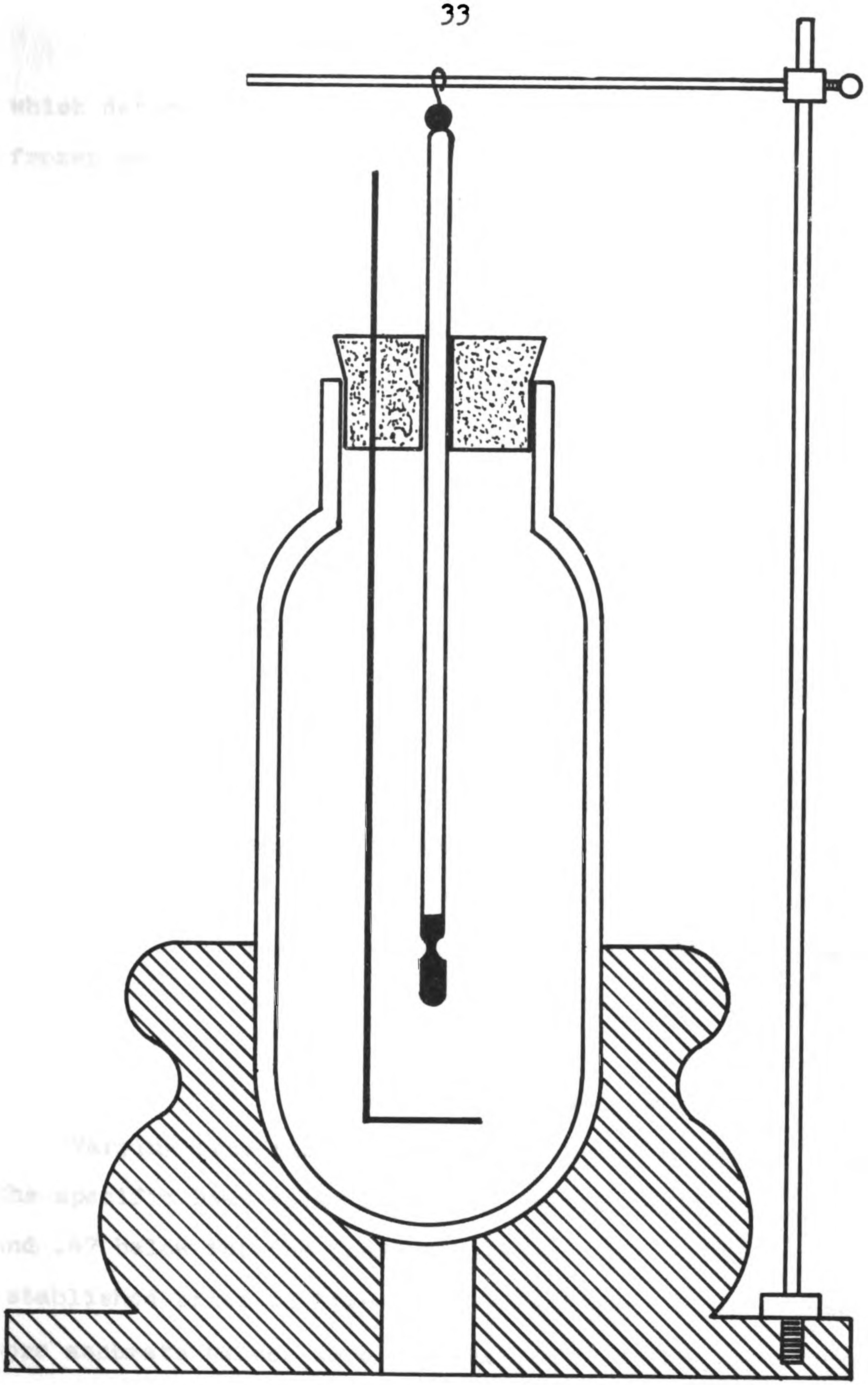

Figure 7. Calorimeter used by Woolrich (1933) and co-workers during the 1930's at the University of Tennessee

$$q = mc_p\Delta T + w \qquad (16)$$

which determines the heat exchanged from the water to the frozen sample with the latent heat being

$$L_h = \frac{q - [(mc_p\Delta T)' + (mc_p\Delta T)'' - w]}{m'} \qquad (17)$$

where:

q = the heat quantity transferred from the water

m = water mass

c_p = specific heat of water

ΔT = temperature initial - temperature final

w = correction for heat exchanged between calorimeter and ambient air (previously determined)

L_h = latent heat of the food sample

$(mc_p\Delta T)'$ = food sample sensible heat below freezing to the freezing point

$(mc_p\Delta T)''$ = sensible heat of the food sample above freezing to the freezing point

m' = the food sample weight.

Varying from Siebel's equation, Woolrich used 0.9 for the specific heat value above the initial freezing point and .47 below for the foods studied. These values were established prior to Siebel's work and were used because more accurate values were not available (Woolrich, 1933). It was shown that by subtracting the sensible heat of the

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food from the total heat transferred from the water to the thawing sample, the latent heat of fusion was derived. It was also demonstrated that the water content of a food, when multiplied by the latent heat of fusion for ice (143.4 BTU), provided a reliable estimate of its latent heat. The formula for the calculation was given as;

$$L_f = 143.4 \frac{P}{100} \tag{18}$$

where:

L_f = the latent heat of fusion of the food in BTU/Lb

P = water percentage of the food sample.

Agreement was found to exist between calculated and experimentally determined values. In a typical example, the calculated value showed an error of -.26% from the experimental value obtained.

Woolrich (1933) further suggested that all water must be frozen in the food sample or a lower value will be obtained when determining the latent heat with his calorimetric method. He noted that the published freezing point values by Smith (1931) were not sufficient as they were measurements of the apparent freezing point of the food. This conclusion was derived from measurements made of the latent heat. If a food sample was frozen to the freezing point suggested by the literature, a lower latent heat value would be obtained than expected. However, if the food was frozen to a temperature significantly below the apparent freezing point, an experimental value more nearly that expected was obtained. This was explained by the freezing point depression resulting from concentration of the solutes in solution as water freezes out of solution. Food products have a freezing range rather than a specific freezing point (Woolrich, 1933). Woolrich et al. (1931) summarized their results as follows: "1) Experiments indicate that the latent heat of fusion of fresh vegetables, fruits, meats, and dairy products is directly proportional to the moisture content by weight. 2) The fusion points of food products are considerably depressed by the presence of salts, starches, fats and sugars. 3) Most foodstuffs have a freezing range of several degrees, such a range often extending from just below the freezing point of water to a temperature near zero degrees Fahrenheit. 4) The presence of any alcohol, by virtue of the breaking down of the starches, or sugars, lowers the fusion point. 5) The presence of fats, starches, sugars, and mineral salts has no measurable effect on the value of the latent heat of fusion of foodstuffs examined."

C. Calculating by Specific Heat of the Principal Constituents and their Weighted Percentage

Subsequent research by Zhadam (1940) proposed a similar scheme for calculating the enthalpy value for a food undergoing a temperature change. He determined the specific heats of the principal constituents of foods as being: carbohydrates, .34; proteins, .37; fats, .40; and water, 1.00. By multiplying the appropriate specific heat value by the component percentage, determined by analysis of the food desired, the heat capacity could be calculated as:

$$C_p = .34P \text{ carbohydrate} + .37P \text{ protein} + .40P \text{ fat} + 1P \text{ water}, \tag{19}$$

where

P = decimal equivalent of percent composition.

The heat of fusion would be calculated by the method of Siebel and Woolrich from equation 18.

The above equation has since been shortened (Charm, 1963) to:

$$C_p = .5P \text{ fat} + .3P \text{ solids} + 1P \text{ water}. \tag{20}$$

The methods discussed for predicting the specific and latent heats for ultimately determining the enthalpy of a food undergoing a temperature change are used extensively today for arriving at refrigeration requirements. These methods are used because of their simplicity and empirical practicality. The workability of the calculations given by Smith and Woolrich is mainly due to: 1) the larger heat enthalpy contributed to freezing or thawing is from the heat of transition for water, 2) the specific heat of water is larger than the specific heat of the food solids. The ASHRAE Guide and Data Book 1968 contains and directs the use of these equations. In the section of the above mentioned handbook frozen foods, "Ice Cream", it was suggested in common practice that the specific heat for ice cream mix of .8 is "generous" for estimating refrigeration requirements. Such empirical values are commonplace for lack of anything more accurate. Also, because of the uncertainty of such values, engineering design usually includes a 5 to 15% addition to the refrigeration load as overdesign would create little problem in processing and/or storage while insufficient refrigeration would be a serious mistake.

D. Inability to Distinguish Latent from Sensible Heats

Woolrich, Bartlett, Short, and Staph during the 1940's at the University of Texas conducted extensive studies on the specific and latent heats of foods. Their work distinguished the freezing of a food as having an extended freezing range rather than a freezing point at which all water becomes solidified. The apparent concern is focused on the difficulty in distinguishing the latent and sensible heats through the freezing region. The calculated values of Siebel and Woolrich assume that all the water became solidified at the apparent freezing point, thus the enthalpy becomes the sensible heat above freezing, the latent heat, and the sensible heat below freezing.

With the latter discussion in mind, it is appropriate to define the terms "specific heat" and "latent heat", as applied by the writer throughout the text. Specific heat was defined by Woolrich (1965) as the ratio between the heat required to change the temperature of a substance one degree and that required to change the temperatue of an equal weight of water by one degree, the unit being calorie per gram per degree centigrade (cal/gm/°C). It is common to consider water as 1 cal/gm/°C above freezing and .5 below. This is not correct. The specific heat of water changes as a function of temperature. The specific heat of water is 1 cal/gm/°C only at 15°C. Heat of fusion is the heat which flows into or out of a solid during melting or freezing without producing a change in temperature of the substance. Because foods have a freezing range, the sensible and latent heat are difficult to separate and distinguish. The term latent heat is not suitable to describe the freezing zone as a change in temperature occurs (Woolrich, 1966). Also, usually experimental measurements are made of the heat required to raise or lower the temperature of a food over several degrees; the value determined is an average specific heat over the temperature interval (Woolrich, 1951). The writer will use the term "apparent specific heat" to designate the heat energy required to induce a 1 degree temperature change in a food system.

E. Electrical Method of Calorimetry

The experimental values found by Short *et al.* (1942) for the specific heat of several food types were in agreement with those calculated using Siebel's or Woolrich's method for values above or below the freezing region, but not for values within the freezing region between 5°F (-15°C) and 40°F (4.4°C), where large discrepancies existed. Thus, it was emphasized that the latent heat of fusion alone would not be sufficient for this region as an extended freezing range is present. Throughout the freezing region, heat energy removed or added is distributed by both the water frozen and the water unfrozen and is dispersed either as latent or sensible heat. In fact some foods are not completely frozen until very low temperatures are reached; orange juice does not completely solidify above -95°C. (Bartlett, 1944). Short et al. (1942) concluded that the specific heat of a food in the freezing region is a function of temperature.

The electrical method of calorimetry was used in their studies. The calorimeter being a conduction type where the heat transfer was minimized and thus considered the heat loss of the system (Figure 8). The sample was placed in the tin container (A) into which was inserted the electrical heater and a mercury well (B) which had a thermometer suspended in it. The container was placed in a double walled vacuum flask (C). This was then placed in a steel container (D) and submerged in calcium chloride brine bath contained in an insulated steel box (E). The calcium chloride brine was refrigerated by Freon to -40°F (-40°C) to -50°F (-45.6°C) thus, freezing the sample. Enough electrical energy was then added to the frozen sample to increase the temperature 5° to 8°F. Records were kept of the energy added and time. The system was then allowed to equilibrate for 4 to 12 hours allowing the brine to increase in temperature to within 4° to 6°F of the calorimeter and sample.

The specific heat was determine using the equation:

$$c_x = \frac{1}{W_x}\left(\frac{q_1 - k\Theta m\Delta t}{\Delta T} - W_cC_c\right) \qquad (21)$$

where:

c_x = specific heat of the foodstuff at the average temperature of the particular

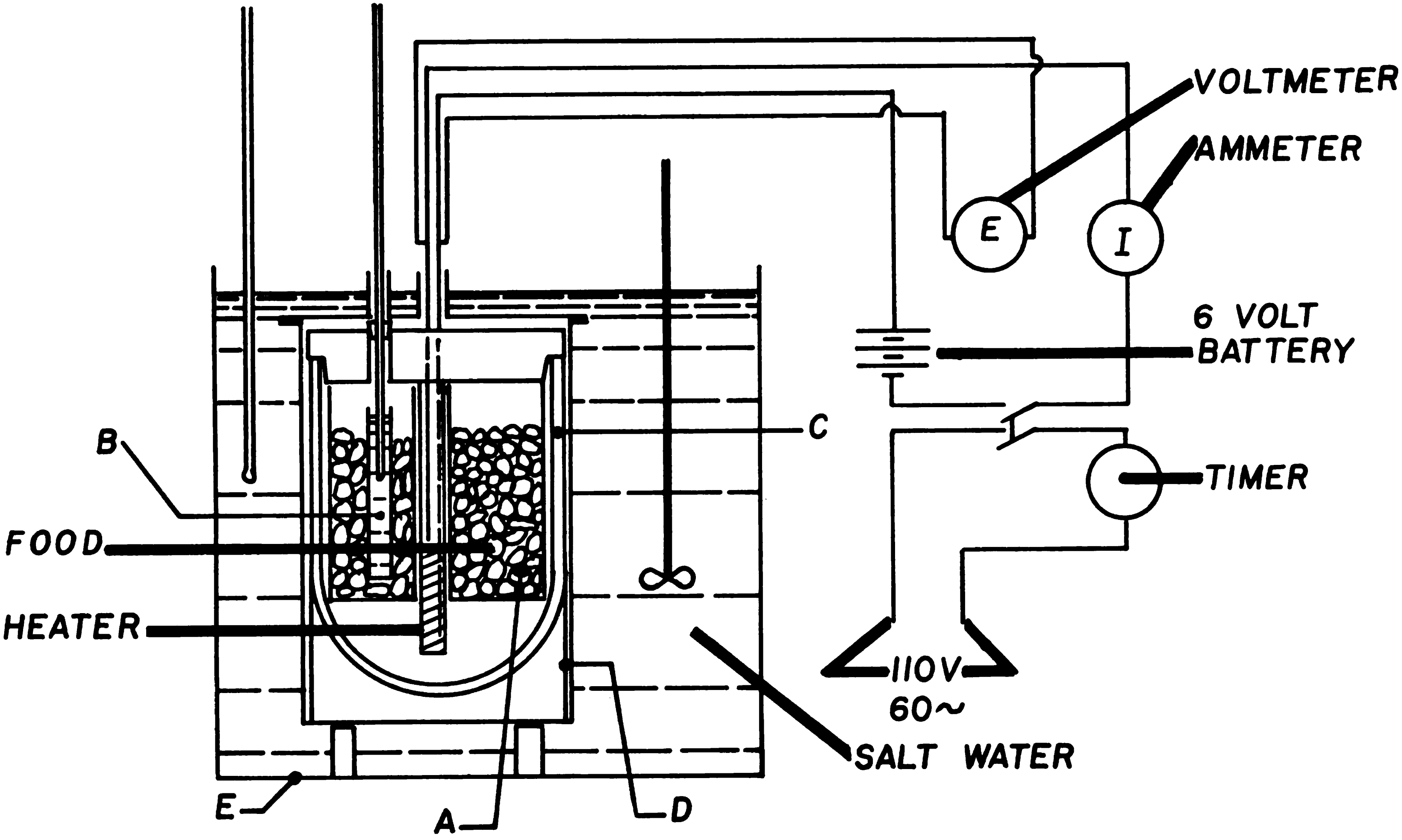

Figure 8. Electrically heated calorimeter used for determining the apparent specific and latent heats of foods. (Short *et al.*, 1944)

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W_x = weight of foodstuff in calorimeter, lb

q_i = energy input, BTU (measured electrically)

k = heat transfer rate of the calorimeter, from calorimeter to brine (BTU/min/°F)

θm = average temperature difference between foodstuff and brine during the period from beginning of heating until the maximum temperature was attained

Δt = time (in minutes) from beginning of heating until maximum temperature rise was attained

ΔT = difference between maximum temperature of the foodstuff and the temperature at the beginning of heating, °F

$W_c C_c$ = thermal leakage of calorimeter at average temperature of foodstuff, BTU/°F (Short *et al.*, 1944).

The specific heat value (c_x) then is an average specific heat determined from 5°F (-15°C) to 10°F (-12.2°C) temperature range. Accompanying Short's experimental work, Bartlett (1944) derived complex mathematical and thermodynamic calculations which enabled prediction of the amount of ice formed, rate of ice formation, and thermal capacity for a particular food.

The results of their research indicated that the apparent specific heat of foods and sugar solutions increased sharply through the partially frozen region as the temperature increased toward initial freezing point and immediately dropped after passing through the initial freezing point. The apparent specific heats of different sugar solution concentrations increase with an increase in concentration in the freezing region as a higher quantity of water will remain unfrozen at a higher sugar concentration at a given temperature in the freezing range. Thus the heat capacity is dependent on sugar concentration. This was not found to be so for foods, however; generally a decrease in the specific heat accompanied those foods lower in water content. Their results exhibited a relationship in the partially frozen region between the amount of water frozen at a particular temperature and the specific heat. They also found that the thermal capacity of a food in the partly frozen region is a function of temperature (Bartlett, 1944). The data obtained did not strictly follow Siebel's rule as some food tested varied widely in moisture content yet had similar specific heat values (Short et al., 1942, 1944).

Continuation of this study by Staph (1949) and Short et al. (1951) further substantiated the relationship previously discussed between the water content and specific and latent heats. Their work increased the number of foods for which the apparent specific heats had been investigated. The research was expanded to encompass the influence or relationship between the heat capacity of foods and their fat, water soluble solids, and water contents. An adiabatic calorimeter replaced the calorimeter previously utilized by the Texas research team.

A food sample was placed in a container which was immersed in kerosene within the calorimeter vessel, both containers were nickel plated copper. The kerosene was in direct contact with the food and continuously circulated by a stirrer. The calorimeter vessel was sealed and itself submerged in a kerosene bath contained within an evaporator system. Both kerosene baths were electrically heated with the outer bath being refrigerated by Freon 12. The entire system was enclosed in an insulated box. The system temperature was allowed to equalize. The inner calorimeter was heated electrically until the sample and calorimeter had risen in temperature 3 to 4 degrees, while the outer bath was maintained constant at the previous equilibrium temperature. The temperature varied throughout the inner kerosene bath at low temperatures as heat was being transferred to both the food sample and outer kerosene bath. The procedure was changed for the work done by Short and Staph in 1951. The innovation included heating the kerosene outer bath electrically as the sample was heated in order to keep the calorimeter and outer bath as near as possible to the same temperature during the test. A difference in the measured apparent specific heat values was found for the two methods. The second procedure described resulted in greater agreement with the previous data.

Kerosene was used as the heat exchange medium because of the low temperature desired. The use of kerosene within the calorimeter vessel increased heat transfer throughout the sample. Kerosene did, however, limit application of the apparatus. Foods and/or samples containing more than 3% fat could not be measured as the kerosene dissolved the fat. A thick jelly resulted which could not be readily stirred; also, the sample composition would be altered as well as the heat exchange medium itself.

A frozen sample was added to the cooled system rather than freezing the sample within the system. Samples frozen in the calorimeter massed together inhibiting circulation of the heat exchange medium (kerosene) through the sample.

In order to compute the energy removed (enthalpy) of a food above -40° C the sensible heats of water, fats, soluble solids and insoluble solids, and the latent heats of transition for water and fats must be considered. Thus the amount of liquid fat and water must be known. Fats were regarded solidified below 32° F (0° C) and only the sensible heat needed to be included in the foods' freezing range. Above 32° F the latent heat of the fat was treated as a separate phase change. By treating the soluble solids and insoluble solids as total solids content, the mathematical calculations can be reduced. The equation to compute the enthalpy change (h_t) between -40° F (-40° C) and 32° F (0° C) (below the solidification of fat) would be:

$$h_t = (dc_{ps} + b_t c_{pf} + a_t c_{pi})(t + 40^\circ) - \frac{a_u c_{pi}}{2}(t - t_x) + \frac{a_u c_{pw}}{2}(t - t_x) + a_u h_{if} \quad (22)$$

where:

a_t = total water content, fraction by weight

a_u = unfrozen water content, fraction by weight

b_t = total fat content, fraction by weight

d = solids content, fraction by weight

c_{pi} = specific heat of ice (varied from 0.43 at -40° F to 0.505 at 32° F)

c_{pf} = specific heat of solidified fat (0.34)

c_{ps} = specific heat of solids (0.24)

c_{pw} = specific heat of water

h_{if} = latent heat of fusion for water (144 BTU/lb)

t = final temperature

t_x = temperature at which all water is frozen. (Short et al., 1951).

The calculated and experimental enthalpy measurements were in very close agreement as shown by the apparent specific heats determined from these values when plotted for comparison.

Included in the scope of their project was demonstrating the relationship between the enthalpy of a food and the sum of the sensible heats from fats, water, soluble solids, and insoluble solids; and the latent heat of transition for water and fats. They found that fats present in a food generally caused the apparent specific heat to increase more rapidly as the thawing range was approached; although no similar tread could be established from the data above freezing. It was later stated by Woolrich (1966) that the fat content has the greatest effect below about 0° F (-17.8° C) and that large amounts of fat reduce the apparent specific heat value.

F. Riedel's Drop Calorimeter for Determining Food Enthalpies

Riedel (1951) worked to determine whether or not a direct relationship could exist between some easily measurable and readily available food property for computing the apparent specific heat and/or enthalpy of a food through a given temperature range. He realized that such relationships would apply only generally to a specific group of foods. Riedel studied fruits and vegetables as his previous research in 1949 found the dry substance content of any juice (soluble solids) could be easily determined by measuring its refractive index. Also, the freezing temperatures taken of several juices when plotted showed a curve that was a function of the dry substance's content. Emphasis was then placed on the soluble solids in solution and their effect within the freezing range. The equations derived by Riedel from his calorimetric results will be discussed in detail under the section "Selected Literature Values and Calculations." His equations were used for comparison with the experimental results of this research.

To collect the experimental values, Riedel used a drop calorimeter technique with the heat quantities being measured by the method of mixtures. The apparatus (Figure 9) was non adiabatic. Thermal leakage was minimized by a large iron block which did not appreciably change in temperature during the test period. A three to five gram sample was placed in a conical copper vessel held in direct contact within a copper cylinder by means of a stretch thread. The sample and vessel were cooled to the desired temperature using

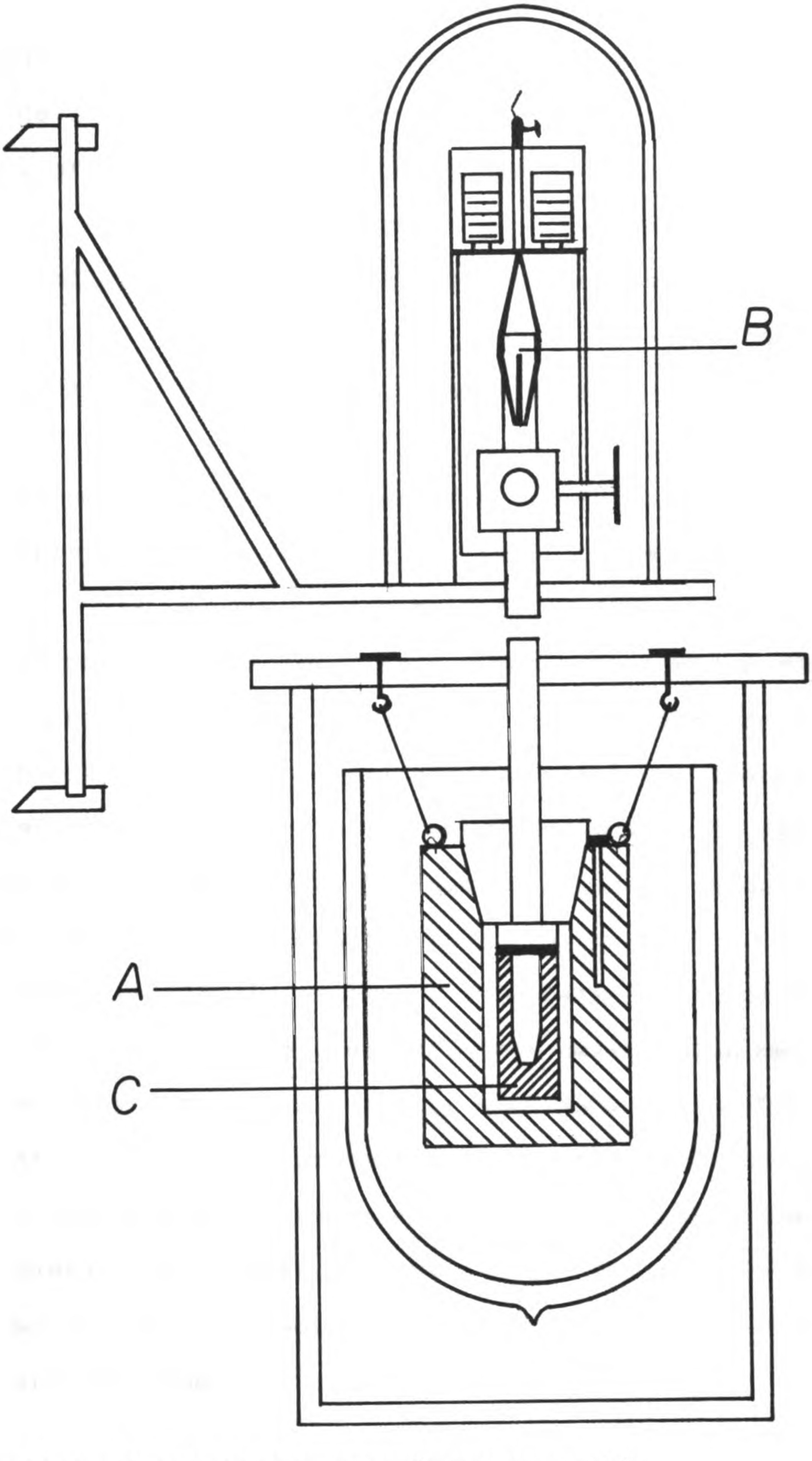

Figure 9. Drop calorimeter (Riedel, 1951)

liquid air within a thermostatic device. When the food sample had reached the desired temperature, about -30° C, the thermostatic device was rotated over the calorimeter apparatus. Delivery of the sample to the calorimeter chamber was accomplished by aligning a glass tube within the thermostat unit with a similar glass tube leading to the calorimeter. The stretch thread was cut by a blade within the thermostat chamber and the sample container released to fall into the calorimeter.

The calorimeter consisted of a copper block (C) with a bore corresponding to the conical sample container (B), Figure 9. This was surrounded by a large iron block (A) which, in turn, was enclosed in a dewar vessel and a wooden box surrounded the entire apparatus. The temperature of the copper block was measured periodically until the temperature was constant and the sample and calorimeter were in equilibrium. The heat energy absorbed by the sample would be calculated by an equation similar to equation 1.

Riedel (1951), in comparing calculated with calorimetrically determined values, stated, "the calculation method as described proved to be universally applicable" (for fruits and vegetables). His results were not compared to the works of those previously discussed as they characterized their values based on the water content and did not provide information as to the juice soluble solids content of the fruits and vegetables studied.

G. Adiabatic Calorimetry

Riedel's more recent work has been greatly facilitated by his development of an adiabatic calorimeter suitable for the investigation of the heat content of food materials and other items which are of importance in food technology. The apparatus, Figure 10, consisted of a small copper calorimeter (A) which contained about a 7 gram sample. A thin walled adiabatic shield (B) surrounded the calorimeter vessel. The shield was electrically heated and automatically regulated to the temperature of the calorimeter. Heat transfer with the surroundings was greatly reduced by controling the shield to the same temperature as the calorimeter. Temperature was maintained to ± .01° C between the calorimeter and adiabatic shield during the experiment. Surrounding the adiabatic shield was a brass, double walled container (C) which, in turn, was enclosed by a dewar vessel. Between these last two partitions was a dry ice-alcohol mixture, melting ice, or some such coolant that would be within the temperature range studied. The temperature bath reduced the temperature differential between the adiabatic shield and external surroundings. An additional vessel (D) partitioned the brass container and adiabatic shield restricting heat transfer between the shield and the enclosed liquid bath (Riedel, 1955, 1956).

The heat energy absorbed by the food sample was directly proportional to the electrical energy constantly supplied in raising its temperature during a recorded time

Figure

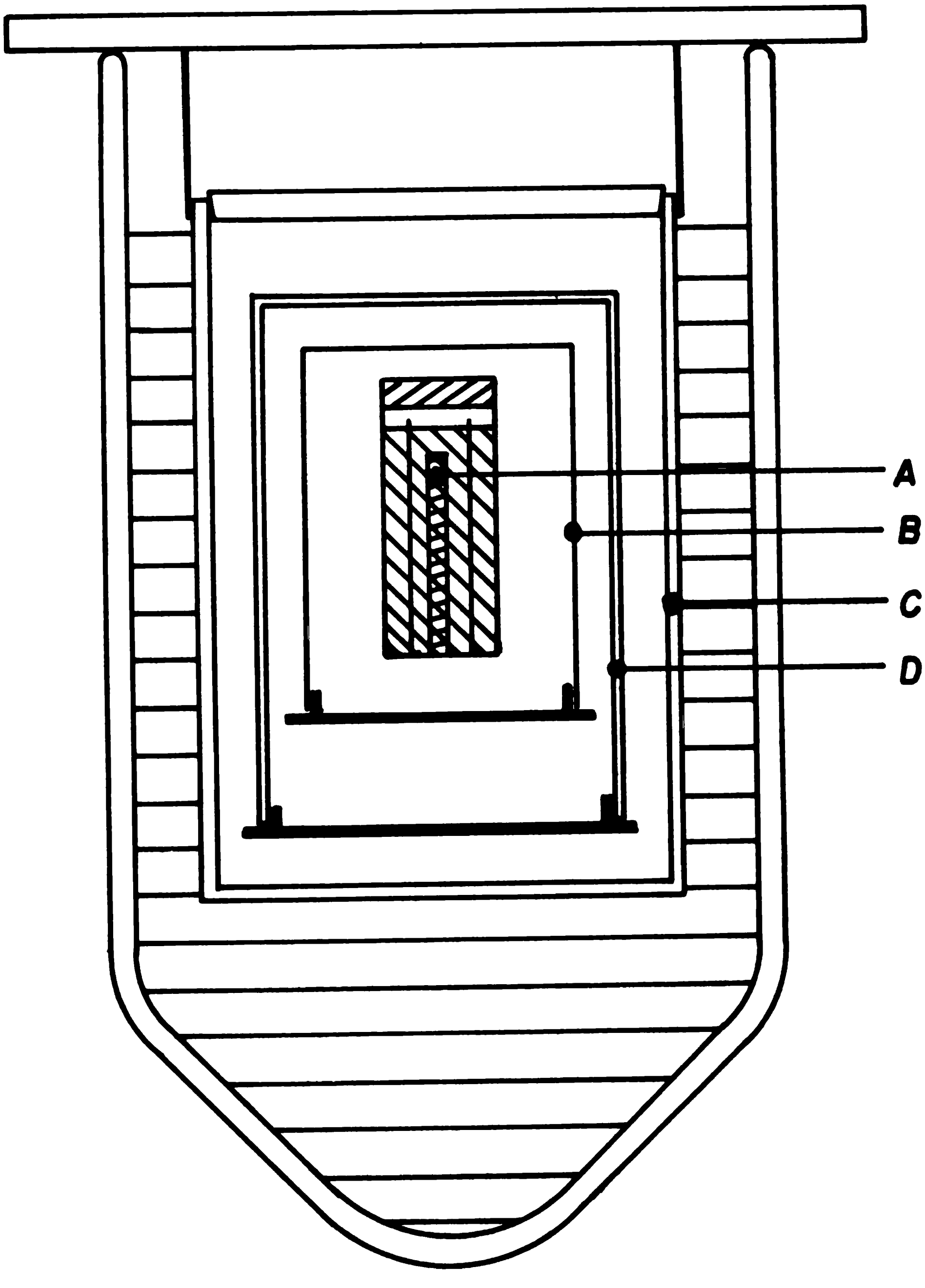

Figure 10. Adiabatic calorimeter used by Riedel (1955) for determining enthalpy and other thermalmatric characteristics of foods.

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period. The measured heat quantities when plotted against the temperature change during warming would provide a direct measure of the enthalpy change for that temperature range. The measured enthalpy value during a one degree temperature increase was equal to the apparent specific heat of the sample (Riedel, 1956). The heat input of 1.5 calories per minute was sufficiently slow for such measurement as to completely melt solidified fat from -50° C in 6 to 8 hours. An accuracy of 1% for the research using the calorimeter was claimed (Riedel, 1955). Calculation of the measured results was as follows:

$$q = 0.239i^2R\Delta t = (mc + L)\Delta T \qquad (23)$$

where:

q = input heat energy absorbed by the system

i = amps through heating element

R = ohms, as resistance of the heating element

t = time is seconds

m = mass of food sample

c = apparent specific heat of the food

L = heat capacity of the calorimeter

ΔT = degrees in temperature range.

The amount of ice melted in warming from -40° C (point at which all free water was frozen) to a desired temperature can be determined from the enthalpy versus temperature plot. This relationship at -40° C being linear was extrapolated to the desired temperature (T) providing the difference in enthalpy between the desired temperature and the enthalpy value at -40°C, which was divided by the latent heat of fusion for ice at T. The value was then considered the amount of ice melted between the two temperatures. The difference between all ice being melted at 0°C (total water content) and the amount of ice melted at the desired temperature identified the quantity of ice remaining. The amount of ice frozen at a particular temperature was related directly to the total water content. Further observations of this relationship were evidenced by varying the water content of a particular food and plotting the specific enthalpy values against their temperature. A moisture content was reached at which no ice formation occurred in the freezing zone, this value was equated to the amount of bound water in the sample (Riedel, 1957). The fraction of water not frozen per gram of dry substance was plotted as a function of the total water content per gram of dry substance giving the value for the amount of bound water which did not freeze per gram of dry substance below -40°C.

Riedel published a series of articles between 1955 and 1964 in which the adiabatic calorimeter just discussed was used. In his observations of the enthalpy values for 27 fats and oils (1955) it was found that each exhibited a characteristic curve plot when apparent specific heat was plotted against temperature. A lipid substance could not be characterized by this method. A model mixture of two different lipid substances revealed the ratio of apparent specific heat to temperature was dependent on the proportions of the mixture, but that the values could not be predicted from the sum of the lipid components and their specific heats. It was also indicated that at -50°C the specific heat of fats and oils was about .35 cal/gm/°C and sharply increased near the melting point and immediately dropped to about .48 cal/gm/°C. The enthalpy values between -50°C (0 enthalpy) and 55°C in one degree increments, and percentage of the lipids solidified at particular temperatures is excellently provided in tabular form for the 27 liquid types (Riedel, 1955).

More work by Riedel (1956) on sea fish (haddock, cod and perch) noted that some water remained unfrozen below -60°C. Drying the samples to different water contents and measuring the enthalpy values indicated that all free water was frozen out at -40°C with 0.39 Kg per Kg dry solids content remaining unfrozen. The enthalpy and apparent specific heat values were comparable between the different fish samples below -2°C even though they had varying water contents. Above freezing, the variation between samples, as an effect of the water content, was more pronounced. Appropriate tables were provided for the amount of ice formed and enthalpy values between -40°C and 20°C (Reidel, 1956).

Extending the 1957 study to meats, Reidel found that a certain amount of water, as with fish, did not freeze at extremely low temperatures (-65°C). In meats, about 0.35 Kg of unfrozen water per Kg of dry substance, or 0.4 Kg of water per Kg of protein, or the equivalent of two molecules of

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water for each amino acid was detected as remaining unfrozen (bound water) (Riedel, 1957a). Water would not freeze out from a sample which had the water content reduced to below 20% (calculated on a dried basis). Freezing began at-1° C and at -2°C about 50% of the water was frozen; at -30°C practically all water was frozen in the meat samples. The enthalpy values for beef, veal, chicken and venison were studied between -60°C and 20°C and found to be similar. An enthalpy diagram was developed as a function of total water content usable for all the mentioned meats.

Subsequent research by Riedel was done with egg white and yolk (1957b) and white bread and flour products (1959). The effects of physical stress on the amount of protein denaturation was observed, as related to the changes in bound water or amount of water unfrozen at -40°C (Riedel, 1964). The enthalpy values for egg white were not noticeably changed by freezing, heating, drying and rehydration, or pulverizing. This indicated that the enthalpy value was not dependent on previous physical stress encountered, such as freezing during calorimetric experimentation. The effect of freezing on the bound water was less than 0.1 Kcal/Kg or not measurable by the instrument. The freezing of beef had no detectable denaturing effect on the protein. Pulverizing, drying and remoistening, and heating do affect the enthalpy values for beef but the change is so small that no generality or conclusion was made (Riedel, 1964).

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H. Calorimeter Designed to Measure the Heat Removed During the Freezing Process

Experiments by Mannheim *et al.* (1955) were to determine the reason for observed discrepancies found in commercial operations utilizing the published methods for calculating refrigeration enthalpy requirements and those actually attained in practice. Most previous investigations concerning the apparent specific heats and enthalpy values for foods were done by freezing the sample and measuring the heat energy required in thawing the food sample. Mannheim *et al.* designed their equipment to also measure the energy removed from the sample during the freezing process. The energy requirement for freezing and thawing was expected to be the same; however, measurements were made for verification and elimination of this as a possible source of discrepancy between the calculated and industrially observed values.

The calorimeter in this study was a 24 liter dewar vessel and the type of calorimetric measurement was the thermometric methods of mixtures. The heat exchange medium was an aqueous solution containing 60% ethylene glycol, refrigerated to -35°C. The cooled solution was added to the dewar calorimeter and the system allowed to equilibrate 4 hours. As the apparatus was of sufficient size, whole intact food samples were studied. Temperature of the sample was determined before it was placed into the dewar. The temperature of the sample and glycol solutions were measured by thermocouples. Temperatures were periodically recorded until an

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equilibrium temperature was established. The solution was stirred by a constant speed mixer which maintained a uniform temperature of 0.05°C throughout the heat exchange medium. Knowing the specific heat of the ethylene glycol solution and the amount of temperature change, the quantity of heat energy absorbed by the glycol in freezing the sample was determined. The reverse of this procedure permitted thawing enthalpy measurements to be made. A correction for the heat loss or gain by the calorimeter was determined by previously established heat transfer rates. No correction was described for the polyethylene bags used to contain the food samples. Nor was consideration given to the possible change in the specific heat of the ethylene glycol solution accompanying changes in temperature.

Their work gave evidence that there was no difference between the thermal effect of freezing and thawing, as the two calorimetric values were essentially the same. Their data agreed with the calculated values. The method of calculation for determining enthalpy values was taken from the Refrigeration Data Book of 1950; although not specified it is assumed that Siebel's equation was used.

Possible explanations which were provided for the difference between calculated enthalpy values and the actual commercially observed or practical values are: 1) allowance must be made for the unfrozen portion at the holding temperature desired. All water is not frozen until - 40°F (-40°C) or lower which would be considerably lower than conventional storage temperatures. Thus, if all water were calculated as

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frozen, higher value would result than was required. 2) The exact water content of the food to be frozen must be known. Tabular values provide averaged results which do not apply to variations in growing conditions, maturity or variety. If a higher tabular value were used in calculating the enthalpy requirements for a food; the actual moisture content being less, a significant error in the calculated value will exist. 3) Finally, if a lower temperature were calculated than was actually achieved, the calculated requirements would be greater than those obtained (Mannheim _et_ _al_., 1955).

I. Cryogenic Calorimetry

Subsequent research by Moline _et_ _al_. (1961) in determining the apparent specific heats of foods by the sum effect of their components was conducted at cryogenic temperatures using liquid nitrogen as a coolant. The calorimeter used was a conduction type and the heat quantity measurement was by differential rates of heat transfer referred to as thermal leakage. The apparatus consisted of a block of polystyrene foam in which a hole was bored to fit an aluminum calorimeter vessel. The sample was placed in the aluminum container, cooled by liquid nitrogen to about -195°C, and placed in the polystyrene block. A polystyrene plug sealed the top of the vessel. The rate of heat transfer to the calorimeter cell was measured.

The heat transfer rate was determined for the polystyrene insulator by cooling a copper slug of known specific heat.

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heat. The slug was permitted to warm inside the insulator box and its temperature recorded as a function of time. The thermal leakage was:

$$q = mc_p \frac{\Delta T}{\Delta t} \tag{24}$$

where:

q = heat leakage, cal/min

m = weight of the copper slug

c_p = specific heat of the copper

$\frac{\Delta T}{\Delta t}$ = the slope of the warming curve of temperature versus time.

After the heat leak was established, the specific heat of an unknown material could be determined as the thermal leakage rate into the cell will be the same for the sample and the copper at any given temperature (Moline, et al., 1961). In determining the apparent specific heat of a food sample, the following calculations were made:

calorimeter plus sample

$$c_p = \frac{q}{m \frac{\Delta T}{\Delta t}} \tag{25}$$

where:

q = heat leakage previously determined

c_p = specific heat or heat capacity of the sample and calorimeter

m = weight of sample and calorimeter

ΔT = temperature change in degrees C

Δt = time in minutes;

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$$c_p' = \frac{c_p m - C}{m'} \qquad (26)$$

where:

c_p' = the apparent specific heat of the food sample

m' = the weight of the food sample

c_p = specific heat of the sample and calorimeter

m = weight of sample and calorimeter

C = the heat capacity of the aluminum vessel (mc_p).

Through plotting the warming curve for a particular sample as temperature versus time; the specific heat could be calculated at a particular temperature by determining the slope of the curve at that temperature. This is particularly helpful when the curve plot is not linear as would occur where phase transitions take place.

Moline _et_ _al_. first established the specific heat values for ice, gelatin and beef fat at -40°to -160°C. A model system was prepared from gelatin (protein), beef fat and water in proportion to simulate the composition of beef. The mixture was homogenized. The experimental apparent specific heat values obtained for the model system were considerably higher than those calculated from the sum of the components weighed percentage multiplied by the previously determined specific heat values. A similar difference was found between the experimental values for the actual beef samples and the calculated values. The results showed that the error in the computed fat, gelatin and

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water, between -40° C and -160° C would be 4.4% average error and 10.5% maximum error after a correction factor of 1.14 was applied.

In summary, foods at -40° F have a low apparent specific heat of about .4 to .5 cal/gm/°C. As the temperature increases toward the initial freezing point the apparent specific heat increases nearly logarithmically to a large value. When the freezing point is reached, the apparent specific heat immediately drops and levels out near .8 or .9 cal/gm/°C. This does not occur in pure water (Short et al., 1942). In foods as water begins to freeze, the solutes become more concentrated and the freezing point of the remaining water is depressed. This continues until all available water is frozen (Woolrich, 1933). Pure water will continue to freeze at a constant temperature until all water is frozen. It is this continued depression of the freezing point in which food and pure water differ in their response to freezing temperatures. Food has a freezing range. Generally when a freezing point is referred to, it is in actuality the initial freezing temperature or apparent freezing point.

The simple mixture rule by Siebel for predicting enthalpy values does not apply within the freezing zone. Siebel's equation is workable at low temperatures near -40° F as most of the water is frozen. The error in using the equation at low temperatures is less than 8%. The calculation is more reliable at temperatures above 40° F (4.4° C), in which case only about 3% variation exists between calorin

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calorimetrically measured enthalpy values and values calculated by Siebel's rule (Staph et al., 1951).

The food system can be considered to consist of two principal components; the dry solid matter and liquid water portions. During thawing of a food, sensible heat is absorbed by the solids, ice, and unfrozen water. Latent heat is absorbed in the phase transition of ice to water. Heat added will be distributed among the food components causing some phase transition to occur in the thawing zone. At the same time an increase in temperature will be recorded as sensible heat of the components. The energy added near the initial freezing point would not produce a proportional change in temperature, some energy is absorbed as latent heat of transition. This explains the large apparent specific heat values found near the initial freezing point. The calorimetric values obtained evidenced the apparent specific heat within the freezing region was a function of temperature (Short et al., 1942). It was found that the enthalpy value for a food could be predicted by considering the effect of the constituents present. Close agreement was found between calculated and experimentally obtained values when the amount of water frozen, liquid water, solidified lipids, liquid lipids, soluble solids, and insoluble solids were calculated using their weighted percentages and appropriate apparent specific or latent heat values (Bartlett, 1944; Staph, 1949; Riedel, 1951).

The apparent specific heat value of a food was found by Riedel to be a function of the water content. The effect was greatest above the freezing region. Egg whites varying by 10% moisture content had similar apparent specific heat values below freezing but a significant difference was observed above the initial freezing point. In general, an increase in water content produces an increase in the apparent specific heat values above the freezing region. Also, as soluble solids increase accompanying a decrease in total water content, the apparent specific heat decreases. In the freezing region the apparent specific heat value was a function of temperature and independent of the initial solute concentration (Riedel, 1951 and Short _et_ _al_., 1942). The enthalpy values were similar for general food classes that varied as much as 10% in water content. This can be explained by the fact that the greatest amount of water freezes out near the initial freezing point. The large change in enthalpy due to the latent heat of fusion is difficult to measure separately from the sensible heat. This characteristic is more recognizable at low temperatures where most of the ice is formed and energy added or removed is mainly sensible heat. The presence of lipids decreased the apparent specific heat in the freezing region. Foods containing large amounts of fat substances exhibited two separate enthalpy temperature curves one being the solidification of lipids and the other the latent heat of fusion for ice (Riedel, 1957b). "The thermal characteristics of all foodstuffs seem to follow the same general pattern regardless of the chemical properties or their amounts.

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The percentage of each of these constituents does, however, determine the relative values of the thermal characteristics" (Woolrich, 1966).

EXPERIMENTAL

A. Apparatus

The calorimeter consisted of a stainless steel vacuum dewar flask (model E-3, Hofman Division, Minnesota Valley Engineering Inc., New Prague, Minnesota). The calorimeter dewar had an internal diameter of 6 inches and an inside depth of 24 inches with a capacity of 10.8 liters. A vacuum of 10^{-5}mm of Hg or less insulated the dewar. Liquid nitrogen was used as the heat exchange medium in the calorimeter. The calorimeter containing liquid nitrogen was placed on a Shadowgraph balance (model 4212, Exact Weight Scale So., Columbus, Ohio) having a 22 pound or 10 kilogram capacity and sensitivity of ±0.75 grams. The scale had a 50 gram over-under range divided in 2 gram increments (Figure 11).

B. Sample Treatment and Preparation

Water samples were prepared from distilled-deionized water. Distilled water was demineralized using a Barnstead demineralizer standard cartridge (model BD-1, Barnstead Still and Sterilizer Co., Boston, Massachusetts). A durable heat sealable triple laminate pouch of mylar-saran-polyethylene was used as a container for the water samples (IKD Super All-Vak #13 pouch; International Kenfield Distributing Co., Chicago, Illinois). Water samples weighed in the range

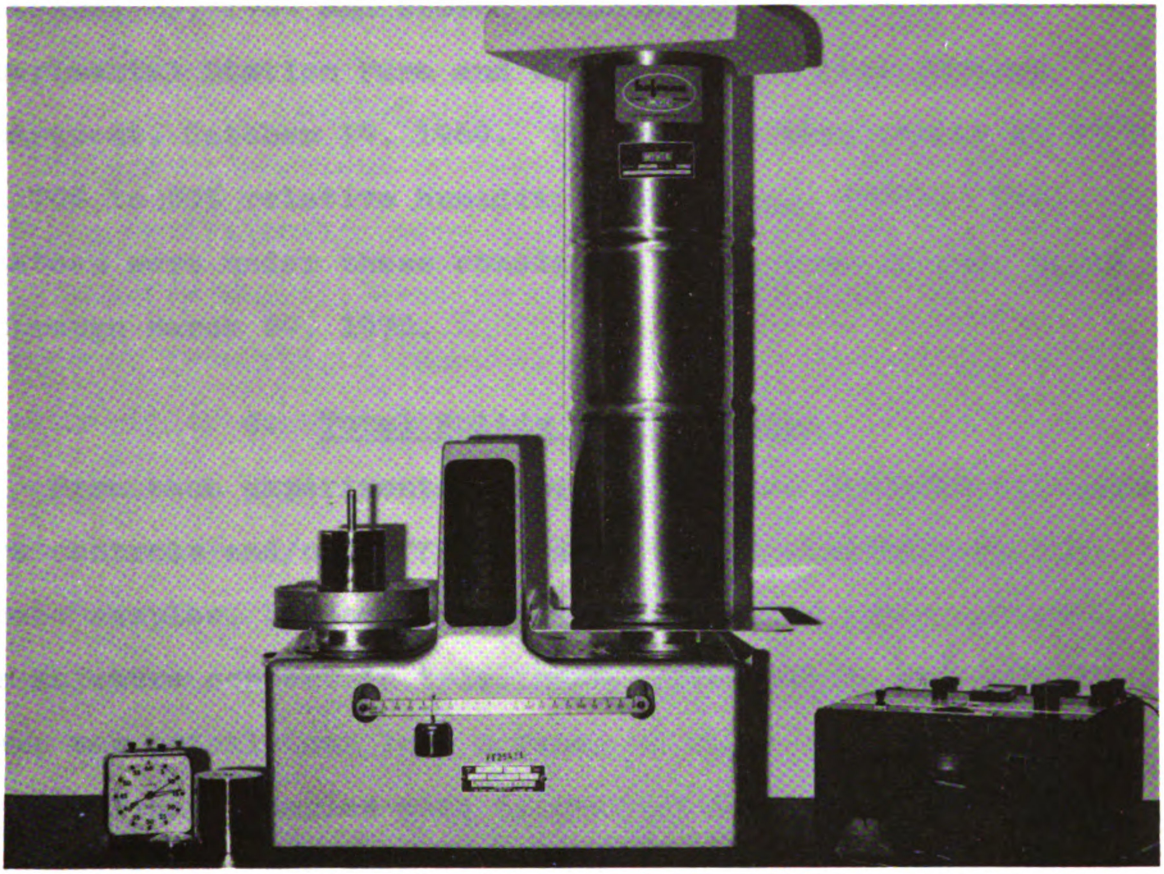

Figure 11. The calorimeter dewar and the measuring instruments.

of 231.0 to 79.29 grams and were contained within 1.43 to 0.98 grams of the triple laminate pouch with most samples weighing about 200 grams in a 1.0 gram pouch.

Russet Burbank variety potato samples used in this study were obtained from the Montcalm County Experiment Station Farm through the Department of Crop and Soil Sciences of Michigan State University. The potatoes were harvested on September 25, 1969 and stored immediately at 45°F at the Experimental Station Farm and brought to the Food Science Department, October 14, 1969. The samples were stored at 45°F and 70% to 80% relative humidity (Lutz <u>et</u> <u>al</u>. 1968). The potatoes were under these conditions until time of use, March 2 through March 29, 1970.

C. Total Solids Determination

From each experimental group held under different temperature controls and/or different days of experimentation, two potato samples, believed to be representative, were analyzed for moisture content in triplicate. Each sample of about 20 grams was quickly cut into a tared moisture dish and weighed. The triplicate samples were transverse sections about 1/8 inch thick cut from each end and the midpoint of the unpeeled potato. The large sample slices were cut into smaller fractions within the same moisture dish. The sample was frozen to -10°F and freeze dried at 150 μ without adding heat for 24 hours in a Stokes Freeze Dryer to a moisture content of approximately 6% (model 2003F-2, Stokes Instrument Co., Philadelphia, Pennsylvania). The freeze dried samples were allowed to equilibrate 6 hours at ambient conditions and reweighed. The sample was ground with mortar and pestle, transferred back to the moisture dish, and reweighed. Moisture analysis was continued using the vacuum oven method (AOAC, 1965). The samples were dried at 70°C and 26-28 inches of mercury for 12 to 14 hours (model 524, Freas Precision Co., Chicago, Illinois). Dry air passing through H_2SO_4 was admitted to the oven at a rate of 2-4 bubbles per second.

D. Soluble Solids and pH Analyses

Remaining portions of the potato sample used in the moisture determination were macerated in a Waring Blendor for 3 minutes and filtered through a milk filter disc (Kleentest Products, Milwaukee, Wisconsin). The pH was immediately determined on the filtrate by a Corning expanded scale pH meter (model 10, Corning Scientific Instruments, Medfield, Massachusetts). Next, the filtrate soluble solids were recorded using an ABBE-56 refractometer (model 53-45-56, Bausch and Lomb Optical Co., Rochester, New York), and all readings were corrected to 20° C.

E. Temperature Measurement and Control

Sample temperature was measured using polyvinyl insulated 24 gauge-duplex copper-constantan thermocouple wire (Industrial Instrument Supply and Mfg. Co., Detroit, Michigan). Copper-constantan thermocouple wire has a standard error limit of ± 0.8°C for the temperature range -59°C to 93°C (Caldwell, 1969). A temperature potentiometer (model 8692-2, Leeds and Northrup, New York) was used, having a limit of error ± 0.2%

of the range span -340°F (-206.67°C) to 230°F (210°C) or ±1.14°F (±0.63°C).

A precise and/or given temperature without variation was not and could not be easily obtained with the conventional refrigeration systems used. A refrigeration system which could be adjusted and maintained continuously at a given temperature without any variation would have been desirable as replicates could have more easily been determined. However, this was not attainable and would not be easily accomplished in industry where commercial refrigeration systems are used. Being unable to readily reproduce a given temperature provided a practical situation under which the method would similarly be used if accepted as an industrial tool.

Because a constant temperature could not repeatedly be used, a large number of water samples were used in the experiments in order to provide replications. The working temperatures selected were 21.67°C, room temperature; 7.22°C, walk-in refrigerator; 2.78°C, refrigerator; -14.44°C, freezer; and -16.11°C, walk-in freezer. All samples on which determinations were made were within a restricted range near these temperatures (range is dependant upon the source of refrigeration).

The principle reason for the use of these temperatures was their availability. However, the temperatures were representative of the temperature ranges to which many foods, at one time or another, are subjected either in processing and/or storage. Another influence in using the above temperatures was the test could not be conducted in the freezer or refrigerator (Puffer-Hubbard, Grand Haven, Michigan). The refrigerator and freezer samples required transfer of the sample from the lower temperature through the ambient room temperature to the apparatus, thus exposing the sample to an environment different from the test conditions. Samples determined at room temperature or while in the walk-in freezer or refrigerator (Chrysler & Koppin, Detroit, Mich.) were at all times held at the same test conditions. A comparison was then made possible as to the effect of transferring the sample versus those samples determined in the temperature controlled environment.

F. Procedure

The experimental procedure involves measurement of the amount of liquid nitrogen vaporized in removing the heat from a sample at a known temperature to -195.803°C (boiling point of liquid nitrogen at 1 atmos.) and bringing the sample to equilibrium with the calorimeter. Theoretically the quantity of heat removed from the sample is proportional to the amount of liquid nitrogen vaporized.

The prepared samples were placed at the desired temperature and permitted to equilibrate 18 hours. The refrigerator and freezer samples had to be weighed after the 18 hour period as weight loss occurred during the time period due to evaporation. The temperature of each sample was determined when removed from the refrigerator or freezer, weighed, and replaced. The temperature was periodically checked to determine when the samples had returned to the original temperature prior to weighing. Return to the initial temperature required about one hour; an additional hour was allotted to ensure the samples had stabilized at the holding temperature.

Those samples tested at room temperature, 21.7°C (71° F); walk-in refrigerator, 7.2°C (45°F); and walk-in freezer, -16°C (3°F) were weighed just before each sample immersion. The apparatus and other instruments were placed in the walk-in areas at the time of sample placement. In both instances, the samples were weighed on a top loading Mettler balance having a magnetic damper which would not be greatly affected by temperature (model P1200, Mettler Instrument Corp., Princeton, New Jersey).

The calorimeter dewar was filled to approximately 3/4 capacity with liquid nitrogen and allowed to come to equilibrium at a uniform heat leak on the Shadowgraph balance (observed as a sharp reduction in boiling rate). Initial weight loss measurements were made by taking consecutive time measurements, using a stop watch having a return to zero button, between 2 gram interval-weight losses and recorded as grams nitrogen per second loss. This value was designated as initial heat leak of the calorimeter. The weight of the calorimeter dewar with nitrogen was recorded upon determination of heat leak and a timer started to record the test duration time.

Immediately after the sample's temperature was measured, it was introduced into the calorimeter, which had the liquid level low enough to prevent liquid nitrogen from boiling over the top of the dewar. Heat loss from the sample produced vigorous boiling of the liquid nitrogen which subsided in about 4 minutes, the time being dependent principally on the sample size; then the rate of liquid nitrogen loss receded until it neared the initial heat leak rate.

The heat leak was again determined. The point at which consecutive timed readings for the 2 gram weight loss did not vary more than 5 seconds was designated the final heat leak rate and termination of the experiment. Simultaneously, the final weight of the calorimeter, liquid nitrogen, and sample was recorded and the duration time clock stopped. The initial and final heat leak rates were averaged with the mean value being designated the thermal leakage for the experimental time span.

The amount of time between 2 gram intervals was greater than 1 minute which was ample time for resetting the duration time clock to zero, making the temperature measurement of the next sample, recording the initial calorimeter weight for the following sample (as final calorimeter weight previous sample minus 2 grams), and obtaining an additional rate time reading for the heat leak. By this procedure consecutive samples were run without loss of time utilizing the final heat leak and weight as the initial measurements for the following sample. Samples were left in the calorimeter dewar and samples were added as long as total immersion of a sample below the liquid nitrogen level was possible. The approximate duration time was 20 minutes or 3 samples were run per hour.

Two timing devices were required. A clock is needed to measure the total time lapse for the experiment which includes establishing the heat leak rates. A stop watch was used for determi

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determining the initial and final heat leak rates in seconds.

G. Selected Literature Values and Calculations

(1) Selected Values for Liquid Nitrogen

The normal boiling point (n.b.p.) and heat of vaporization values at n.b.p. for liquid nitrogen selected to be used in this work were 77.34°K (-195.803°C) and 1334.8 cal/gm mole (47.6442 cal/gm), respectively. These values were from the work of Ziegler and Mullins (1963) who made a literature survey and selected the best experimental values that were available. They averaged the values from which evolved a value they termed "selected value."

(2) Method of Calculating Experimental Enthalpy

The gross amount of liquid nitrogen vaporized was found by subtracting the final weight of the system from the initial weight of the dewar and liquid nitrogen plus the sample weight. The final weighing was taken after vigorous boiling had subsided from the immersed sample and the system was equalized. Once the amount of nitrogen vaporized by the test sample had been measured, it was possible to determine the enthalpy change of the sample itself, using:

$$\Delta h = \Big[(\mathrm{LIN} \times k)(\rho \mathrm{liquid}/\rho \mathrm{liquid} - \rho \mathrm{vapor}) - (t \times r \times k)(\rho \mathrm{liquid}/\rho \mathrm{liquid} - \rho \mathrm{vapor}\Big]\, 1/m \qquad (27)$$

where:

Δh = heat evolved from the samples as cal/gm going from temperature T to reference temperature -195.803°C measured as cal/gm

LIN = mass of liquid nitrogen vaporized, grams

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k = constant of 47.6442 cal/gm the latent heat of vaporization for liquid nitrogen

t = test duration time in seconds

R = heat leak average of the determined initial and final rates, gm/sec

$\dfrac{\rho\text{liquid}}{\rho\text{liquid} - \rho\text{vapor}}$ = corrects for the vapor formed that does not leave the dewar, occupying the space left by the vaporized nitrogen

m = test sample mass in grams.

Use of the factor ρliquid/ρliquid - ρvapor does not take into account the sample volume or density. This factor permitted closer correlation of the experimental with calculated values.

(3) Correction Factors

The factor ρliquid/ρliquid - ρvapor corrected for the amount of nitrogen vaporized that remained in the dewar vessel occupying the space vacated by the vaporized liquid nitrogen. The correction ρliquid/ρliquid - ρvapor, ρ being density, was based on the relative densities of the liquid and the vapor of the liquid nitrogen at the temperature existing in the dewar (Falk, 1959 and Vance *et al.*, 1962). Strobridge (1962), using mathematical expressions derived from the literature, computed an extensive table for internal energy, enthalpy, entropy, and specific volume of nitrogen. The density of the nitrogen vapor was taken as the reciprocal of the specific volume at temperature T. Determination of the vapor temperature was accomplished using a multi-riter recorder (Texas Instruments Inc., Houston, Texas).

An additional correction for water samples above freezing was required. Nitrogen vaporized by the pouching material or energy evolved from the pouch was subtracted from the gross amount of nitrogen vaporized. As specific heat values for the pouch were not available for the low temperatures encountered; the average specific heat from 25°C to -195.803°C was experimentally determined. The average specific heat of the pouch material was found to be 0.24 cal/gm/°C. This value was determined using the calorimetric procedure described. Addition of a lead weight was required to submerge the pouching material in the liquid nitrogen. Once the average specific heat of the pouch had been determined, the bag correction was calculated by $c_p \times m \times \Delta T$.

(4) Thermal Properties of Water used to Evaluate the Experimental Systems

A measurement was required to determine the accuracy of the calorimetric method. It was decided to use the usual comparison between experimentally measured enthalpies and the calculated enthalpies derived from the best specific heat data given in the literature for water and/or ice. A literature search was made to find reliable specific heat values for water and ice. The low temperatures to which the ice was subjected (-195.803°C, liquid nitrogen) caused the author to desire a more recent reference than provided by either Hodgman et al. (1959) or Washburn (1926). Johnson (1964) made an extensive literature survey to select and present in tabular form the "best values" for the specific heats of ice. Whenever possible, the values selected by Johnson were used in preference to those presented by Hodgman and Washburn. A summary of the specific heat values for ice used in this study from the three mentioned sources is provided in Table 2.

TABLE 2

Literature Summary of Specific Heat Values for Ice

Temp °C	cp cal/gm	Rf	Temp °C	cp cal/gm	Rf	Temp °C	cp cal/gm	Rf
-250.00	.0309	b	-100.00	.3322	b	-23.70	.4599	c*
	.0361	c		.3290	c	-20.80	.4668	c
-203.15	.1499	a	-93.15	.3418	a	-20.00	.4637	b*
-200.00	.1561	b	-80.00	.3681	b	-14.80	.4782	c
	.1620	c	-73.15	.3752	a	-14.60	.4779	c*
-193.15	.1711	a	-60.00	.4015	b	-13.15	.4804	a
-183.15	.1914	a		.3920	c	-11.00	.4861	c
-180.00	.1990	c	-53.15	.4111	a	-8.10	.4896	c
-173.15	.2108	a	-40.00	.4350	b	-4.90	.4932	c
-160.00	.2300	c	-38.30	.4346	c*	-4.50	.4984	c
-153.15	.2462	a	-34.30	.4411	c	-4.30	.4989	c
-150.00	.2462	b,c	-33.15	.4446	a	-3.15	.4971	a*
-140.00	.2620	c	-31.80	.4454	c	-2.60	.5003	c
-133.15	.2772	a	-30.60	.4488	c	-2.20	.5002	c
-113.15	.3083	a	-24.50	.4605	c	0.00	.5019	a

Rf. [a]

Johnson, V. J. 1964. WADD Tech Rept. 60-56, Natl. Bur Standards.

[b] Washburn, E. W. 1926. "International Critical Tables" Natl. Research Council.

[c] Hodgman, C. D. et al. 1959. "Handbook of Chemistry and Physics". Chemical Rubber Co.

[*] Specific heat values that are out of sequence.

Johnson also prepared a graphical presentation of the specific heat values for ice. The graph showed that a slight curvilinear relationship existed between specific heat and temperature of ice. This indicated that an enthalpy calculated between two temperatures would not be correct using the arithmetic mean of specific heat value for the desired temperature range. The enthalpies for uneven increments were calculated between -195.803°C and 0° C.

The sum of the calculated enthalpy changes taken from -195.805°C through the desired temperature T, below 0° C, provided the total enthalpy change of that particular range, Table 3. The specific heat for a given temperature T was found by interpolating between specific heat values given in Table 2. All of the experimental measurements for ice were made from above -20° C; hence the base enthalpy total would be 55.9267 cal/gm. The enthalpy change was calculated for a temperature T (below 0° C) going to -195.803°C by:

$$\Delta h = h + \left(\frac{c_p + c_p'}{2}\right)\left(T - T'\right) \qquad (28)$$

or

$$\Delta h = 55.9267 \text{ cal/gm} + \left(\frac{c_p + .4652 \text{ cal/gm/}^\circ\text{C}}{2}\right)$$

$$\left[T - (-20.40^\circ\text{C})\right]$$

where:

h = enthalpy from -195.803° to -20.40°C (55.9267 cal/gm)

c_p = interpolated specific heat from Table 2 for the desired temperature T

T = temperature of the experimental sample, below 0°C

c_p' = specific heat of ice at -20.40°C or specific heat value below the interpolated sample's specific heat value (.4652 cal/gm/°C)

T' = temperature coinciding with c_p' (-20.40°C).

TABLE 3

Calculated Enthalpy Increments for Ice[a]

Temp °C	c_p	Avg. c_p	ΔT	cal/gm
-195.803	.1653			
-183.15	.1914	.1788	12.653	2.2569
-173.15	.2108	.2011	10.00	2.0112
-153.15	.2462	.2285	20.00	4.5698
-133.15	.2772	.2617	20.00	5.2342
-113.15	.3083	.2926	20.00	5.8526
-100.00	.3322	.3203	13.15	4.2115
-93.15	.3418	.3370	6.85	2.3084
-80.00	.3681	.3549	13.15	4.6672
-73.15	.3752	.3717	6.50	2.5458
-60.00	.4075	.3885	13.15	5.1073
-53.15	.4111	.4063	6.85	2.7832
-40.00	.4350	.4230	13.15	5.5630
-36.60	.4488	.4419	9.40	4.1538
-20.40	.4652	.4570	10.20	4.6616
				55.9267[b]
-13.15	.4804	.4728	7.25	3.4279
-3.15	.4971	.4888	10.00	4.8877
0.00*	.5019	.4995	3.15	1.5735
				65.8158[c]

[a] Specific heat values from Table 2

[b] Enthalpy value going from -195.803°C to -20.40°C

[c] Enthalpy value going from -195.803°C to 0°C

*Water is in solid state.

Water samples above 0° C were similarly calculated. The enthalpy change between -195.803°C and 0° C was derived from the sum of enthalpy increments within the range taken from Table 3 as 65.8158 cal/gm. As the specific heat for water was not exactly 1.0 except at 15°C; the specific heat value for the desired temperature T was interpolated from Table 4 given by Lange (1967).

TABLE 4

Specific Heat Values and Calculated Enthalpy Changes for Water from 21.7°C to 0°C[a]

Temp	c_p	Avg. c_p	ΔT	cal/gm
+21.7	.99828			
+15.0	1.00000	.99914	6.67	6.66092
+10.0	1.00184	1.00092	5.00	5.0046
+5.0	1.00477	1.00331	5.00	5.01653
0.0*	1.00874	1.00676	5.00	5.03375
				21.71580

[a]Values taken from Lange, 1967

*Water is in liquid state.

Again the enthalpy change was calculated going from temperature T (above 0°C) to 0°C by the summation of enthalpy increments as shown in Table 4. The enthalpy value going from a temperature above 0°C to -195.803° was found by:

$$\Delta h = h + L_h + \left(\frac{cp + cp'}{2}\right)\left(T - T'\right) \qquad (29)$$

where:

h = enthalpy going from -195.803° to 0°C (65.8158 cal/gm)

L_h = latent heat of fusion for ice (79.71135 cal/gm)

c_p = interpolated specific heat from Table 4 for desired temperature T

T = temperature of the experimental sample at above 0°C

c_p' = specific heat value below the interpolated sample heat value

T' = temperature coinciding with c_p'.

The value selected for the latent heat of fusion for water was 1436 cal/mole (79.71135 cal/gm) (Perry, 1963 and Hodgman, 1959). It appears that other commonly used values were derived from this value, such as: 80 cal/gm, 144 BTU/lb (80 cal/gm x 1.798823 $\frac{\text{BTU/lb}}{\text{cal/gm}}$ = 143.9 BTU/lb), 143.4 BTU/lb (79.71135 cal/gm x 1.798823 $\frac{\text{BTU/lb}}{\text{cal/gm}}$ = 143.39 BTU/lb).

(5) Riedel's Method for Calculating Fruit and Vegetable Enthalpy Change

The accuracy of the experimental procedure used in this study for determining food enthalpies was further shown by comparing the results obtained for potatoes with the equation developed by Riedel (Riedel, 1951). Riedel's investigations are regarded as the most reliable of those available in the literature. Riedel (1951) showed that a direct relationship existed between the dry substance content of any juice and its apparent specific heat. This was shown by plotting the apparent specific heat between 0° and 20° C for different fruit and vegetable juices against their dry substance content arriving at a linear relation expressed as:

$$c_j = 1.00 - .57x_o \qquad (30)$$

where:

c_j = the apparent specific heat for a juice

x_o = the dry substance content (refractive index of the juice).

The enthalpy change Δh of a partially frozen juice at temperature (T) in warming to 20°C is determined by:

$$\Delta h = x_i L + c_j\ (20^\circ C - T) \qquad (31)$$

where:

x_i = amount of ice present at T.

The latent heat of fusion for ice is a function of temperature (T) and can be calculated by:

$$L = 79.82 + .506T - .00187T^2. \qquad (32)$$

With x_o being the dry substance content of the unfrozen juice, Riedel said put x_s as the dry substance content of the unfrozen solution at the freezing temperature (T) then:

$$x_o = (1 - x_i)x_s \text{ or } x_i = 1 - \frac{x_o}{x_s}. \qquad (33)$$

The universal curve for juice prepared by Riedel in 1949 gives x_s as a function of T which can be expressed:

$$T(^\circ C) = -10x_s - 50x_s^3, \qquad (34)$$

giving for the temperature (T) the dry substance content of the unfrozen fraction for any fruit or vegetable juice (Riedel, 1951).

Riedel then introduced the terms x_i and c_j in equation 31 thus having all terms dependent on x_o or the dry solids content of the juices:

$$\Delta h_j = (L + 20 - T) - [L/x_s + .57(20 - T)\}x_o \qquad (35)$$

where:

Δh_j = enthalpy change of the juice.

"This equation permits calculation of the quantity of heat to be removed when cooling any juice with a known value of x_o to any freezing temperature T" (Riedel, 1951). For temperatures above the initial freezing point the x_i and terms containing L drop out giving:

$$\Delta h_j = (1.00 - .57x_o)(20 - T). \tag{36}$$

The insoluble solids must be considered when predicting the enthalpy for the whole fruit or vegetable. The total solids content x_{tot} was measured and the insoluble solids x_u then found by $x_{tot} - x_o$. The specific heat of .29 for the insoluble matter was established from the results of several tests and considered accurate for any temperature and any kind of fruit or vegetable (Riedel, 1951). The enthalpy change of the insoluble matter (x_u) was found by:

$$\Delta h_{xu} = .29x_u\Delta t. \tag{37}$$

The enthalpy change of the whole fruit or vegetable was the sum of the separately calculated values for the juice and insoluble substances:

$$\Delta h = (1 - x_u)\ h_j + .29x_u\Delta T \tag{38}$$

where:

Δh = enthalpy change of the whole fruit or vegetable.

The term dry substance content of a juice rather than the familiar soluble solids content was so used to call attention to the fact that Riedel did not express the soluble solids as percent sucrose. Riedel (1949) prepared a refractive index reference table for fruit and vegetable juices based on known concentrations of sucrose and glucose, the principle sugars present in many fruits and vegetables. The preparation of the table was prompted by the difficulty in determining the soluble solids of juices chemically by sugar analysis or by evaporation, both being laborious and uncertain. In this research the refractive index was found for the potato samples and the percent soluble solids (dry substance content) taken from Riedel's tabulated values. Refer to Table 8 under Results and Discussion.

RESULTS AND DISCUSSION

A. Selection of Moisture Determination Procedure

Moisture determination methods for fresh vegetables are not given in the AOAC Methods of Analysis. The analyses for total solids of fresh and canned fruits (method 20.010) and for total solids of processed and canned vegetable products (method 30.003), although not strictly followed, were used. Sample analysis using either method produces results that varied among individual potatoes sampled and between the triplicate determinations of a sample. The 20 gram sample prepared by cutting the potato in 1/4 inch cubes into a tared moisture dish of 2-1/2 inches diameter produced a lower moisture content than other methods tried. Blending the sample 3 to 5 minutes caused variations probably due to separation of the solid and liquid portions. The liquid fraction settled to the bottom of the blendor. Stirring the mascerated sample before taking sample triplicates did not ensure representative sampling. A 20 gram sample was too small for the Waring blendor. Adding a known sample weight to the blender plus water prior to masceration followed by water to flush out all of the sample required more water then desired. The original weighed sample would have required 3 or 4 moisture dishes filled nearly full. A Wiley mill was too small for the 20 gram sample even when cut into small pieces. Other problems posed by the sample slurry were: 1) a weighed sample placed immediately in a vacuum oven would foam over the moisture dish. The moisture dish had a 2-1/2 inch diameter and 1-3/4 inch height; 2) preliminary drying in the vacuum oven at 70° F with the release valve open resulted in gelatinization of the starch forming a hard residue. This also occurred when using a steam table; 3) as starch gelatinizes it is more likely to retain water that would otherwise be free to vaporize during drying, thus resulting in a lower apparent moisture value than the true value. As AOAC 30.003 analysis suggested three methods for preliminary drying, each requiring heat that would affect the starch-water absorption, the freeze dryer was used to achieve preliminary drying with the least starch gelatinization effect. Initial freeze drying at 150 μ to remove the larger water portion, grinding the partially dried sample, and final vacuum oven drying at 70° C under 26 to 27 inches of mercury provided better reproducibility between moisture determinations. These data are presented in Table 5.

TABLE 5

Comparison of Results Obtained with Various Methods of Moisture Analysis

Method	%Moisture^c	Range	Avg.	Sample
1. Vacuum oven^a	77.35 78.24 77.71 77.92	.89	77.81	cut up
2. Vacuum oven	79.42 79.97 80.17 77.85	2.32	79.36	blended
3. Freeze dry & V.O.^{b}	78.79 78.44 78.74 78.83	.39	78.70	blended
4. Freeze dry & V.O.	78.71 78.76 78.56 78.39	.37	78.61	cut up, ground after freeze drying

[a] conditions: 70°C, 26 to 28 inch Hg, 12 to 14 hours

[b] freeze dried at 150 μ, no heat added, 24 hours, vacuum oven dried as above

[c] % moisture values represent an average of 6 replicates or triplicate determination of 2 potatoes.

Method number 4 was preferred over number 3 because of uncertainties in getting a uniform and representative sampling from the blended mixture. Also, method number 4 was reproducible as found by comparing the range for the 6 samples of the different methods. In method number 4, a 20 gram sample of 1/4 inch potato cubes was tared into a 2-1/2 inch diameter moisture dish. Samples removed from the freeze dryer were equalized at ambient conditions prior to weighing and grinding so as to reduce possible moisture pick-up from the atmosphere during the grinding process. Joslyn (1950) remarked about the importance of particle size for dehydrated carrots and stated that moisture loss was significantly affected by the sieve size. Samples of smaller particle size, when vacuum oven dried under the same conditions would lose more water in a given period of time than larger size particles. Grinding of the freeze dried potato sample with a mortar and pestle resulted in 95.5% of the particles passing through a 30 mesh screen with 5.5% being larger than 30 mesh. Josyln stated that the largest weight loss takes place within 12 hours during drying fruits in vacuo at 70° C and that subsequent drying 1 or 2 hours longer would not appreciably change the results.

B. Sample Temperature Control

Several methods were tried and utilized to minimize sample temperature fluctuations when placed in different refrigerators. Range restriction provided the best means to achieve temperature replication in this study. Temperature range for a given refrigerator at one thermostat setting was termed the restricted range.

There were three areas in which experiments were conducted: laboratory, room temperature 22°C (71°F); walk-in refrigerator, 7°C (45°F); and walk-in freezer, -16°C (3°F). Magnitude of the restricted range was influenced by several variables. Sample temperatures from the refrigerator and freezer were dependent upon the air circulation cycle, compressor and fan functioning, and opening and closing the door during removal. Variation in temperature of the walk-in refrigerator and freezer was caused by the presence of the researcher, entering and leaving the walk-in, and turning off the forced air circulation. The temperature in the walk-in always increased from the initial temperature as the refrigeration was shut down during experimentation to reduce the influence of air currents affecting the reading of the scale and affect of the rate of nitrogen vaporized. After an increase of 5°F was reached, experimentation was stopped; however, this did not occur until about 3 hours had elapsed.

Several techniques were used to minimize sample temperature change. Samples were handled with tongs which had the tips covered with rubber hose reducing heat transfer from the handler. Two sets of tongs were kept in the refrigeration source and were used interchangeably during the experiments. As previously mentioned, samples in the refrigerator or freezer had to be weighed prior to experimentation as moisture evaporated from the sample during the temperature equilibration time. Samples removed from refrigeration to be weighed

were protected from the scale heat by a tared layer of styrofoam placed on the balance pan. Also to be certain that all samples had returned to the temperature recorded prior to weighing, the control sample containing thermocouples for monitoring sample temperatures was removed and weighed last. A styrofoam picnic type cooler was used to hold and minimize temperature variation due to ambient air entering while removing the sample. This technique was unsuccessful; however, the procedure of alternating experimental samples held at different temperatures located in the same area was more satisfactory. The refrigerator and freezer were adjacent to each other making it possible to set the apparatus in a position where it was readily accessible to both. In addition, room temperature samples could be run enabling observations to be obtained on samples held at three different temperature ranges during experimentation. Each sample required 20 to 30 minutes test duration requiring a minimum of one hour to examine a set of three samples. This permitted the samples time to recover from any temperature fluctuation caused by removing the previous test sample from that same temperature source.

Transfer of a sample from the refrigerator or freezer affected the sample temperature as heat energy was absorbed when the cooler sample contacted warmer air. Also slight condensation on the sample from the atmosphere would affect the sample temperature. Placement of the apparatus directly in front of the refrigerated rooms reduced the sample exposure time to the ambient. A sample could be transferred in 7 to 9 seconds from the time the refrigerator door was opened until the sample was placed in the dewar and the test initiated. The actual exposure time in the ambient was about 5 seconds.

The walk-in refrigerator and freezer provided additional reference temperatures and a means to check the effect that transferring a sample from the refrigerator to the apparatus had on the sample temperature and experimental results. The samples and all instruments used were at the same temperature of the refrigerated room. The primary source of temperature fluctuation was attributed to researcher's presence in the walk-in. Familiarity of the method permitted the researcher to leave the walk-in once the sample run was begun and return when the test was near completion. The Shadowgraph scale associated with the apparatus had a silicone fluid filled dashpot which was by-passed or disconnected while in the walk-ins to prevent the possible adverse influence temperature might have on the balance precision.

(1) Precautions Against Nitrogen Asphyxiation

Precautions were also taken to guard against nitrogen asphyxiation. According to Sax (1968) the minimum safety level for oxygen should be set at 13.33%. A thermal conductivity analyzer (model 7C, Beckman Instruments, Inc., Palo Alto, California) was used to indicate oxygen level in the walk-in during an experimentation period. The oxygen level dropped to 18% during a 4 hour testing period. However, to ensure safety at the end of an experimentation the forced air circulation was turned back on while the door to the walk-in remained open. To aid in replacing the air balance, a fan was placed in the door way to flush in air. The flushing procedure took about 3 to 5 minutes and did not significantly increase the walk-in temperature which would hinder other commodities stored in the room.

(2) Control Temperature Baths

Control temperature baths were unsuccessfully attempted to maintain a specific sample temperature. Freon 12 was refrigerated by adding dry ice (-109° F). The resulting temperature bath varied between -90° F and -109° F with a similar range when acetone was substituted for Freon 12 (-86° F to -96° F). The method was abandoned because the temperature could not be closely regulated, being dependent on the amount of dry ice present. Also, the heat transfer liquid adhered to the sample surface creating a source of error in the experiment, as the amount of liquid adhering to each sample could not be accurately determined.

C. Establishing Dewar Correction Factor

As the correction factor for the actual amount of liquid nitrogen vaporized by the sample was a function of the liquid and vapor densities, temperature of the vapor had to be determined. This required triplicate tests to be conducted at the three test areas. Vapor temperature was recorded continually prior to addition of a sample. The sample was added and the temperature recorded until it equalized near the original temperature and remained constant. Three thermocouples were located within the dewar at the liquid level, the upper lip of the dewar, and mid way between. Table 6 shows the results obtained from triplicate experiments. An average correction value was calculated for the vapor using the temperature at the liquid nitrogen surface and the vapor temperature at the dewar top. Comparing the recorded vapor temperature it was found that an even gradient did not exist between the liquid surface and dewar top. However, it was decided the average value was suitable as the correction factor was so small in magnitude that the effect of the uneven gradient would be negligible.

TABLE 6

Average Correction Factor (ρliquid/ρliquid $-\rho$ vapor)

For Rooms in which Experiments were Conducted

Temp. of areas in which testing was conducted °C	Vapor temp. top of dewar °C	ρliquid[b]	ρvapor	ρliquid/ ρliquid - ρvapor	Avg. cor. factor
	-195.803[a]	.8074	.0046	1.0057	
23.3	-13.3	.8074	.0013	1.0016	1.0037
7.2	-15.0	.8074	.0013	1.0016	1.0037
-17.8	-59.0	.8074	.0015	1.0019	1.0038

[a] Temperature of liquid nitrogen.

[b] Strobridge, T. R. 1962. Natl. Bur. of Stand. Tech. Note 129.

D. Heat Leak Rate and Duration Time

The results of these experiments also confirmed the relationship between the thermal leakage rate and test duration time. The principal experimental measurement was the amount of liquid nitrogen vaporized during the vigorous boiling period immediately following addition of the sample. At this point most of the energy absorbed from the sample took place. The vigorous boiling persisted through the first 3.5 to 4.5 minutes of the experiment. During this time the rate of nitrogen vaporized was so rapid it was impossible to manually record. Also, the rate of heat leakage could not be separated from the energy evolved from the test sample. Because of this the thermal leakage for the test duration time was considered to be an average of the initial and final heat leakage rates. The time from when the dewar vapors began to return to their original temperature and their arriving at the final equilibrium temperature (usually slightly less than the initial vapor temperature) required about 50 ± 8 minutes with an average rate of return being 1.22^{0} C/minute. Water and potato samples of about 227 grams were used with vapor temperatures measured by thermocouples placed at the top of the dewar.

The change in heat leak rate was slow, allowing accurate determinations shortly after the boiling had subsided. The thermal leakage rate did not return to the initial rate but remained somewhat less. A possible explanation for this was the cooling effect the vapors had on the exterior of the dewar and the immediate surroundings. The vapors being more dense than air flowed down the outer surface of the dewar. Twenty minutes was the approximate experimentation time. This allowed sufficient time for temperature recording, establishing of the heat leak rate, and preparation for the following sample. After 20 minutes, the vapor temperature had returned to 70.6% of its final temperature which would be reached after 50 minutes. After about 20 minutes the rate of change was so slight (0.5°C/minute) detection was difficult thus the experiment was terminated. The end of the experiment was determined by measuring the rate of weight loss of the dewar and its contents until an apparent constant rate was reached.

E. Effect of Atmospheric Pressure Changes

Pressure affects the latent heat of vaporization and normal boiling point of liquids. The effect of atmospheric pressure on the liquid nitrogen vaporization calorimetric system was investigated for possible correction factors. Hodgman *et al*. (1959) provided an equation to calculate the boiling point of liquid nitrogen as a function of pressure changes:

$$\text{boiling point} = -195.803^{\circ}\text{C} + 0.0109\,(p - 760) \quad (39)$$

where:

195.803°C = the normal boiling point of liquid nitrogen at 760 mm Hg

0.0109 = constant

p = the barometric pressure mm Hg.

Gold *et al*. (1969) in his review of thermophysical properties of liquids gave a formula which could be used for calculating the latent heat of vaporization in relation to temperature of the liquid:

$$\lambda = \lambda_B\left(\frac{1 - T_R}{T_{B,R}}\right)^{0.38} \quad (40)$$

where:

λ = corrected latent heat of vaporization

λB = latent heat of vaporization at the normal boiling point, 47.6442 cal/gm for liquid nitrogen

$T_R = \frac{T}{TC}$

T = boiling point from equation 39, °K

TC = critical temperature, 126.26°K

$T_{B,R} = \frac{T_B}{TC}$

T_B = normal boiling point, 77.347°K

Established values from Strobridge (1962) for liquid nitrogen at 0.7 atm. were used to substantiate the two above methods of calculation. Comparisons of Strobridge's values with those calculated are boiling point -198.7°C (calculated -198.3°C) and latent heat of vaporization 48.51 cal/gm (calculated 48.53 cal/gm).

During a week of experimentation the barometric pressure was recorded at the beginning and end of all experiments. The lowest reading was 737.3 mm Hg or 0.97 atm. (700 mm Hg equals 0.92 atm.). The average barometric reading for the week, 747.4 mm Hg, was used to calculate the boiling point of nitrogen and latent heat of vaporization changes. The boiling point of nitrogen at 747.4 mm Hg was -195.9°C (normal boiling point -195.8°) and latent heat of vaporization 47.68 cal/gm (at 760 mm Hg 47.64 cal/gm). Enthalpies found during the week changed in the second and third decimal place using the corrected boiling point and latent heat of vaporization. The corrections did not make a significant difference in the final enthalpy values of samples. Corrections for atmospheric pressure changes were not used in any of the data collected.

F. Experimentally Determined Enthalpy Changes for Water and Ice

Table 7 is composed of the average values for water and ice replicates taken at each temperature listed. Each experimental determination is found in the appendix, pages A1 through A 8. Values represent the enthalpy change going from the initial holding temperature to -195.803°C, the reference temperature of liquid nitrogen. The experimental values are in close agreement with those calculated using literature values available for the specific heat of water and ice. The maximum per cent deviation between calculated value and experimental mean was 2.0%; the average per cent deviation for the Table 7 data as a whole was 0.5%. The difference between the experimental and the calculated value was divided by the calculated value to obtain the per cent deviation, 100(experimental - calculated/calculated), as presented in Table 7.

Relying on the accuracy of the literature values for water (Tables 2 through 4) it was found that the liquid nitrogen calorimeter is accurate to within 2.0% when using the wide temperature range to -195.803°C. The precision of this method was observed from particular temperatures where several replicate enthalpies were obtained. No significant variation occurred between replicates. Appendix A for

TABLE 7

Experimental Enthalpy Differences (Δh) for Water and Ice in cal/gm between T and -195.803°C

Refrigeration source	T°C	No. of Replicates	Experimental mean[a] cal/gm	Calculated[b] cal/gm	Deviation[c]	%Deviation[d]
laboratory room temp.	21.7	17	167.50	167.24	0.26	0.2
walk-in refrigerator	10.6	2	156.73	156.15	0.60	0.4
	9.4	1	156.41	155.02	1.39	0.9
	8.3	3	155.97	153.91	2.06	1.3
	8.0	1	154.66	153.63	1.03	0.7
	7.8	3	153.64	153.35	0.29	0.2
	7.2	7	154.13	152.79	1.34	0.9
	6.7	5	154.27	152.24	2.03	1.3
refrigerator	6.7	1	152.45	152.24	1.68	1.1
	4.9	1	149.06	150.56	-1.50	-1.0
	4.4	3	150.09	150.01	0.08	0.0
	3.9	8	149.29	149.44	-0.15	-0.1
	3.3	8	149.78	148.89	0.89	0.6
	3.0	10	149.18	148.61	0.57	0.4
	2.8	17	149.11	148.33	0.78	0.5
	2.5	2	149.06	148.05	1.01	0.7
	2.2	2	147.17	147.77	-0.61	-0.4
freezer	-13.3	2	59.96	59.27	0.67	1.2
	-13.9	7	58.96	59.00	-0.04	-0.1
	-14.2	6	59.06	58.87	0.19	0.3
	-14.4	8	59.14	58.74	0.40	0.7
	-15.0	2	57.94	58.47	-0.53	-0.9
	-16.1	1	57.33	57.94	-0.61	-1.1
	-17.5	3	58.45	57.29	1.16	2.0
	-17.8	6	57.29	57.15	0.14	0.2
	-17.9	2	57.28	57.10	0.18	0.3
walk-in freezer	-14.7	2	58.97	58.60	0.37	0.6
	-15.0	2	58.71	58.42	0.29	0.5
	-15.6	3	58.29	58.20	0.09	0.2
	-15.8	2	58.51	58.07	0.44	0.8
	-16.1	3	58.04	57.94	0.10	0.2
	-16.7	4	57.69	57.68	0.01	0.0

[a] Mean experimental values from Appendix, pages A1 through A 8.

[b] The sources for calculated values are listed in Tables 2, 3 and 4.

[c] Deviation of experimental, E, from the calculated, C; E - C.

[d] 100(E - C)/C.

individual water enthalpies has a maximum of +3.0 to -2.5% deviation between experimental and calculated enthalpy values. All experiment enthalpies (144) were within 3.0% variation with 91.2% varying less than 2.0% from the calculated and 64.4% of the values were below 1.0% deviation.

The conditioning areas that were large enough to set up the experimental apparatus were the laboratory, walk-in refrigerator and walk-in freezer. Samples that were run in these areas were at the same temperature as their environment and did not undergo a transfer from the refrigeration source. Samples conditioned in the upright refrigerator and freezer required the apparatus to be set up outside the source of refrigeration. These samples had to be transferred from the refrigeration source to the apparatus which was at room temperature. The laboratory room temperature, walk-in refrigerator and walk-in freezer, where the refrigeration source was the same temperature as the testing area, did show slightly less deviation than the refrigerator and freezer samples. Water samples were affected by transferring from the refrigeration source to the test area (at room temperature). The magnitude of this effect does not appear to be significant. No large differences between experimental and calculated values existed for water samples determined in the different testing areas. The transfer time was less than 10 seconds. Thermocouples indicated that a slight temperature increase of 3° to 6°F occurred at the sample surface during this period. No change was found for the sample interior. The sensitivity of this calorimetric method was not sufficient to detect the small sensible heat increase at the sample's surface. Detectable differences were not apparent in samples determined at the different refrigeration areas.

G. Experimentally Determined Values for Change in Enthalpy of Potatoes

Experimentally determined values for change in enthalpy of potatoes are given in Appendix B1 through B 3. The values are for various ranges from each conditioning temperature to -195.803° C. Previous results are not available to substantiate values found for samples brought to this low temperature. To use this calorimetric method to obtain meaningful data, it was necessary to subtract the value for change in enthalpy undergone by the sample between a given temperature and -195.803°C from the value for enthalpy change between a second (and higher) temperature and -195.803° C. Thus, the enthalpy difference between any two temperatures can be calculated by subtracting $\Delta h_2 - \Delta h_1$.

(1) Potato Analyses

In order to utilize Riedel's method for calculating fruit and vegetable enthalpies, representative potato samples were analyzed for moisture, total solids, soluble solids and/or "dry substance content" of the juice. The results of the analyses are listed in Table 8. Each moisture value represents the average of 6 determinations. Two potatoes were used, one large and one small size. Three moistures were run on each potato using a section from each end and a middle portion. The analyses for the two potatoes were averaged arriving at the values given in Table 8.

TABLE 8

Potato Analyses

Date[a]	3/2	3/10	3/11	3/21	3/22	3/26	3/28	avg.
moisture %	78.71	78.76	78.56	78.39	78.70	78.65	78.87	78.66
total solids %	21.29	21.24	21.44	21.61	21.30	21.35	21.13	21.34
soluble solids %	6.37	6.77	6.77	6.22	6.22	6.77	6.22	6.0
dry substance component[b]	6.6	7.0	7.0	6.5	6.5	7.0	6.5	7.0
pH	6.06	6.02	6.00	6.04	6.03	6.00	5.96	6.0

[a] Harvested September 25, 1969.
[b] Riedel (1949), soluble solids refractive index reference table for fruit and vegetable juices.

The values for Table 8 were in close agreement for the different days in March, 1970 that calorimetric measurements were made. The average values from the analyses were used to simplify the calculations. The moisture content found agrees with published values of Lutz _et al_. (1968) at 77.8% and Pope (1969) 77.7%. The pH of 6.0 was the same as tabulated by Whiteman (1957) but the experimentally determined soluble solids was slightly higher than his 5.9% value. This may be attributed to the shorter storage period given by Whiteman.

(2) Compensation for Moisture Lost in Temperature Equalization

Potato samples held at different refrigerated temperatures lost moisture by evaporation. The amount was detected by weighing the sample before placement in the desired temperature unit. A final weight was determined about 2 hours prior to conducting the calorimetric experiment. The difference between the two weighings was considered that amount of moisture evaporated during the time required for temperature equilibration of the test sample. The greatest moisture loss was found for those samples held in the walk-in freezer and freezer; the moisture content being 78.60% and 78.63%, respectively. The amount of water present initially was calculated using 78.66% moisture from Table 8 and the weight loss between weighings subtracted as water evaporated. The per cent moisture was recalculated using the adjusted water content and dividing by the final sample weight. The adjusted moisture values obtained are averages of all the experimental samples determined for a particular refrigeration source. The moisture values and other necessary values for calculating the potato sample enthalpies are given in Table 9.

(3) Interpolated Potato Enthalpies

The interpolated values used for Table 10 were taken from the averaged replicate values found in Appendix B1 through B 3 for potato samples. Experimental change in enthalpy, column 1, was found by interpolating the difference between the enthalpy at two experimental temperatures going

TABLE 9

Values for Calculating Interpolated Potato Enthalpies Using Riedel's Equation

	Refrigeration Source			
	Room Temp. and walk-in Refrigerator	Refrigerator	Walk-in Freezer	Freezer
moisture %	78.66	78.65	78.60	78.63
total solids % content (X_{tot})	21.34	21.35	21.40	21.37
dry substance % content (X_o)	7.00	7.00	7.00	7.00
solids insoluble % (X_u)	14.34	14.35	14.40	14.37

to the temperature of -195.803°C ($\Delta h_2 - \Delta h_1$). Column 2, calculated enthalpy, was derived using equation 30 through 38, Riedel's method of calculating change in enthalpy for fruits and vegetables (Riedel, 1951). Variation, listed in column 3, between the two enthalpy values was found by subtracting the calculated value from the experimental. The variation was divided by the calculated giving per cent that experimental enthalpy change deviated from the calculated change in enthalpy, column 4, 100 (experimental - calculated)/ calculated. It was found that 88.6% of the interpolated enthalpy changes (70 values) varied less than 5% from the calculated value. The maximum per cent variation between calculated values and experimental mean was 8.4%, The average per cent variation for Table 10 data as a whole was 2.8%.

TABLE 10

Changes in Enthalpy of Potatoes Over Various Temperature Ranges as Determined Experimentally and as Derived by Use of the Riedel Equations

		Enthalpy Difference (Δh) in cal/gm Between 26.1°C (Laboratory Room Temperature) to T°C			
Refrigeration Source	T°C	(1) Experimental mean^a cal/gm	(2) Calculated^b cal/gm	(3) Variation^c	(4) % Variation^d
walk-in freezer	-14.4	91.94	89.05	2.89	3.2
	-15.0	92.28	89.43	2.85	3.2
	-15.6	92.38	89.82	2.56	2.9
	-16.4	92.54	90.33	2.21	2.4
freezer	-15.6	92.08	89.80	2.28	2.5
	-16.1	92.78	90.18	2.60	2.9
	-16.7	92.07	90.54	1.53	1.7
		Enthalpy Difference (Δh) in cal/gm Between 25.0°C (Laboratory Room Temperature) to T°C			
walk-in freezer	-14.4	89.84	88.09	1.75	2.0
	-15.0	90.18	88.48	1.70	1.9
	-15.6	90.28	88.86	1.42	1.6
	-16.4	90.44	89.37	1.07	1.2
freezer	-15.6	89.93	88.83	1.10	1.2
	-16.1	90.68	89.22	1.46	1.6
	-16.7	89.97	89.58	0.39	0.4
		Enthalpy Difference (Δh) in cal/gm Between 23.9°C(Laboratory Room Temperature) to T°C			
walk-in freezer	-14.4	84.99	87.13	-2.14	-2.5
	-15.0	85.33	87.52	-2.19	-2.5
	-15.6	85.43	87.91	-2.48	-2.8
	-16.4	85.59	88.41	-2.82	-3.2
freezer	-15.6	85.08	87.88	-2.80	-3.2
	-16.1	85.83	88.26	-2.43	-2.8
	-16.7	85.12	88.62	-3.50	-3.9

(TABLE 10 cont.)

		Enthalpy Difference (Δh) in cal/gm Between 8.1°C (Walk-in Refrigerator Temperature) to T°C			
		(1)	(2)	(3)	(4)
Refrigeration Source	T°C	Experimental mean[a] cal/gm	Calculated[b] cal/gm	Variation[c]	% Variation[d]
walk-in freezer	-14.4	72.62	73.50	-0.88	-1.2
	-15.0	72.96	73.89	-0.93	-1.3
	-15.6	73.06	74.27	-1.21	-1.6
	-16.4	73.22	74.78	-1.56	-2.1
freezer	-15.6	72.71	74.24	-1.53	-2.1
	-16.1	73.46	74.63	-1.17	-1.6
	-16.7	72.75	74.98	-2.23	-3.0
		Enthalpy Difference (Δh) in cal/gm Between 7.5°C (Walk-in Refrigerator Temperature) to T°C			
walk-in freezer	-14.4	70.28	72.98	-2.70	-3.7
	-15.0	70.62	73.36	-2.74	-3.7
	-15.6	70.72	73.75	-3.03	-4.1
	-16.4	70.88	74.25	-3.37	-4.5
freezer	-15.6	70.37	73.72	-3.35	-4.5
	-16.1	71.12	74.10	-2.98	-4.0
	-16.7	70.41	74.46	-4.05	-5.4
		Enthalpy Difference (Δh) in cal/gm Between 7.2°C (Walk-in Refrigerator Temperature) to T°C			
walk-in freezer	-14.4	72.15	72.74	-0.59	-0.8
	-15.0	72.49	73.12	-0.63	-0.7
	-15.6	72.59	73.50	-0.91	-1.2
	-16.4	72.75	74.01	-1.26	-1.7
freezer	-15.6	72.24	73.48	-1.24	-1.7
	-16.1	72.99	73.86	-0.87	-1.2
	-16.7	72.28	74.22	-1.94	-2.6
		Enthalpy Difference (Δh) in cal/gm Between 6.7°C (Walk-in Refrigerator Temperature) to T°C			
walk-in freezer	-14.4	69.38	72.26	-2.88	-4.0
	-15.0	69.72	72.64	-2.92	-4.0
	-15.6	69.82	73.03	-3.21	-4.4
	-16.4	69.98	73.54	-3.56	-4.8
freezer	-15.6	69.47	73.01	-3.54	-4.8

Refrigeration Source	T^{o} C	(1) Experimental mean[a] cal/gm	(2) Calculated[b] cal/gm	(3) Variation[c]	(4) % Variation[d]
freezer (cont.)	-16.1	70.22	73.39	-3.17	-4.3
	-16.7	69.51	73.74	-4.23	-5.7
		Enthalpy Difference (Δh) in cal/gm Between 3.3°C (Refrigerator Temperature) to T°C			
walk-in freezer	-14.4	69.48	69.38	0.10	0.1
	-15.0	69.82	69.76	0.06	0.1
	-15.6	69.92	70.15	-0.23	-0.3
	-16.4	70.88	70.66	-0.58	-0.8
freezer	-15.6	69.57	70.12	-0.55	-0.8
	-16.1	70.32	70.50	-0.18	-0.3
	-16.7	69.61	70.86	-1.25	-1.8
		Enthalpy Difference (Δh) in cal/gm Between 3.1°C (Refrigerator Temperature) to T°C			
walk-in freezer	-14.4	68.55	69.15	-0.60	-0.9
	-15.0	68.89	69.53	-0.64	-0.9
	-15.6	68.99	69.91	-0.92	-1.3
	-16.4	69.15	70.42	-1.27	-1.8
freezer	-15.6	68.64	69.89	-1.25	-1.8
	-16.1	69.39	70.27	-0.88	-1.3
	-16.7	68.68	70.63	-1.95	-2.8
		Enthalpy Difference (Δh) in cal/gm Between 2.8°C (Refrigerator Temperature) to T°C			
walk-in freezer	-14.4	64.25	68.90	-4.55	-6.6
	-15.1	64.69	69.28	-4.59	-6.6
	-15.6	64.79	69.67	-4.88	-7.0
	-16.4	64.95	70.18	-5.23	-2.5
freezer	-15.6	64.44	69.65	-5.21	-7.5
	-16.1	65.19	70.03	-4.84	-6.9
	-16.7	64.48	70.38	-5.90	-8.4

[a] Mean experimental enthalpy changes for temperatures are from pages B1 through B 3. Experimental mean values were obtained by $\Delta h_2 - \Delta h_1$.

[b] Calculated values derived using Riedel's equations, numbers 30 through 38.

[c] Variation of experimental, E, from the calculated, C; E - C.

[d] 100(E - C)/C.

H. Riedel's Experimental and Calculated Fruit and Vegetable Enthalpies

Table 11 represents Riedel's (1951) experimental enthalpy values of fruits and vegetables for comparison with the values calculated by the author using the equations given by Riedel. The reason for preparing this table was to measure the magnitude of disagreement between Riedel's experimental and calculated values. The graphic representation of this data by Riedel showed there was a deviation between experimental and calculated values but it was difficult to determine the amount the values varied from the graph. All of Riedel's data are not presented in this table nor is each sample shown calculated at all temperatures. The per cent that the experimental varied from calculated values was obtained by dividing the deviation by the calculated value , 100(experimental - calculated)/calculated. Per cent deviation from Table 11 was as great as 15.1% for onions, 10.2% for peas at -4.17°C, and -8.5% for spinach at -9.34° C. The closest agreement between calculated and experimental enthalpy was at temperatures below -10.0°C (14°F).

Tressler et al. (1968) also calculated enthalpy of the fruits and vegetables investigated by Riedel. Tressler used equation 38 and the Mollier chart (enthalpy concentration chart) developed by Riedel. The Mollier chart provided by Riedel made it possible to estimate enthalpy using equation 38 only. The writer felt that accurate reading of the Mollier chart was difficult and would create possible

TABLE 11

Comparison of Riedel's Experimental Data with Calculated Enthalpy Differences (Δh) in cal/gm Between T and 20°C

T°C	carrots	peas	spinach	Onions	strawberries	raspberries
-29.92						
experimental[a]	99.40	-	103.00	-	103.30	93.20
calculated[b]	98.68	-	102.36	-	100.82	94.19
deviation[c]	0.72	-	0.64	-	2.48	-0.99
% deviation[d]	0.7	-	0.6	-	2.5	-1.1
-19.65						
experimental[a]	93.30	86.60	-	91.50	-	87.10
calculated[b]	93.58	81.68	-	90.66	-	89.04
deviation[c]	-0.28	4.92	-	0.84	-	-1.94
% deviation[d]	-0.3	6.0	-	0.9	-	-2.2
-14.50						
experimental[a]	89.60	79.10	-	87.80	93.80	83.20
calculated[b]	89.63	76.94	-	86.20	92.29	84.96
deviation[c]	-0.3	2.16	-	1.60	1.51	-1.76
% deviation[d]	0.0	2.8	-	1.9	1.6	-2.1
-9.34						
experimental[a]	84.50	73.30	82.90	82.90	89.00	78.10
calculated[b]	84.06	69.88	90.64	79.69	87.33	79.14
deviation[c]	0.44	3.42	-7.74	3.21	1.67	-1.04
% deviation[d]	0.5	4.9	-8.5	4.0	1.9	-1.3
-4.17						
experimental[a]	74.20	58.40	82.60	74.40	78.50	66.60
calculated[b]	71.80	53.01	82.10	64.62	77.20	66.06
deviation[c]	2.40	5.39	0.50	9.78	1.30	0.54
% deviation[d]	3.3	10.2	0.6	15.1	1.7	0.8
-0.05						
experimental[a]	18.58	16.90	18.40	18.20	18.70	17.60
calculated[b]	18.30	17.20	18.84	18.37	18.79	17.99
deviation[c]	0.28	-0.30	-0.44	-0.17	-0.09	-0.39
% deviation[d]	1.5	-1.7	-2.3	-0.9	-0.5	-2.2

[a] Experimental cal/gm (Riedel, 1951).

[b] Calculated cal/gm, derived by the author using Riedel's (1951) equations and data.

[c] Deviation of experimental, E, from the calculated, C; E - C.

[d] 100(E - C)/C.

additional errors as compared with values derived from equation 30 through 38 without the Mollier chart. Because of the difference in calculation, the author and Tressler do not agree exactly on the maximum enthalpy deviation. Except for plums and onions, the values calculated by Tressler varied from Riedel's measured values by less than 5.0%. Tressler found the experimental enthalpy change for plums and onions varied 12.0% from the calculated. Tressler (1968) stated that in working with fruit and vegetable juices, Riedel found the enthalpy data varied within approximately 2.0% between calculated and experimental values.

Riedel mentioned the range of application could have been exceeded for peas and onions which were observed from the graph provided to have varied significantly from the calculated value. However, of the 29 fruits and vegetables or juices studied by Riedel, 11 deviated noticeably from the calculated enthalpy at -4.17° C (24.5° F). The larger deviation between values occurred near the initial freezing point; however, most frozen foods are stored below 0° F (-17.8° C) or lower. Riedel stated the "deviations of the measured values from the calculated ones are negligible at those low temperatures (0° F) even for peas and onions" (Riedel, 1951).

I. Interpolated Water and Ice Enthalpies

Interpolated changes in enthalpy for water and ice using the average replicate values from Appendix A1 through A8 are presented in Table 12. Experimental enthalpy changes

TABLE 12

Enthalpy Values for Water and Ice Calculated by Interpolation between Experimentally Determined Enthalpies

		Enthalpy Difference (Δh) in cal/gm Between 21.7°C (Laboratory Room Temperature) and T°C			
		(1)	(2)	(3)	(4)
Refrigeration Source	T°C	Experimental mean[a] cal/gm	Calculated[b] cal/gm	Deviation[c]	% Deviation[d]
walk-in refrigerator	10.6	11.37	11.07	0.30	2.7
	8.3	11.53	13.38	-1.85	-13.8
	7.8	13.84	13.88	-0.04	-0.3
	7.2	13.37	14.48	-1.11	-7.7
	6.7	13.23	14.98	-1.75	-11.7
refrigerator	4.4	17.41	17.29	0.12	0.7
	3.9	18.21	17.79	0.42	2.4
	3.3	17.72	18.40	-0.68	-3.7
	3.0	18.32	18.70	-0.38	-2.0
	2.8	18.39	18.90	-0.51	-2.7
	2.2	20.33	19.51	0.82	4.2
freezer	-13.9	108.54	108.25	0.29	0.3
	-14.2	108.44	108.39	0.05	0.0
	-14.4	108.36	108.49	-0.13	-0.1
	-15.0	109.56	108.78	0.78	-0.7
	-17.5	109.05	109.96	-0.91	-0.8
	-17.8	110.21	110.10	0.11	0.1
	-17.9	110.22	110.15	0.07	0.1
walk-in freezer	-14.7	108.53	108.63	-0.10	-0.1
	-15.0	108.79	108.78	0.01	0.0
	-15.6	109.21	109.06	0.15	0.1
	-16.1	109.46	109.30	0.16	0.1
	-16.7	109.81	109.58	0.23	0.2
		Enthalpy Difference (Δh) in cal/gm Between 7.2°C (Walk-in Refrigerator) and T°C			
walk-in refrigerator	10.6	2.00	3.41	-1.41	-41.3
	8.3	1.84	1.10	0.74	67.3
	7.8	0.47	0.60	-0.13	-21.7
	6.7	0.14	0.50	-0.36	-72.0
refrigerator	4.4	4.04	2.81	1.23	43.8
	3.9	4.84	3.31	1.53	46.2
	3.3	4.35	3.92	0.43	11.0
	3.0	4.95	4.22	0.73	17.3

Refrigeration Source	T°C	(1) Experimental mean[a] cal/gm	(2) Calculated[b] cal/gm	(3) Deviation[c]	(4) % Deviation[d]
refrigerator (cont)	2.8	5.02	4.42	0.60	13.6
	2.2	6.96	5.03	1.93	38.4
freezer	-13.9	95.17	93.77	1.40	1.5
	-14.2	95.07	93.91	1.16	1.2
	-14.4	94.99	94.01	0.98	1.0
	-15.0	96.19	94.30	1.89	2.0
	-17.5	95.68	95.48	0.20	0.2
	-17.8	96.84	95.62	1.22	1.3
	-17.9	96.85	95.67	1.18	1.2
walk-in freezer	-14.7	95.15	94.15	1.00	1.1
	-15.0	95.42	94.30	1.12	1.2
	-15.6	95.86	94.58	1.28	1.4
	-16.1	96.09	94.82	1.27	1.3
	-16.7	96.44	95.10	1.34	1.4
		Enthalpy Difference (Δh) in cal/gm Between 2.8°C (Refrigerator) and T°C			
walk-in refrigerator	10.6	7.07	7.83	-0.76	-9.7
	8.3	6.86	5.52	1.34	24.3
	7.8	4.55	5.02	-0.47	-9.4
	7.2	5.02	4.42	0.60	13.6
	6.7	5.16	3.92	1.24	31.6
refrigerator	4.4	0.98	1.61	-0.63	-39.1
	3.9	0.18	1.11	-0.93	-83.8
	3.3	0.67	0.50	0.17	34.0
	3.0	0.07	0.20	-0.13	-65.0
	2.2	1.94	0.61	1.33	68.6
freezer	-13.9	90.15	89.35	0.80	0.9
	-14.2	90.05	89.49	0.56	0.6
	-14.4	89.97	89.59	0.38	0.4
	-15.0	91.17	89.88	1.29	1.4
	-17.5	90.66	91.06	-0.40	-0.4
	-17.8	91.82	91.20	0.62	0.7
	-17.9	91.83	91.25	0.58	0.6
walk-in freezer	-14.7	90.14	89.73	0.41	0.5
	-15.0	90.40	89.88	0.52	0.6
	-15.6	90.82	90.16	0.66	0.7
	-16.1	91.07	90.40	0.67	0.7
	-16.7	91.42	90.68	0.74	0.8

		Enthalpy Difference (Δh) in cal/gm Between -14.4°C (Freezer) and T°C			
Refrigeration Source	T°C	(1) Experimental mean[a] cal/gm	(2) Calculated[b] cal/gm	(3) Deviation[c]	(4) % Deviation[d]
walk-in refrigerator	10.6	96.99	97.42	-0.43	-4.4
	8.3	96.83	95.11	1.72	1.8
	7.8	94.52	94.61	-0.09	-0.1
	7.2	94.99	94.01	0.98	1.0
	6.7	95.13	93.51	1.62	1.7
refrigerator	4.4	90.95	91.20	-0.25	-0.3
	3.9	90.15	90.70	-0.55	-0.6
	3.3	90.64	90.09	0.55	0.6
	3.0	90.04	89.79	0.25	0.3
	2.8	89.97	89.59	0.38	0.4
	2.2	88.03	88.98	-0.95	-1.1
freezer	-13.9	0.18	0.24	-0.06	-25.0
	-14.2	0.08	0.10	-0.02	-20.0
	-15.0	1.20	0.29	0.91	75.8
	-17.5	0.69	1.47	-0.78	-53.1
	-17.8	1.85	1.61	0.24	14.9
	-17.9	1.86	1.66	0.20	12.0
walk-in freezer	-14.7	0.17	0.14	0.03	21.4
	-15.0	0.43	0.29	0.14	48.1
	-15.6	0.85	0.57	0.28	49.1
	-16.1	1.10	0.81	0.29	35.8
	-16.7	1.45	1.09	0.36	33.0

		Enthalpy Difference (Δh) in cal/gm Between -16.7°C(Walk-in Freezer) and T°C			
walk-in refrigerator	10.6	98.44	98.51	-0.07	-0.1
	8.3	98.28	96.20	2.08	2.2
	7.8	95.97	95.70	0.27	0.3
	7.2	96.44	95.10	1.34	1.4
	6.7	96.58	94.60	1.98	2.1
refrigerator	4.4	92.40	92.29	0.11	0.1
	3.9	91.60	91.79	-0.19	-0.2
	3.3	92.09	91.18	0.91	1.0
	3.0	91.49	90.88	0.61	0.7
	2.8	91.42	90.68	0.74	0.8
	2.2	89.48	90.07	-0.59	-0.7
freezer	-13.9	1.27	1.33	-0.06	-4.5
	-14.2	1.37	1.19	0.18	15.12
	-14.4	1.45	1.09	0.36	33.0

Refrigeration Source	T°C	(1) Experimental mean[a] cal/gm	(2) Calculated[b] cal/gm	(3) Deviation[c]	(4) % Deviation[d]
freezer (cont.)	-15.0	0.25	0.80	-0.55	-68.8
	-17.5	0.76	0.38	0.38	50.0
	-17.8	0.40	0.52	-0.12	-23.1
	-17.9	0.41	0.57	-0.16	-28.1
walk-in freezer	-14.7	1.28	0.95	0.33	34.7
	-15.0	1.02	0.80	0.22	27.5
	-15.6	0.60	0.52	0.08	15.4
	-16.1	0.35	0.28	0.07	25.0

[a] Mean experimental enthalpy changes for temperatures are from Appendix A1 through A8. Experimental mean value was obtained by $\Delta h_2 - \Delta h_1$.

[b] The source for the calculated values are listed in Tables 2, 3 and 4.

[c] Deviation of experimental, E, from the calculated, C; E - C.

[d] 100(E - C)/C.

from Table 12 which vary more than 5.0% from the calculated numbered 44 out of the 111 values or 39.6% of the samples determined. Changes in enthalpy for temperature ranges that included the freezing point for water had no more than 5.0% deviation between the 58 experimental and calculated values. The average per cent deviation for those enthalpy changes which included the latent heat of fusion for ice was 0.8%. A temperature range of 15.0°C or more resulted in a deviation between the experimental and calculated enthalpy changes of no more than 5.0%, the average per cent deviation was 1.0%. Temperature ranges of 5.0°C or more had 91.7% of the interpolated enthalpy changes within 5.0% deviation of experimental from calculated values, the average deviation for interpolated values for temperature ranges 5.0°C or more was 2.0%.

As the temperature range of the interpolation was reduced, the per cent deviation became significantly larger. The smaller the temperature range, the greater the per cent deviation between the interpolated experimental enthalpies and the calculated values. The interpolated experimental values for temperature ranges less than 15.0°C had 44 out of 47 or 93.6% varying more than 5.0% from the calculated values with the average per cent deviation of 31.9% between experimental and calculated values. All the interpolated experimental values for temperature ranges less than 5.0°C varied more than 5.0% from the calculated changes in enthalpy with the average per cent deviation being 35.7% for the 40 values.

The range of application for the experimental method, liquid nitrogen boil-off calorimetry, for determining changes in food enthalpy may have been exceeded when measuring sensible heat within a temperature range of 15.0°C. The magnitude of deviation was significant enough to indicate that sensitivity of this calorimetric method was not capable of accurate measurement of such small enthalpy changes. It should be observed that a small variation is a significant percentage of the total change in enthalpy, as shown by 8.3°C series, Table 12. The variation between values was less than 2 calories/gm but represent a significantly large percentage (13.8% deviation). The average of the net experimental calories from Appendix A was 36,616.10 calories, averaging 167.50 calories/gm of water going from 21.7°C to -195.803°C. The averaged net calories going from 8.3°C to -195.803°C was 13,806.06 or 155.97 calories/gm. Subtracting the two for the interpolated enthalpy gives 11.53 calories/gm for water between 21.7°C and 8.3°C.

J. Potato Enthalpy Changes Above 0°C

Enthalpy changes interpolated for potatoes at tempertures above freezing, Table 13, do not exhibit the close correlation between experimental and calculated values as did the water and ice calibration samples, Table 7 and 12, or the potato enthalpies from Table 10. Of the 33 interpolated experimental values from Table 13, 9.1% were within 5.0% variation from the calculated. The 21 interpolated experimental values having temperature ranges greater than 15.0° C, 9.5% of the values were within 5.0% variation of the calculated change in enthalpy. Enthalpy values for temperature ranges greater than 5.0° C had 8.7% of the experimental values within 5.0% variation from the calculated.

The data for interpolated potato enthalpies, Table 10, had good correlation between the experimental and calculated values with the average per cent variation for the Table 10 data being 2.8%. The interpolated experimental enthalpy values for Table 13 were calculated using the same experimental values as used in Table 10. An important difference between the data for Table 13 and Table 10 is that all the interpolated changes in enthalpy include the latent heat of fusion for ice in Table 10. These values are larger because they include the latent heat of fusion in addition to the sensible heat removed. The measured enthalpies for Table 13, potato enthalpy changes above 0° C, are of sensible heat above

TABLE 13

Changes in Enthalpy of Potatoes Over Various Temperature Ranges Above 0° C as Determined Experimentally and as Derived by Use of the Riedel Equations

		Enthalpy Difference (Δh) in cal/gm Between 26.1° C (Laboratory Room Temperature) and T°C			
		(1)	(2)	(3)	(4)
Refrigeration Source	T° C	Experimental mean^a cal/gm	Calculated^b cal/gm	Deviation^c	% Deviation^d
walk-in refrigerator	8.1	19.32	15.60	3.72	23.8
	7.5	21.66	16.08	5.58	34.7
	7.2	19.79	16.32	3.47	21.3
	6.7	22.56	16.80	5.76	34.3
refrigerator	3.3	22.46	19.07	3.39	17.8
	3.1	23.39	19.92	3.47	17.4
	2.8	27.56	20.16	7.4	36.7
		Enthalpy Difference (Δh) in cal/gm Between 25.0° C (Laboratory Room Temperature) and T°C			
walk-in refrigerator	8.1	17.22	14.64	2.58	17.6
	7.5	19.56	15.12	4.44	29.4
	7.2	17.69	15.36	2.33	15.2
	6.7	20.46	15.84	4.62	29.2
refrigerator	3.3	20.36	18.72	1.64	8.8
	3.1	21.29	18.96	2.33	12.3
	2.8	25.49	19.20	6.29	32.8
		Enthalpy Difference (Δh) in cal/gm Between 23.9°C (Laboratory Room Temperature) and T°C			
walk-in refrigerator	8.1	12.37	13.68	-1.31	-9.6
	7.5	14.71	14.16	0.55	3.9
	7.2	12.84	14.40	-1.56	-10.8
	6.7	15.61	14.76	0.85	5.8
refrigerator	3.3	15.51	17.76	-2.25	-12.7
	3.1	16.44	18.00	-1.56	-8.7
	2.8	20.64	18.24	2.4	1.3

		Enthalpy Difference (Δh) in cal/gm Between 8.1° C (Walk-in Refrigerator) and T°C			
Refrigeration Source	T°C	(1) Experimental mean[a] cal/gm	(2) Calculated[b] cal/gm	(3) Deviation[c]	(4) % Deviation[d]
refrigerator	3.3	3.14	4.09	-0.95	-23.2
	3.1	4.07	4.32	-0.25	-5.8
	2.8	8.24	4.56	3.68	80.7
		Enthalpy Difference (Δh) in cal/gm Between 7.5°C (Walk-in Refrigerator) and T°C			
refrigerator	3.3	0.8	3.60	-2.8	-77.8
	3.1	1.73	3.84	-2.11	-54.9
	2.8	5.93	4.08	1.85	45.3
		Enthalpy Difference (Δh) in cal/gm Between 7.2°C (Walk-in Refrigerator) and T°C			
refrigerator	3.3	2.67	3.36	-.69	-20.5
	3.1	3.60	3.59	0.01	0.28
	2.8	7.80	3.84	3.96	10.31
		Enthalpy Difference (Δh) in cal/gm Between 6.7°C (Walk-in Refrigerator) and T°C			
refrigerator	3.3	0.10	2.89	-2.79	-96.5
	3.1	0.83	3.12	-2.29	-73.4
	2.8	5.03	3.36	1.67	49.7

[a] Mean experimental enthalpy changes for temperatures are from Appendix B1 through B 3. Experimental mean was obtained by $\Delta h_2 - \Delta h_1$.

[b] Calculated values derived using Riedel's equations, numbers 30 through 38.

[c] Deviation of experimental, E, from the calculated, C; E - C.

[d] 100(E - C)/C.

freezing. The enthalpy values are smaller and a slight variation becomes a significantly large per cent deviation.

The interpolated experimental enthalpy changes of sensible heat above the freezing range do not agree with the calculated values using Riedel's equations. However, because Riedel's method for calculating food enthalpies was considered the most accurate method available, it was used. Riedel's equations, like others for calculating food enthalpies, are empirically derived to fit the available experimental data with emphasis in calculating enthalpies for the freezing or thawing region. As mentioned, in the freezing region the latent heat becomes a significantly large fraction of the energy added or removed. Because of this larger amount of energy, methods of calculation can be slightly inaccurate and not result in a significant error when calculating enthalpy changes over temperature ranges which include the freezing region. For enthalpy values above freezing, where small degrees of sensible heat are measured, a slight error in calculation would cause a large percentage in variation between theoretical and experimental values. The use of Riedel's equations for calculating food enthalpy changes may not be appropriate for comparison with the experimental data in Table 13. For defense of the experimental values of Table 13 the author emphasizes the correlations for the experimental water and ice enthalpy changes, Tables 7 and 12, and the interpolated potato values in Table 10 with the calculated values.

An attempt was made to establish another standard of comparison by using Siebel's equations for calculating food enthalpy changes. The values calculated were lower than Riedel's, making an even greater disagreement between the experimental and calculated enthalpy values. Another possible cause of the discrepancy in the interpolated potato enthalpies was the possibility of starch conversion during the temperature conditioning period preceding each calorimetry test. This was investigated by placing potato samples in a refrigerator at 3.3°C (38.0°F) and a freezer at -16.1°C (3.0°F). Soluble solids analyses were made every 2 hours for 12 hours and a final determination was made at the end of 24 hours. No great change occurred between the determinations in this short period of time in the soluble solids content of the potato. The initial value was 6.9% for freezer and 7.0% for refrigerator samples with the final reading being 6.8%, respectively. An additional experiment was made to be certain that enzymatic activity was not a factor in the analysis. Soluble solids determinations were made as quickly as possible during the calorimetric procedure. Sometimes the grinding or extraction procedure was interrupted during a calorimetric experiment to obtain a measurement or begin a new sample. Two of the samples used for soluble solids above were permitted to stand one hour after the soluble solids were measured. The samples were rechecked at the end of the one hour with no apparent change from their initial readings.

CONCLUSIONS AND RECOMMENDATIONS

A liquid nitrogen vaporization calorimeter, in which changes in enthalpy were measured by the amount of liquid nitrogen vaporized, is described. From the results obtained, it appears that the method is satisfactory for determining enthalpy changes in foods for given changes in temperature.

Water and ice enthalpy changes from any temperature to -195.803°C agreed within 3.0% with the literature values considered the most accurate available. At any given temperature to -195.803°C the experimental mean values of temperature replicates for water and ice enthalpy changes were within 2.0% of the respective calculated values and had an average per cent deviation of 0.5%. The average per cent deviation for interpolated enthalpy changes which included the latent heat of fusion for ice was 0.8%. The range of application for the experimental method may have been exceeded when measuring sensible heat within a temperature range of 15.0°C. Interpolated changes in enthalpy for temperature ranges less than 15.0°C had 93.6% of the values varying more than 5.0% from the respective calculated values. The sensitivity of this calorimetric method may not be capable of accurate measurement of such small enthalpy changes. A temperature range of 15.0°C or more resulted in a maximum deviation between experimental and calculated enthalpy changes of 5.0%. The average per cent deviation was 1.0%.

Interpolated potato enthalpy changes that included latent as well as sensible heats correlated well with calculated values derived using Riedel's equation. Potato enthalpy changes where the interpolated ranges included the initial freezing point had a maximum per cent variation of 8.4% from the respective calculated values; the average per cent variation was 2.8%. Experimental data did not support Riedel's equations for enthalpy changes of sensible heat above or below the initial freezing point.

The methodology and feasibility have been established for utilizing liquid nitrogen vaporization calorimetry in determining enthalpy changes of food substances. Further investigations with a greater variety of foods may show the method to have limitations which are not apparent at this time. The speed and accuracy of the method lends itself to possible commercial use in determining refrigeration requirements of foods as well as in determining the effects of product composition and other variables on refrigeration requirements. With only minor changes in test procedure and calculation method, packaged products may be tested while still in their packages. Adaptation of the method to other types of materials (e.g., non-foods) and for other end purposes are also possible.

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APPENDIX

TABLE A

Experimental Data for Water and Ice Enthalpy Differences (Δh)

in cal/gm Between T and -195.803°C

T	T-(-195.803°C)	Water (grams)	Nitrogen vaporized[a] (grams)	Net[b] calories	Experimental[c] (cal/gm)	Calculated[d] (cal/gm)	Deviation[e]	% Deviation[f]
				Room Temperature				
21.7°C (71.0°F)	217.47	194.38	714.38	32513.22	167.27	167.24	0.03	0.0
		189.98	695.98	31868.84	167.75		0.51	0.3
		220.55	798.55	36974.38	167.65		0.41	0.2
		183.13	644.13	30563.24	166.89		-0.35	-0.2
		205.25	751.25	34322.51	167.22		-0.02	0.0
		184.68	674.80	30965.58	167.67		0.43	0.3
		210.23	770.23	35114.25	167.03		-0.21	-0.1
		206.64	761.64	34826.50	168.54		1.30	0.8
		192.52	704.52	32197.91	167.24		0.00	0.0
		220.02	803.02	36616.10	166.42		-0.82	-0.5
		205.12	761.12	34754.22	169.43		2.19	1.3
		189.50	700.50	31842.97	168.04		0.80	0.5
		198.80	727.80	33305.92	167.53		0.29	0.2
		213.73	776.73	35759.76	167.31		0.07	0.0
		206.27	746.27	34420.97	166.87		-0.37	-0.2
		201.25	725.25	33359.82	165.76		-1.48	-0.9
		205.65	771.65	34725.16	168.86		1.62	1.0
					**167.50		0.26	0.2
				Walk-in Refrigerator				
10.6°C (51.0°F)	206.36	188.54	641.92	29447.92	156.19	156.13	0.06	0.0

T	T-(-195.803°C)	Water (grams)	Nitrogen vaporized[a] (grams)	Net calories[b]	Experimental[c] (cal/gm)	Calculated[d] (cal/gm)	Deviation[e]	% Deviation[f]
		210.77	720.2	33148.01	157.27		1.14	0.7
					**156.73		0.60	0.4
9.4°C (49.0°F)	205.25	196.58	667.00	30746.08	156.41	155.02	1.39	0.9
8.3°C (47.0°F)	204.14	88.98	317.96	13806.06	155.16	153.91	1.25	0.8
		87.91	318.91	13709.68	155.95		2.04	1.3
		76.65	277.62	12018.09	156.79		2.88	1.9
					**155.97		2.06	1.3
8.0°C (46.5°F)	203.86	96.45	345.49	14917.14	154.66	153.63	1.03	0.7
7.8°C (46.0°F)	203.58	184.72	622.02	28180.76	152.56	153.35	-0.79	-0.5
		82.48	299.48	12590.00	152.64		-0.71	-0.5
		110.17	389.23	17156.39	155.73		2.38	1.5
					**153.64		0.29	0.2
7.2°C (45.0°F)	203.03	206.37	687.78	31244.25	151.96	152.79	-0.83	-0.5
		209.27	704.70	32079.36	153.29		0.50	0.3
		219.91	725.29	33670.77	153.11		0.32	0.2
		222.49	729.90	33942.35	152.56		-0.23	-0.2
		90.20	327.19	14099.65	156.32		3.53	2.3
		227.52	765.42	35501.01	156.03		3.24	2.1
		100.96	361.97	15716.01	155.67		2.88	1.9
					**154.13		1.34	0.9
6.7°C (44.0°F)	202.47	225.03	747.45	34447.23	153.08	152.24	0.84	0.6
		181.59	602.70	27738.82	152.76		0.52	0.3
		198.40	647.10	31102.11	156.76		4.52	3.0

T	T-(-195.803°C)	Water (grams)	Nitrogen vaporized^a (grams)	Net calories^b	Experimental^c (cal/gm)	Calculated^d (cal/gm)	Deviation^e	% Deviation^f
		199.75	674.10	31102.11	155.71		3.47	2.3
		201.59	683.01	30854.67	153.06		0.82	0.5
					**154.27		2.03	1.3
				Refrigerator				
6.7°C (44.0°F)	202.47	174.32	581.72	26575.03	152.45	152.24	1.68	1.1
4.9°C (41.0°F)	200.80	195.18	647.18	29093.38	149.06	150.56	-1.50	-1.0
4.4°C (40.0°F)	199.70	212.20	695.60	31919.70	150.42	150.01	0.41	0.3
		186.90	612.30	27891.91	149.23		-0.78	-0.5
		217.12	724.12	32700.18	150.61		0.60	0.4
					**150.09		0.08	0.0
3.9°C (39.0°F)	199.79	184.14	614.14	27496.86	149.33	149.44	-0.11	-0.1
		211.96	723.96	32287.79	152.33		2.89	1.9
		187.04	621.04	27610.03	147.62		-1.82	-1.2
		214.01	712.01	32101.72	150.00		0.56	0.4
		196.55	650.55	29222.11	148.68		-0.76	-0.5
		212.30	698.30	31629.40	148.98		-0.46	-0.3
		190.97	646.97	28442.33	198.94		-0.50	-0.3
		177.12	600.55	26293.96	148.45		-0.99	-0.7
					**149.20		-0.15	-0.1
3.3°C (38.0°F)	199.14	227.72	770.72	34719.25	152.46	148.89	3.57	2.4
		181.43	608.43	27436.26	151.22		2.33	1.6
		191.08	639.08	28810.25	150.78		1.89	1.3
		224.12	739.12	33425.12	149.14		0.25	0.2
		191.85	628.85	28529.07	148.71		-0.18	-0.1

T	T-(-195.803°C)	Water (grams)	Nitrogen vaporized^a (grams)	Net^b calories	Experi- mental^c (cal/gm)	Calcu- lated^d (cal/gm)	Devia- tion^e	% Devia- tion^f
		231.00	753.00	34311.47	148.53		-0.36	-0.2
		187.79	610.79	27896.38	148.55		-0.34	-0.2
		206.26	683.66	30693.39	148.81		-0.08	-0.1
					**149.78		0.89	0.6
3.0°C (37.5°F)	198.86	183.41	612.81	27185.40	148.22	148.61	-0.39	-0.3
		202.61	664.64	30066.76	148.40		-0.21	-0.1
		178.13	599.49	26676.96	149.76		1.15	0.8
		207.13	690.56	30883.53	149.10		0.49	0.3
		211.57	694.96	31634.77	149.52		0.91	0.6
		212.61	696.05	31683.09	149.02		0.41	0.3
		204.80	677.80	30486.45	148.86		0.25	0.2
		191.08	639.08	28810.34	150.78		2.17	1.5
		196.20	650.20	29399.71	149.85		1.24	0.8
		191.00	644.40	28415.28	148.77		0.44	0.3
		227.30	728.70	33605.80	147.85		-0.48	-0.3
		224.26	732.26	33617.85	149.91		1.58	1.1
		205.43	674.45	30828.61	150.07		1.74	1.2
		196.99	647.99	29438.07	149.44		1.11	0.7
		199.45	642.45	29321.56	147.01		-1.32	-0.9
		219.97	704.97	32292.74	146.81		-1.52	-1.0
					**149.11		0.78	0.5
2.8°C (37.0°F)	198.68	196.64	650.03	29186.42	148.43	148.33	0.10	0.1
		197.69	665.03	29392.45	148.68		0.35	0.2
		197.95	649.32	29057.07	146.79		-1.54	-1.0
		174.07	593.51	26319.91	151.20		2.87	1.9
		186.07	637.42	28082.00	150.92		2.59	1.7
		201.38	660.38	30039.48	149.17		0.84	0.6
		222.97	726.97	33379.49	149.70		1.37	0.9
		183.80	602.80	27337.41	148.73		0.40	0.3
		185.27	620.27	27809.68	150.10		1.77	1.2

T	T-(-195.803°C)	Water (grams)	Nitrogen vaporized[a] (grams)	Net[b] calories	Experimental[c] (cal/gm)	Calculated[d] (cal/gm)	Deviation[e]	% Deviation[f]
		179.03	600.03	27081.72	151.27		2.94	2.0
		213.65	702.65	31681.13	148.29		-0.32	-0.2
					**149.18		0.57	0.4
2.5°C (36.5°F)	198.30	195.65	657.04	29273.07	149.62	148.05	1.57	1.1
		177.25	596.57	26320.99	148.50		0.45	0.3
					**149.06		1.01	0.7
2.2°C (36.0°F)	198.03	221.92	707.92	32667.87	147.19	147.77	-0.58	-0.4
		224.18	768.18	35486.44	147.14		-0.63	-0.4
					**147.17		-0.61	-0.4
Freezer								
-13.3°C (8.0°F)	182.47	180.33	247.33	10861.09	60.23	59.27	0.96	1.6
		197.88	268.88	11809.36	59.68		0.41	0.7
					**59.96		0.67	1.2
-13.9°C (7.0°F)	181.91	218.18	295.18	13047.42	59.80	59.00	0.80	1.4
		197.95	266.95	11638.59	58.80		-0.20	-0.4
		182.30	249.30	10726.71	58.84		-0.16	-0.3
		189.35	254.35	11177.37	59.03		0.03	0.0
		196.03	260.03	11415.03	58.23		-0.77	-1.3
		134.68	186.68	7914.05	58.76		-0.24	-0.4
		136.00	188.00	8061.03	59.27		0.27	0.5
					**58.96		-0.04	-0.1
-14.2°C (6.5°F)	181.64	204.28	277.28	12085.57	59.16	58.87	0.29	0.5
		213.32	269.32	12500.04	58.60		-0.27	-0.5
		247.60	310.60	14518.91	58.64		-0.23	-0.4
		211.30	265.30	12265.73	58.05		-0.82	-1.4
		92.08	132.08	5457.66	59.27		0.40	0.7

T	T-(195.803°C)	Water (grams)	Nitrogen vaporized[a] (grams)	Net calories[b]	Experimental[c] (cal/gm)	Calculated[d] (cal/gm)	Deviation[e]	% Deviation[f]
		104.02	150.02	6258.09	60.16		1.29	2.20
					**59.06		0.19	0.3
-14.4°C (6.0°F)	181.36	200.12	273.12	11845.05	59.19	58.74	0.45	0.8
		225.62	298.62	13193.60	58.48		-0.26	-0.4
		218.25	293.25	12912.10	59.16		0.42	0.7
		106.20	150.20	6275.66	59.09		0.35	0.6
		189.09	265.09	11339.96	59.97		1.23	2.1
		200.00	275.00	11942.98	59.71		0.97	1.7
		225.45	302.45	13347.73	59.20		0.46	0.8
		124.34	176.35	7250.09	58.31		-0.43	-0.7
					**59.14		0.40	0.7
-15.0°C (5.0°F)	180.80	150.02	198.02	8686.30	57.90	58.47	-0.57	-1.0
		151.88	201.88	8804.56	57.97		-0.50	-0.9
					**57.94		-0.53	-0.9
-16.1°C (3.0°F)	179.69	249.33	324.33	14293.41	57.33	57.94	-0.61	-1.1
-17.5°C (0.5°F)	178.30	169.14	247.14	9787.50	57.87	57.29	0.58	1.0
		190.96	266.96	11216.31	58.74		1.45	2.5
		174.76	266.76	10264.30	58.73		1.44	2.5
					**58.45		1.16	2.0
-17.8°C (0.0°F)	178.03	193.04	277.04	11182.56	57.93	57.15	0.78	1.4
		186.58	272.58	10958.61	58.73		1.58	2.8
		194.54	272.54	11117.37	57.15		0.00	0.0
		176.41	252.41	10171.06	57.66		0.51	0.9
		194.63	268.63	11004.03	56.54		-0.61	-1.1
		202.28	266.28	11275.69	55.74		-1.41	-2.5
					**57.29		0.14	0.2

T	T-(-195.803°C)	Water (grams)	Nitrogen vaporized[a] (grams)	Net calories[b]	Experimental[c] (cal/gm)	Calculated[d] (cal/gm)	Deviation[e]	% Deviation[f]
-17.9°C (-0.2° F)	177.91	202.36	284.36	11526.07	56.96	57.10	-0.14	-0.3
		188.78	278.78	10872.17	57.59		0.49	0.9
					**57.28		0.18	0.3
				Walk-in Freezer				
-14.7°C (5.5°F)	181.08	192.30	268.30	11405.38	59.31	58.60	0.71	1.2
		190.82	260.82	11185.29	58.62		0.02	0.0
					**58.97		0.37	0.6
-15.0°C (5.0°F)	180.80	176.65	248.65	10438.00	59.09	58.42	0.67	1.1
		167.11	231.11	9746.84	58.33		-0.09	-0.2
					**58.71		0.29	0.5
-15.6°C (4.0°F)	180.25	208.00	288.00	12221.07	58.76	58.20	0.56	1.0
		195.09	261.09	11219.95	57.51		-0.69	-1.2
		197.30	273.30	11561.62	58.60		0.40	0.7
					**58.29		0.09	0.2
-15.8°C (3.5°C)	179.97	183.70	259.70	10704.07	58.27	58.07	0.20	0.3
		223.17	305.17	13112.34	58.75		0.68	1.2
					**58.51		0.44	0.8
-16.1°C (3.0° F)	177.69	190.19	268.19	10990.25	57.79	57.94	-0.15	-0.3
		185.19	259.19	10880.07	58.75		0.81	1.4
		164.12	238.12	9448.07	57.57		-0.37	-0.6
					**58.04		0.1	0.2
-16.7°C (2.0°F)	179.14	195.58	271.58	11372.68	58.15	57.68	0.47	0.8
		170.72	252.72	9690.48	58.76		1.08	1.9

T	T-(-195.803°C)	Water (grams)	Nitrogen vaporized[a] (grams)	Net calories[b]	Experimental[c] (cal/gm)	Calculated[d] (cal/gm)	Deviation[e]	% Deviation[f]
		195.38	275.38	11205.41	57.35		-0.33	-0.6
		181.00	245.00	10222.00	56.48		-1.20	-2.1
					**57.69		0.01	0.0

[a] Total grams of liquid nitrogen vaporized during experiment duration.

[b] Net calories for the water sample changing from temperature T to -195.803°C, derived using equation 27. Calories corrected for can be obtained by subtracting net calories, C_n, from nitrogen vaporized, V, times 47.6442; $47.6442 V - C_n$.

[c] Derived by dividing net calories, C_n, by the water mass, m; C_n/m.

[d] From Tables 2, 3, and 4.

[e] Deviation of experimental, E, from the calculated, C; E - C.

[f] 100(E - C)/C

**Mean values for temperature replicates.

TABLE B

Experimental Data for Potato Enthalpy Differences (Δh)

in cal/gm Between T and -195.803°C

T	T-(-195.803°C)	Potato (grams)	Nitrogen[a] vaporized (grams)	Net[b] calories	Experi-mental[c] (cal/gm)
		Room Temperature			
26.1°C	221.91	228.48	748.48	34382.35	150.48
(79.0°F)		294.87	934.87	43383.62	147.13
		262.85	867.85	40181.71	152.87
		249.80	772.80	35515.11	142.17
		356.10	1101.10	51511.66	144.65
					**147.46
25.0°C	220.80	388.60	1210.60	56529.81	145.47
(77.0°F)		203.40	641.40	29541.40	145.24
					**145.36
23.9°C	219.69	232.39	722.39	32835.27	141.29
(75.0°F)		249.36	773.36	35436.75	142.11
		192.56	592.56	27019.88	140.31
		220.15	692.15	31036.10	140.98
		201.26	625.26	28276.78	140.50
		237.64	707.64	32425.70	136.43
		321.68	975.68	44974.93	139.81
		214.90	676.90	30727.05	142.98
		237.80	743.80	34042.69	143.16
		282.69	852.69	39121.32	138.39
		239.82	743.82	33901.45	141.36
		263.25	803.25	36785.67	139.74
		219.97	677.97	30705.95	139.59
		204.91	640.91	29108.00	142.05
		227.43	709.43	32389.33	142.41
		220.48	686.48	31237.60	141.68
		259.04	771.04	35373.71	136.56
		260.90	804.90	36502.85	139.91
					**140.51
		Walk-in Refrigerator			
8.1°C	203.86	150.58	432.58	19132.38	127.06
(46.5°F)		117.98	343.98	15081.92	127.83
		60.79	196.79	7874.11	129.53
					**128.14
7.5°C	203.30	405.81	1113.81	51462.03	126.81
(45.5°F)		291.62	765.62	34833.73	119.45
		226.46	622.46	27927.36	123.32
		206.31	592.31	26082.34	126.42
		225.39	643.39	29654.42	131.57
		87.29	257.29	10992.31	125.93
		79.29	245.79	10078.09	127.10
					**125.80

T	T-(-195.803°C)	Potato (grams)	Nitrogen[a] vaporized (grams)	Net[b] calories	Experimental[c] (cal/gm)
7.2°C	203.03	228.39	628.39	28705.63	125.69
(45.0°F)		213.71	597.71	27187.42	127.22
		175.68	499.68	22297.98	126.92
		90.19	274.19	11466.61	127.14
		149.01	437.01	19339.48	129.79
		91.91	269.91	11492.68	125.04
		224.41	652.41	29494.49	131.45
		225.47	717.47	32733.24	128.13
					**127.67
6.7°C					
(44.0°F)	202.47	151.20	419.20	18460.84	122.10
		95.11	285.11	11935.36	125.49
		222.89	628.89	28305.50	126.99
		113.02	327.02	14129.26	125.02
					**124.90
		Refrigerator			
3.3°C	199.10	178.96	512.96	22112.96	123.56
(38.0°F)		202.11	560.11	24986.92	123.63
		264.76	714.76	32352.71	122.20
		267.10	773.10	35669.26	133.54
		240.68	663.68	30673.68	127.45
		275.92	758.92	35159.33	127.43
		227.39	628.39	28924.95	127.20
		304.20	816.20	38097.43	125.24
		247.32	654.32	30358.59	122.75
		297.70	803.70	37579.24	126.23
		266.04	620.04	27915.35	123.50
		197.80	547.80	24332.79	123.02
		260.81	722.81	32666.75	125.25
		231.71	617.71	28115.73	121.34
		188.58	520.58	22983.79	121.40
		251.21	669.21	30323.14	120.71
		217.04	625.04	28352.94	130.63
					**125.00
3.1°C	198.86	246.27	672.27	30081.03	122.15
(37.5°F)		163.77	471.77	20631.28	125.98
					**124.07
2.8°C	198.58	162.29	448.29	19360.21	119.73
(37.0°F)		271.14	727.14	32868.05	121.67
		253.60	657.60	29869.34	118.22
					**119.87
		Walk-in Freezer			
-14.44°C	181.36	522.59	638.59	28836.23	55.18
(6.0°F)		367.79	455.79	20541.80	55.85
					**55.52

T	T-(-195.803°C)	Potato (grams)	Nitrogen[a] vaporized (grams)	Net[b] calories	Experimental[c] (cal/gm)
-15.0°C (5.0°F)	180.80	258.91	340.91	14320.78	55.31
		274.08	348.08	14991.10	54.70
		208.31	272.31	11545.11	55.42
		400.19	496.19	21995.35	54.96
		252.32	318.32	13921.92	55.18
		246.09	312.09	13683.38	55.60
		217.67	287.67	11995.87	55.11
					**55.18
-15.6°C (4.0°F)	180.25	233.81	301.81	12771.95	54.63
		202.65	288.65	11341.08	55.96
		268.08	336.08	14679.35	54.76
		282.52	354.52	15534.35	54.98
					**55.08
-16.4°C (2.5°F)	179.41	218.81	284.81	11927.89	54.51
		271.47	317.47	13286.46	48.94
		202.16	268.16	11109.15	54.95
		259.20	389.20	15901.22	61.35
					**54.94
		Freezer			
-15.6°C (4.0°F)	180.25	387.52	503.52	21725.49	56.06
		294.82	388.82	16190.31	54.92
		312.50	396.50	17288.35	55.32
					**55.43
-16.1°C (3.0°F)	179.69	398.77	484.77	21514.19	53.95
		189.86	259.86	10444.14	55.01
		269.32	359.32	14971.39	55.59
		154.27	230.27	8592.24	55.70
		242.55	310.55	12896.30	53.17
					**54.68
-16.7°C (2.0°F)	179.14	536.63	662.63	29726.00	55.39
		209.86	283.86	11899.31	56.70
		249.41	323.41	14093.63	56.51
		214.06	298.06	12191.80	56.96
					**56.39

[a] Total grams of liquid nitrogen vaporized during experiment duration.

[b] Net calories for the potato sample in changing from temperature T to -195.803°C, derived using equation 22. Calories corrected for can be obtained by subtracting net calories, C_n, from nitrogen vaporized, V, times 47.6442; $47.6442V - C_n$.

[c] Derived by dividing net calories, C_n, by the potato mass, m; C_n/m.

**Mean values for temperature replicates.