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A CALORIMETER FOR MEASURING SPECIFIC HEATS AND HEATS OF VAPORIZATION OF LIQUIDS. THE SPECIFIC HEAT AND HEAT OF VAPORIZATION OF LIQUID ETHYL ETHER AT 0° AND 12°

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Introduction

This investigation was carried out some years ago, and was concerned with the design of a calorimeter for the accurate determination of latent heats of vaporization of liquids, and of specific heats of liquids and compressed gases. The advantage of the apparatus is that it can be used over a wide series of temperatures, especially the range from room temperature down. The apparatus described in this article was used in determining some of the thermal properties of liquid ethyl ether at two temperatures below that of the room. With the aid of the experience so obtained the calorimeter has been redesigned and is being used for a study of the thermal properties of some other substances.

The usual method of determining specific heats is to place a known quantity of the substance in a calorimeter, to introduce a measured amount of energy, and to determine the rise in temperature. Corrections must be applied for the amount of energy absorbed by the calorimeter and for the various heat leakages, which often introduce great uncertainties into the result. Many special types of calorimeters have been designed to reduce or compensate one or both of these corrections for certain ranges of temperature, especially in the region near room temperature where thermostats can be accurately controlled.

The ordinary method of determining heats of vaporization of liquids is to draw off a measured portion of the dry saturated vapor, and determine the drop in temperature of the liquid remaining behind. The accuracy of the result is reduced by the many necessary corrections, as well as by any uncertainties in the specific heat of the liquid. In this field also, many special types of apparatus have been proposed and used.

Previous Work

For the heat of vaporization of ethyl ether Regnault[1] gives the equation $r = 94.00-0.07901\,t-0.0008514\,t^2$ and Winkelmann[2] from a recalculation of Regnault's results obtained the equation $r = 93.50-0.1082\,t - 0.0005033\,t^2$ where t is the temperature in degrees centigrade, and r the heat of vaporization in calories per gram.

Ramsay and Young,[3] substituting their measured values of specific volumes and vapor pressures in the Clapeyron equation, arrived at the value 93.27 calories per gram at 0° and 90.77 at 10°; and Mills[4] calculated 92.52 calories per gram at 0° and 87.54 at 20°.

As to the specific heat of liquid ether, the only values in the range from 0° to 12° are by Regnault,[5] whose data were represented by the equation $C = 0.529 + 0.000592\,t$, where C is the specific heat of the liquid in calories per gram, along the saturation curve, and t is the temperature in degrees centigrade. In Table I are given the values calculated from the above equations for the temperatures used in this investigation.

The Apparatus

The apparatus consisted of a silver calorimeter enclosed in a glass vessel, so arranged that the space between could be evacuated when desired. Provision was made for withdrawing known amounts of dry saturated vapor at the temperature of the liquid, and for introducing measured quantities of electrical energy. The temperature of the liquid in the calorimeter was measured by means of a platinum thermometer placed in good thermal contact with it.

The calorimeter is shown in Fig. 1. A vessel A of silver 2 mm. thick, and 105 mm. long by 25 mm. in diameter, contained a re-entrant tube B, which reached almost to the bottom and enclosed a platinum thermometer. By means of a platinum ferrule this tube was connected to a glass tube, which carried the thermometer leads to the head C from which the usual connections were made to the temperature-measuring bridge, capable of indicating 0.0005°.

The tube carrying the thermometer leads was connected to the glass vacuum jacket by means of De Khotinsky cement. This vessel also possessed tubes for the introduction of the current wire and for the vapor exit tube, as well as a connection to a mercury

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[1] Regnault, See Winkelmann, "Hand. d. Physik," J. H. Barth, Leipzig, **1906,** Vol. 3, p. 1093.

[2] Winkelmann, *Wied. Ann.*, **9,** 358 (1880).

[3] Ramsay and Young, *Phil. Trans.*, **178A,** 88 (1887).

[4] Mills, THIS JOURNAL, **31,** 1123 (1909).

[5] Ref. 1, p. 196.

diffusion pump for evacuation. This latter tube (not shown in the drawing) was of sufficient size, 1 cm. inside diameter, so that very high vacua could be quickly produced.

The vapor exit coil D was a silver tube 4.5 meters long and about 0.5 mm. inside diameter. It was doubly wound in the manner of a non-inductive resistance, one end projecting into a small cap E on the top of the calorimeter vessel, and the other passing out through the vacuum jacket to the volumenometer, a shut-off valve being in the line. (See also Fig. 2.) In order to leave the calorimeter, the vapor had to travel to the top of the cap, thence down through the tube to the bottom of the liquid and up again. By this means, it is believed that only dry saturated vapor at the temperature of the liquid was withdrawn. That part of the vapor tube which was outside of the calorimeter was much larger in diameter than the part inside.

The heating coil F consisted of an asbestos covered Nichrome wire drawn through a silver tube and soldered to it at the bottom end. The tube was soldered to the container and the wire projecting through was connected to a copper wire at K. The other electrical connection was made to the vapor-exit tube. The resistance of the heater was about 12 ohms.

The *accessory apparatus* is shown in Fig. 2. The calorimeter A was immersed in a bath at the desired temperature. The electrical current was furnished by a 3-cell lead storage battery E connected in parallel. In series with the battery were a standard resistance F, a variable resistance B, the heating coil of the calorimeter, and a switch D. Two leads from the standard resistance and two from the calorimeter were connected to the potentiometer J, through the double-throw double-pole switch G in such a manner that the potential drop across either could be measured. The voltage characteristics of the storage battery were studied with a view to determining the best time for using it. It was found that if after charging, it was allowed to discharge for several days through a resistance of about the same as that in the heating coil of the calorimeter, the voltage became very constant, changing less than one part in 300 during 24 hours.

The temperature was measured on the resistance bridge H.

The method of determining the amount of vapor distilled was to condense it into the volumenometer K, which consisted of a series of 5 calibrated bulbs, three of 1 cc. capacity and two of 10 cc., connected by calibrated capillary tubing. In making a determination of latent heat, this volumenometer was placed in a bath at a sufficiently low temperature to give the desired rate of distillation and the weight of ether distilled determined from its volume and independent measurements on the density.

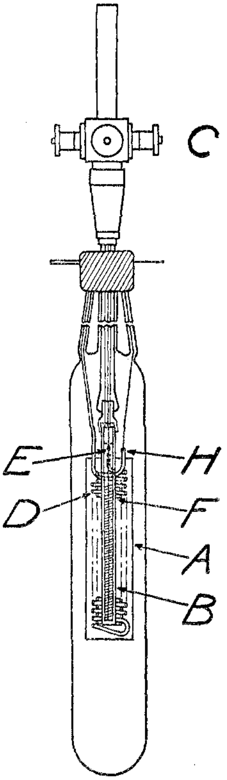

Fig. 1.—The calorimeter.

The *loading device* is also shown in Fig. 2. Because of the method used in determining the amount of ether distilled it was necessary to have no permanent gases present. The entire apparatus was evacuated until the pressure read less than 0.0001 mm. after standing. The glass tip from the tube N was broken under the surface of liquid ether which had been treated with sulfuric acid according to Willstätter's method, dried over calcium chloride and finally distilled over sodium to fresh sodium. The liquid was thus drawn into N. By the use of liquid ammonia it was distilled back and forth many times between the tubes M and N through a greaseless stopcock, the entire vapor phase being removed each time by evacuation. The removal of all the permanent gases was shown by the complete collapse of the vapor phase in the small inverted bell-shaped device under the hydrostatic pressure of the liquid. The stopcock L was opened and the liquid distilled into the volumenometer until full, the cock C being closed, and the loading apparatus sealed off at L. Before the final filling, the apparatus was rinsed out several times with ether vapor and evacuated to insure the complete removal of permanent gases. The amount of ether in the apparatus was thus known from the volume of liquid in the volumenometer, and the amount of vapor in the space above up to the cock C.

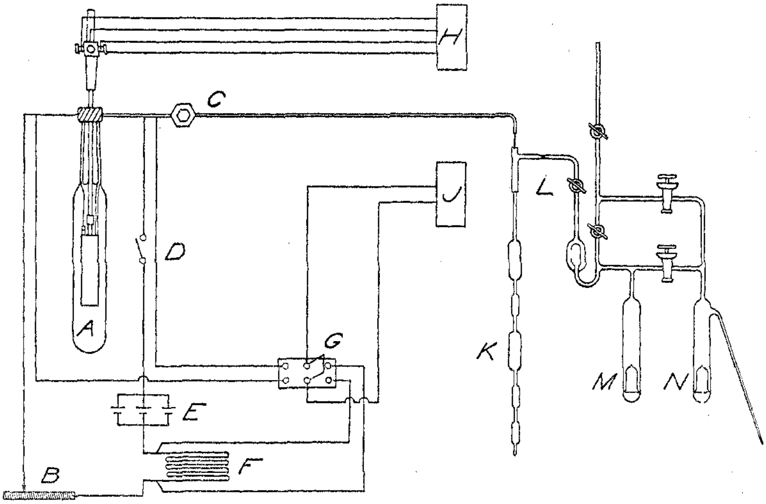

Fig. 2.—The accessory apparatus.

Experimental Method

Heat of Vaporization.—The ether was distilled into the calorimeter by cooling it. The calorimeter was immersed in a thermostat at constant temperature and when the platinum thermometer indicated the same temperature as that of the bath, the glass jacket was evacuated.

The volumenometer was surrounded by a bath at a somewhat lower temperature than that of the calorimeter, using ice for the 12° run, and liquid ammonia for the 0° measurement, and cock C opened, thus causing the liquid to distil from the calorimeter. The sliding resistance in the battery circuit was so adjusted that the temperature indicated on the platinum thermometer remained constant, the temperature being read every minute. As the bulbs of the volumenometer filled, the bath around it was raised so that only the bulbs already filled, and that being filled, were cooled, thus preventing condensation in the bulbs above. As the meniscus passed along the capillaries between the bulbs, the time was read. It required about 30 minutes to fill one of the smaller bulbs, and four hours and a half for the larger.

During the filling of the first bulb no measurements were taken, since the current was being changed so as to keep the temperature in the calorimeter constant. After that only very small changes in the resistance were necessary. The energy input was determined by measuring the potential drops across the heating coil and standard resistance every two minutes and integrating with respect to the time the EI products so obtained.

Two corrections were necessary to obtain the heat of vaporization from the amount of ether distilled, and the energy input. The first is applied to the weight of liquid evaporated and is due to the fact that the space occupied by the distilled liquid in the calorimeter at the beginning of a measurement was filled with vapor at the end; this can be calculated from the vapor density and the volume of the liquid distilled.

The second is caused by the Joule-Thomson cooling of the vapor due to the drop in pressure from the vapor pressure of the liquid in the calorimeter to that of the liquid in the volumenometer. Since the vapor tube outside the calorimeter was quite large and short, all this cooling was considered to have taken place in the calorimeter. The value of the Joule-Thomson coefficient μ was calculated from the Keyes equation of state for ether vapor. The heat withdrawn by W grams of vapor dropping from a pressure of p_1 to p_0 is then, $Q = \mu\, C_p\, (p_1 - p_0)\, W$, assuming that μ and C_p are constant over the pressure range p_1 to p_0.

This latter correction is due to the fact that it is the reversible heat of vaporization which is desired. The heat input measured in the calorimeter corresponds to an irreversible change, namely liquid ether at $t°$ converted into vapor at a pressure less than the vapor pressure at $t°$, the drop in pressure being carried out in the calorimeter by the vapor flowing through a fine tube. The irreversibility in the change in state is this latter process, and the correction can evidently be calculated by the Joule-Thomson coefficient as given above. The heat thus corrected is the reversible heat corresponding to the conversion of liquid ether at $t°$ to its vapor under the vapor pressure at $t°$.

The first of these two corrections amounts to about 0.1 calorie per gram, and the second, 0.15 calorie per gram at 0°, and although the latter could not be made with great accuracy (perhaps 10%), there were other factors which influenced the results more than the uncertainty in this correction.

Specific Heat.—Instead of measuring the heat capacity of the calorimeter empty and making a correction for it when determining the heat capacity of the liquid filling it, a procedure was employed which eliminated the necessity of such a measurement. All of the ether in the system was condensed into the calorimeter and a heat-capacity determination made, the cock C being closed. Then about half of the liquid was distilled into the volumenometer, the cock C closed and another determination made. In each case the exact weight of liquid in the calorimeter was known.

This gives two equations connecting the specific heat of ether and the heat capacity of the calorimeter, from which the latter could be eliminated.

The determinations were carried out in the ordinary manner. The calorimeter was placed in the thermostat and after taking readings of temperature for ten minutes the switch D was closed and the temperature read every half minute until the total rise was about 2°. The switch was then opened and the cooling curve followed for about 15 minutes. The energy input was determined by measuring the voltage drops across the heating coil and the standard resistance every minute and integrating, with respect to the time, the *EI* products so obtained.

In these measurements the temperature of the thermostat remained constant. However, the heating curve rose very steeply and was quite sharp at the top, indicating only a small heat leak.

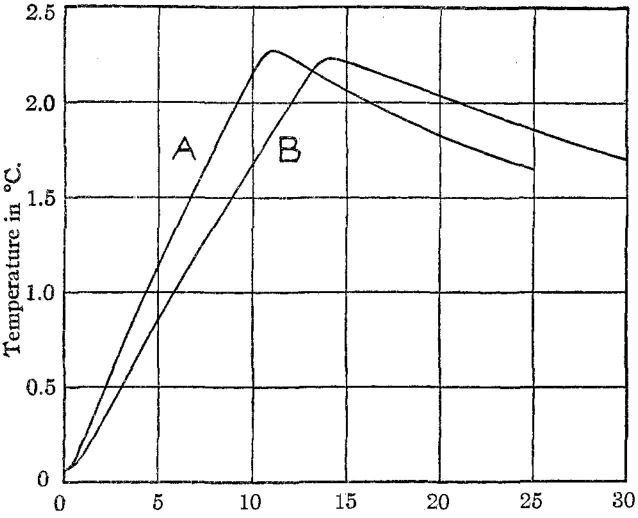

Fig. 3.—Heating curves for specific-heat determination. Curve A, Calorimeter half full. Curve B, Calorimeter full.

By raising the temperature of the thermostat at even approximately the same rate as that in the calorimeter, it is believed that the experimentally-determined temperature rise will require no correction.

There was, however, a temperature lag of from one half to one minute, due to the time required to transmit energy to the thermometer from the walls of its container. This can be greatly reduced by the use of platinum resistance thermometers of the flat type, for which the lag is practically zero.

A typical set of heating curves is shown in Fig. 3. The observed temperature increase was corrected for the radiation loss in the following manner. If t_r is the radiation loss expressed in degrees and τ the time, then Newton's law of cooling gives $\frac{dt_r}{d\tau} = k\ (t-t_s) = k\ (f(\tau)-t_s)$, where t is the temperature of the calorimeter at the time τ, and is some function of τ, and t_s is the temperature of the thermostat. Integration gives $t_r = k\int_{\tau_1}^{\tau_2} [f(\tau) - t_s]\ d\tau = k \times$ (area under the heating curve) (Fig. 3). Now $k = \frac{dt_r}{d\tau}\left(\frac{1}{t - t_s}\right)$, and since the cooling curve at the end of the run is due to the loss of heat by radiation alone, the value of k can be obtained from the slope of this line at any point, and its height above the initial temperature. This tangent can be accurately obtained since the cooling curves are so nearly straight lines. The magnitude of this correction was about 0.3° on an observed temperature rise of 2.2°.

It will be noticed that at the beginning of a measurement the calorimeter was at the temperature of the thermostat so that no correction need be applied for the radiation loss at the start.

The energy input must be corrected for the small amount of vaporization which occurred due to the change in vapor pressure when the temperature was increased. In the case of the measurement with the calorimeter full, this was negligible.

Results

In Tables I and II are given the results of the measurements taken in this investigation together with those of other observers. The references are given in an earlier paragraph.

TABLE I

HEAT OF VAPORIZATION OF ETHYL ETHER

Calories per gram

Temp. °C.	Keyes and Beattie	Regnault	Winkelmann	Mills	Ramsay and Young
0.1	90.50	93.99	93.49	92.52[a]	93.27[a]
11.8	88.83	92.95	92.15	87.54[b]	90.77[c]

[a] At 0°. [b] At 20°. [c] At 10°.

TABLE II

SPECIFIC HEAT OF LIQUID ETHYL ETHER

Calories per gram per degree

Temp. °C.	Keyes and Beattie	Regnault
1.2	568	530
13.4	577	537

Accuracy of the Results

A comparison of the results of this investigation with those obtained by other observers shows that the present measurements lead to a higher value for the specific heat and a lower value of heat of vaporization than those measured by previous investigators.

An analysis of the various factors entering into the calculations of the specific heat and heat of vaporization leads to the conclusion that the probable accuracy of the present results is within about 1% in each case. By far the greatest factor entering into this uncertainty is that caused by the lag in the temperature measurement.

Further work is being carried out with a calorimeter of the same type as the one described in this investigation. It has been redesigned to permit the use of a platinum thermometer of the flat type, which the work of the present investigation indicated was very necessary in such a calorimeter, several other improvements being also incorporated.

Summary

A new type of calorimeter for the determination of the specific heats and heats of vaporization of liquids is described. It can also be used for the determination of the specific heats of compressed gases. This calorimeter can be used over wide ranges of temperature and is especially suited for use in the range under room temperature.

The heat of vaporization and specific heat of liquid ethyl ether were determined for the temperatures 0° and 12°, with an accuracy within about 1%.

The main factor in reducing the accuracy of the results was determined, and the method of avoiding it given. Work is proceeding with the calorimeter in its improved form.

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THE SYSTEM MAGNESIUM SULFATE-SODIUM SULFATE-WATER AND A METHOD FOR THE SEPARATION OF THE SALTS

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In order that a method might be devised for the separation by fractional crystallization of sodium sulfate from magnesium sulfate or *vice versa* it was necessary to know the solubility relationships of these salts over the entire range of temperature from the freezing points to the boiling points of their solutions. The data given by Roozeboom,[1] van't Hoff,[2] Hildebrand,[3] Blasdale,[4] D'Ans,[5] and Seidell[6] apply to only a few temperatures.

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[1] Roozeboom, *Rec. trav. chim.*, **6**, 333 (1888).

[2] van't Hoff, "Über die Bildungsverhältnisse der ozeanischen Salzablagerungen," Leipzig, **1912**.

[3] Hildebrand, *J. Ind. Eng. Chem.*, **10**, 96 (1918).

[4] Blasdale, *ibid.*, **10**, 344 (1918); *ibid.*, **12**, 164 (1920).

[5] D'Ans, *Kali*, **9**, 177 (1915).

[6] Seidell, "Dictionary of Chemical Solubilities," D. Van Nostrand Co., **1920**.