

HEAT OF VAPORIZATION

OBJECT: To measure the heat of vaporization of water.

METHOD: A condenser is placed in a calorimeter containing a measured quantity of water, and steam is passed into the condenser where it is converted into water. The heat absorbed by the calorimeter cup and its contents (water, thermometer, stirrer and condenser) is computed from their combined thermal capacity and the rise in temperature. The heat given up by the condensing vapor is expressed in terms of the mass of the vapor, the heat of vaporization and the fall in temperature of the water resulting from the condensation. The heat absorbed by the cup and its contents is set equal to the heat given up by the steam, and this equation is solved for the heat of vaporization. A correction is made for the heat lost to the surroundings.

THEORY: 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 applied to particular situations. 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 and in some cases to the opening up of whole new fields of physics.

A necessary corollary of 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. During this interval 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. Again the heat is converted into potential energy since, 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. 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

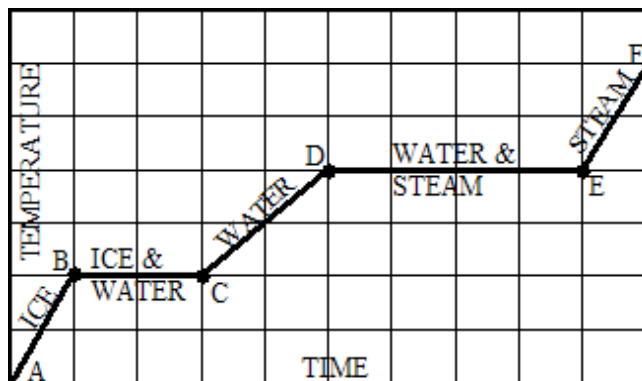


Fig. 1. Heat may either raise the temperature of a substance or change its state. This graph is not constructed accurately to scale.

the 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.

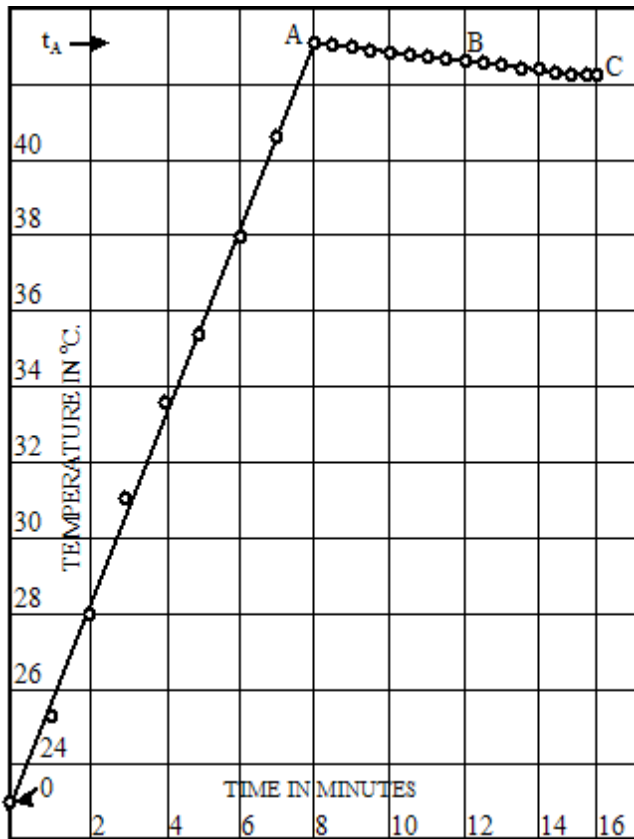


Fig. 2. Body is heated and then cools by radiation to the surroundings.

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 ($\text{cal}/\text{gm}^\circ\text{C}$). 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 ($\text{cal}/^\circ\text{C}$). 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 specific heat of water with temperature is negligible.

The quantity of heat required to change material from the liquid to the vapor state is proportional to the mass m of the material. Stated algebraically

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

where the constant of proportionality L_v depends upon the kind of substance and is called the *heat of vaporization*; sometimes it is called the latent heat of vaporization. In the metric system L_v is expressed in calories per gram (cal/gm). Obviously, the heat of vaporization is numerically equal to the heat required to change one gram of the substance from the liquid to the vapor state. The heat required to vaporize a liquid may be recovered, for if the vapor is allowed to condense, L_v calories of heat are liberated for each gram of vapor that condenses.

Method of Mixtures: The simplest method of measuring the heat of vaporization is the method of mixtures. In this method steam is condensed in a vessel of water, and the heat given up by the steam in condensing and coming to the final temperature of the mixture is set equal to the heat gained by the rest of the system. Since the only unknown in this equation is the heat of vaporization L_v , the equation may be solved for L_v .

Suppose that a condenser K (Fig. 5) is placed in a cup, containing water and equipped with thermometer and stirrer, and that a mass m_v of water vapor is condensed. The temperature of the cup and its contents rises from an initial temperature t_o to a final temperature t_A . The steam condenses at a temperature t_s (the temperature at which water boils under the existing atmospheric pressure) and the resulting water falls in temperature to t_A . Setting the heat given up by the steam and resulting water equal to the heat absorbed by the cup and its contents plus the heat H_R radiated to the surroundings, yields the equation

$$L_v m_v + m_v c_w (t_s - t_A) = (C_w + C_c + C_T + C_S + C_K)(t_o - t_A) + H_R \quad (3)$$

in which c is specific heat, C is thermal capacity, m is mass

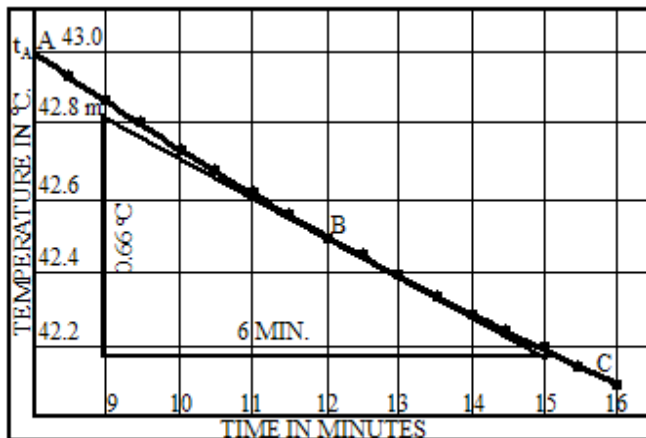


Fig. 3. The rate of cooling is determined from the slope of the curve.

and the subscripts V , W , C , T , S and K refer to vapor, water, cup, thermometer, stirrer and condenser, respectively.

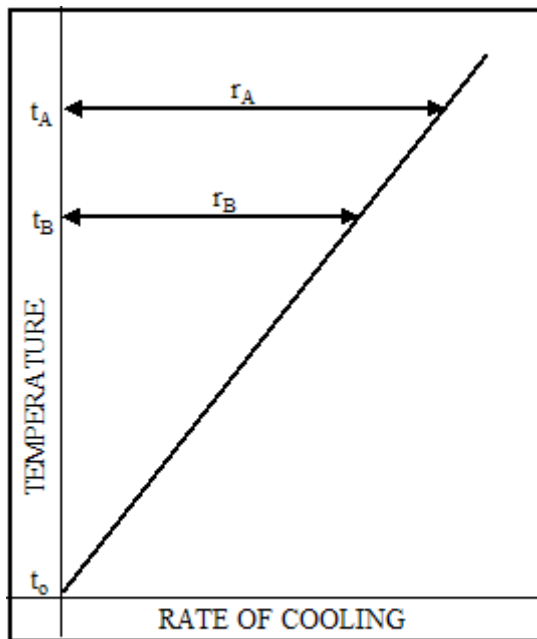


Fig. 4. The rate of cooling is proportional to the difference in temperature between the body and its surroundings.

Correction for Heat Lost to the Surroundings: In this experiment most of the heat given up by the vapor is used to raise the temperature of the cup and its contents, but some of the heat is radiated to the surroundings. It is necessary, therefore, to determine how much heat has been lost to the surroundings. Suppose that heat is added at a uniform rate to a body which is originally at the temperature t_0 of the surroundings. The temperature of the body is read at regular intervals and the temperature t plotted against the time T as indicated in Fig. 2. It is evident that heat was being added to the body during the interval OA and in the interval AC the

body was cooling owing to radiation to the surroundings. Of course heat was also being radiated during the interval OA , and it is for this loss that correction must be made.

There are several methods of correcting for the heat lost by a body to its surroundings, and the choice of method depends upon the conditions of the experiment. For the case where the temperature rises at a uniform rate, particularly if a vacuum-jacketed calorimeter is used, the method outlined below is recommended. To study the cooling of the body it is advisable to construct the portion ABC of the curve on a much larger scale as indicated in Fig. 3. Newton's law of cooling states that, provided 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 rate of cooling r_B at the temperature t_B is found from the slope of the tangent (mn) drawn to the curve at the point B . The point B is any convenient point near the middle of the section ABC of the curve. It follows from Newton's law that the graph obtained by plotting rate of cooling against temperature (Fig. 4) is a straight line and that

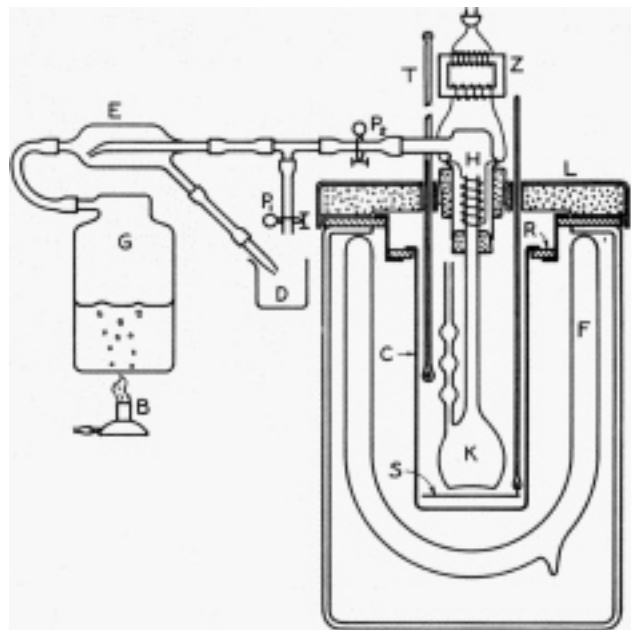


Fig. 5. Arrangement of the apparatus.

the rate of cooling r_A at temperature t_A may be obtained by proportion. Since, while the temperature was rising, the rate of cooling increased uniformly from zero to r_A , the average rate of cooling \bar{r} during the interval OA is $\frac{1}{2}r_A$. From this it follows that

$$r = \frac{1}{2}r_B \frac{t_A - t_0}{t_B - t_0} \quad (4)$$

It should be obvious that the heat H_R lost during the interval OA is equal to the product of the average rate of cooling, the thermal capacity and the elapsed time ($T_A - T_0$). In the present experiment the thermal capacity of the cooling body is $(C_W + C_C + C_T + C_S + C_K + m_V c_W)$ and it follows that

$$H_R = \frac{1}{2} r_B \frac{t_A - t_o}{t_B - t_o} (C_W + C_C + C_T + C_S + C_K + m_V c_W)(T_A - T_O) \quad (5)$$

APPARATUS: Vacuum jacketed calorimeter, condenser equipped with heating coil, water trap, steam generator, centigrade thermometer graduated in one-tenth degree divisions, ring stand, stop watch, Bunsen burner, beaker, two pinch cocks, T-tube and transformer are required. Two balances should be available: a sensitive balance for weighing the collector and condensed vapor, and a rough balance for all other weighings. The vacuum-jacketed calorimeter is illustrated in Fig.6 and shown in cross section in Fig. 5. The aluminum cup C is suspended inside the vacuum flask F from an insulating ring R. To minimize heat conduction the cover L is lined with a thick layer of cork insulation and the handle of the stirrer S is made of glass. Temperatures are read by means of the precision thermometer T.



Fig. 6. The Vacuum Jacketed Calorimeter

The Bunsen burner B is used to boil the water in the steam generator G (illustrated in Fig. 7) and the resulting steam passes through the water trap E (Fig. 8) where the water that has condensed in the connecting tubes is drained off into the beaker D. When the pinchcock P₁ is closed and P₂ is open, the steam passes into the condenser K where it is condensed and collected. A heating coil H is wound around the entrant tube of K. Without the heating coil a considerable amount of steam condenses at the entrance and the resulting water flows into the condenser.



Fig. 7. The Steam Generator

This should be prevented since the steam that condenses at this point does not deliver its heat of condensation to the water in the calorimeter. Condensation is prevented at this point by raising the temperature to the boiling point and the most convenient method of raising the temperature is by means of the heating coil. The step-down transformer Z provides the coil with 2.5 to 3.0 amperes of current. If the output voltage of the transformer is too high, a fixed resistance should be inserted in the circuit to give the correct current.

PROCEDURE: Weigh the aluminum cup C, fill it about two-thirds full of water at room temperature and weigh again 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. Remove the lower glass part of

the condenser K from the rest of the assembly and weigh it (to hundredths of a gram) on the sensitive balance. Assemble the apparatus as shown in Fig. 5, place the Bunsen burner under the steam generator and turn on the current in the heating coil. During this preliminary heating, the pinchcock P₂ should be closed and P₁ open. After the water in the generator has been boiling for a few minutes, proceed to take observations in the following manner. Stir the water thoroughly to make sure thermal equilibrium has been established, and read the temperature t_o to hundredths of a degree. Turn off the current in the heating coil H, open P₂, close P₁ and start the stopwatch. While the temperature is rising (interval OA, Fig. 2) the thermometer T should be read to tenths of a degree and at one-minute intervals. When the temperature has risen about 15°C (point A) the flow of steam to the condenser is stopped by opening P₁ and closing P₂. For about 8 minutes thereafter (interval ABC) the thermometer should be read to hundredths of a degree at one-half minute intervals. The water should be stirred throughout the experiment, but care should be taken that no water is splashed from the cup. Again remove the lower part of the condenser, wipe the outside dry and weigh on the sensitive balance. Since water always collects in the upper part of the condenser, care must be exercised while taking the apparatus apart that none of this water runs into the lower part.



Fig. 8. The Water Trap

Construct curves similar to the ones shown in Figs. 2 and 3. From the second curve determine the final temperature t_A and the rate of cooling r_B. Read the barometer and, using steam tables, determine the temperature t_s of the steam. Determine the thermal capacities of the thermometer, the stirrer, the calorimeter cup and the condenser. 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 submerged portion of the thermometer. The thermal capacities of the cup, condenser and stirrer may be computed from their respective masses and specific heats. The specific heat of aluminum is 0.22cal/gm/°C and of Pyrex glass is 0.20cal/gm/°C. The

specific heat of the stirrer may be assumed to be $0.21\text{cal/gm}^\circ\text{C}$. In case a copper cup is used, its specific heat is $.092\text{cal/gm}^\circ\text{C}$. For very precise work the fact that the upper parts of condenser and stirrer are not heated by the water should not be neglected in computing the thermal capacities.

Use Eq. (5) to determine HR and Eq. (3) to determine L_v .

QUESTIONS: 1. What percentage error in the determination of L_v would be caused by each of the following: (a) an error of 5% in the combined thermal capacity of the cup, stirrer, condenser and thermometer? (b) an error of 1gm in the mass of water? (c) an error of 10% in the value of t_B ? (d) an error of 0.5°C in the value of t_s ? (e) an error of 0.1°C in t_A ?

2. In this experiment does the temperature of the surroundings remain constant? Explain.

3. The curve ABC (Fig. 3) is slightly concave upward. Explain why.

4. 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.

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

6. Express the value of L_v , as determined in this experiment, in British thermal units per pound.

7. When a 100gm metal object, originally at a temperature of 20°C , is held in a steam chamber, 2.2gm of water condense on it. What is the specific heat of the metal? Assume that the temperature of the steam is 100°C .