

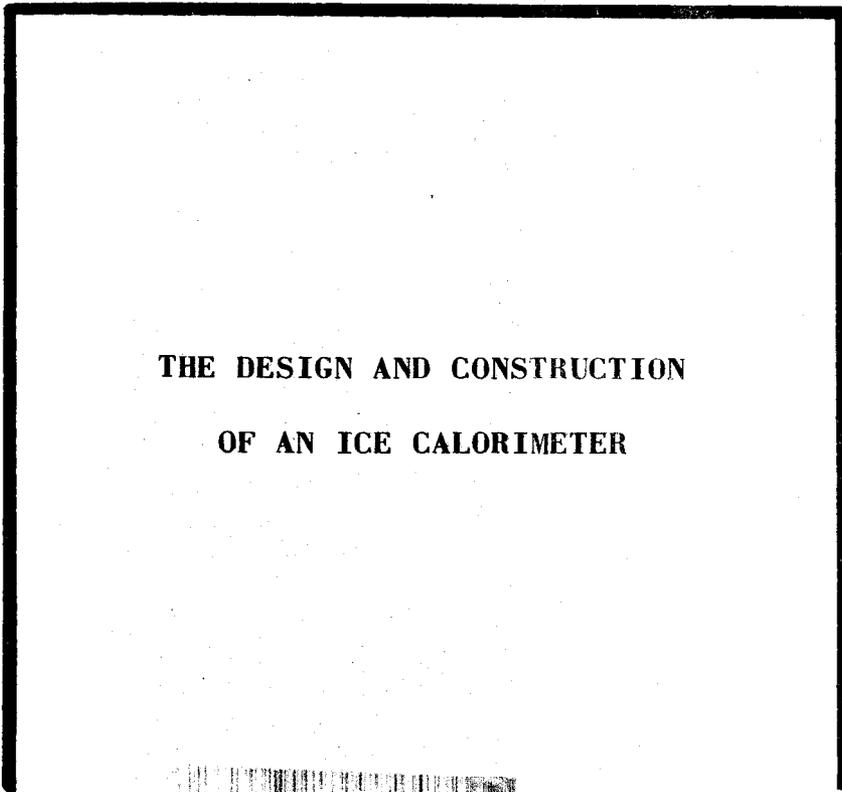
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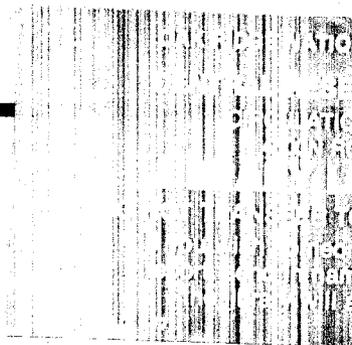
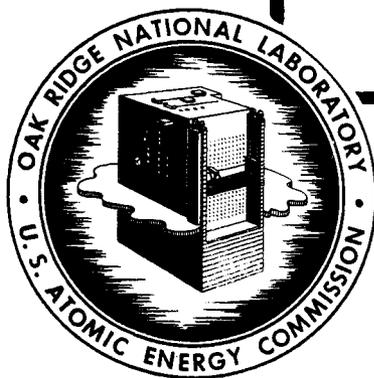
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THE DESIGN AND CONSTRUCTION
OF AN ICE CALORIMETER



OAK RIDGE NATIONAL LABORATORY
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THE DESIGN AND CONSTRUCTION OF AN ICE CALORIMETER

R. F. Redmond
J. Lones

DATE ISSUED:

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SUMMARY

An isothermal ice calorimeter has been designed and constructed for use in obtaining heat capacity data within $\pm 5\%$ in the temperature range 100 - 1000 °C. Relative enthalpies are measured by the amount of volume change that occurs in a two phase ice-water mixture which gains heat from a heated sample. Using a synthetic sapphire calorimetric standard the calorimeter was checked for performance and was found to give heat capacity values with an accuracy greater than 95%.

INTRODUCTION

In conformance with the program initiated at ORNL for the purpose of obtaining physical property data for materials at elevated temperatures (100 - 1000°C), an ice calorimeter has been designed, constructed and tested for use in determining heat capacity values within $\pm 5\%$.

The ice calorimeter was originated by Robert Bunsen (1) in 1870. The ice calorimeter belongs to a class of isothermal calorimeters in which the heat quantity is measured by the amount of an isothermal phase change the heat produces. In the case of the ice calorimeter, ice in a two phase mixture of ice and water undergoes a phase change proportional to the amount of heat gained from a heated sample. The phase change is measured by means of a volume change in the two phase mixture. This is possible because of the difference in densities of ice and water at 0°C.

To determine the proportionality constant to be used in calculating the heat exchange from the indicated volume change, the densities of ice and water at 0°C, and the latent heat of fusion of water must be used. This information is known quite accurately (2) (4) (5).

$$\begin{aligned}\Delta H_f &= 79.72 \text{ cal/g} \\ \rho_{\text{water}} &= 0.99987 \text{ g/ml} \\ \rho_{\text{ice}} &= 0.91671 \text{ g/ml}\end{aligned}$$

The proportionality constant calculated from these values is

$$K = \Delta H_f / \left[\frac{1}{\rho_{\text{ice}}} - \frac{1}{\rho_{\text{water}}} \right]$$
$$K = 878.7 \text{ cal/ml.}$$

As the heat capacity is to be determined by first determining the enthalpy-temperature relation of each substance, and then calculating the slope of the enthalpy-temperature curve at various temperatures, it was thought necessary to have enthalpy data within $\pm 3\%$ to obtain the desired heat capacity accuracy.

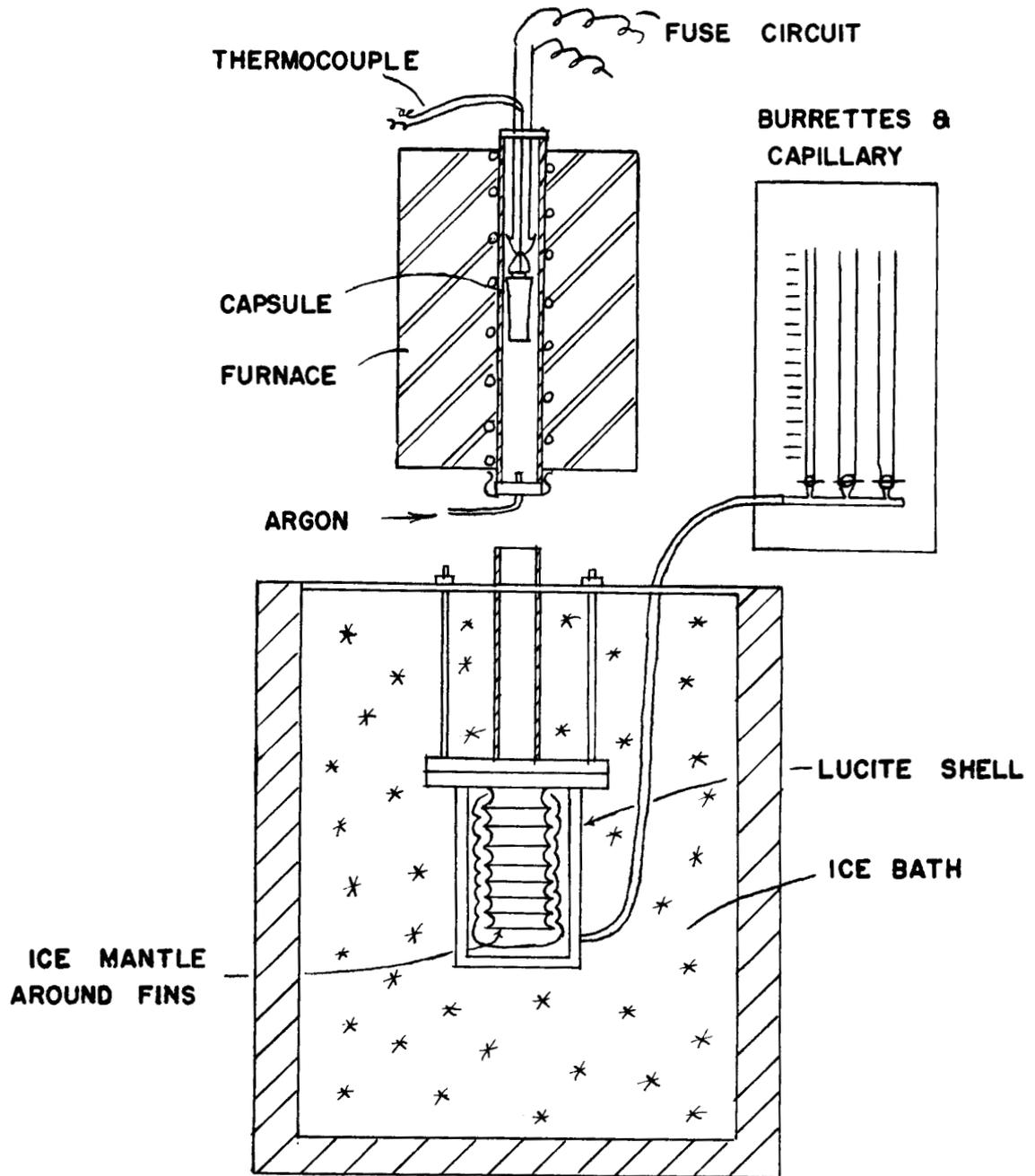
Of the many types of calorimeters that might have been selected to determine relative enthalpies, the ice calorimeter seems to be the most appealing because of its simplicity and adaptability. The ice calorimeter is easily constructed and simple to operate. High temperatures impose no great difficulty, and corrosion is isolated to the capsule used to contain the material being investigated.

This is the first of a series of reports to be published concerning heat capacity determinations. Future reports will refer the reader to this preliminary report for a description of method and apparatus.

DESIGN

A. General

The components necessary to utilize the ice calorimeter principle are shown schematically in figure 1. To make an enthalpy determination the capsuled material is heated to the desired temperature in the furnace, and in the meantime ice has been frozen in the calorimeter by means of dry ice. When the furnace and calorimeter both have reached equilibrium, the furnace is positioned over the calorimeter and the hot capsule is dropped. The net volume change is measured when the calorimeter has again reached equilibrium. From



SCHEMATIC DRAWING OF APPARATUS

FIGURE 1

the weight of the sample, the enthalpy of the capsule, the temperature before dropping, and the volume change, the enthalpy of the sample above 0°C is calculated.

The basic components of the apparatus are as follows:

1. Furnace for heating the sample to the desired temperature.
2. Calorimeter for measuring the heat contained by the capsuled sample.
3. Volume change indicator for detecting volume changes that occur in the two phase ice-water system.

While these are the fundamental features of the apparatus, precautions must be taken to insure that the components fulfill their intended purpose. Thus, considering the heating phase of the sample, it is necessary that the sample be heated to a uniform temperature; and that the temperature measured represent the actual sample temperature.

As the calorimeter is to be primarily used for measuring relative enthalpies of liquid metals and molten salts, a problem of secondary nature is introduced. That is, the sample material is not easily handled and must be sealed in a suitable capsule. This necessitates the determination of the enthalpy-temperature relation for the capsule material as the capsule enthalpy must be subtracted from the total enthalpy of the filled capsule to obtain the desired sample enthalpy. It would be desirable to have the capsule enthalpy small compared to the total enthalpy; and this requires a capsule of large volume capacity but with small actual volume. On the other hand the capsule wall must be thick enough to withstand a certain amount of corrosion.

B. Capsule

The following design features for the capsule must be considered:

1. Wall must be thick enough to withstand corrosion and internal pressure.
2. Enthalpy ratio of capsule to sample must be made small.
3. Capsule must be in good thermal contact with calorimeter receiver.

The capsule was designed with a 1/16 inch wall thickness; although, for some sample materials this thickness could be substantially reduced.

With the wall thickness decided, the general shape of the capsule was chosen as a frustum of a cone. The taper permits the capsule to wedge into the calorimeter receiver when the capsule is dropped and thereby insures good thermal contact. A taper of approximately 3° is used.

With the general shape and the thickness of the capsule determined the ratio of the capsule material volume to the capsule capacity volume was diminished as much as possible.

A typical capsule is shown in figure 2. The sample is sealed into the capsule by heli-arc welding around the capsule cover. A thermocouple well is tapped in the capsule cover.

C. Calorimeter

The task of designing the calorimeter was eased considerably by referring to the work of Ginnings and Corruccini (2)(3). Because of the care and precision of their work it became a simple matter to modify their apparatus for more rapid construction and operation while still obtaining data of sufficient accuracy. In view of the reduced accuracy requirements for the current equipment many precautionary features of Ginnings' apparatus were either eliminated or altered in designing the calorimeter.

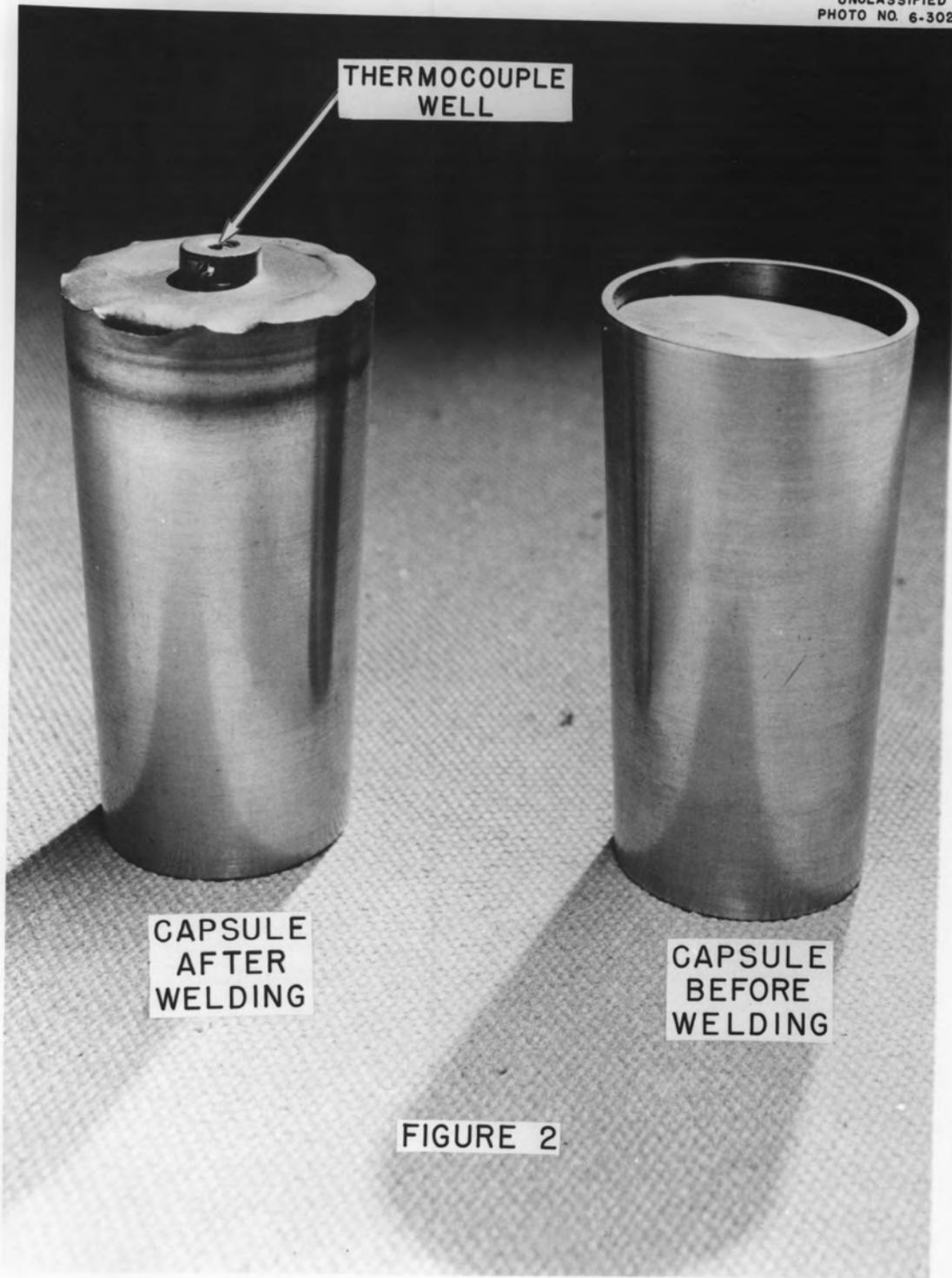


FIGURE 2

The purpose of the calorimeter is, of course, to measure accurately the heat content of material at some temperature above 0°C . This requires that no heat be exchanged with the surroundings, or that the heat exchanged with the surroundings be corrected for in the final analysis.

One advantage of an isothermal calorimeter is that the exchange of heat with the surroundings can be practically eliminated because the constant temperature of the calorimeter is easily matched in the surroundings. By immersing the ice calorimeter in an ice bath, heat exchange with the surroundings is negligible.

The core of the calorimeter consists of a copper receiver which has a tapered well to hold the capsule. The copper receiver separates the capsule from the two phase ice-water mixture contained in the calorimeter. The receiver is machined from a cylindrical piece of copper. Circumferential fins are machined on the outside of the receiver to permit rapid transfer of heat to the ice-water mixture, and a thin coating of cadmium is plated onto the fins to prevent corrosion.

The receiver is threaded at the top and fitted to a lucite flange. The lucite flange in turn is bolted and sealed to a lucite container with a mating flange top. The closed volume between the lucite shell and the finned copper receiver contains the ice-water mixture; and volume changes that occur in the two phase mixture are transmitted to a burette system by a connecting copper tube.

The assembly of the lucite shell and copper receiver is shown in figure 3.

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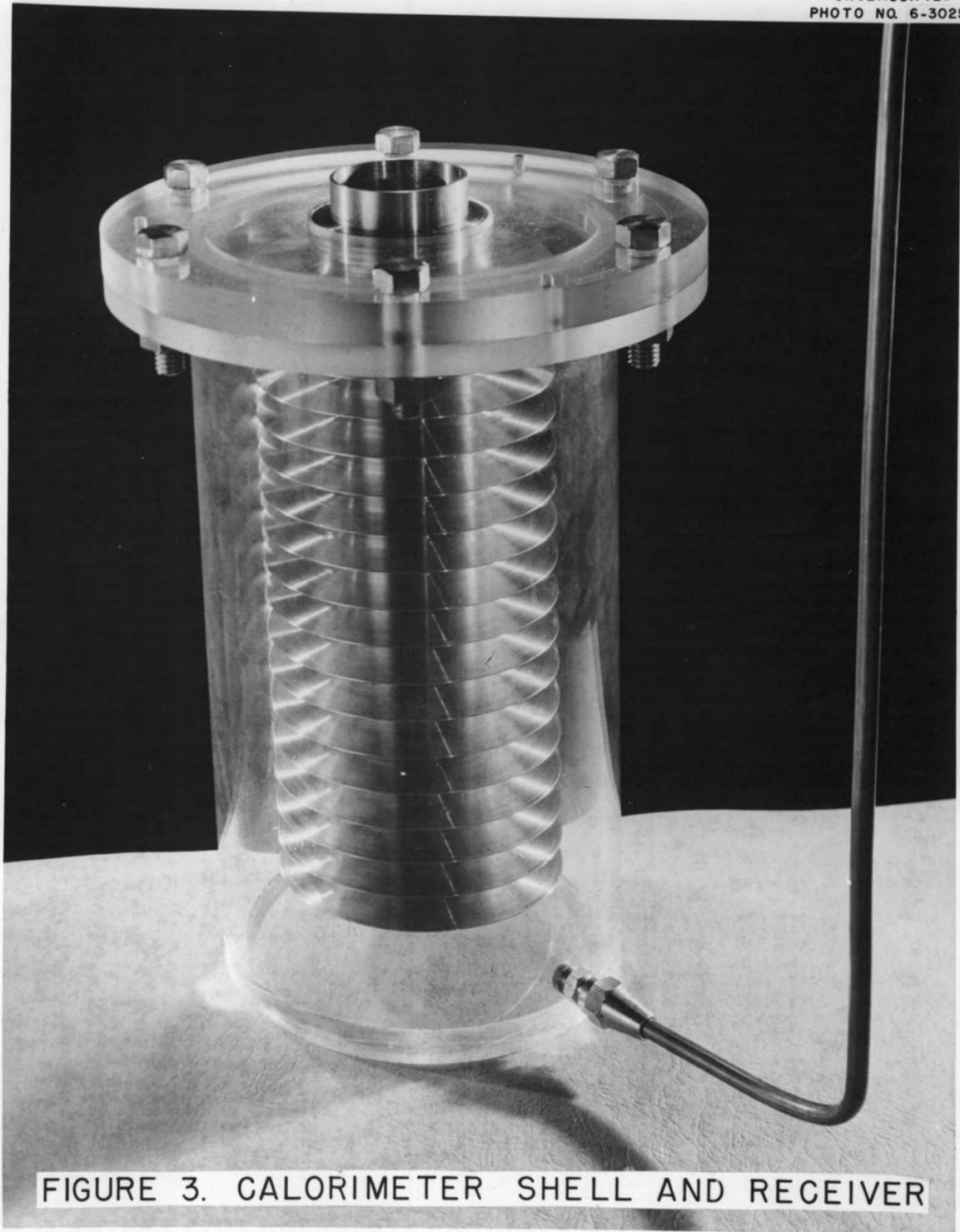


FIGURE 3. CALORIMETER SHELL AND RECEIVER

This assembly is then suspended by three steel rods and is immersed in an ice bath. A water proofed tube of alundum connects the assembly to the top of the bath container. This tube provides a passageway between the furnace and the calorimeter through which the capsule is dropped.

Lucite is used as the calorimeter container material because of its transparency and ease of fabrication. When the calorimeter is filled with degassed water, it is important that no air bubbles be trapped and visual inspection is readily possible if the container is transparent.

The container is fabricated from lucite sheet and tubing. A mixture of ethylene chloride and lucite is used as the sealing cement in joining the tube to the lucite flange and lucite container bottom. Glyptal is used to make the threaded connection of the lucite flange and the copper receiver water-tight. Before the lucite flanges are joined, a layer of the lucite cement is applied to the flange faces to insure a water-tight seal.

D. Furnace

To heat the capsule to the desired temperature, a Hoskin's furnace with a tube two inches in diameter and ten inches in length is used. The line voltage is kept constant with a Sola constant voltage transformer; the furnace temperature is regulated with a Variac auto-transformer.

As an isothermal heating zone is required, a longer furnace than the ten inch furnace used would be desirable, but tests on the furnace used have indicated it is adequate for the purpose. A six-inch section of steel pipe is inserted into the center of the furnace tube to extend the isothermal heating zone. At both ends of the steel pipe short sections of alundum tube are placed and these extend to the furnace ends.

While heating, the capsule is suspended into the center portion of the furnace by two steel rods that pass through the furnace lid. A strand of nichrome wire, hooked to the lower ends of the rods, passes through the capsule hanger. The upper ends of the rods which extend outside the furnace are connected to an electrical switch box. When the switch is closed, the strand of wire fuses and releases the capsule. Figure 4 shows this assembly.

Through the furnace lid there is also passed a thermocouple that extends down with the bare junction resting in a small well in the capsule cover.

While heating, the furnace is capped at the bottom, and through the cap a tube is inserted which admits argon gas to the furnace to maintain an inert atmosphere. When the capsule is dropped the bottom furnace cap is temporarily removed. Both the furnace lid and bottom cap are machined from Lavite.

F. Volume Change Indicator

Volume changes that occur in the calorimeter are indicated by a burette system connected to the closed volume of the calorimeter. Volume changes, other than those caused by the phase change, arise because the lucite container is rather elastic and different water levels in the burettes cause different internal pressures to be exerted on the lucite container. This effect is noticeable when the pressure on the system is suddenly changed.

But since the capillary tube must be calibrated anyway, it is found that the pressure correction will be inherent in the calibration if the calibration is conducted while the capillary and burettes are connected to the calorimeter system.



The capillary tube is very useful when slow volume changes are to be measured, such that occur when the calorimeter is approaching equilibrium.

Water is used throughout the burette and capillary system and has been found satisfactory if the glass system is cleaned periodically. The amount of water evaporated from the burettes at room temperature is small compared to the volume change characteristic of an enthalpy determination.

PERFORMANCE

After the calorimeter has been filled with degassed water and assembled, the capillary is calibrated while connected to the calorimeter.

Tests are made to determine the most nearly isothermal region and the capsule suspension rods are adjusted to position the capsule in this region.

The apparatus as it appears during operation is shown in figure 5. Actually five calorimeters have been constructed to speed the accumulation of data. Two enthalpy determinations are possible with each instrument for each eight hour day of operation.

A synthetic sapphire calorimetric standard was obtained from the Bureau of Standards to check the calorimeters for accuracy. The sample of synthetic sapphire was sealed in a capsule of stainless steel (Type 316) and enthalpy determinations were made on both the empty capsule and the filled capsule. The enthalpy of the synthetic sapphire was obtained by subtracting the measured value for the capsule enthalpy from the total enthalpy of the filled capsule and dividing the result by the sample weight. As both the empty and filled capsules are subject to the same experimental errors, there should be a tendency for the errors to be eliminated in the subtraction operation. An example of



FIGURE 5. CALORIMETER AS OPERATED

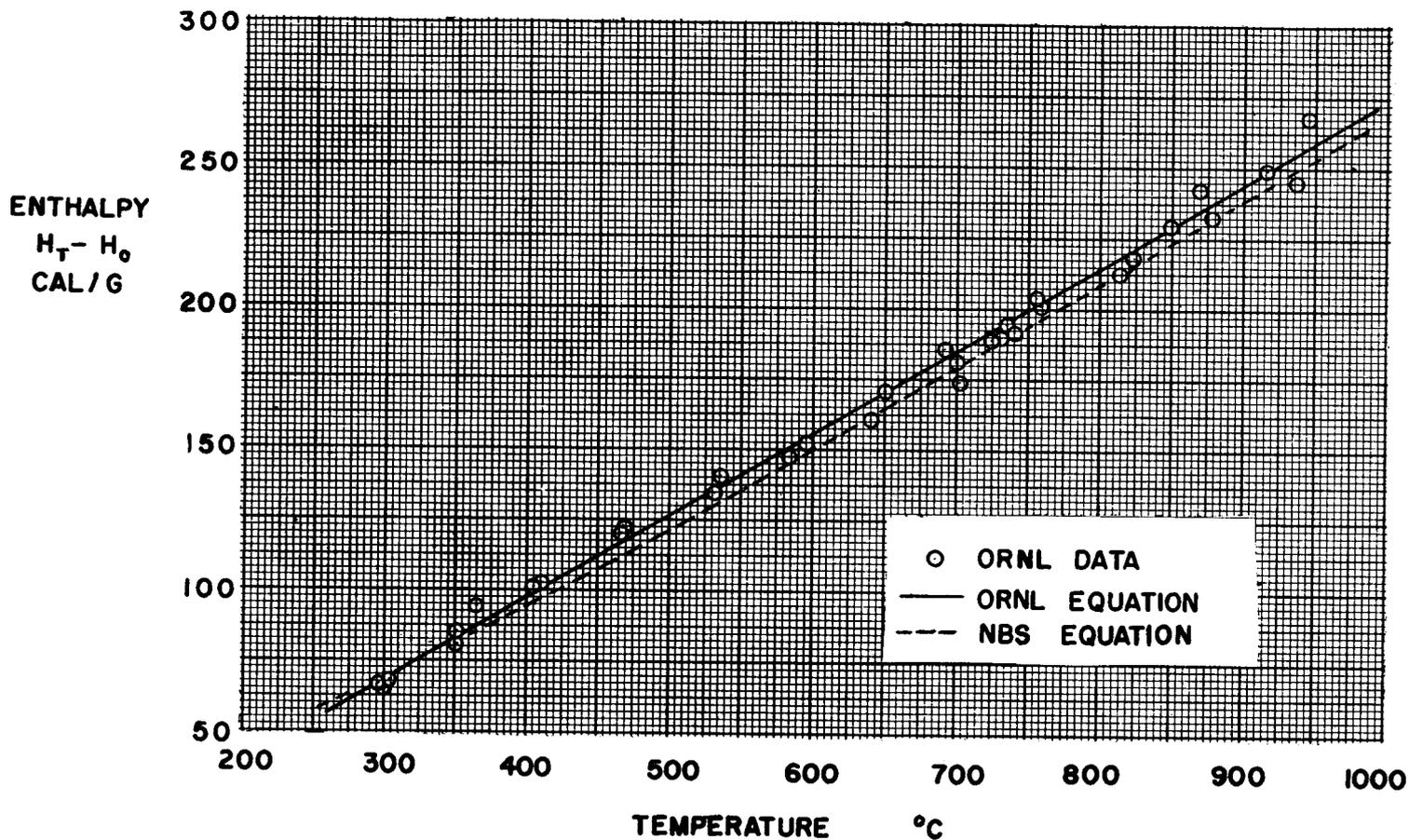
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this is the heat loss that occurs during a capsule drop. Both capsules experience radiation and convection losses when passing from the furnace to the calorimeter. As the capsules have the same external structure, at the same temperature, and are dropped in the same manner, the error should be approximately the same and should therefore disappear in the subtraction of enthalpy values.

The results of the enthalpy measurements for synthetic sapphire are shown in figure 6. Many of the points were obtained from a calorimeter system where evaporation from the burettes was considerable. This excessive evaporation was caused by the furnace which swung near the burette system and heated the burettes. The evaporation was indicated by the condensation of water droplets on the cold side of the burette. Presently this is the only reason that can be offered for the high enthalpy values as sufficient data are not available from the remaining calorimeters which are not subject to the furnace heating of the burettes.

In spite of this, the accuracy of the enthalpy data is satisfactory for the program planned. As the slope of the enthalpy-temperature curve is the desired result $\left[c_p = \left(\frac{\partial H}{\partial T} \right)_p \right]$, the values of the slope, determined analytically from the least squares enthalpy-temperature equation, are compared to the values derived from the Bureau of Standards enthalpy-temperature equation. This comparison is shown in Table I.



GRAPH OF ENTHALPY CURVE
FOR SYNTHETIC SAPPHIRE

FIGURE 6

TABLE I

HEAT CAPACITY VALUES FOR SYNTHETIC SAPPHIRE

<u>T °C</u>	<u>c_p NBS</u>	<u>c_p ORNL</u>	<u>ORNL % Deviation</u>
400	0.2719	0.2854	+ 4.97
500	0.2799	0.2898	+ 3.54
600	0.2865	0.2941	+ 2.65
700	0.2919	0.2985	+ 2.26
800	0.2960	0.3028	+ 2.30
900	0.2995	0.3072	+ 2.57

These data have been calculated from the following equations:

$$\text{NBS(6), } c_p(\text{cal/g } ^\circ\text{C}) = 0.3462 - 8.021 \times 10^{-6}T - \frac{47.78}{T + 273.2}$$

$$\text{ORNL, } c_p(\text{cal/g } ^\circ\text{C}) = 0.2636 + 4.358 \times 10^{-5} T$$

CONCLUSION

As the results given in Table I are within the desired accuracy ($\pm 5\%$), only several enthalpy comparisons are contemplated for the remaining calorimeters.

Currently, one of the calorimeters is being used for experimental purposes to improve the ice bath. After prolonged periods of operation the ice bath becomes impure, apparently, and causes a lowering of the melting point. This is evidenced by the freezing of ice in the calorimeter caused by the lower melting point of the external ice bath. Eventually ice freezes in the copper connecting tube and plugs the line. The normal volume changes inside the calorimeter then causes the calorimeter container to rupture.

While the freezing problem can be avoided by frequently changing the ice bath, it is hoped that by increasing the thermal resistance between the two ice regions the effect of the small temperature gradient can be neglected entirely. Some insulating materials are being tested for this purpose.

The impurities initially present in the ice used may be the cause of the freezing problem and this possibility is being investigated.

The program for measurement of heat capacities is to be included in a classified report by Major A. R. Frithsen (ORNL-1039), which will outline the physical properties program at ORNL in general.

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