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### Authors

McKisson, Raleigh L.  
Bromley, LeRoy A.

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A NEW HIGH-TEMPERATURE CALORIMETER

Raleigh L. McKisson and LeRoy A. Bromley

May 1, 1950

Berkeley, California

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A New High-Temperature Calorimeter.

Raleigh L. McKisson and LeRoy A. Bromley

May 1, 1950

Abstract

A high-temperature calorimeter, designed for use in the temperature interval 600°K. to 1500°K., is described. This calorimeter consists of a thermostat of molten tin surrounding a cavity in which the sample is placed. The calorimeter is resistance-heated and control of the thermostat temperature to  $\pm 1/2$  °C. is effected by means of a modified "single-speed floating" control. Equations which allow calculation of the data are derived and their use explained.

## Introduction

Alloys and intermetallic compounds represent an important group of chemical substances about which relatively little is known. While it is true that much effort has been directed toward the measurement of basic thermodynamic data pertaining to alloys, one finds relatively poor agreement in the reported heats of formation. A summary of such data was made by McKisson and Bromley<sup>(9)</sup>, and it is apparent that there is a need for work in this field.

Attack of the problem of heats of formation of alloys is readily carried out by conventional calorimetry, although the complications of gas evolution, reaction rates, and the fact that the desired result is obtained by taking the small difference of large numbers, frequently gives the final result a high degree of inaccuracy. However, if one could measure the heat liberation when the elements were mixed, one would be directly measuring the desired quantity, and although these measurements be of lower precision than those of conventional calorimetry, the result might be more reliable. Such measurements would have to be made at elevated temperatures so that a high-temperature calorimeter must be developed.

Few calorimeters have been designed which permit the measurement of heats of reaction at elevated temperatures. Those which have been applied to the measurement of heats of formation of intermetallic compounds are the calorimeters described in the articles by Biltz et al.<sup>(2)</sup>, Kubaschewski and Walter<sup>(5)</sup>, Chipman and Grant<sup>(3)</sup>, Barber et al.<sup>(1)</sup>, and Kawakami<sup>(4)</sup>. Biltz's calorimeter was used in solution measurements of elements and alloys, and its thermostat was held at about 100°C. Kubaschewski and Walter devised an adiabatic unit using a nickel-chromium steel clock which could be held at temperatures up to 700°C. Heats of reaction were measured at this temperature with an estimated uncertainty of  $\pm 2.5\%$ . Chipman and Grant used a high frequency induction coil as a calorimeter and were able to measure

the heat of solution of silicon in molten iron at a temperature of 1600°C. Bromley's calorimeter, described by Barber et al., was patterned after that of Chipman and Grant, but was constructed on a smaller scale\*. Bromley successfully operated this apparatus at 1150°C.\*\* It was later operated at about 600°C. yielding results with a probable error of ±6-8% in direct measurements of the heats of formation of the intermetallic compounds NaSn and LiSn. Kawakami used an electric tube furnace as the basis of his calorimeter, and measured the heats of isothermal mixing of metals at around 700°C.

Of the calorimeters above, only that of Kubaschewski seems acceptable, although his measurements, consisting of measuring the  $(H_T - H_{298})$  function for elements separately, then, measuring the same function when the elements are allowed to react, also gives the result as a difference of larger numbers. Biltz's calorimeter is limited to 100°C. Bromley found that the operation of his calorimeter was not altogether satisfactory in that the power supply, an Ajax 20 kx. spark-gap converter, was erratic and difficult to control to the required constancy of power output. Kawakami uses a calorimeter of very small heat capacity, and a very small thermostat, so that it seems that good temperature control would be quite difficult.

After an examination of these calorimeters, and their means of measuring the heats of formation of alloys, it was decided that the measurement method outlined by Barber et al.<sup>(1)</sup> had promise; that is, the actual measurement of but a small fraction of the desired heat of reaction, and conversion to the desired heat of reaction by use of heat capacity data of high accuracy. This is effected by adding cold samples to a hot melt, which then uses a large fraction of the liberated heat in heating up the samples.

The new calorimeter consists essentially of a resistance-heated constant

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\* Chipman and Grant used a melt of 65-90 lbs., Bromley used a melt of 100-200 grams.

\*\* Private communication, unpublished work of L. A. Bromley.

temperature bath of molten tin, completely surrounding the sample chamber, except for a loading tube opening. These internal parts are surrounded by a layer of powdered graphite insulation which is contained in a water-cooled shell. The temperature of the bath is maintained within  $\pm \frac{1}{2}^{\circ}\text{C}$ . of the desired equilibrium temperature.

### Derivation of Equations

The data obtained from the apparatus consist of a temperature-time trace of the crucible and its charge, together with a number of checks of temperatures on this curve from readings taken on the potentiometer (Leeds and Northrup Precision Potentiometer). The problem is, then, to devise a method of calculating the heat liberated in a reaction using this data. McKisson<sup>(7)</sup> previously analysed a system similar to the one concerned here, and this derivation will follow a similar approach.

The rate of heat transfer from the crucible at temperature,  $T$ , when the surroundings are at temperature,  $t$ , is:

$$-q = \sigma A_1 \epsilon (T^4 - t^4) + hA_2 (T - t). \quad (1)$$

We can expand  $(T^4 - t^4)$  in terms of  $(T - t)$ , and letting

$$(T - t) = \Delta T, \quad (2)$$

we find,

$$(T^4 - t^4) = 4t^3 \Delta T + 6t^2 \Delta T^2 + 4t \Delta T^3 + \Delta T^4. \quad (3)$$

The error introduced when the first two terms of the expansion (Eqn. 3) are used for  $(T^4 - t^4)$  in Eqn. (1) can be readily determined. In general, this error will be less than 2%. Then Eqn. (3) becomes

$$(T^4 - t^4) \approx 4t^3 \Delta T + 6t^2 \Delta T^2. \quad (4)$$

Now, substituting Eqn. (4) and Eqn. (2) into Eqn. (1), we find,

$$-q = \sigma A_1 \epsilon \left[ 4t^3 \Delta T + 6t^2 \Delta T^2 \right] + h A_2 \Delta T, \quad (5)$$

or

$$-q = (4\sigma A_1 \epsilon t^3 + h A_2) \Delta T + (6\sigma A_1 \epsilon t^2) \Delta T^2. \quad (6)$$

The Boltzman constant,  $\sigma$ , is a constant for all conditions. The emissivity,  $\epsilon$ , is a function of  $T$ , but can be considered constant during a run. The effective area for radiative heat transfer,  $A_1$ , and the effective area for convective heat transfer,  $A_2$ , are functions of melt-height. The convection heat-transfer coefficient,  $h$ , is a function of melt-height, melt temperature,  $T$ , and  $\Delta T$ , but the dependence on  $\Delta T$  is small. In spite of the variability of these quantities, they can be considered to be constant during an individual addition.

Now let

$$(4\sigma A_1 \epsilon t^3 + h A_2) = P, \quad (7)$$

and

$$(6\sigma A_1 \epsilon t^2) = R. \quad (8)$$

Substituting Eqn. (7) and Eqn. (8) in Eqn. (6), we find

$$-q = P \Delta T + R \Delta T^2. \quad (9)$$

Equation (9) gives an expression which relates the rate of heat transfer from the crucible, in calories per minute, to the temperature difference between the crucible and the cavity,  $\Delta T$ , through the quantities  $P$  and  $R$ . Now since

$$q = \frac{dQ}{d\theta}, \quad (10)$$

plotting  $q$  against time,  $\theta$  will give an area which is proportional to the heat liberated in the reaction. Such a plot may be constructed if  $P$  and  $R$  are known. Examination of Eqn. (7) and Eqn. (8) shows that the ratio of  $P$  to  $R$  can be

calculated as:

$$\frac{P}{R} = \frac{4\sigma A_1 \epsilon t^3 + hA_2}{6\sigma A_1 \epsilon t^2} \quad (11)$$

In Eqn. (11) if we assume  $hA_2 = 0$ , we can calculate the minimum value of the ratio (P/R) as

$$(P/R)_{\min} = \frac{2t}{3} \quad (12)$$

Equation (12) shows that the ratio of P/R will be greater than 250°K. at temperatures suitable for operation of the calorimeter. In general,  $R\Delta T^2$  represents a correction term in equation (9), and as such, it is not necessary that R be known to high accuracy. With this in mind, we can analyse the system by means of heat transfer correlations given by McAdams<sup>(6)</sup> and the ratio P/R can be estimated from this analysis. The results of such an analysis are shown in Figure 1. Details of this calculation are given by McKisson<sup>(8)</sup>. These values are used only in estimating R, once P is known. The problem, then, is to obtain the best value for P.

When no heat is being liberated in the system, the expression relating the heat, Q, to the heat capacity of the system is:

$$dQ = C_p dT. \quad (13)$$

When Eqn. (13) is combined with Eqn. (9) and Eqn. (10), we find,

$$-q = C_p \frac{dT}{d\theta} = PAT + R\Delta T^2. \quad (14)$$

Now, since

$$\Delta T = (T - t), \quad (2)$$

then

$$d\Delta T = dT. \quad (15)$$

Combining Eqn. (14) and Eqn. (15), and rearranging, we find

$$\frac{d\Delta T}{P\Delta T + R\Delta T^2} = -\frac{1}{C_p} d\Theta \quad (16)$$

Equation (16) is integrable, yielding

$$\frac{\Theta}{C_p} = \frac{1}{P} \ln \frac{P + R\Delta T}{\Delta T} + C, \quad (17)$$

or,

$$\Theta = -\frac{C_p}{P} \ln \frac{\Delta T}{1 + (R/P)\Delta T} - \ln P + C. \quad (18)$$

Equation (18) can be re-written,

$$\Theta = -\frac{C_p}{P} \ln \frac{\Delta T}{1 + (R/P)\Delta T} + C_1. \quad (19)$$

Equation (19) indicates the relation between  $\Theta$  and  $\Delta T$  for the system when no reaction is taking place. Using Eqn. (19), we can plot  $\Theta$  vs.  $\ln \frac{\Delta T}{1 + (R/P)\Delta T}$  and draw the best straight line whose slope is  $-(P/C_p)$ . In place of  $\Delta T$  one may use  $\Delta mv.$ , the millivolt difference reading of the melt thermocouple over the equilibrium millivolt value. When  $C_p$  is known this yields  $P$ , and the  $q$  vs.  $\Theta$  plot can be made as previously described. The  $C_p$  of the system can be determined from the addition of an inert material to the melt. The procedure is outlined below:

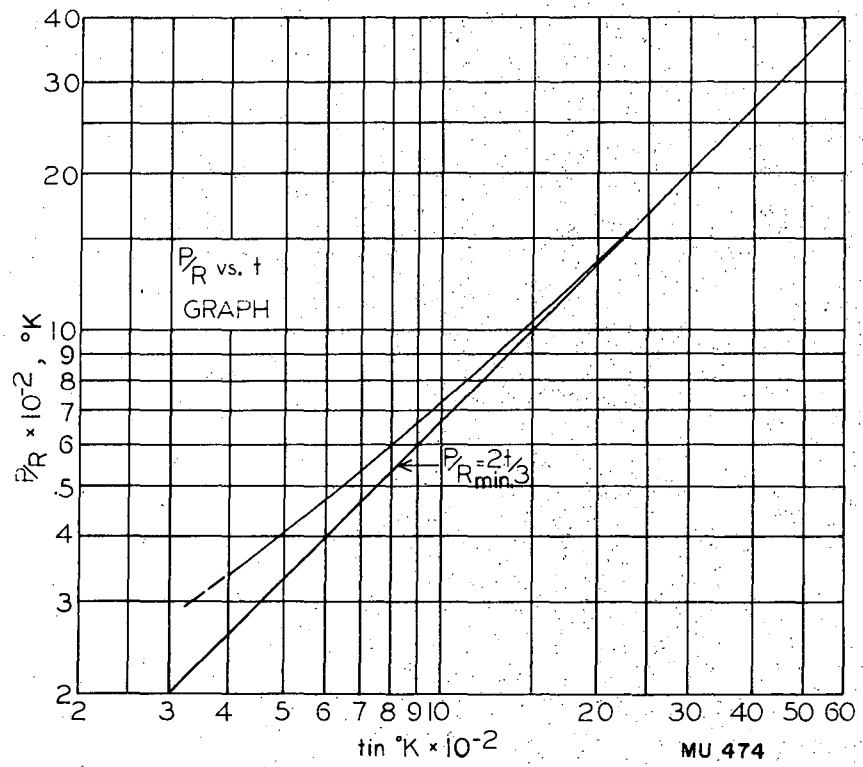
a) Plot the  $T - \Theta$  curve or the  $\Delta mv. - \Theta$  curve using the data of an addition of an inert material (see Figure 2), and estimate the average temperature of the addition.

(b) Refer to Figure 1 and find the value of  $P/R$  corresponding to this average temperature.

(c) Calculate values of  $\frac{\Delta T}{1 + (R/P)\Delta T}$  \* and plot  $\ln \frac{\Delta T}{1 + (R/P)\Delta T}$  vs.  $\Theta$  (Fig. 3).

---

\* If  $\Delta mv.$  is used in the expressions here written in terms of  $\Delta T$ , then  $P$ ,  $R$  and  $(R/P)$  should be converted to the proper units.  $\Delta mv$  can only be substituted for  $\Delta T$  if there is a linear relation between  $mv.$  and temperature.



$P/R$  vs.  $t$  CURVE.  
FIG. 1

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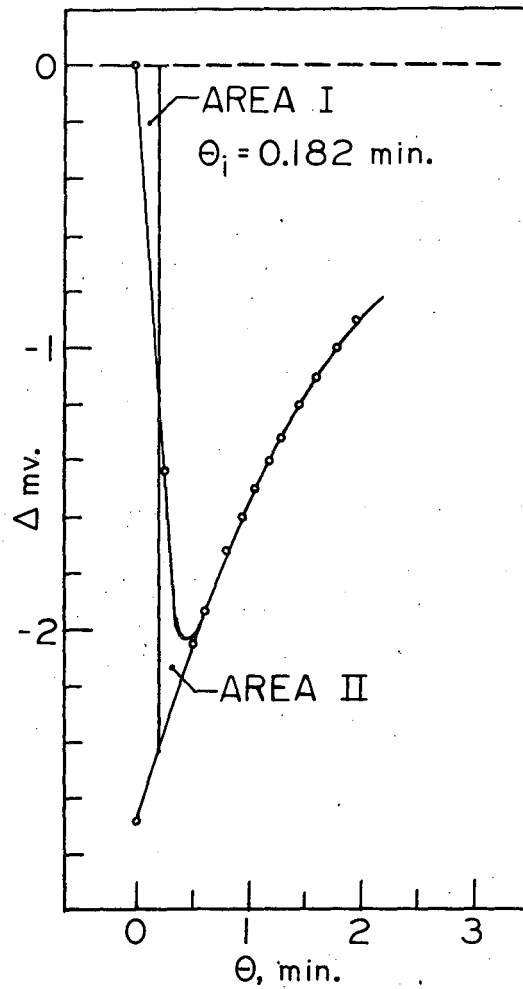


FIG. 2

mv.- TIME CURVE FOR THE FIRST MOLYBDENUM  
ADDITION OF THE FOURTH SODIUM-TIN RUN.

MU 473

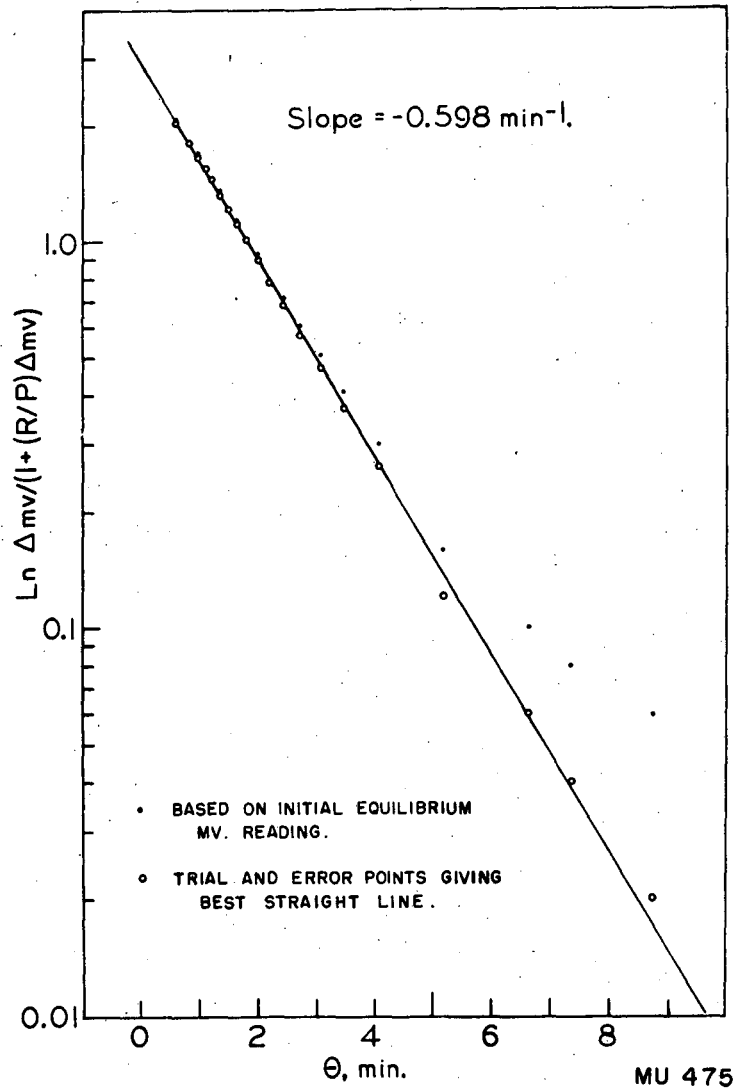


FIG. 3  
 $\text{Ln } \Delta mv / (1 + (R/P) \Delta mv)$ -TIME CURVE FOR THE  
 FIRST MOLYBDENUM ADDITION OF THE FOURTH SODIUM-TIN RUN.

In Figure 3, an incorrect choice of the true final equilibrium temperature was chosen for the calculation of the solid points. On such a plot, if the chosen final equilibrium temperature is incorrect, a curved line is found. A curve convex downward indicates the equilibrium temperature was too high, a curve convex upward indicates the equilibrium temperature was too low. This effect is noticed only when the thermostat temperature changes during the addition, and if the initial temperature was taken as reference (as was the case for the solid points in Fig. 3) then these deviations occur. In such cases, the lines are straightened out by adjusting the equilibrium temperature to its final value.

(d) Extrapolate the  $\ln \frac{\Delta T}{1 + (R/P)\Delta T}$  vs.  $\Theta$  curve back to low values of  $\Theta$  and plot the corresponding extrapolated curve of  $\Delta T$  vs.  $\Theta$ , (Figure 2).

e) Estimate  $\Delta t_i$  on the  $T$  vs.  $\Theta$  curve by adjusting  $\Theta_i$  so that Area I equals Area II (Figure 2).

f) Calculate the value of  $C_{p_i}$  corresponding to  $\Delta t_i$  from the known heat content of the inert material,

$$\Delta H_{\text{inert}} = (C_{p_i} - C_{p_{\text{inert}}}) \Delta t_i \quad (20)$$

In Eqn. (20),  $C_{p_{\text{inert}}}$  is calculated at the average temperature of the addition. The heat capacity,  $C_{p_i}$ , which is operative in the warming process is larger than the heat capacity found by the method of mixtures, and it is larger by just the heat capacity of the inert material added.

g) Evaluate the slope of the  $\ln \frac{\Delta T}{1 + (R/P)\Delta T}$  vs.  $\Theta$  curve, calculate  $P_i$  from this slope and the value of  $C_{p_i}$  calculated from Eqn. (20), and find the corresponding value of  $R$ ,  $R_i$ , from the  $P/R$  ratio.

h) Calculate values of  $q_i$ ,

$$q_i = P_i \Delta T + R_i \Delta T^2 \quad (21)$$

and plot  $q_i$  vs.  $\Theta$  (Figure 4), including values corresponding to the extrapolated  $\Delta T$ 's from d).

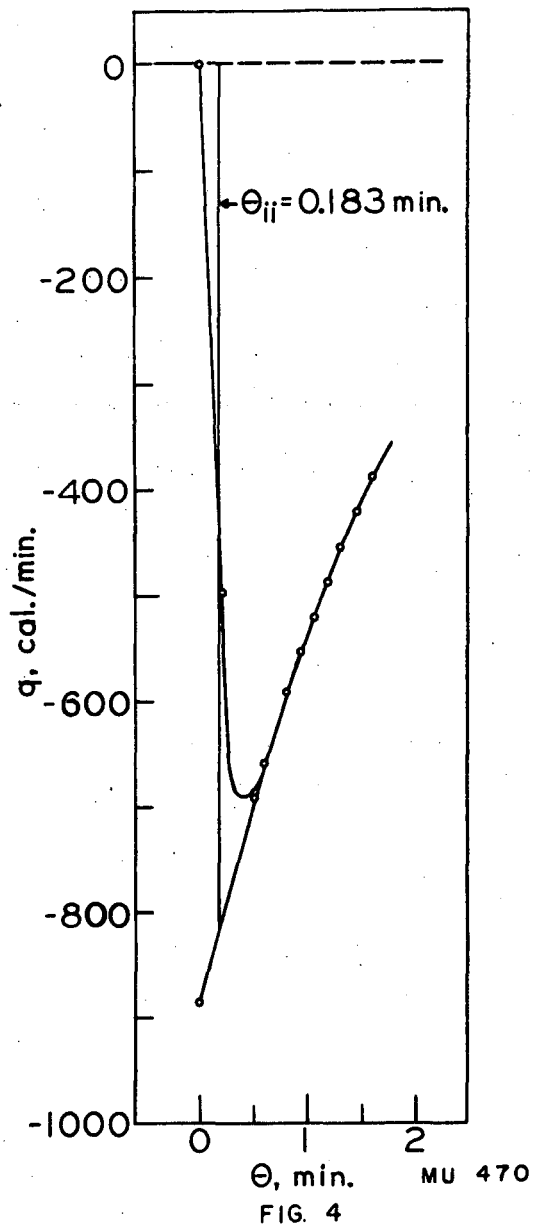
i) Find  $\Delta t_{ii}$  and  $\Theta_{ii}$  on the  $q_i$  vs.  $\Theta$  curve in the same manner that  $\Delta t_i$  and  $\Theta_i$  were located on the  $T$  vs.  $\Theta$  curve. Since areas on the  $q$  vs.  $\Theta$  plot are equivalent to heat, this procedure is equivalent to finding the  $\Delta T$  for an instantaneous temperature equilibration when the inert material is added. In general,  $\Theta_{ii}$  will be slightly smaller than  $\Theta_i$ , and  $\Delta t_{ii}$  will be slightly larger than  $\Delta t_i$ . Further, the total area under a  $q$  vs.  $\Theta$  plot for an inert addition should be equal to the heat required to heat the inert material from its base temperature to the final temperature.

j) Calculate the value of  $C_{p_{ii}}$  using  $\Delta t_{ii}$  in Eqn. (20). Then calculate the corrected values  $P_{ii}$  and  $R_{ii}$ .

k) Evaluate the values of  $q_{ii}$  using Eqn. (21) and repeat steps h) through j) until successive calculations show  $P$  and  $C_p$  to be constant. In most cases, it is not necessary to calculate  $q_{ii}$ , since  $\Theta_i$  and  $\Theta_{ii}$  will differ only slightly, if at all.

The final values of  $P$  and  $C_p$  calculated as above apply only to the alloy melt to which the inert material was added. In order that an individual heat of reactive addition be calculable, a value of  $P$  for that particular addition is needed. The estimation of  $P$  for any particular addition can be effected by interpolation between quantities directly determined. These points must be taken from the addition of non-reacting material, since this is the only way one can be certain that there are no rate of reaction effects to affect  $P$ . An initial point can be readily obtained by adding a piece of the melt metal to the crucible containing only this metal. Other points must be taken by the addition of an inert material.

Once the values of  $P$  for the various additions are obtained, the heat effects can be readily calculated by constructing the  $q - \Theta$  plot. A difficulty is encountered in making the  $q - \Theta$  plot in that it is impossible to measure an area out to infinite time. However, it is simple to calculate the heat liberated from any



given time out to infinite time if one assumes that the curve is an exact cooling curve in this region. This derivation is explained fully by McKisson<sup>(8)</sup> and only the result will be used here. This heat,  $Q'$ , is found to be calculable by Eqn. 22,

$$Q' = \Delta T_o C_p. \quad (22)$$

### Design

The design of an instrument can be divided into two phases, the design of the working parts and their interrelationships, and the selection of the materials of construction. The first phase usually requires the bulk of the work for equipment to be used at room temperature, but for high temperature applications, the second phase becomes dominant. High temperature equipment is of necessity much less complex because of the difficulty of maintaining alignment of mechanisms when large temperature gradients are present. Further, since conventional building materials are not suitable for use in equipment operating above 1000°C., a challenge is presented in the selection of a suitable group of materials which can withstand these temperatures for an extended period. For these reasons, it behooves a designer of high-temperature equipment to consider very carefully the various chemical reactions possible at operating temperatures, and to attain the greatest simplicity in any mechanisms which must function in the region of high temperatures, or high temperature gradients.

An extended discussion of the considerations involved in the design appears in the thesis of McKisson<sup>(8)</sup>, and a summary of the conclusions follows.

The internal configuration of this calorimeter is subject to the limitations outlined in the section on the derivation of equations. The problem is to maintain a cavity with a constant wall temperature. This can be very closely attained

by using a good heat conductor in a massive cavity wall so that the large heat capacity can absorb heat with a relatively small change in temperature, and the rapid conduction of heat minimizes local variations in wall temperature. These conditions were fulfilled by using an inner graphite chamber with wall thickness of  $3/4$ " , surrounded on all sides by a vat of about 70 lbs. of molten tin (used only when operating temperature is above  $450^{\circ}\text{C}$ .). The tin is contained in an external graphite vat with an average wall thickness of  $1/2$ " (see Fig. 5). The composition heat capacity is about 7000 cal/deg. C. The molten tin is circulated by four stirrers and thus thermal equilibrium is constantly maintained.

The reaction crucible is placed inside the inner chamber, and for all systems herein described, consisted of a  $1/32$ " wall  $1\ 5/8$ " I.D. x 2.5" high molybdenum crucible, sitting on a zircon stand (see Fig. 5). This size was chosen since it has a capacity of about 4 g.-mols of metal and these crucibles are readily available. This amount of melt is sufficient to give sensible heat effects, even with systems in which the heat of mixing is small, and the consumption of starting materials is not excessive.

The heating unit, which surrounds the tin vat, consists of a graphite spiral machined from a cylinder  $1/2$  inch thick,  $10\ 1/4$  inch inner diameter and  $15\ 1/4$  inch high. The cross-sectional area of the spiral is  $1/2$ " x  $3/4$ " and it has an effective length of 38.9 ft. Its resistance at room temperature is about one-half ohm.

The electrical insulators upon which the heating unit rests are made of alumina. The insulator-separators, which are inserted in the heating spiral every one-third turn for support, are also made of alumina. The insulation on the molybdenum power leads consists of cylinders of McDanel High-temperature porcelain. These parts will limit the extended period operating temperature to an estimated  $1620^{\circ}\text{K}$ . ( $1350^{\circ}\text{C}$ .), and will probably limit the short-period operating temperature

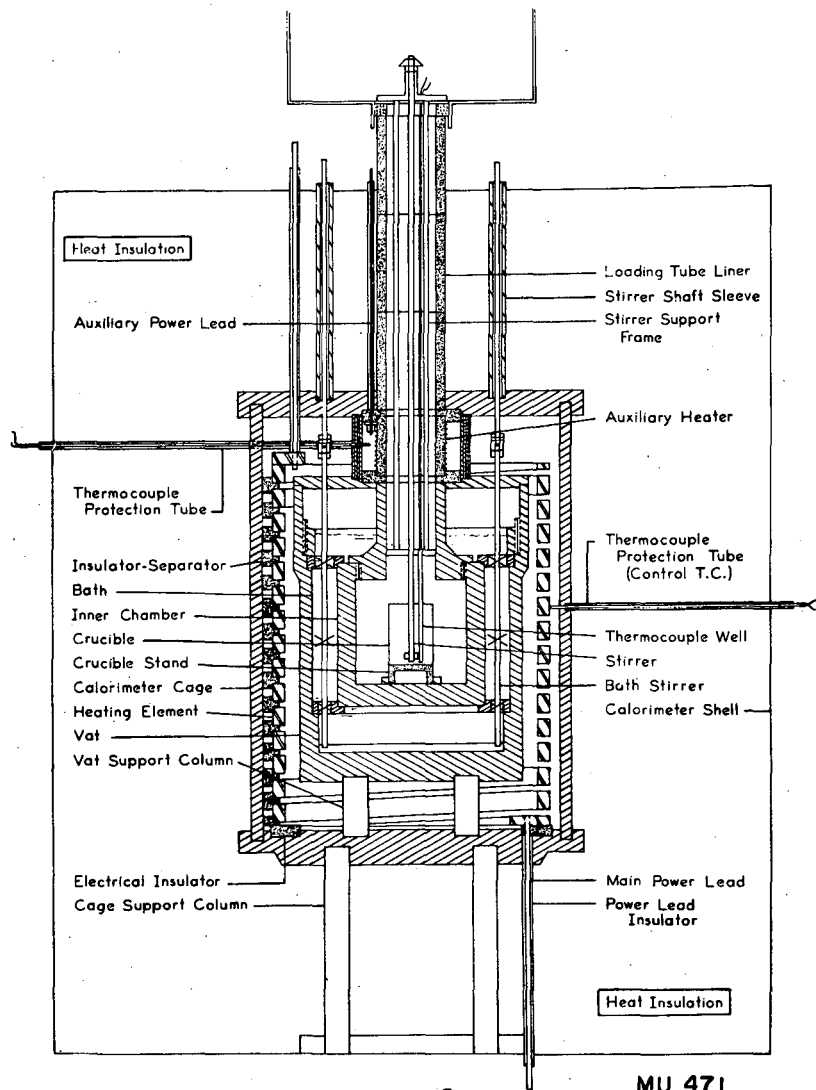


FIG. 5

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to about 1670°K. (1400°C.), since graphite attacks both alumina and porcelain at this temperature.

The calorimeter cage, which surrounds the heating-unit, consists of a cylinder of graphite, set into a graphite bottom, and closed by a graphite top. The cylinder has a wall thickness of 1/2 inch, a height of 17 3/4 inches, and an inner diameter of 12 inches. The cage is supported from below by four 1" diameter graphite rods. The top of the cage is tapped for the graphite protection tubes which enclose each of the stirrer shafts and the thermocouples. The vent and the gas inlet tube also are threaded and screw into seats on the cage top.

Between the top of the inner graphite chamber and the cage top, an auxiliary heating element is provided to help compensate for the heat losses in the loading tube. This heater element is a molybdenum wire, wound on an alumina core. Longer life would be expected if the molybdenum were replaced by platinum. The loading tube consists of three alumina cylinders, as shown in Fig. 4, each two inches I.D. with a 1/4" wall, and 4" high. This loading tube passes through the cage top and the insulation to the top of the calorimeter.

The insulation used is graphite powder, about 100 mesh or finer. It is an excellent insulator, but quite messy to handle. The cage is completely surrounded by an eight-inch layer of this powder. The external container for the insulating powder is a cylindrical copper shell, 29 inches in diameter, 35 inches high, and 1/16 inch thick, upon which copper tubes are soldered to serve as cooling coils. The cooling water flow can be regulated so that the shell is cool to the touch.

The sample dispenser unit, Fig. 6, rests on the top of the loading tube, and carries the samples to be added down to within 2" of the top of the melt before dropping them into the melt. It consists essentially of a 1/2" I.D. stainless-steel tube, to which is affixed a rack. A gear train connects the rack and an operating crank. The sample tube runs on two sets of three ball-bearing guides

and one can add a sample and return the tube to its rest position in less than two seconds. The lower end of the sample tube rests in the sample chamber between additions. This chamber is enclosed and is provided with two clamps which can be manipulated externally, and has storage space for several samples. The clamps are used to transfer the samples from the sample store to the sample tube. A frame carrying a stirrer and a thermocouple well for the melt is supported by the sample chamber. This frame rests against the wall of the loading tube, leaving enough room for passage of the sample tube. The lower parts of the frame, the stirrer, and the thermocouple well are made of molybdenum; the upper parts are made of stainless steel. The auxiliary equipment consists of the main power supply, the control unit for the main power supply, the storage vat for the tin bath metal, the gas system, and the recording instruments.

The main power supply consists of a 220 v., 7.5 K.V.A. Variac, whose secondary feeds a bank of three 4:1 voltage step-down transformers, wired in parallel. The output from these three transformers is wired in parallel and is fed into the main heating coil of the calorimeter.

The control of the main power supply is obtained by varying the Variac setting to correct the temperature of the heating element. This temperature is continuously read by a Wheelco Potentiostat unit which operates from a thermocouple in contact with the main heating element. The Potentiostat unit is wired to control a reversible motor which is geared to the Variac shaft. When the temperature of the heating element is low, the motor increases the e.m.f. delivered by the Variac; when the temperature is high, the e.m.f. is decreased. In addition to this control, moveable limiting switches are mounted so that the maximum variation in the Variac e.m.f. can be set to give the best degree of constancy in the temperature cycle of the tin bath.

The storage vat for the tin bath metal consists of a closed vat made by welding end-plates on an 8" extra heavy steel pipe. This vat is heated by a gas burner

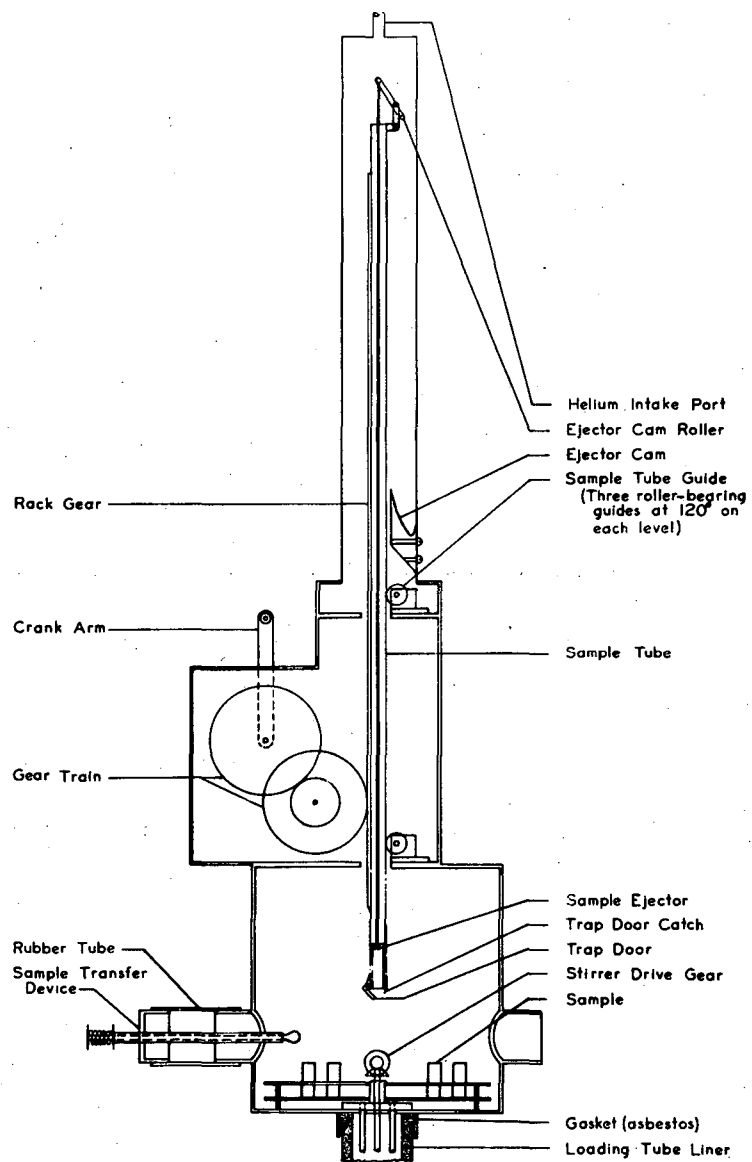


FIG. 6

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system and both pressure and vacuum are available. One can empty the vat by melting the tin, and applying gas pressure, which forces the tin out a delivery tube discharging into the tin bath. The reverse operation is effected by the use of vacuum.

The gas system used consists of a tank of argon and a tank of helium, each piped through manometers and drying tubes to the calorimeter. The drying tube on the argon line consists of a bubbler unit in which the gas bubbles through the liquid alloy of sodium and potassium to remove water and oxygen. The dry argon then flows into the heating element region, and also into the inner graphite chamber, providing an inert atmosphere around the heating element, and around the sample. The drying tube on the helium line consists of a column of phosphorous pentoxide. The dry helium then flows to the top of the sample dispenser unit. Thus the argon fills the inner graphite container displacing any lighter gas and overflows into the sample chamber where it meets the helium which displaces heavier gas in the upper part of the dispenser unit. The sample chamber does not have a gas-tight seal with the loading tube and the two gasses escape through this joint, and thus provide the calorimeter with an inert atmosphere.

The recording instruments are the Leeds and Northrup Micromax controller-recorder, the Leeds and Northrup Precision potentiometer, and a timer. In normal operation, the Micromax unit is used to record the temperature-time trace of the sample, the Wheelco unit controls the tin-bath temperature as previously described, and the potentiometer in conjunction with the timer is used to read the temperatures of the sample, at known times. The Micromax trace, and the potentiometer-timer reading, constitute the data obtained from the calorimeter.

A thermocouple selector switch is used with each instrument so that any thermocouple may be connected to any instrument. In addition, the Micromax unit is wired so that it can be used to control and record the temperature of the

heating unit. Further, since the range of expected operating temperatures exceeded that of the Micromax unit and the Wheelco unit, a "buck-boost" system of e.m.f. was designed. This system allows the operator to "boost" or "buck" the e.m.f. of the selected thermocouple by any amount required so that the resultant e.m.f. is in the range of the instrument.

### Discussion

The overall calorimeter design proved satisfactory with but few exceptions. It was anticipated that the problem of a suitable heating element would be a difficult one. A unit consisting of eight 1/2" D. x 15" long globar elements in parallel was tried first. The low resistance sections of the elements were found to attack molybdenum, and since molybdenum was the only available material at all suitable for use in making bus bars, elements with 15" of heating section were used and the ends cut off. This presented the problem of making suitable contacts since the contact resistance of molybdenum and the silicon carbide rod was higher than the resistance of the rod. The first attempts consisted of trying to electroplate a thin layer of metal on the end of the rods. Nickel, chromium, and platinum were tried but none of these yielded a suitable plate. Then copper was tried, and this plated on, giving a nice-looking plate, which could be covered by any of the above metals. However, the contact resistance of such plated contacts was not appreciably lower than that of the molybdenum-silicon carbide contact and this approach was abandoned.

The next approach consisted of dipping the ends of the rods into a crucible of molten titanium metal. This metal alloys with silicon and also forms a very stable carbide so that this approach was successful in getting some titanium metal to adhere firmly, and with low contact resistance between the titanium and the silicon carbide. However, the surface was so rough that an appreciable contact

resistance was encountered between the molybdenum and the titanized end of the silicon carbide rod. The final contact was made by wrapping a piece of platinum foil around the end of the titanized rod, slipping the wrapped end under the molybdenum clips in the molybdenum bus bar (bus bar was laminated molybdenum, 3/4" x 3/16" in total section, and having 8 contact clips equally spaced on the outer circumference) and then adding a few drops of molten tin to each joint after the unit was assembled. The fact that tin has a low melting point, alloys with platinum and has a low vapor pressure makes it ideal for this application. The tin melts, contacts both the rod and the molybdenum at the same time, and alloys with the platinum, making a good contact. This element was operated at a temperature of about 600°C. in an argon atmosphere with a control of  $\pm 1.5^\circ\text{C}$ . in the tin bath when the control thermocouple was placed next to one of the heating elements. However, when a mixed atmosphere of argon and hydrogen was used at this temperature it resulted in a break down. First, the hydrogen gas (or possibly water vapor in the hydrogen gas or in the argon) attacked the gas intake port area and corroded this region badly. The laminated molybdenum bus bar was fastened together with tantalum rivets, since these were more easily fabricated and used than molybdenum, and the hydrogen attacked these rivets to such an extent that the bus bar fell apart. Although this, at first sight, seems disastrous, the bus bars could be readily repaired by using molybdenum rivets. The molybdenum parts themselves were practically unaffected except for a very light surface coating of oxide, presumably  $\text{MoO}_2$ .

The second heating element tried was one of molybdenum wire. The fact that the molybdenum attack in the globar unit was light gave the false impression that the atmosphere in the region of the heating element was relatively free of oxygen. The molybdenum wire heater was made of 0.050" diameter wire, and was operated satisfactorily at temperatures up to 200°C. However, this element was inadvertently burned out, and upon unpacking the calorimeter it was found that the entire

surface lining the heating element region was coated with the oxide of molybdenum  $\text{MoO}_3$ . Although, at the time, the argon had been off for several days, the destruction of the element was proof that oxygen attack was an ever-present peril to such an element, and particularly so because of the small mass of molybdenum involved. It became apparent then that a massive element was desirable, if the material were susceptible to attack by oxygen or water vapor.

The third and final heating element used consisted of a graphite spiral. This element was very successful and was operated at  $600^\circ\text{C}$ . for over a month, and at  $1050^\circ\text{C}$ . for two days. Upon examination, after the heatings, the element proper was practically unchanged although the contact between the power lead and the contact tab was very poor. The fact that this contact was poor was noted several days before breakdown, but it was possible to operate at  $600^\circ\text{C}$ . for a week and at  $1050^\circ\text{C}$ . for two days in spite of this partial failure.

The run at  $1050^\circ\text{C}$ . was an attempt to measure the heat of formation of cerium-silver alloys but before the run was well started, it was noted that the calorimeter was behaving peculiarly. The run was stopped and the calorimeter opened, when it was noted that the inner cavity had flooded with tin.

When the calorimeter was unpacked, the difficulty was readily located. The collar on the inner cavity had corroded to such an extent that the tin had run over through the top of the inner chamber and had partially filled the chamber. This break-down was the result of two effects, the abrasion of the stirrer support whose lower end rested against the collar, and the greater attack by oxygen of the air while the parts were at the higher temperature, and the argon flow was turned low. During the operation of the calorimeter at  $600^\circ\text{C}$ ., for a month this attack must have been small, but at the higher temperature which would cause much more vigorous convection currents in the loading tube, the resulting attack was sufficient to result in breakdown.

The difficulties mentioned above can be overcome. A new design of the contact is desirable, and the most promising design is one which utilizes a spring or weight-loaded contact of larger area than the previous one. The redesigned contact tab would have a hemispherical depression cut in it, into which a matching hemisphere of molybdenum seats. The seat would be coated with silicon powder, whose purpose is to provide a firm bond between the two materials, since silicon forms alloys with molybdenum, and forms silicon carbide with the carbon. The pressure on the seat would maintain a good contact.

Since the difficulty with the collar of the inner chamber is primarily due to inward leakage of air into the sample chamber and thence into the loading tube, all possible sources of leakage must be corrected. The most probable leak is in the asbestos gasket between the loading tube liner and the sample chamber. This could be replaced by a sponge rubber gasket which should improve the seal at this point. In addition, the tube liner sections could be cemented together. A third alteration consists of redesigning the sample transfer mechanism so that when they are in use less air is displaced by their movement.

It was anticipated that the cooling of the calorimeter with the tin bath in place might cause either the vat or the inner chamber to crack when the tin solidified. The tin did solidify once due to the development of the bad connection in the heating coil. A check was made upon re-melting and indications were that neither element cracked. When the calorimeter was unpacked after the 1050°C. trial, these conclusions were verified. No tin was present outside the vat, and the level of the solid tin in the vat was just below the top level of the broken part, indicating that the tin merely ran over the top of the inner chamber, and not through a crack, since the level in the chamber was quite a bit below the level in the vat.

It appears, then, that the tin may be allowed to solidify in the calorimeter without damage. This solves the question of whether to keep the calorimeter warm



over a short period of dis-use or whether to transfer the tin to the storage vat.

A preliminary estimate of the power requirement was made before design of the main power supply, which estimate resulted in a calculated power requirement of about 4 kw. to maintain the calorimeter at 1500°K. In the runs at 600°C. (870°K.) the power requirement was about 1.8 kw., at 1050°C. (1320°K.) the power requirement was about 4 kw. Hence the power supply of 7.5 kw. will probably be sufficient to operate up to 1300°C. (1570°K.).

The control system used with the graphite heating element was adequate in that the temperature variation of the tin bath could be limited to  $\pm 0.5^\circ\text{C}$ . at 600°C. for periods of an hour or more. An improvement might be obtained by using a voltage regulator in the 220v. line.

The preliminary data for the run at 1050°C. indicate a maximum variation of one °C. over a period of two hours. This degree of control is quite satisfactory at this temperature.

The system sodium-tin was chosen for investigation to examine the operation of the calorimeter. The results of this investigation are reported by McKisson and Bromley<sup>(10)</sup>, and on the basis of these results, it is felt that the calorimeter operates successfully. It is of interest to note that the calorimeter's use is not limited to measurements in alloy systems, but could be applied as well to measurements of mixed oxide systems, or mixed halide systems; provided, of course that the system being investigated was liquid below 1300°C. Further, it should be possible to use the calorimeter for measurement of heat effects of materials which are not themselves liquid at 1300°C., if a suitable solvent could be found.

#### Conclusion

A new high-temperature calorimeter has been designed, constructed, and operated with some measure of success. Means have been presented by which its faults may be corrected.

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Definition of Symbols

$A_1$	Area of crucible system for radiative heat transfer, cm. <sup>2</sup>
$A_2$	Area of crucible system for convective heat transfer, cm. <sup>2</sup>
$C$	Constant of integration.
$C_1$	Constant.
$C_p$	Heat capacity at constant pressure, cal./deg.
$C_{p_i}$	First approximation on heat capacity of system, cal./deg.
$C_{p_{ii}}$	Second approximation on heat capacity of system, cal./deg.
$C_{p_{inert}}$	Heat capacity of inert material cal./deg.
$d$	Prefix, differential operator.
$H_T$	Heat content at T, cal./mol., kcal./mol.
$H_{298}$	Heat content at 298°K, cal./mol., kcal./mol.
$\Delta H_{inert}$	Heat content change of inert material, cal./mol., kcal./mol.
$h$	Heat transfer coefficient for convection BTU/hr. ft. <sup>2</sup> °F., cal./min. cm <sup>2</sup> °C.
$\ln$	Natural logarithm.
$mv.$	Millivolts.
$\Delta mv$	Difference of mv. from the equilibrium value, millivolts.
$P$	Parameter in developed equations, defined by Eqn. (7), cal./min. deg., cal./min. mv.
$P_i$	First approximation of P, cal./min. deg., cal./min. mv.
$P_{ii}$	Second approximation of P, cal./min. deg., cal./min. mv.
$Q$	Heat, cal.
$Q'$	Heat in the "tail" of the $q - \Theta$ plot, cal.

$q$	Rate of heat transfer, cal./min.
$q_i$	First approximation of rate of heat transfer, cal./min.
$q_{ii}$	Second approximation of rate of heat transfer, cal./min.
$R$	Parameter developed in equations, defined by Eqn. (8), cal./min. deg. <sup>2</sup> , cal./min. mv. <sup>2</sup>
$R_i$	First approximation of $R$ , cal./min. deg. <sup>2</sup> , cal./min. mv. <sup>2</sup>
$R_{ii}$	Second approximation of $R$ , cal./min. deg. <sup>2</sup> , cal./min. mv. <sup>2</sup>
$T$	Temperature of crucible, °K.
$\Delta T$	Temperature difference, $(T - t)$ , °K.
$\Delta T_o$	Temperature difference between a point on the ideal region of a cooling curve and the equilibrium temperature, °K.
$t$	Temperature of cavity, °K.
$\Delta t_i$	First approximation of temperature drop of mixing, when inert material is added, $(T - t)$ at $\theta_i$ , °K.
$\Delta t_{ii}$	Second approximation of temperature drop of mixing, when inert material is added, $(T - t)$ at $\theta_{ii}$ , °K.
$e$	Emissivity, dimensionless.
$\theta$	Time, min.
$\theta_i$	First approximation to the time for the fictitious "instantaneous" reaction, min.
$\theta_{ii}$	Second approximation to the time for the fictitious "instantaneous" reaction, min.
$\theta_o$	Time corresponding to temperature difference $\Delta T_o$ , min.
$\sigma$	Boltzman constant, BTU/hr. ft. <sup>2</sup> °F. <sup>4</sup> , cal./min. cm. <sup>2</sup> °K. <sup>4</sup> .

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