

SPECIFIC HEAT OF A LIQUID

OBJECT: To measure accurately the specific heat of various liquid specimens, using the method of mixtures.

METHOD: A thin-walled copper flask containing a known mass of the liquid under investigation is lowered from a steam jacket into a calorimeter containing a measured mass of cold water. The initial temperature of the test liquid is assumed to be the temperature of boiling water under existing atmospheric pressure, and this temperature is determined by reference to steam tables. The change in temperature of the water is read from a thermometer. The heat given up by the liquid and flask is set equal to the heat absorbed by the water and calorimeter, and this equation is solved for the specific heat of the liquid. A correction is made for the heat lost by radiation.

THEORY: Temperature is a measure of the relative hotness or coldness of a body, and any instrument designed to measure temperature is called a thermometer. In order to raise the temperature of a body, heat must be added to it and the quantity of heat *H* required is proportional to the mass m of the body and to the rise in temperature Δt . Stated algebraically

$$H = c \cdot m \cdot \Delta t \tag{1}$$

where the constant of proportionality c is called the specific heat of the material. 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 per cent, 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 specific heat of most liquids changes considerably with temperature, and this fact should not be ignored when comparing the results in this experiment with values given in tables.

Method of Mixtures: The simplest way of measuring specific heat is the method of mixtures. In this method, as the experiment is usually performed, a sample of the material under investigation is heated and then lowered into a vessel of cold water. The heat lost by the specimen is set equal to the heat gained by the rest of the system. If the only unknown quantity in this equation is the specific heat c_x of the specimen, this equation may be solved for c_x .

If, for example, a flask of liquid at the temperature of steam t_s is lowered into a cup, filled with water and equipped with thermometer and stirrer, the temperature of the cup and its contents rises from an initial temperature t_s to a final temperature t_F . Setting the heat lost by the flask and liquid

equal to the heat gained by the cup and its contents yields the equation

$$(C_x + C_K)(t_s - t_F) = (C_W + C_C + C_T + C_S)(t_F - t_I)$$
(2)

in which *C* symbolizes thermal capacity and the subscripts *X*, *K*, *W*, *C*, *T* and *S* refer to specimen, flask, water, cup, thermometer and stirrer, respectively. Since $C = c \cdot m$ it follows that the specific heat c_x of the liquid is given by the equation

$$c_{x} = \frac{\left(C_{W} + C_{C} + C_{T} + C_{S}\right)\left(t_{F} - t_{I}\right) - C_{K}\left(t_{S} - t_{F}\right)}{m_{x}\left(t_{S} - t_{F}\right)}$$
(3)

where m_X is the mass of liquid.

Correction far Heat Losses: Assume that a cup and its contents are initially at the temperature $t_{\rm R}$ of the surroundings and that, when a hot specimen is lowered into the cup, the relation between the temperature of the cup and elapsed time is represented by the solid-line curve of Fig. 1. The maximum temperature read by the thermometer is $t_{\rm M}$.



Fig. 1. Illustration of the method of correcting for loss of heat to surroundings.

When the temperature of the cup is above the surrounding temperature, heat is being lost to the surroundings and the problem is to determine what the final temperature would have been had no heat been lost. There are several methods of correcting for heat losses and the choice of method depends upon the conditions of the experiment. For the case represented in Fig. 1, one method of correcting may be best; whereas in special cases simpler and more accurate methods may be found. For example, it is seen in Fig. 1 that the rise in temperature from I to M has not taken place at a uniform rate. It is a reasonable assumption that in the special case where the temperature rise is uniform, correcting for heat losses is more simple. It is also seen (Fig. 1) that it takes considerable time for the temperature of the water to reach its maximum value. From this it may be concluded that the specimen is a poor thermal conductor. The case where the specimen is a good thermal conductor and the temperature rise is so rapid that the section IM of the curve cannot be constructed must be solved by other methods. In the discussion that follows only the case represented by Fig. 1 is considered.

The final temperature for the case illustrated in Fig. 1 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 IAR and AFBM are equal. The ordinate of the point F is the final temperature $t_{\rm F}$. 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 of a body is proportional to the difference in temperature between the body and its surroundings. The height of each point on the graph above the horizontal line at $t_{\rm R}$ is, therefore, proportional to the rate of cooling. Multiplying any given time interval by the corresponding rate of cooling gives the temperature loss during this interval. Referring to Fig. 2, where the area between the curve and the horizontal line at $t_{\rm R}$ is divided into thin slices, the height of a slice (for example, the shaded one) is proportional to the rate of cooling at that particular time and the width of the slice is equal to the time interval ΔT .



Fig. 2. The temperature loss is proportional to the area under the curve.

From this it follows that the area of the slice is proportional to the temperature loss during the interval ΔT . Upon summing the areas of all the slices, it is evident that the temperature deficiency due to loss of heat in the time interval IG is proportional to the area IAMBG. This temperature deficiency is the same as if the body had started at the temperature represented by the point *R*, risen instantly to temperature t_F and then cooled as indicated by the line FBC. The temperature loss in one case is proportional to the area IAMBG and in the other case to the area RFBG. These two areas are equal, since FR was drawn to make area IAR equal to area AFBM. It may be concluded, therefore, that if

no heat had been lost the thermometer reading would have risen from $t_{\rm I}$ to $t_{\rm F}$ and then have remained constant.

APPARATUS: A vacuum jacketed calorimeter, stirrer, centigrade thermometer graduated in one tenth degree divisions, steam jacket, steam generator, specific heat flask, two Bunsen burners, two beakers, ring stand, balance, various liquid specimens, watch and access to a barometer are required.

The vacuum jacketed calorimeter is illustrated in Fig. 3 and



Fig. 3. The Vacuum Jacketed Calorimeter

shown in cross section in Fig. 4. The aluminum cup C is suspended inside the vacuum flask V from an insulated 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.

The steam generator is shown in Fig. 5 and steam jacket in Fig. 6. The arrangement if the apparatus used for holding the specimen at the temperature of boiling water is illustrated schematically in Fig. 7. The water in the steam generator G is boiled by means of the Bunsen burner B, and the resulting steam passes through the double wall of the steam jacket J and out the tube F. The beaker R catches the water resulting from condensation. The specimen X is suspended inside the steam jacket by means of a string and a small clamp on the cover C of the chamber. The lower end of the heating chamber is closed with a cork stopper.

The specific heat flask (Fig. 8) has thin walls of copper. After the flask has been filled with the liquid under investigation, a cork stopper, with an attached string, is firmly inserted into the neck of the flask. The string is used to suspend the flask within the steam jacket.

PROCEDURE: Light both Bunsen burners, placing one under the steam generator, which should be at least half full of water, and the other under the beaker of water. While waiting for the water to boil, weigh the copper flask, fill it with glycerin and weigh again. Place the cork stopper in the flask and, by means of the attached string, lower the specimen into the beaker of boiling water.

When the specimen has come to the temperature of boiling water, remove it and suspend it in the steam jacket. This dries the specimen and maintains it at the temperature of boiling water until time to transfer it to the calorimeter.

Weigh the aluminum cup, fill it with water at room temperature and weigh again. Assemble the apparatus as shown in Fig. 4 with the thermometer and stirrer in position. Stir the water and observe the thermometer reading for several minutes to make sure that the temperature is constant.



Fig. 4. Diagram of the Vacuum Jacketed Calorimeter.

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.



Fig. 5. The Steam Generator

Read the barometer. Use the observed barometric height and steam tables to compute the temperature of saturated water vapor under the existing atmospheric pressure. This is assumed to be the temperature within the steam jacket and therefore the initial temperature t_s of the specimen. With the calorimeter directly under the steam jacket, read carefully and record the temperature t_i of the water. Remove the cork stoppers and, when the watch reads on the minute, lower the specimen into the cup of water. Replace the cork stopper in the calorimeter. Read the temperature each halfminute until the temperature has reached its maximum and has fallen for at least eight minutes.



Fig. 6. The Steam Jacket

The water should be gently stirred during this period and, except when the temperature is changing rapidly, the thermometer readings should be estimated to hundredths of a degree centigrade.





Fig. 7. Arrangement of the apparatus used in holding the temperature of the specimen at the temperature of boiling water.

Plot a curve, similar to the one in Fig. 1, which shows the relationship between these temperature readings and elapsed times. Extrapolate this curve to the axis of ordinates, and, using the method of equal areas, construct the line FR. As explained above, the ordinate of the point *F* is the final temperature t_F . It is considerably more accurate, however, if the section BC of the curve is redrawn on a much larger scale, like the one shown in Fig. 9, and t_F determined from this second curve. Construct such a graph and determine t_F . Determine the thermal capacities of the thermometer, the stirrer, the calorimeter cup and the copper flask. 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 (0.46cal/cm³/°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



Fig. 8. The Specific Heat Flask

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 can not be weighed separately (or estimated with sufficient accuracy) the value of the thermal capacity will be supplied by the instructor. The thermal capacities of the cup and flask may be computed from their respective masses and specific heats. The specific heat of aluminum is 0.22cal/gm/°C and of copper is 0.093cal/gm/°C.

Using Eq. (3), compute the value of the specific heat of glycerin.

Repeat the experiment, using other liquids suggested by the instructor.



Fig. 9. The final temperature ty is the ordinate of the point F.

QUESTIONS: 1. Give three reasons why it is advisable to place the specimen in the steam jacket rather than transfer it

directly from the boiling water to the calorimeter.

2. Compare the errors introduced into this experiment by a one-degree error in ts and an error of one-tenth degree in t_F.

3. What percentage error in the determination of the thermal capacity of the thermometer would cause a one tenth percent error in the specific heat of glycerin?

4. The glass wall of the thermometer bulb is very thin. What are the advantages and disadvantages of this?

5. If the burner under the steam generator is turned too high, the steam is ejected with considerable velocity. Discuss the nature of the error caused by this.

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

7. It is frequently suggested that loss of heat from the calorimeter cup may be minimized by so choosing the initial temperature that it is as far below the temperature of the surroundings as the final temperature is above. Criticize this method as it applies to this experiment.

8. Assume that the temperature of the surroundings, for the case shown in Fig. 1, is not equal to the initial temperature but is midway between the initial and maximum temperature. For what fractional part of the time in the interval from I to M does the cup absorb heat from the surroundings?

9. Explain why the experiment as outlined above could not be used to determine the specific heat of alcohol.

10. What effect does the high viscosity of glycerin have on the shape of the curve in Fig.1?

11. In using Fig. 1 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 rises during the experiment, how are the results affected?