

HEAT OF FUSION

OBJECT: To measure the heat of fusion of ice, using the method of mixtures.

METHOD: A piece of ice of known mass is dropped into a calorimeter containing a measured quantity of water. The heat given up by the calorimeter cup and its contents (water, thermometer and stirrer) is computed from their combined thermal capacity and the change in temperature. The heat absorbed by the ice is expressed in terms of the mass of the ice, the heat of fusion and the change in temperature of the water from the melted ice. The heat given up by the cup and its contents is set equal to the heat absorbed by the ice, and this equation is solved for the latent heat of fusion. A correction is made for the exchange of heat between the calorimeter cup and its surroundings.

THEORY: Temperature is a measure of the relative hotness or coldness of a body, and any instrument designed to measure the temperature of a body is called a thermometer. The principle of the *conservation of energy* is one of the most fundamental and most useful laws of physics. It is fundamental in that it has not been derived from more basic relationships. Its utility is indicated by the fact that many equations in physics are merely the algebraic statement of this principle. If, in an experiment, the principle of conservation of energy seems to be violated, physicists do not question the validity of the principle but look for possible experimental errors and, if no experimental errors are found, for errors in existing theories. Such studies have frequently led to the discovery of new laws.

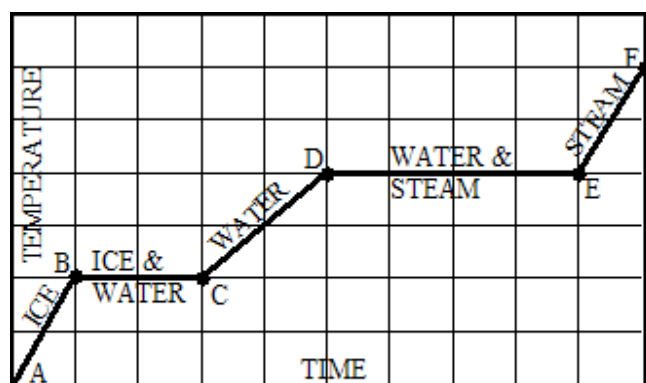


Fig. 1. Heat may either raise the temperature of a substance or change its state.

A necessary corollary to the principle of conservation of energy is the *first law of thermodynamics*. According to this

law *heat is a form of energy*. The energy that seems to be lost when work is done in overcoming frictional resistance is not lost but is converted into heat energy. Conversely, heat energy may be converted into other forms of energy. If, for example, heat is added to a system, it may be expended in anyone (or any combination) of the following ways: (a) raise the temperature of the system, (b) change the state of the material in the system, (c) perform mechanical work. In this experiment only the first two need be considered. Suppose a piece of ice, originally at a temperature considerably below its melting point, is placed in a vessel and that heat is added to it at a constant rate. The relationship between the temperature of this substance and the elapsed time is shown schematically in Fig. 1. From A to B the absorbed heat raises the temperature of the ice. What has become of the heat energy? The kinetic theory of heat indicates that, as the temperature of the ice rises, the random vibratory motion of the molecules increases and the heat energy which the ice has absorbed exists in the form of molecular kinetic energy. At the point B the ice begins to melt and from B to C, although heat is being absorbed, there is no change in temperature and, therefore, no increase in molecular kinetic energy. As the ice changes from the solid to the liquid state, the heat energy is expended in changing the arrangement of the molecules and the absorbed heat is converted into molecular potential energy. At point C the ice is all melted and from C to D the absorbed heat raises the temperature of the water. At point D the water begins to boil and from D to E the absorbed heat changes the water into steam without changing its temperature. In separating the water molecules, as the water passes from the liquid to the vapor state, work must be done to move the molecules against attractive forces. It is clear, therefore, that in the interval DE the absorbed heat energy is converted into potential energy. Beyond point E, where the water has all been converted into steam, the added heat raises the temperature of the steam. Assuming that there is no change in state, the quantity of heat H required to produce a certain temperature change is proportional to the mass m of the body and to rise in temperature Δt . Stated algebraically

$$H = c \cdot m \cdot \Delta t \quad (1)$$

where the constant of proportionality c is called the *specific heat*. Since heat is a form of energy, the quantity of heat H might be expressed in ordinary energy units, for example, joules or foot-pounds. It is customary, however, to measure heat in special heat-energy units. It has been found convenient to adopt as the unit of heat energy the amount of

heat required to raise the temperature of a unit mass of water one-degree.

In the metric system this unit is called the calorie. The *calorie* is defined as the heat required to raise the temperature of one gram of water one degree centigrade. If, in Eq. (1), H is expressed in calories, m in grams and Δt in degrees centigrade, the specific heat c is given in calories per gram per degree centigrade (cal/gm °C). Obviously, the specific heat of a substance is numerically equal to the number of calories of heat required to raise the temperature of one gram of the substance one degree centigrade: In the British system the unit of heat energy is the *British thermal unit* (Btu) which is defined as the heat necessary to raise the temperature of one pound of water one degree Fahrenheit. In this system the specific heat of a substance is measured in British thermal units per pound per degree Fahrenheit and is numerically equal to the quantity of heat required to raise the temperature of one pound of the substance one degree Fahrenheit.

The product $c \cdot m$ is called the thermal capacity C of the body. It should be obvious that the thermal capacity of a body is numerically equal to the quantity of heat required to raise the temperature of the body one-degree. Since a mass m of any substance is thermally equivalent to a mass of water equal to $c \cdot m$ (or C), the thermal capacity of a body is sometimes called the "water equivalent" of the body. When a body is composed of several kinds of materials, the quantity of heat required to produce a certain temperature change is most easily determined by adding the thermal capacities of the individual parts and multiplying the sum by the change in temperature. In the metric system C is expressed in calories per degree centigrade (cal/°C). It should be noted that specific heat is a property of a substance and is, therefore, an important physical constant; whereas thermal capacity is a property of a particular body.

In the discussion above it was assumed that the quantity of heat required to raise the temperature of water one degree is independent of the initial temperature; that is, it requires the same amount of heat to raise the temperature from 0°C to 1°C as to raise the temperature from 50°C to 51°C, say. This is true to a fairly high degree of accuracy, but for very precise work the exact temperature range must be specified. For example, the 15 degree calorie is defined as the amount of heat required to raise the temperature of one gram of water from 14.5°C to 15.5°C; whereas the mean calorie is defined as one hundredth of the heat required to raise the temperature of one gram of water from 0°C to 100°C. Since the difference between these two calories is only 0.024 of one percent, it is obvious that it is almost never necessary in practice to specify the kind of calorie. In this experiment the slight variation in the thermal capacity of water with temperature is negligible.

The quantity of heat required to change a body from the solid to the liquid state is proportional to the mass m of the body. Stated algebraically

$$H = L_f \cdot m \quad (2)$$

where the constant of proportionality L_f depends upon the kind of substance and is called the *heat of fusion*; sometimes it is called the latent heat of fusion. In the metric system it is expressed in calories per gram (cal/gm). Obviously, the heat

of fusion is numerically equal to the heat required to change one gram of the substance from the solid to the liquid state with no change in temperature. Similarly, the heat of vaporization is numerically equal to the quantity of heat required to change one gram of the substance from the liquid to the vapor state with no change in temperature.

Method of Mixtures: The simplest method of measuring the heat of fusion of ice is the method of mixtures. In this method, a piece of ice is dropped into a vessel of water, and the heat absorbed by the ice in melting and coming to the final temperature of the mixture is set equal to the heat lost by the rest of the system. If the only unknown in this equation is the heat of fusion L_f , the equation may be solved for L_f .

If, for example, a piece of ice is dropped into a cup, containing water and equipped with thermometer and stirrer, the temperature of the cup and its contents falls from an initial temperature t_U to a final temperature t_F . The ice melts at a temperature t_o and the resulting water rises in temperature to t_F . Setting the heat absorbed by the ice and resulting water equal to the heat given up by the cup and its contents yields the equation

$$L_f m_I + m_I c_W (t_F - t_o) = (C_W + C_C + C_T + C_S)(t_U - t_F) \quad (3)$$

in which c is specific heat, C is thermal capacity, m is mass and the subscripts I , W , C , T and S refer to ice, water, cup, thermometer and stirrer, respectively.

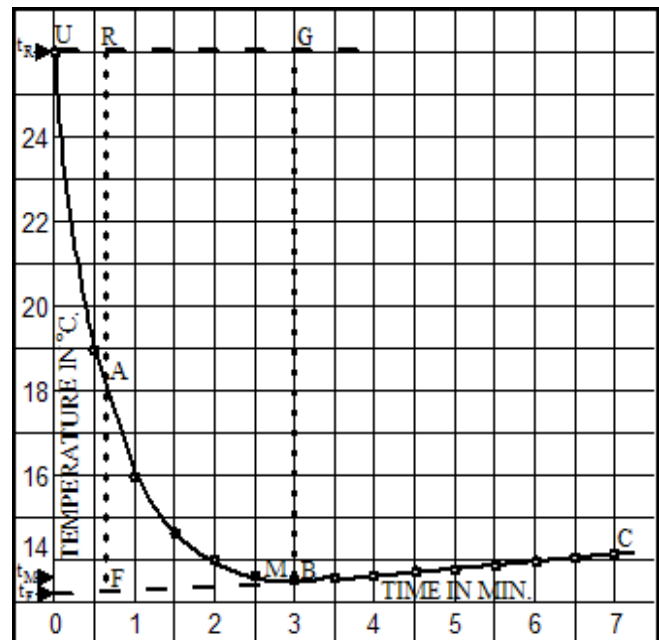


Fig. 2. Illustration of the method of correcting for the heat absorbed from the surroundings.

Correction for Heat Exchange with Surroundings: Assume that the cup and its contents are initially at the temperature t_R of the surroundings and that the relation

between the temperature of the cup and elapsed time is represented by the solid-line curve of Fig. 2. The minimum temperature read by the thermometer is t_M . When the temperature of the cup is below the temperature of its surroundings, heat is being absorbed from the surroundings, and the problem is to determine what the final temperature would have been had no heat been gained.

There are several methods of correcting for the heat exchanged between a body and its surroundings, and the choice of method depends upon the conditions of the experiment. In the case represented in Fig. 2 the rate of change of temperature is not uniform; considerable time is required for the temperature to fall to its minimum value and thereafter the rise in temperature is quite slow. Under these conditions the method of temperature correction suggested below is recommended. In a different type of experiment some other method of correction might be better.

The final temperature for the case illustrated in Fig. 2 is determined in the following manner. Extrapolate the portion CB of the curve back until it intersects the ordinate axis, and construct the vertical line FR so that the areas UAR and AFBM are equal. The ordinate of the point F is the final temperature t_F . The justification of this procedure is based upon Newton's law of cooling which states that, if the difference in temperature is not large, the rate of cooling (or warming) of a body is proportional to the difference in temperature between the body and its surroundings. The distance of each point on the graph below the horizontal line at t_R is, therefore, proportional to the rate of warming. Multiplication of any given time interval by the corresponding rate of warming gives the temperature gain during this interval.

Referring to Fig. 3, where the area between the curve and the horizontal line at t_R is divided into thin slices, the height of a slice (for example, the shaded one) is proportional to the rate of warming at that particular time and the width of the

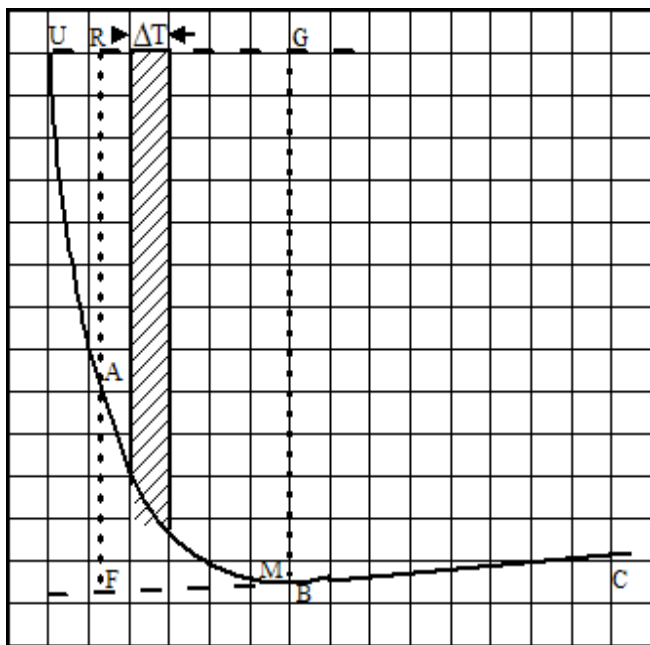


Fig. 3. The temperature gain is proportional to the area between the curve and the line UG.

slice is equal to the time interval ΔT . From this it follows that the area of the slice is proportional to the temperature gain during the interval ΔT . Upon summing the areas of all the slices it is evident that the temperature excess due to heat absorbed from the surroundings in the time interval UG is



Fig. 4. The Vacuum Jacketed Calorimeter

proportional to the area UAMBG. This temperature excess is the same as if the body had started at the temperature represented by the point R, fallen instantly to temperature t_F and then warmed as indicated by the line FBC. The temperature gain in one case is proportional to the area UAMBG and in the other case to the area RFBG. These two areas are equal, since FR was drawn to make area UAR equal to area AFBM. It may be concluded, therefore, that if no heat had been gained, the thermometer reading would have fallen from t_U to t_F and then have remained constant.

APPARATUS: A vacuum jacketed calorimeter, ice, stirrer, centigrade thermometer graduated in one tenth degree divisions, beaker, balance and stopwatch are required. The vacuum-jacketed calorimeter is illustrated in Fig. 4 and shown in cross section in Fig. 5. The aluminum cup C is suspended inside the vacuum flask V from an insulating ring R. The cover L is lined with a thick layer of cork insulation and is provided with a cork stopper K. To minimize heat conduction the handle of the stirrer S is made of glass. Temperatures are read by means of the precision thermometer T.

PROCEDURE: Weigh the aluminum cup and the stirrer. Place the stirrer in the cup, fill the cup about two thirds full of water at room temperature and determine the combined weight of cup, stirrer and water. Assemble the apparatus as shown in Fig. 5 with the thermometer and stirrer in position. Stir the water and observe the temperature reading for several minutes to make sure that the temperature is constant. To provide a supply of water at room temperature it is suggested that a tank of water be kept standing in the laboratory for this purpose.

Dry a piece of ice, weighing approximately 25gm, with a paper towel and, when the watch reads on the minute, drop the dry ice into the calorimeter cup. Replace the cork stopper and, while keeping the water thoroughly stirred, read the thermometer every half-minute for 7 or 8 minutes. The thermometer readings should be estimated to hundredths of a degree. Although the water should be thoroughly stirred, care should be taken that no water is splashed from the cup. Plot a curve, similar to the one in Fig. 2, which shows how temperature of the cup varies with time. Construct a vertical line FR such that the area UAR is approximately equal to the area AFBM. The line FR may be located with sufficient accuracy by inspection, without actually measuring the areas. The final temperature t_F is the ordinate of the point F and might be read directly from the graph. It is considerably

more accurate, however, if the section BC of the curve is drawn on a much larger scale, like the one shown in Fig. 6 and t_F determined from this second curve. Construct such a graph and determine t_F .

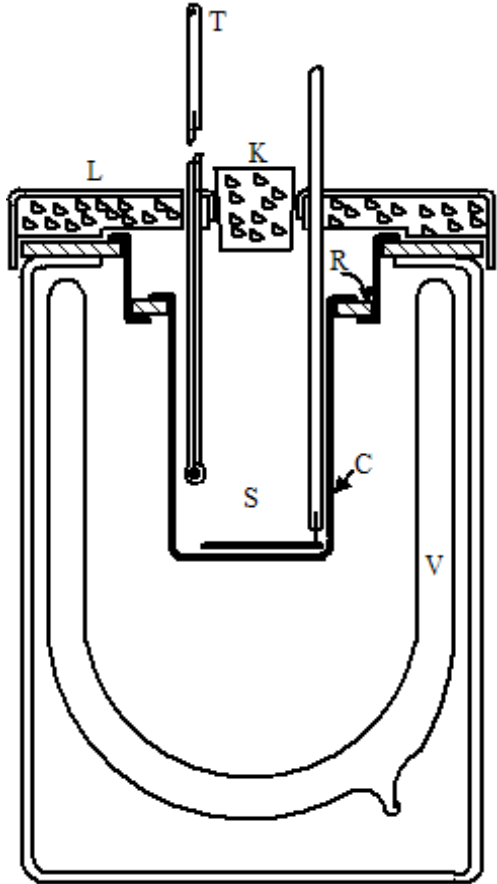


Fig. 4. Diagram of the Vacuum Jacketed Calorimeter.

Determine the thermal capacity of the thermometer and of the stirrer. Since glass is a poor conductor of heat, only that portion of the thermometer which is immersed in the water need be considered in calculating its thermal capacity. Although the specific heats of glass and mercury are quite different, fortunately equal volumes of these two materials have approximately the same thermal capacity ($0.46 \text{ cal/cm}^3 \text{ } ^\circ\text{C}$). The volume of the submerged portion of the thermometer may be determined in the following manner. Place a vessel of water on the balance and weigh. Then, holding the thermometer in the hand, immerse it in the water to the same depth as in the experiment and observe the apparent increase in weight. The increase in weight in grams is numerically equal to the volume in cubic centimeters of the submerged portion of the thermometer. The thermal capacity of the stirrer may be computed from the mass and specific heat of the metal part and the volume of the submerged portion of the glass stem. If the metal part cannot be weighed separately (or estimated with sufficient accuracy) the value of the thermal capacity will be supplied by the instructor. Using Eq. (3) determine the value of the heat of fusion of ice L_f .

If time permits redetermine L_f using a somewhat different

mass of ice. If undecided whether to use more or less, ask an instructor.

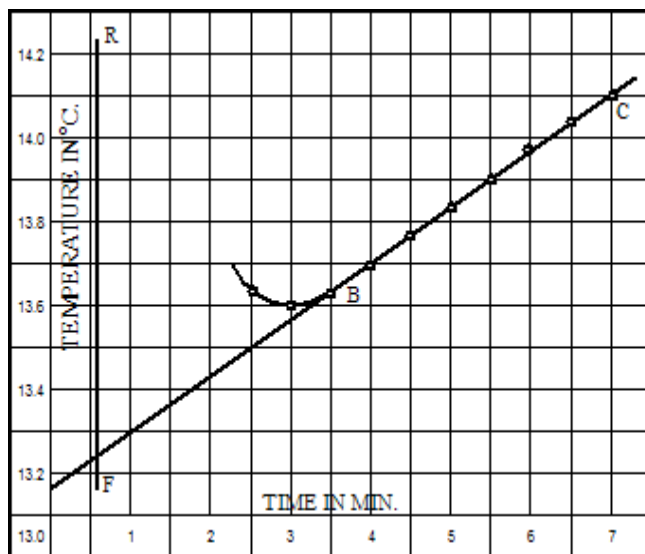


Fig. 6. The final temperature t_F is the ordinate of the point F.

QUESTIONS: 1. What percentage error in the determination of the latent heat of fusion would be caused by one half gram of water adhering to the ice?

2. Name some materials that do not have definite melting points. What class of materials do have definite melting points?

3. Discuss the significance of the difference in slope in various parts of the curve in Fig. 1. Show that this curve is not drawn accurately to scale.

4. The calorimeter cup is highly polished. Explain why.

5. What percentage error in the determination of the thermal capacity of the thermometer would cause a one tenth percent error in the heat of fusion?

6. Since the heat that flows to the thermometer must flow through the thin glass wall of the bulb, there is a certain lag of the thermometer reading behind temperature changes of the water. How does this lag affect the results in this experiment?

7. In using Fig. 2 it was assumed that the temperature of the surroundings remained constant. The surroundings in this case consist primarily of the inner wall of the vacuum jacket. If the temperature of this wall falls during the experiment how are the results affected?

8. It is frequently suggested that the exchange in heat between the calorimeter cup and its surroundings may be minimized by choosing the initial temperature so that it is as far above room temperature as the final temperature is below. Criticize this method as it applies to this experiment.

9. Assume that the temperature of the surroundings, for the case shown in Fig. 2, is not equal to the initial temperature but is midway between the initial and final temperatures. For what fractional part of the time in the interval from U to M does the cup lose heat to the surroundings?

10. When a 16gm metal ball at a temperature of 112°C is dropped into a cavity in a block of ice it melts 2.5gm of the ice. What is the specific heat of the metal?