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Application of an adiabatic calorimeter to the determination of the heats of fusion and heats of formation of several metallic compounds

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Application of an adiabatic calorimeter to the determination of the heats of fusion and heats of formation of several metallic compounds

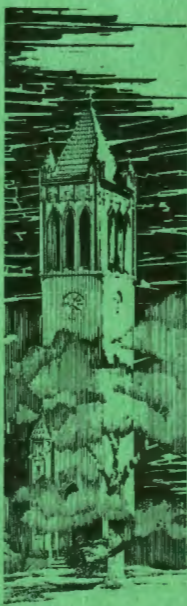
Abstract

High temperature thermodynamic properties of metal alloys and refractory materials are important in both research and engineering. Reliable and precise measurements are difficult to make and require rather elaborate equipment. In recent years a commercial adiabatic calorimeter has been made available by the Rigaku Denki Company, Ltd., of Tokyo, Japan. The general operating principles of this apparatus are summarized; its application to the measurement of heats of fusion and transformation of materials, and heats of formation of intermetallic phases is described. The results of the heat of formation experiments are: MgZn_2 @863° K, -4.30 kcal/ g-atom; CaMg_2 @532° K, -3.12 kcal/ g-atom; and CeZn @623° K, -10.6 kcal/ g-atom. The results of the heat of fusion of the materials are: MgZn_2 , 9.687 kcal/mole; CaMg_2 , 11.744 kcal/mole; CeZn , 7.826 kcal/mole. The average values for the heats of fusion are accurate to ± 2 pct.

Disciplines

Ceramic Materials | Metallurgy

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IOWA STATE UNIVERSITY

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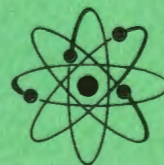
by

Gerald J. Gartner and Premo Chiotti

AMES LABORATORY

**RESEARCH AND
DEVELOPMENT
REPORT**

U.S.A.E.C.



PHYSICAL SCIENCES READING ROOM

IS-1070

Metals, Ceramics, and Materials (UC-25)
TID-4500, December 1, 1964

UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

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February, 1965

Ames Laboratory

at

Iowa State University of Science and Technology
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Gerald J. Gartner and Premo Chiotti

ABSTRACT

High temperature thermodynamic properties of metal alloys and refractory materials are important in both research and engineering. Reliable and precise measurements are difficult to make and require rather elaborate equipment. In recent years a commercial adiabatic calorimeter has been made available by the Rigaku Denki Company, Ltd., of Tokyo, Japan. The general operating principles of this apparatus are summarized; its application to the measurement of heats of fusion and transformation of materials, and heats of formation of intermetallic phases is described. The results of the heat of formation experiments are: MgZn_2 @ 863°K , -4.30 kcal/g-atom; CaMg_2 @ 532°K , -3.12 kcal/g-atom; and CeZn @ 623°K , -10.6 kcal/g-atom. The results of the heat of fusion of the materials are: MgZn_2 , 9.687 kcal/mole; CaMg_2 , 11.744 kcal/mole; CeZn , 7.826 kcal/mole. The average values for the heats of fusion are accurate to ± 2 pct.

*This report is based on a M. A. thesis submitted by Gerald J. Gartner, February, 1965, to Iowa State University, Ames, Iowa.

INTRODUCTION

Entropy and energy are the two most important thermodynamic properties of a substance. Values of these two properties, appropriately combined, yield information on the thermodynamic stability of chemical substances. Modern trends toward higher operating temperatures for nuclear reactors, turbines and jet engines, processes for purifying reactor fuels, etc., emphasize the need for quantitative data on the physical and chemical behavior of materials at high temperatures. As a result, high temperature thermodynamic properties of metals, alloys, and refractory materials in general are rapidly becoming more important both in research and engineering. Enthalpies of transformation and heat capacities are needed to relate high-temperature equilibrium data to room-temperature thermodynamic properties. The design of an operative nuclear reactor could hardly be possible without a previous knowledge of the thermodynamic properties of the reactor materials.

Measurements of entropy and energy can be obtained from thermal data, the most important of which are heats of reaction and formation, heat capacities, heats of transformation and fusion (1). Calorimetric methods afford a means for

the measurement of these quantities. Many different types of calorimeters have been designed for the direct measurement of thermal properties, but basically each can be classified into one of the three following categories:

1. Drop methods
2. Differential thermal methods
3. Adiabatic methods

In the drop method, the change in heat content of a sample for a temperature span, between the furnace temperature and the calorimeter temperature, is determined. The Bunsen ice calorimeter (2) is an example of a calorimeter which employs the drop method. The sample is dropped from a furnace into an ice bath and the heat liberated by the sample on cooling is found by measuring the amount of ice melted. Generally speaking, the results obtained are quite accurate, but a few serious limitations do exist. The drop methods are not suitable for those substances which undergo metastable transitions and which do not give a thermodynamically reproducible state on quenching (3). It is often not feasible to use drop calorimetry to measure the heat content of an alloy for temperatures above the melting point of the alloy. Segregation will almost always occur, causing the final states to be indefinite. Even when the cooling takes place entirely

within a single-phase region, there may be order-disorder changes with heat effects of several hundred calories per g-atom (1).

In the differential thermal method, the sample and a standard are heated or cooled in a massive metal block. By measuring the difference in temperature of the sample and standard, it is possible to measure heats of transformation or reaction. This method, although quite well suited for finding the temperature of a transformation, is not as good as the other two for determining heats of transformation or reaction. Extreme care taken in experimental design and operation produce results which are mediocre at best.

In the adiabatic method, the temperature of the sample surroundings is made to follow that of the sample. Thus, there is no transfer of heat between the sample and its surroundings. The sample is heated at a known wattage and the energy required to raise the sample an increment of temperature is recorded, making it possible to directly determine heat capacities, heats of transformation, heats of fusion, and heats of reaction.

The adiabatic method was used in this investigation. The drop method is probably more accurate, but the adiabatic

method is much faster and has a wide range of applications. The adiabatic method surpasses the differential thermal method in both accuracy and convenience.

Several types of adiabatic calorimetry are now in use. In the Sykes method (4), the sample is heated at a constant rate ($dT/dt = \text{const.}$). This method is suitable for the measurement of specific heats, but not for the determination of enthalpies of transformation since it is virtually impossible to maintain a constant heating rate through a transformation. In another method, developed by Nagasaki and Takagi (5), the sample is warmed by a heater which is powered by a constant wattage supply and the amount of heat required to traverse an interval of temperature is determined by measuring the time. This is the method which was employed in this work.

Stated briefly, the objectives of this investigation were: 1) To adapt a commercial calorimeter based on the method developed by Nagasaki and Takagi to the measurement of thermal properties of various zinc and magnesium alloys which are of particular interest in the pyrometallurgical methods being developed by Metallurgy Group IV, and 2) To apply the calorimeter to the measurements of the heats of fusion and formation of the compounds MgZn_2 , CeZn , and CaMg_2 and the heats of fusion and transformation of ThCl_4 .

OPERATION OF THE APPARATUS

The apparatus used in this investigation was an automatic recording differential thermal analyzer and adiabatic calorimeter, manufactured commercially by the Rigaku Denki Co., Ltd., of Tokyo, Japan. The apparatus, shown in Figure 1, combines facilities for differential thermal analysis (DTA) and specific heat measurement (SHM) into a compact and fully automatic unit. In this investigation, only the SHM capabilities were utilized.

The principle of operation is actually quite straightforward. Briefly, a specimen is encased in a cylindrical tantalum crucible and supported at the center of a metal sphere (Figure 2). The temperature of the surrounding metal sphere is maintained the same as the temperature of the sample by an electronic control circuit. A small resistance heater is inserted into the sample and powered by a constant wattage source. A temperature measuring thermocouple is in contact with the sample, and the time required to heat the sample an increment of temperature is automatically recorded. Knowing this time and the power dissipated by the heater, it is possible to determine the heat capacity of the sample by the equation,



Figure 1. Rigaku Denki automatic recording differential thermal analyzer and adiabatic calorimeter

$$C_p = \frac{(W)(\Delta t)(0.239 \text{ cal/watt-sec})}{\Delta T}, \quad (1)$$

W = heater power = volt-amperes

Δt = time to raise sample temperature ΔT

ΔT = increment of temperature in Centigrade degrees.

The heat of an isothermal transformation of a substance can be determined by measuring the time required for the transformation to occur, knowing the heater power:

$$\Delta H = (W)(\Delta t)(0.239 \text{ cal/watt-sec}). \quad (2)$$

The enthalpy of formation of a compound can be found by measuring the heat required to raise the sample, initially consisting of the pure reactants, through a temperature range and subtracting from this the heat required to raise the temperature of the sample consisting of only the compound through the same temperature range. The two end temperatures are chosen such that during the first run the reaction will go to completion. The measurement of the heats of transformation and heats of reaction are discussed in Chapter III of this work.

The unit actually measures the heat capacity of everything within the metal sphere. Therefore, obtaining the heat capacity of the sample material requires various corrections. Also, heat transfer due to non-adiabatic conditions was one

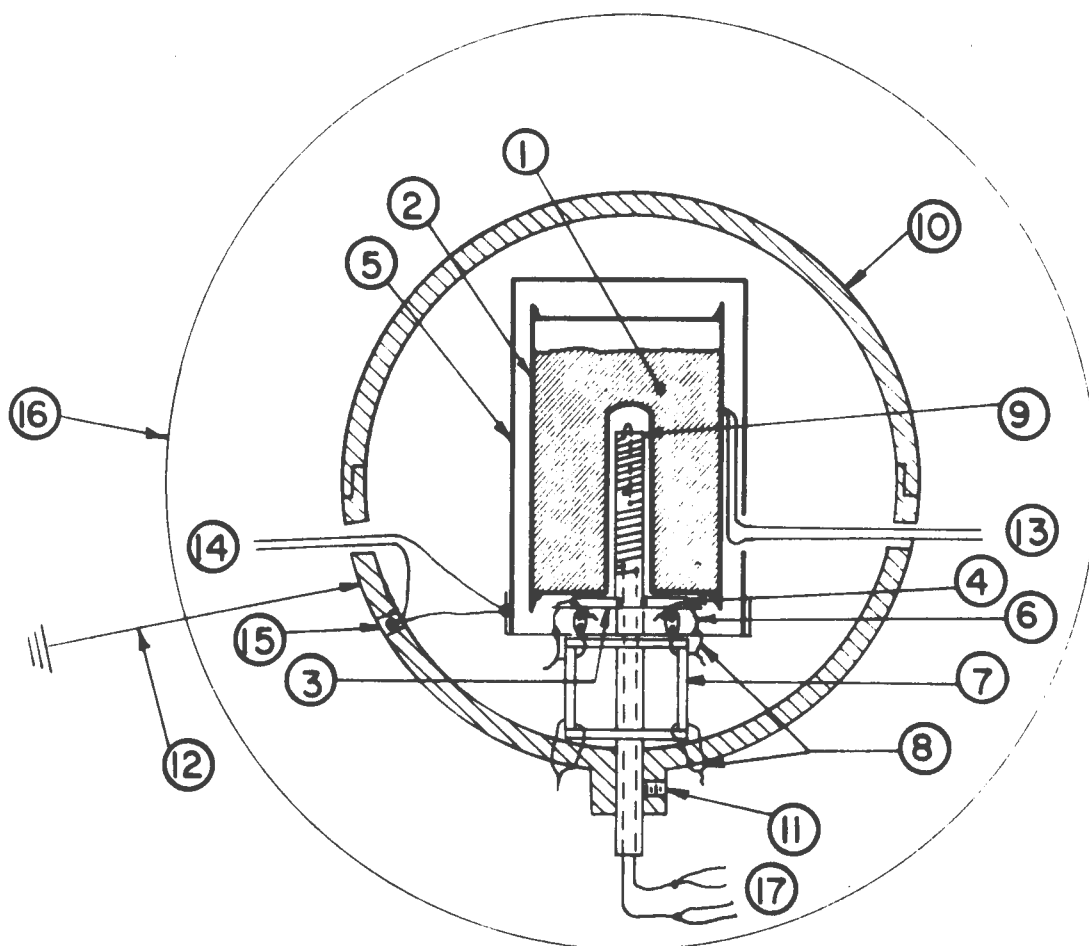
of the most serious problems encountered. Consequently, the actual determination of specific heats has been postponed and the effort has been concentrated in the development of procedures for measuring heats of transformation and reaction. As will be shown later, the heat capacity of the container and other extraneous, but necessary materials within the calorimeter, need not be known for these measurements. However, heat transfer must be accounted for and much of the work in this investigation has been directed toward reducing it to a minimum.

Even though the principle of operation is simple, actually achieving adiabatic conditions requires a very complicated electrical control circuit. . . Basically, the calorimeter can be divided into four sections: the sample chamber, the adiabatic control section, the wattage stabilizer section, and the temperature measurement and timer section. These four sections will be discussed in some detail.

A. Sample Chamber

A section drawing of the sample chamber is shown in Figure 2. The sample itself is located at the geometric center. The substance investigated is sealed in a tantalum crucible consisting of a piece of one-inch tantalum tubing,

Figure 2. Sample chamber



- | | |
|---|---|
| 1. Sample | 10. Nickel adiabatic ball (three-inch diameter) |
| 2. Tantalum crucible | 11. Set screw |
| 3. Nickel base plate | 12. Adiabatic ball ground wire |
| 4. Insulating spaghetti (0.060-inch diameter) | 13. Temperature measuring thermocouple |
| 5. Platinum radiation shield | 14. Differential thermocouple |
| 6. Insulating spaghetti (0.150-inch diameter) | 15. Ball junction of differential thermocouple |
| 7. Quartz stand | 16. External furnace |
| 8. Nickel binding wire | 17. Nickel heater leads |
| 9. Internal heater | |

1½ inches high and wall thickness of 0.015 inch , closed at both ends by 0.015-inch tantalum caps. A piece of ¼-inch tantalum tubing, sealed at one end, extends about one inch through the bottom cap, forming a well for the resistance heater. All the joints of the crucible are made by arc welding in an argon atmosphere.

The crucible is supported by a 0.75-inch nickel disc or base plate, and insulated from it by a triangular arrangement of 1/16-inch alumina thermocouple insulator, "insulating spaghetti". The base plate is insulated from the base of the radiation shield by a triangular arrangement of 1/8-inch insulating spaghetti. The base of the platinum radiation shield rests on a quartz stand which is tied to the adiabatic ball. All the above components constitute the sample stand and are rigidly held together by pieces of 0.010-inch nickel wire. Although nickel wire, an electrical conductor, is used to hold the sample stand together, the sample container is electrically "floating" from the rest of the system. It has been found that adiabatic control is virtually impossible if there is electrical contact between the sample container and the other parts of the sample chamber.

Surrounding the crucible is a cylindrical, platinum

radiation shield. Its function is to diminish radiative heat transfer between the sample and the ball. Runs have been made with the shield removed showing conclusively that adiabatic control is hampered.

The internal heater (Figure 3) is made by wrapping Kanthal resistance wire around the top of a piece of four-hole insulating spaghetti. The ends of the heater wire are welded to nickel leads which are then wound several times around the spaghetti. The purpose of the latter winding is to minimize the heat loss due to conduction along the heater leads. The total resistance of the heater is about 8 ohms. A thin coating of Sauereisen high-temperature insulating cement covers all exposed wires to prevent possible electrical contact of the heater with the sample.

The sample is located approximately at the center of a 3-inch O.D., 2 7/8-inch I.D. nickel sphere called the "adiabatic ball", which is split in a horizontal plane; the two halves come apart exposing the sample, stand, etc. At the bottom of the sphere there is a hole through which the heater stem passes. A set screw holds the heater stem in place. The adiabatic ball is grounded by a 0.010-inch nickel wire.

Two thermocouples are used in the sample chamber. One is

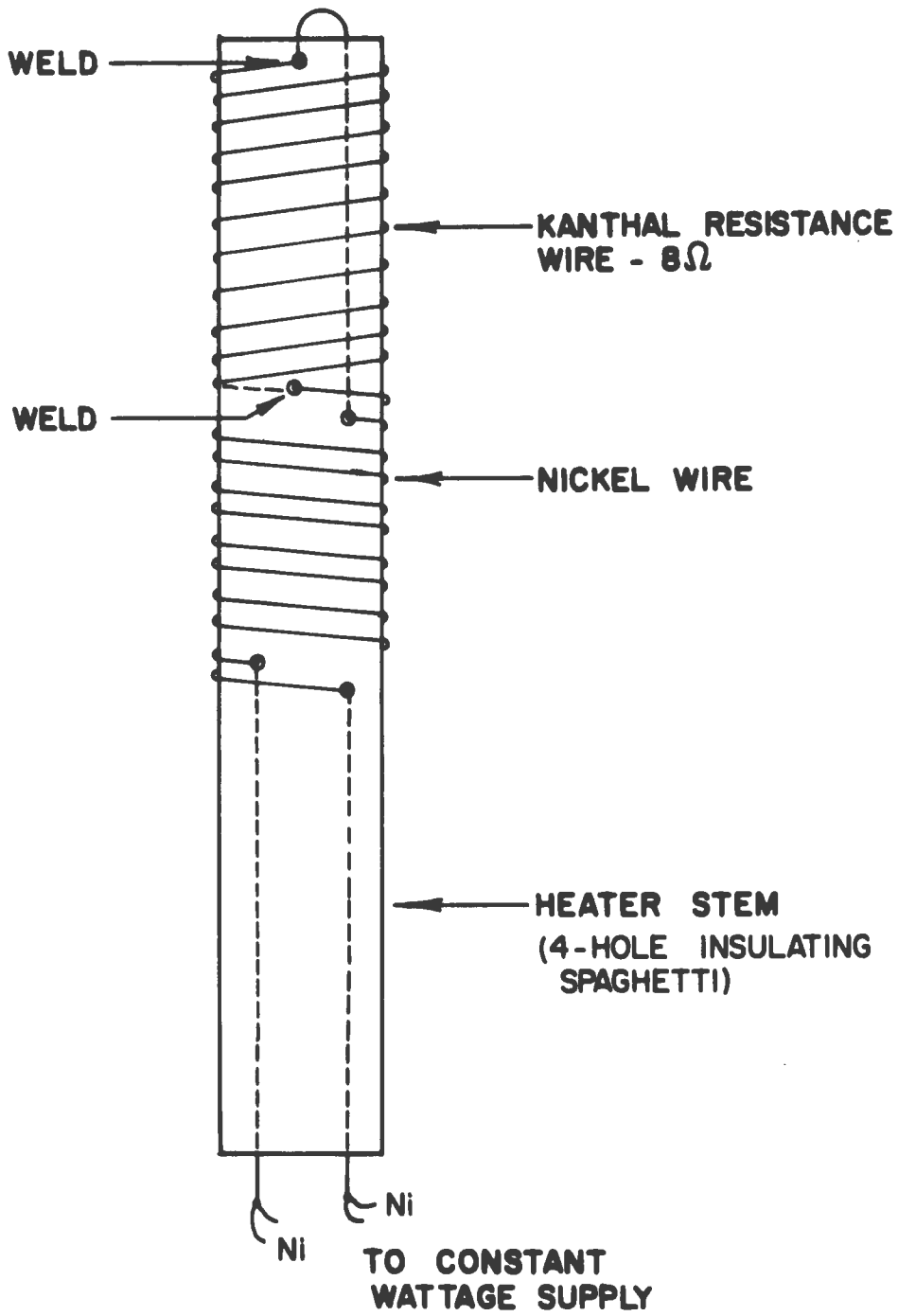


Figure 3. Sample heater

the chromel-alumel temperature measuring thermocouple which is placed between the sample and the platinum radiation shield. This thermocouple measures the temperature of the sample. The output of the temperature measuring thermocouple is fed into the temperature measurement and timer section which is explained later. The other thermocouple is an alumel-chromel-alumel differential thermocouple. One junction is spot welded to the base of the platinum radiation shield and the other junction is imbedded in Saureisen cement in a hole in the ball. Thus, there is no electrical contact between the radiation shield, or sample, and the adiabatic ball.

The output of the differential thermocouple is amplified by the differential amplifier and adiabatic control section of the unit which in turn controls the external furnace power. When the adiabatic ball is hotter than the sample the furnace power is decreased, and when the adiabatic ball is colder than the sample the power is increased.

The external furnace is spherical in shape and symmetrically wound with Nichrome wire such that the energy dissipated per unit area of the furnace is approximately constant over the surface.

The furnace is surrounded by an alumina-ceramic radiation

shield which is surrounded by a stainless steel radiation shield. Like the radiation shields, the furnace, and the adiabatic ball, the outer water-cooled housing is spherical, consisting of two hemispheres separated by a large rubber "O" ring which makes a vacuum-tight seal. The entire system is evacuated by an oil diffusion pump and mechanical pump acting in series. The normal operating pressure is about 1×10^{-4} mm of Hg, eliminating the heat loss due to convection and gas conduction. Runs have also been made with an inert atmosphere and adiabatic control was improved at lower temperatures. However, all runs reported in this work were made under vacuum.

A photograph of the sample chamber is shown in Figure 4. The sample, platinum radiation shield, and top halves of the adiabatic ball, external furnace, alumina-ceramic radiation shield, stainless steel radiation shield, and water cooled jacket have been removed.

Two factors are very important in achieving adiabatic control at high temperatures. First, it is necessary to have the entire sample arrangement mechanically rigid. If the components of the calorimeter are not firmly bound together, slight vibrations cause control to become erratic. For this



Figure 4. Photograph of sample chamber

reason, all of the calorimeter parts have been tightly secured with nickel wire. The second factor is proper insulating and grounding of the sample chamber. The sample must not make electrical contact with the platinum radiation shield, the differential thermocouple must be electrically insulated from, but in good thermal contact with the adiabatic ball, and the adiabatic ball must be kept at ground potential. Other electrical arrangements have been found to be less satisfactory.

B. Adiabatic Control Section

The adiabatic control section of the calorimeter is the heart of the system. Its ability to control the external furnace such that there is no net heat flow between the sample and ball determines whether or not the calorimeter is useful as a research tool. For this reason, a sophisticated electronic system is employed, keeping the temperature difference of the ball and sample within ± 0.04 degrees, and doing so automatically.

The principle of operation of the adiabatic control section is shown in Figure 5. If the temperature of the ball is different from the temperature of the sample, a potential difference, e_d , will be generated by the junctions of the differential thermocouple. This emf is then amplified by the

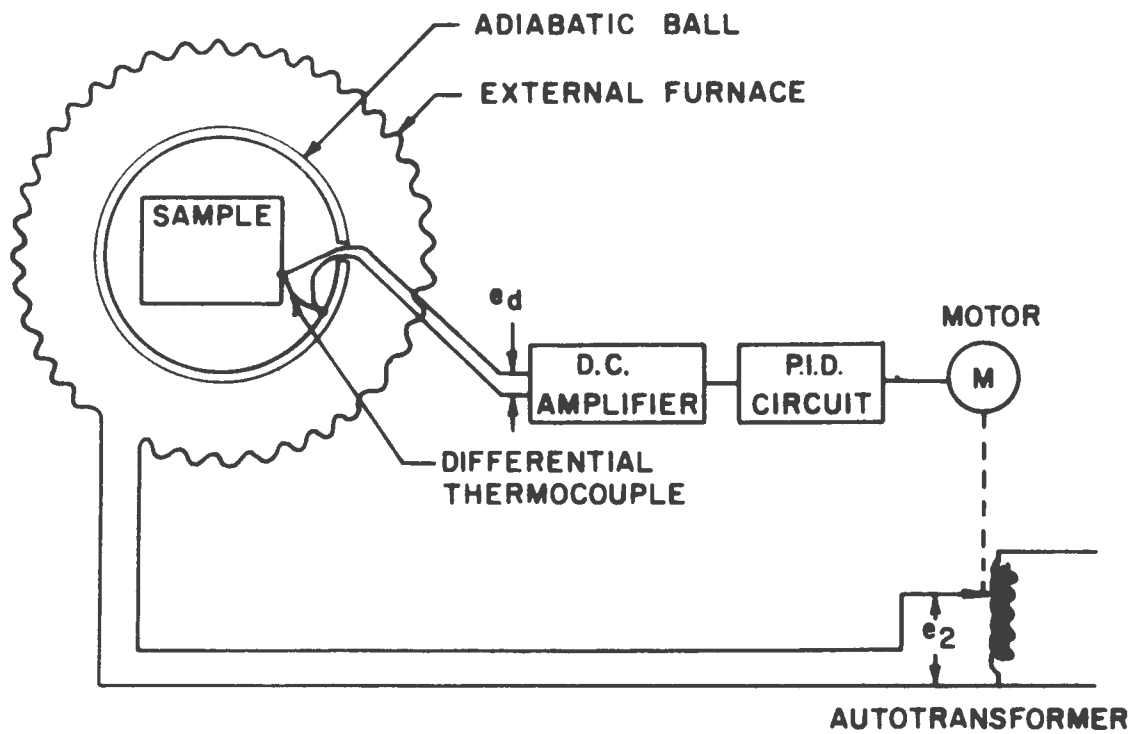


Figure 5. Schematic of adiabatic control section

D.C. amplifier and fed into the proportional-differential-integral (PID) circuit.

The PID circuit is best explained in parts. The proportional (P) part will be discussed first. Let us assume that there is a temperature difference between the ball and sample of ΔT , the sample being hotter. This temperature difference generates a characteristic emf in the differential thermocouple, e_d , which is amplified by the D.C. amplifier and proportional amplifier in series. By a complex system of relays, the motor will drive the autotransformer until the voltage supplied to the external furnace is e_2 . This voltage is proportional to e_d and hence the name "proportional control".

If proportional control were used exclusively, the control action would be disturbed by hunting since e_2 becomes zero only when e_d is zero. Proportional control makes no allowance for the rate of change of e_d . However, by employing a proportional-differential amplifier, the first time derivative of e_d is considered and the control action becomes much smoother and more stable.

The differential part of the circuit consists of a capacitive feedback network on the proportional amplifier. The

overall effect of the proportional-differential amplifier is represented in the equation,

$$e_2 \propto [ae_d + b\frac{de_d}{dt}], \quad (3)$$

where e_2 is the external furnace voltage, and a and b are constants. Thus the external furnace is supplied a voltage which is proportional to both the output potential of the differential thermocouple and its time derivative. The constants, a and b , can be varied: a is changed by regulating the amplification of the D.C. amplifier, and b is changed by varying the capacitance of the feedback network.

If proportional-differential control were used alone, the furnace voltage would be reduced to zero when the ball and sample temperatures became the same. This is desirable only when the sample is at room temperature. At a higher temperature e_2 cannot be zero because the adiabatic ball must be held at a temperature greater than room temperature. If it were not, the ball would lose heat to the outer water-cooled housing. The integrating (I) part of the PID control automatically sets the furnace voltage to a value greater than zero when the sample temperature is above room temperature.

Thus, adiabatic conditions are achieved when the temperature of the two junctions of the differential thermocouple,

and presumably of the sample and ball, are the same, causing e_d to be zero. This presumption, although it appears to be valid, was not borne out and an experiment was performed showing that it was not true.

If the adiabatic ball were not uniform in temperature, the average temperature^a of the ball could be different from the sample temperature, even though the ball and sample junctions of the differential thermocouple were the same temperature. If, for example, the top of the adiabatic ball were hotter than the ball junction of the differential thermocouple, there could be a net heat flow into the sample. Thus it was decided to spot weld differential thermocouples to several points on the inside of the adiabatic ball in order to detect differences in temperature. Chromel-alumel thermocouples were used throughout. The experimental setup is shown in Figure 6. By using this arrangement it is possible to measure the temperature of the ball and also the differences in temperatures of the top and side, side and bottom, and top and bottom of the ball. The results of this experiment, shown in Table 1,

^aAverage temperature: Consider a surface consisting of n points, each point at a different temperature, T_1, T_2, \dots, T_n . The weighted mean of these temperatures would be the "average temperature".

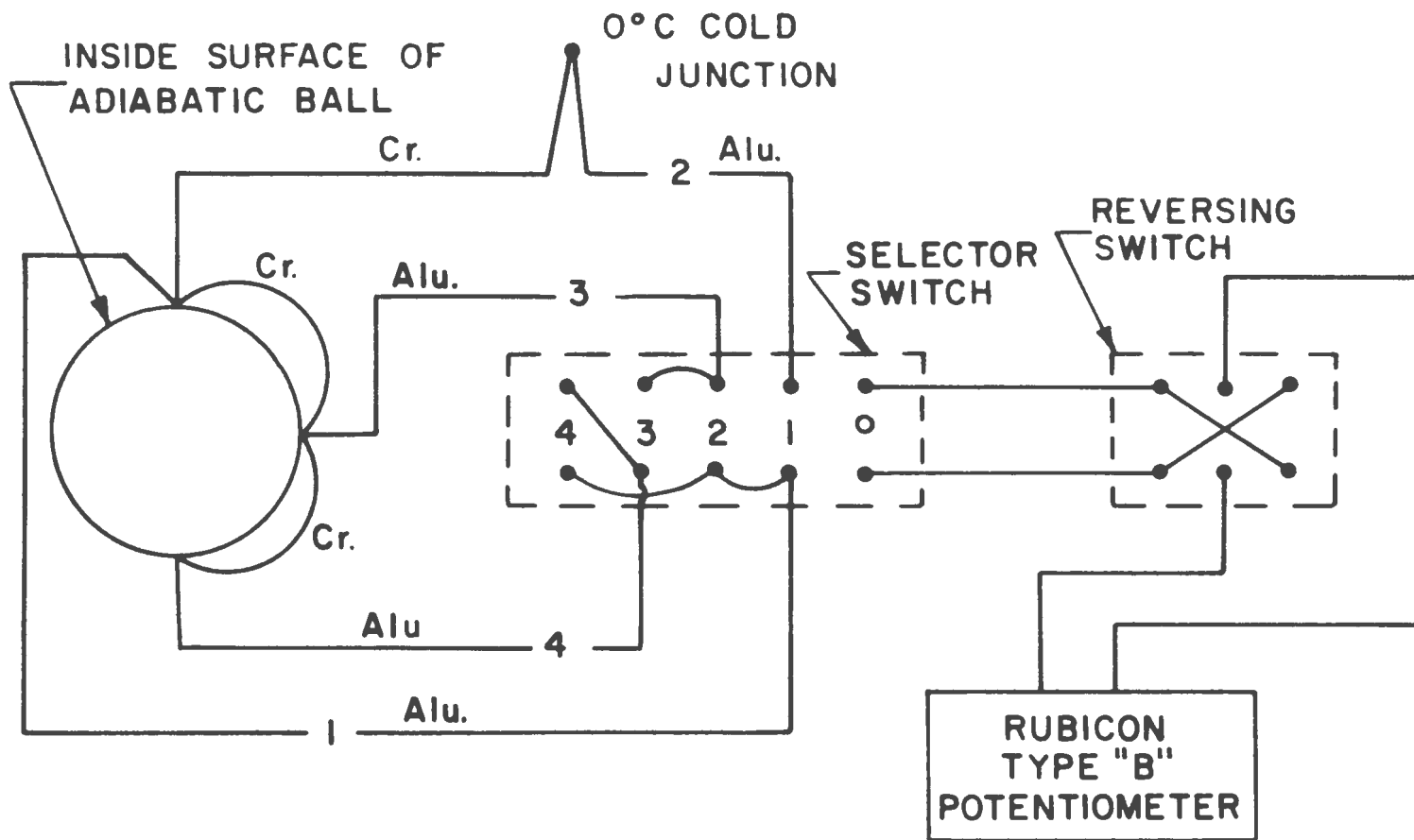


Figure 6. Experimental setup for detecting temperature gradients in the adiabatic ball

indicate that a temperature gradient does exist in the adiabatic ball and that it varies with temperature. The sample temperature was measured by the temperature measuring thermocouple.

Table 1. Temperature gradients in the adiabatic ball

Sample temp.	T_T °C	$T_T - T_S$ °C	$T_S - T_B$ °C	$T_T - T_B$ °C
146	142			
154		1.1		
158			0.0	
160				1.1
226	227			
230		0.8		
232			0.1	
234				0.9
374	381			
378		0.0		
380			1.1	
382				1.1
628	633			
632		1.3		
634			0.3	
636				1.7
828	832			
832		2.0		
834			0.4	
838				2.4

Because a gradient does exist in the adiabatic ball, then non-adiabatic conditions would be expected. This was also experimentally verified. The sample was heated to a temperature, the internal heater turned off, and the output of the temperature measuring thermocouple was observed

over a period of time. The output of this thermocouple would be a constant function of time if adiabatic conditions existed; however, the sample temperature increased even though e_d was zero (± 0.5 microvolt). Obviously, the average temperature of the ball was greater than the average temperature of the sample, and adiabatic conditions did not exist.

There are two ways by which this problem can be solved. First, an experiment or calculation could be made to determine the rate of heat flow into the sample. This could then be applied to the results as a correction factor. Second, an improvement could be made to the unit actually making the calorimeter adiabatic. The second method was chosen.

The problem of non-adiabatic conditions could be caused by one or a combination of many undesirable factors. One such factor, non-uniformity of temperature in the adiabatic ball, was found experimentally and discussed above. This problem might be eliminated by designing a new external furnace which would be more nearly symmetric than the present one. The possibility also exists of surrounding the adiabatic ball with a spherical metal heat sink a small distance away. The heat sink would be heated like the adiabatic ball is presently. This would smooth out the temperature gradi-

ents of the adiabatic ball, but adiabatic control would probably be much more sluggish than with the current design.

It must be kept in mind, though, that eliminating temperature gradients on the ball does not insure adiabatic conditions. The possibilities exist of stray currents in the differential thermocouple, non-uniformity of sample temperature, and a host of other unknown ailments.

As complex as the problem is, the solution is quite basic. It is not necessary to know all the factors causing a non-adiabatic condition. If such a condition exists in the apparatus, then there must be a net heat flow between the sample and ball. If by some means the rate of heat flow could be varied, and actually reversed in direction, then it would be possible to attain the state where the net heat flow rate is zero and adiabatic conditions exist. This is precisely what has been done.

A very small, variable emf source was inserted into the differential thermocouple circuit as shown in Figure 7. This emf source is called the "bucking potentiometer", or simply "bucking pot". The bucking pot adds to e_d a voltage, e_p . Thus, the total voltage fed to the adiabatic control section is

$$e_d + e_p = e_d^1. \quad (4)$$

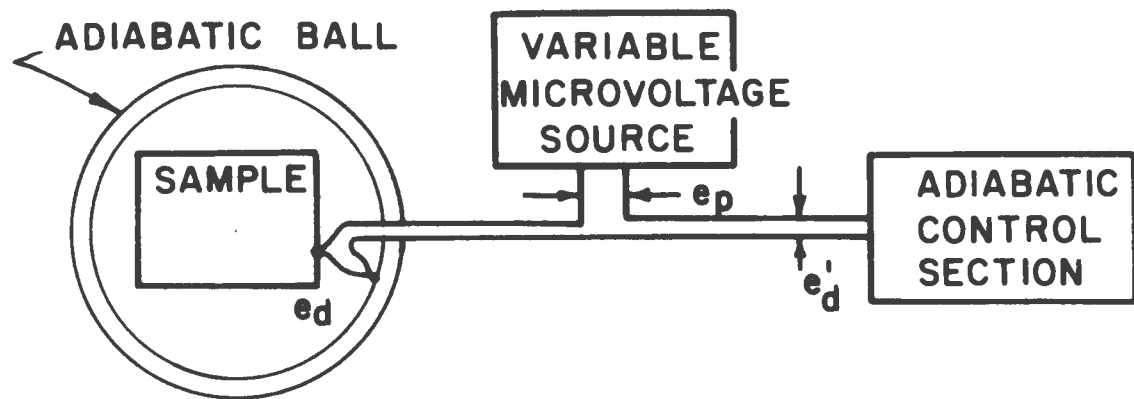


Figure 7. Location of the variable microvoltage source

However, the adiabatic control section cannot discriminate between e_d and e_p . All it detects is the total potential e_d' and controls the furnace until e_d' is zero. When control is attained,

$$e_d = -e_p. \quad (5)$$

It is therefore possible to make e_d any value, within reasonable limits, by varying the output of the bucking pot. The voltage e_d represents the temperature difference of one point on the ball and one point on the sample, not the difference in average temperatures of ball and sample. However, there is a relationship between the point temperatures and average temperatures. Raising the point temperature of the ball, for example, is accompanied by an increase in the average temperature of the ball. Thus it is possible to control the average temperature of the ball by the bucking pot, and to make the average temperature of the ball the same as the sample temperature, resulting in adiabatic conditions.

The procedure for determining the correct potentiometer setting for zero heat leak, called the "zero pot setting," will now be explained. The sample is heated to a temperature, T , and the internal heater is turned off. The bucking pot is then set to some value, e_p , and the system is allowed to come

to equilibrium. Then the output of the temperature measuring thermocouple is observed over a period of time and the rate of temperature change is recorded. The bucking pot setting is changed and the same procedure is repeated. The data are then plotted on a graph of heat leak rate vs. bucking pot setting and a smooth line is drawn through the points. The pot setting indicated by the point where the curve crosses the zero-heat-leak axis is taken as the zero pot setting.

A series of experiments were designed to determine what factors influenced the zero pot setting. It was desired to know: a) if the zero pot setting was a function of temperature, b) if the zero pot setting was the same for different runs with the same sample, and c) if changing samples affected the zero pot setting. It was found that the variance of the zero pot setting was negligible for different runs on the same sample. The variability, however, increased somewhat for different samples. This was attributed to the fact that it is impossible to set up each sample exactly the same. The furnace, sample, platinum radiation shield, etc. may be in slightly different positions causing differences in the zero pot setting. Most striking, though, is the pronounced relationship between temperature and zero pot setting. In all

cases, the required bucking potential for no heat leak showed an increase with temperature. A graph of zero pot setting vs. temperature is shown in Figure 8. The data for this graph were obtained from many different runs on different samples.

A special emf source was designed for use as the bucking pot. It was necessary to have good control and resetability in the microvolt range. This was accomplished by using the design shown in Figure 9. The voltage divider was a ten-turn, 100,000 ohm precision potentiometer fitted with a ten-turn dial having 100 divisions per turn. Both the potentiometer and dial were manufactured by Beckman Instruments, Inc., Helipot Division, Fullerton, Calif. Precision resistors were used in the circuit and all solder joints were made with special "EMF" solder, distributed by Alpha Metals, Inc., Jersey City, New Jersey. This solder was used to eliminate stray currents arising from dissimilar metal junctions. A 1.35 volt mercury battery was used as an extremely constant power supply. A reversing switch made it possible to change the polarity of the output, but for all zero pot settings the adiabatic ball side of the output was positive and the adiabatic control section side was negative.

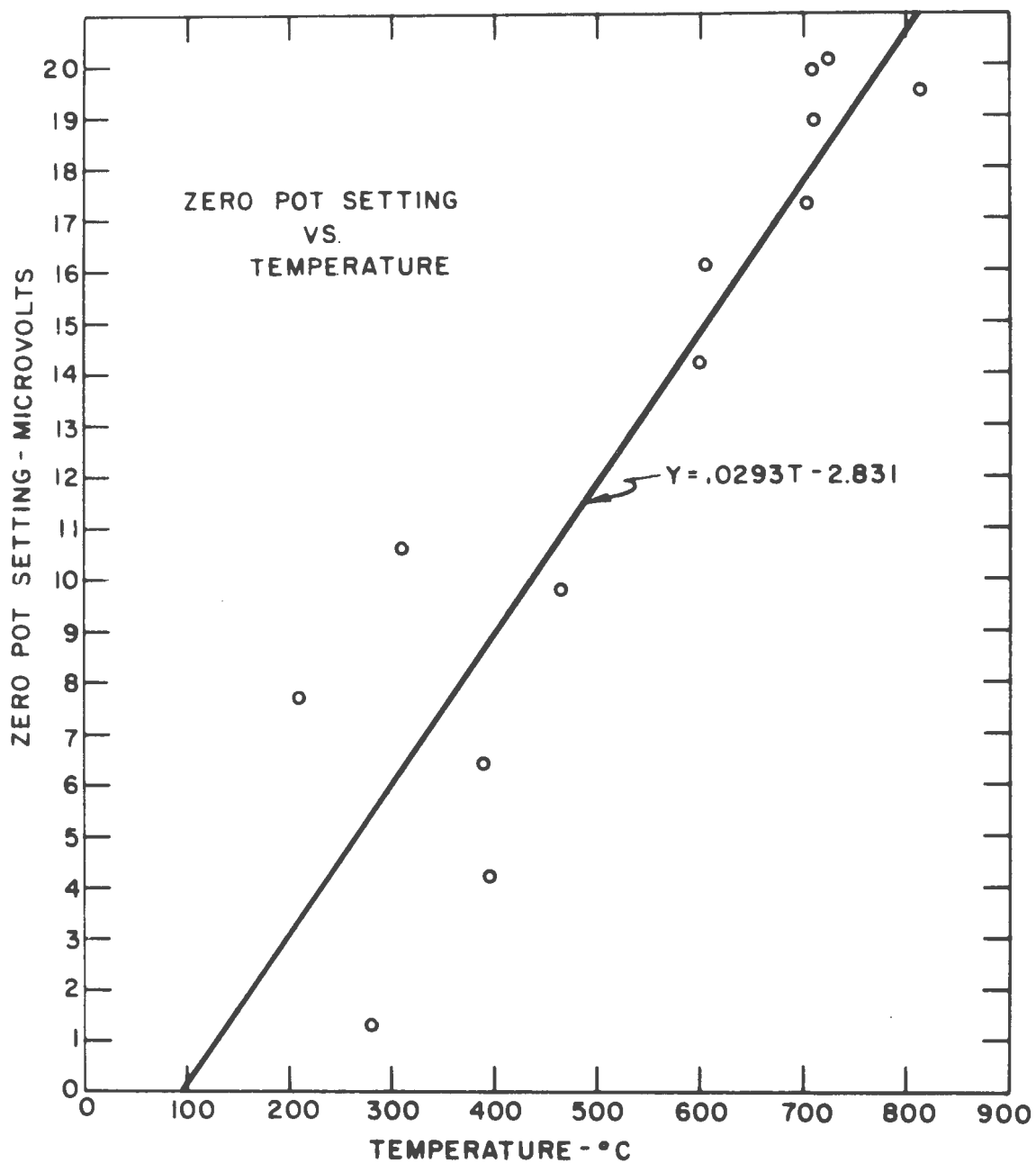


Figure 8. Bucking pot setting for adiabatic conditions as a function of temperature

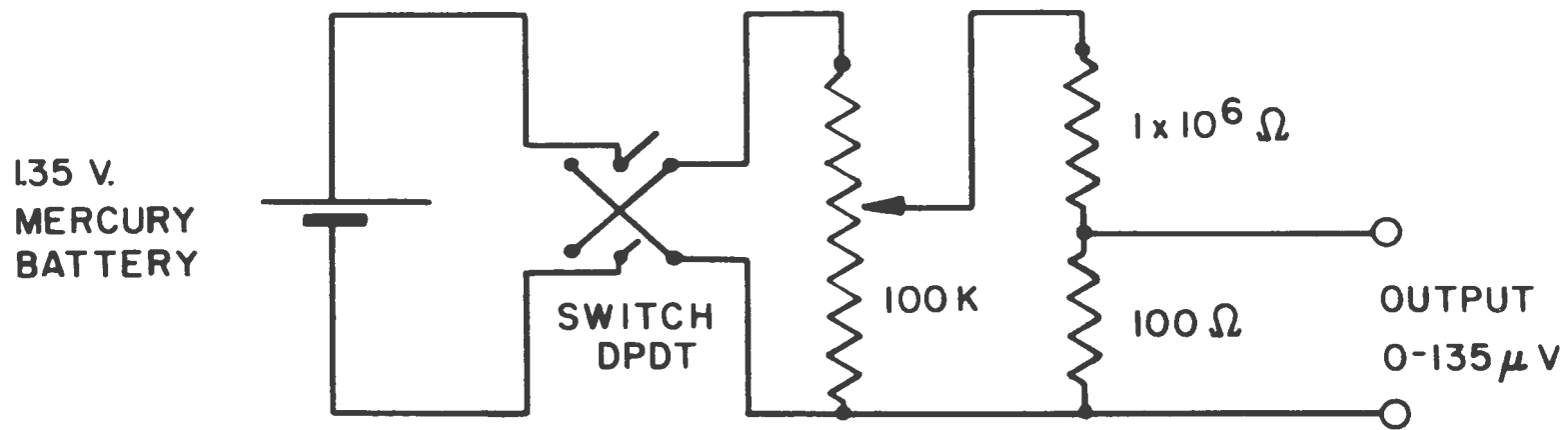


Figure 9. Wiring diagram of the variable microvoltage source

C. Wattage Stabilizer Unit

The power dissipated to the sample must be stable over a long period of time. Since the electrical resistance of the internal heater changes with temperature, a constant wattage source, rather than a constant voltage or current supply, must be used. The wattage stabilizer unit of the Rigaku Denki apparatus is a standard type employing a multiplication circuit.

Heater power for all runs of this investigation was about 1.1 watts. The wattage stabilizer unit maintained this power to ± 0.002 watts over long periods of time and temperature spans of 25 to 900°C.

D. Temperature Measurement and Timer Section

The temperature measurement and timer section automatically measures and records the time required to raise the temperature of the sample a constant, preset increment. A signal is sent to this section via the temperature measuring thermocouple. It is the only section which actually takes a measurement on the sample. The other sections, as previously explained, serve in controlling capacities.

The schematic diagram of the temperature measurement and timer section is shown in Figure 10. The D.C. amplifier is

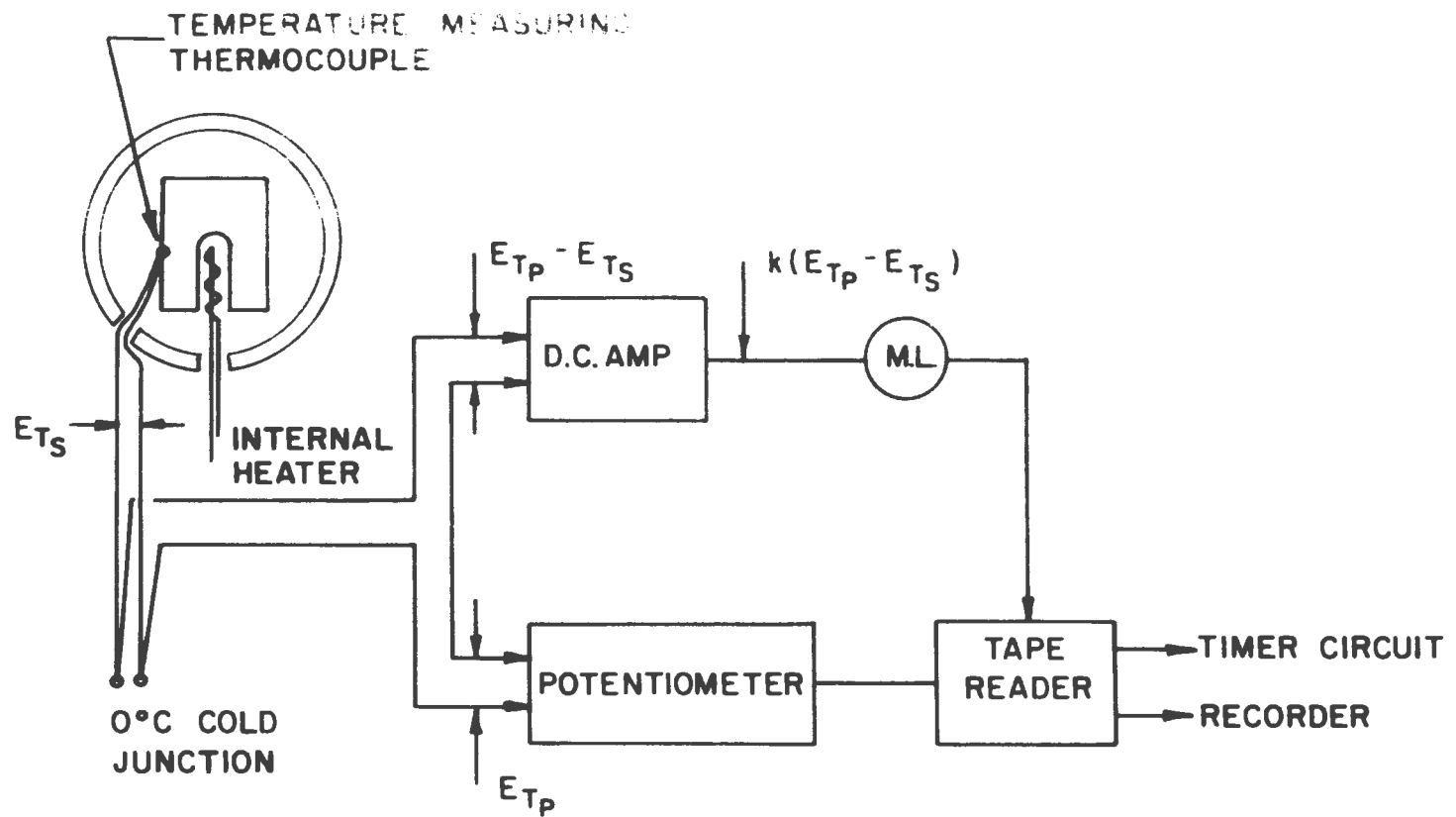


Figure 10. Schematic of temperature measurement and timer section

similar in design to the one used in the adiabatic control section, but it is not the same one. The meter relay (ML) operates when the voltage to it reaches a certain, preset value. The tape reader interprets signals from a perforated tape and sends the information of the potentiometer which generates a potential corresponding to the tape signal.

The operation of the temperature measurement and timer section is cyclic. The meter relay will be used as a starting point in the explanation. Assume that the signal to the meter relay is zero volts, and this is the potential at which the meter relay operates, closing a switch to the timer and to the tape reader motor. The motor operates until one series of perforations of the tape is read, each series corresponding to a temperature, ΔT degrees higher than the previous one. Assume that the tape has just read the temperature T_1 . The potentiometer, commanded by the tape reader, will produce an emf (E_{T_1}) which is equal to the output of a chromel-alumel thermocouple at temperature T_1 , referred to 0°C . The polarity of this emf is opposite the polarity of the temperature measuring thermocouple output, E_{T_S} , and

$$|E_{T_1}| > |E_{T_S}| \quad . \quad (6)$$

However, the magnitude of E_{T_S} is increasing because the sample

is being heated. Finally, the situation is reached such that

$$|E_{T_1}| = |E_{T_S}| \quad (7)$$

and the amplified voltage sent to the meter relay,

$$k(E_{T_1} - E_{T_S}), \quad (8)$$

is zero. The meter relay again closes the switch to the tape reader motor, the elapsed time is recorded, the timer is reset to zero and started, and the whole cycle again proceeds.

Thus, as previously stated, the temperature measurement and timer section records the time required to raise the temperature ΔT degrees. The temperature increment can be varied by using differently punched tapes.

The resulting data are recorded as shown in Figure 11. Time for increment of temperature is the ordinate, and temperature is the abscissa. The abnormally large time interval, Δt_6 , is characteristic of an endothermic phase transformation.

A block diagram showing how all the different sections tie together to function as a unit is shown in Figure 12.

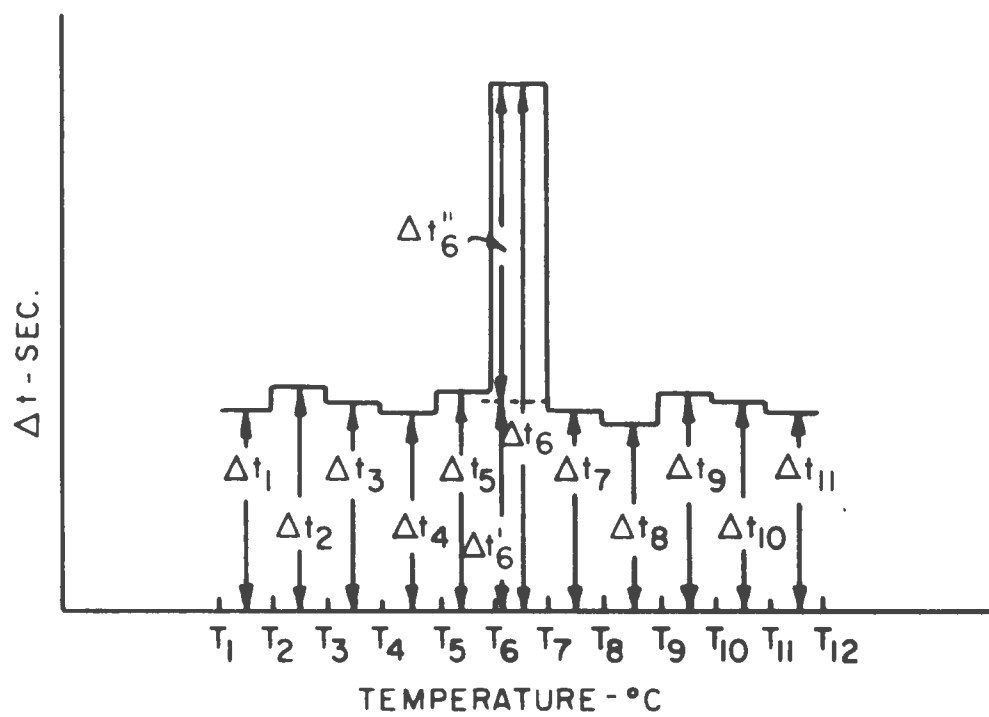


Figure 11. Method of recording data

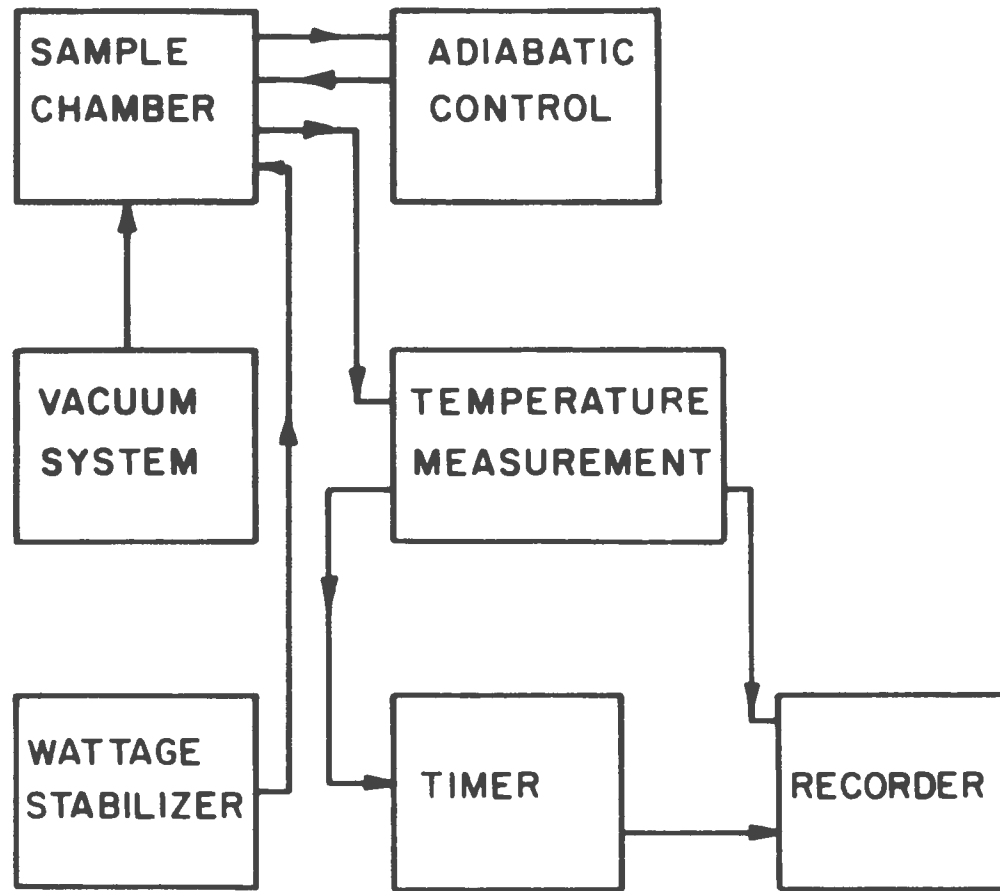


Figure 12. Block diagram showing the coordinate functions of the various components

MATERIALS AND EXPERIMENTAL PROCEDURE

A. Materials

The purities of the elements used were as follows:

Bunker Hill slab zinc, 99.99 pct pure; Ames Laboratory magnesium containing 13 ppm nitrogen, 195 ppm carbon, and trace amounts of silicon, manganese, iron, aluminum, copper, and calcium; United Mineral and Chemical Corp. cerium, 99.6 pct pure, which was arc melted and electron-beam melted to 99.7 pct pure, containing as final impurities 50 ppm calcium, 50 ppm copper, 400 ppm magnesium, 300 ppm iron, 300 ppm silicon, 200 ppm oxygen, 5 ppm nitrogen, and 5 ppm hydrogen; and Ames Laboratory calcium containing 200 ppm carbon, 50 ppm nitrogen, 100 ppm oxygen, 5 ppm iron, and 250 ppm magnesium.

The intermetallic compounds studied in this investigation were $MgZn_2$, $CeZn$, and $CaMg_2$, which were prepared by a direct combination of the elements during Run I of a heat of formation experiment. The amounts of each element were chosen such that the resulting alloy would have the stoichiometry of the compound in question.

The heats of fusion and transformation of thorium tetrachloride were determined. The $ThCl_4$ was prepared at the Ames Laboratory (6,7). At present it is impossible to accurately

analyze thorium tetrachloride for impurities. So, the purity was determined by preparing thorium metal from the ThCl_4 and analyzing the metal for impurities. By this method, the following impurities were accessed to the ThCl_4 : 35 ppm carbon, 1050 ppm oxygen, 40 ppm nitrogen, 50 ppm aluminum, 140 ppm chromium, 50 ppm iron, and 30 ppm nickel (6).

The materials used in this project do not react with tantalum, so no contamination from the sample container was encountered.

B. Experimental Procedure

1. Heat of fusion

The Rigaku Denki unit actually measures the time to heat the sample through a temperature increment of several degrees. In this work, the temperature increment was two degrees. If a transition occurs within the temperature interval (fusion or allotropic transformation), the unit measures the time to raise the sample through the temperature increment plus the time to transform it. The heat of fusion of a substance can be determined directly; the procedure is to heat the substance to its melting point and measure the heat required to melt it. Since the wattage of the internal heater is constant, the aforementioned times are directly related to heat by the

following equation:

$$q = (0.239 \text{ cal/watt-sec})(\Delta t)(W), \quad (9)$$

q = heat in calories

Δt = time required to raise sample temperature
through the increment of temperature

W = heater power in watts.

The quantity q is a direct measure of the enthalpy change, as shown in Equations 10 through 17 below. The extensive variable, enthalpy, is defined as

$$H = E + PV, \quad (10)$$

which on differentiation gives

$$dH = dE + PdV + VdP. \quad (11)$$

The internal energy, E , may be represented as

$$dE = \delta q - \delta w = \delta q - PdV - \delta w', \quad (12)$$

where w is the work done by the system on the surroundings and w' is the work over and above pressure-volume work done by the system. Combining Equations 11 and 12, one obtains

$$dH = \delta q + VdP - \delta w'. \quad (13)$$

If no work is done other than against pressure,

$$dH = \delta q + VdP, \quad (14)$$

and if the pressure is constant, as it is in the system studied,

$$dH = \delta q. \quad (15)$$

Thus, the change in enthalpy is equal to the heat input to the system, or

$$\Delta H = q. \quad (16)$$

Equation 9 can be rewritten as

$$\Delta H = (0.239 \text{ cal/watt-sec})(\Delta t)(W). \quad (17)$$

The heat required to raise the temperature of the sample through an increment, ΔT , is therefore measured directly. If a transformation occurs within this increment of temperature, the measured enthalpy is

$$\Delta H = \Delta H_{\text{trans}} + \int_{T_1}^{T_2} C_p dT, \quad (18)$$

where C_p is the total heat capacity of everything within the adiabatic ball (specimen, crucible, stand, heater, etc.) and $T_2 - T_1 = \Delta T$. The minimum temperature interval employed was two Centigrade degrees. Theoretically, a fusion or transformation is an isothermal process for a pure substance and under the conditions employed should occur within one temperature interval. However, premelting phenomena were observed in some instances and indicated that fusion occurred over several temperature intervals. Even in the case of high purity zinc (99.99 pct pure) the fusion process was spread over a temperature span of two to six degrees. This is probably due to the dynamic conditions of the calorimeter; that is, a finite

heating rate must result in a finite temperature gradient and consequently fusion appears to occur over a temperature span.

In order to calculate the heat of transition, it is necessary to subtract the integral term from the total enthalpy change, ΔH , in Equation 18. The procedure for this step is quite simple. When the sample is not undergoing a transformation, the unit measures only the heat to raise the sample temperature through an increment,

$$\Delta H = \int_{T_1'}^{T_2'} C_p dT, \quad (19)$$

where $T_2' - T_1' = \Delta T$ and again C_p is the heat capacity of everything within the adiabatic ball. Thus one can eliminate the second term of Equation 18 by interpolating the plot of time to go ΔT degrees vs. temperature though the transformation discontinuity, saying that the time above the line is the time required for transformation and the time below the line is the time required to raise the sample, stand, etc. through ΔT degrees, neglecting the transformation. Referring to Figure 10, for example, Δt_6 is the total time required to traverse the sixth temperature interval, $\Delta t_6'$ is the time required to raise the sample, stand, etc. through ΔT degrees neglecting any transformation, and $\Delta t_6''$ is the time required for the

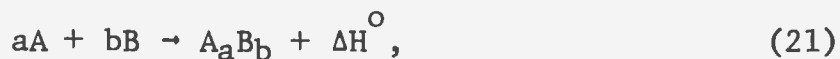
transformation. Thus, the heat of transformation can be calculated from Equation 9 by substituting $\Delta t''$ for Δt :

$$\Delta H_{\text{trans}} = (0.239 \text{ cal/watt-sec})(\Delta t'')(W). \quad (20)$$

As previously mentioned, it is necessary to turn the bucking pot to a zero pot setting at the melting point in order to obtain adiabatic conditions during fusion. Since melting is an isothermal process, it is impossible to directly determine the zero pot setting at the fusion temperature. This is because the temperature of a partially molten sample does not change with the addition or subtraction of a small quantity of heat. However, a zero pot setting can be found by a linear interpolation of two measured zero pot settings--one above, and one below the fusion temperature. The two pot settings are found by the method outlined on page 27 of this work.

2. Heat of reaction

The method of adiabatic calorimetry also affords a straightforward procedure for determining the heat of formation of a compound. In this work, reactions of the following type were investigated:



where A and B are metals. The heat of reaction is found by

continuously measuring the specific heat of the sample, consisting of the pure solid reactants, as it is heated by a constant wattage source to a sufficiently high temperature for the reaction to go to completion. When a reaction occurs, the specific heat shows an apparent decrease because some of the heat required to raise the sample temperature is being supplied by the sample in an exothermic reaction. After the reaction run is completed, another run is made and the heat capacity of the pure compound is measured. This time there is no apparent decrease in the specific heat curve on heating because the reaction is complete. These two specific heat vs. temperature curves are plotted on the same graph and the area under the second curve is subtracted from the area under the first curve. The difference is equal to the heat of reaction, or formation, of the compound, ΔH° . All the reactions investigated in this work were exothermic, but a similar scheme could be followed for endothermic reactions.

A theoretical justification will now be given for the above procedure. The experimental part for the determination of the heat of formation of a solid metal compound requires two runs:

Run I: Solid metal A and solid metal B are heated in a sealed tantalum crucible. The heat

required to raise the sample temperature between two temperatures, T_I and T_F , is measured to be q_1 . T_I is selected high enough to insure smooth operation of the unit, but below any critical temperatures (melting points, etc.). A normal value for T_I would be 300°C , but, of course, this may be different with different samples. T_F is selected such that the sample is entirely molten and the reaction has gone to completion. During Run I the components react to form A_aB_b compound. Since the process is carried out at constant pressure,

$$q_1 = H_{A_aB_b}(T_F) - aH_A(T_I) - bH_B(T_I) = \Delta H_1. \quad (22)$$

Run II: The sample, now consisting entirely of A_aB_b compound, is allowed to cool below T_I and another run is made. The heat required to raise the sample temperature between T_I and T_F is measured to be q_2 . Again, since this is at constant pressure,

$$q_2 = H_{A_aB_b}(T_F) - H_{A_aB_b}(T_I) = \Delta H_2. \quad (23)$$

Using the data from the two runs it is possible to directly determine the heat of formation of the compound.

Subtracting Equation 23 from Equation 22, one gets

$$q_1 - q_2 = \Delta H_1 - \Delta H_2 = H_{A_aB_b}(T_I) - aH_A(T_I) - bH_B(T_I). \quad (24)$$

Thus, by the definition of the enthalpy of formation of a solid, A_aB_b ,

$$q_1 - q_2 = \Delta H_{T_I}^{\circ}. \quad (25)$$

To find the enthalpy of formation at some other temperature, T' , the following relationship (8) must be used:

$$\Delta H_T^O = \Delta H_{T_I}^O + \int_{T_I}^{T_1} \Delta C_p' dT \pm \Delta H_{\text{trans}} + \int_{T_1}^T \Delta C_p'' dT \quad (26)$$

The enthalpy of transition, occurring at temperature T_1 , takes a minus sign if it is for one of the reactants and a positive sign if it is for one of the products.

It was desired to evaluate the standard enthalpy of formation of the compound MgZn_2 at its melting point, 863°C .

Using Equation 26, the following equation is obtained.

$$\begin{aligned} \Delta H_{863}^O = \Delta H_{T_I}^O + \int_{T_I}^{692} \Delta C_{\text{PMgZn}_2}' dT - 2\Delta H_{\text{fus}}(\text{Zn}) \\ + \int_{692}^{863} \Delta C_{\text{PMgZn}_2}'' dT, \end{aligned} \quad (27)$$

where

$$\Delta C_{\text{PMgZn}_2}' = C_{\text{PMgZn}_2}(\text{s}) - C_{\text{PMg}}(\text{s}) - 2C_{\text{PZn}}(\text{s}), \quad (0-692^\circ\text{K}) \quad (28)$$

and

$$\Delta C_{\text{PMgZn}_2}'' = C_{\text{PMgZn}_2}(\text{s}) - C_{\text{PMg}}(\text{s}) - 2C_{\text{PZn}}(\ell). \quad (692-863^\circ\text{K}) \quad (29)$$

EXPERIMENTAL RESULTS

A. Heat of Fusion

The heats of fusion of the following metallic compounds were determined in this investigation: CeZn, CaMg₂, MgZn₂, and ThCl₄. The experimental procedure is outlined in Chapter III of this thesis.

The results of the experiments performed in this work were subjected to a statistical analysis to determine the random error. To do this, the standard deviation and standard error were evaluated. These two parameters give a measure of the precision and reproducibility of the measurements. There is no way to mathematically test for a systematic error, so minimizing it is accomplished by taking care in the experimental procedure. The measurement of the heat of formation of a compound depends on the subtraction of two quantities of heat, lessening the effect of a systematic error.

The estimate of the standard deviation is s_x and it is calculated from the formula,

$$s_x = \left(\sum_{i=1}^n \frac{(\bar{x} - x_i)^2}{n-1} \right)^{\frac{1}{2}} \quad (30)$$

where x_i , $i = 1$ to n , are the individual measurements, \bar{x} is the arithmetic mean of the measurements, and n is the number

of measurements (9). The standard deviation of the mean, often referred to as the "standard error," is inversely proportional to the square root of the number of observations. It is calculated by the equation,

$$s_{\bar{x}} = \frac{s_x}{\sqrt{n}} . \quad (31)$$

Table 2 presents the results of the heat of transformation and heat of fusion experiments.

Table 2. Heats of fusion and heat of transformation of compounds in cal/mole

	$\frac{\text{MgZn}_2}{\Delta H_{\text{fus}}}$ @ 590°C	$\frac{\text{CeZn}}{\Delta H_{\text{fus}}}$ @ 825°C	$\frac{\text{CaMg}_2}{\Delta H_{\text{fus}}}$ @ 714°C	$\frac{\text{ThCl}_4}{\Delta H_{\text{fus}}}$ @ 769°C	$\frac{\text{ThCl}_4}{\Delta H_{\text{trans}}}$ @ 406°C
	9,693	6,875	11,624	14,302	1,386
	9,717	6,818	11,542	14,952	1,057
	9,653		11,623	14,569	1,153
	9,686		11,982	14,938	
			11,854		
			11,839		
Ave: ^a	9,687	6,846	11,744	14,690	1,198
s_x^b	26	---	172	314	---
$s_{\bar{x}}^c$	15	---	77	181	---

^aAverage value.

^bStandard deviation.

^cStandard error.

B. Heat of Formation

The heats of formation of the following intermetallic compounds were determined in this investigation: CaMg_2 , MgZn_2 , and CeZn . The method used is explained in Chapter III of this thesis with one further refinement. By closely examining the C_p vs. T graphs of the MgZn_2 runs, it was noticed that the reaction was not complete after the first run (Run I) and that there was some reaction in subsequent runs. The heat liberated by reaction in these runs was also accounted for. If reaction is completed during the n^{th} run, then

$$\Delta H_{T_I}^{\circ} = (\Delta H_1 - \Delta H_n) + (\Delta H_2 - \Delta H_n) + \dots + (\Delta H_{n-1} - \Delta H_n) \quad (32)$$

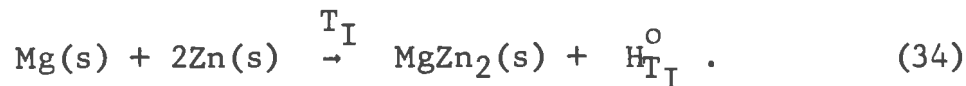
where ΔH_i , $i = 1$ to n , are the enthalpy changes for the various runs between the temperatures T_I and T_F . Equation 32 can be simplified by using summation notation,

$$\Delta H_T = \sum_{i=1}^{n-1} \Delta H_i - (n - 1)\Delta H_n . \quad (33)$$

The reaction was usually complete after two runs; therefore, a normal value for n in Equations 32 and 33 was three. Also, using the data for sample MgZn_2 III, it was observed that about 80 pct of the reaction occurred during the first heating and about 20 pct during the second heating.

The enthalpy of formation of MgZn_2 was determined two

times. The compound is formed according to the chemical reaction:



It was observed that this reaction proceeded when zinc melted (at 692°K). The melting point of the compound is 863°K.

Therefore, the temperatures T_I and T_F were chosen to be 623°K and 923°K, respectively. This temperature range includes all critical temperatures of the Mg-Zn system (10).

It was desired to refer the heat of formation of MgZn_2 to the standard states of the components at the melting point of the compound, 863°K. To do this, Equation 27 must be used:

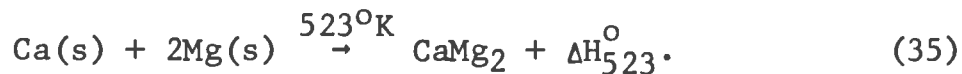
$$\begin{aligned} \Delta H_{863}^{\circ} = \Delta H_{623} + \int_{623}^{692} \Delta C_{P\text{MgZn}_2} dT - 2\Delta H_{\text{fus}}(\text{Zn}) \\ + \int_{692}^{863} \Delta C_{P\text{MgZn}_2} dT . \end{aligned} \quad (27)$$

An average value of -0.375 cal/deg/g-atom for $\Delta C_{P\text{MgZn}_2}$ was evaluated from the data presented by Hultgren (11); and the heat of fusion of zinc is 1678 cal/mole as presented by Chiotti, Stevens, and Gartner (12). Using these quantities and the experimentally determined values for the heats of formation of MgZn_2 at 623°K, the value of ΔH_{863}° can be calculated. Table 3 shows the results of three determinations.

Table 3. Standard enthalpy of formation in kcal/g-atom

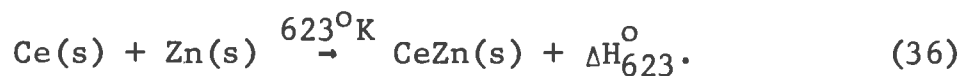
MgZn ₂		CeZn	CaMg ₂
623°K	863°K	623°K	523°K
-3.12	-4.32	-10.6	-3.12
-3.07	-4.27		

The compound MgZn₂ is formed according to the reaction presented as Equation 34. The reaction was complete after three heatings. Only two runs were necessary for the formation of CaMg₂ to go to completion. This compound is formed as



For CeZn, four runs were necessary for the reaction to finish. As the other compounds, CeZn was formed from the elements.

The reaction for this is



DISCUSSION

A. Heat of Fusion

The "hole theory" of liquid structure states that the molten state is similar to the solid state except that in the liquid some of the lattice sites are empty and the lattice is distorted (8). The empty sites are called "holes" or "vacancies" and they reduce the coordination number of the structure. As a rough approximation, the liquid of a close-packed solid would have a coordination number of 11 whereas the solid has a coordination number of 12. The hole theory accounts for the heat of fusion. To melt a metal, it is necessary to break one of every eleven nearest neighbor bonds. Evaporation requires that all eleven nearest neighbor bonds be broken. Thus, the expected ratio of the entropy of evaporation to the entropy of fusion should be 11:1 which is quite close to that predicted by a comparison of Trouton's rule (the entropy of evaporation = 23 cal/deg) with Richard's rule (the entropy of fusion = 2 cal/deg).

Various methods for estimating thermodynamic properties of substances have been presented by Kubaschewski and Evans (13). The heat of fusion of a metal can be estimated by estimating the entropy of fusion and knowing the melting

temperature, since for an isothermal and isobaric process,

$$\Delta S = \Delta H/T. \quad (37)$$

It is known from statistical thermodynamics that the entropy change in Equation 37 is made up of a change in the configurational entropy and a change in the vibrational entropy (14),

$$\Delta S = \Delta S_v + \Delta S_c. \quad (38)$$

If an alloy is completely ordered, the configurational entropy change on fusion is given by (13),

$$\Delta S_c = -R(N_1 \ln N_1 + N_2 \ln N_2) \quad (39)$$

where N_1 and N_2 are the atomic fractions of the two components and R is the gas constant.

The state of order for the alloy phases may not always be known, but as an approximation, phases with narrow concentration ranges are considered to be ordered. Since phase diagram studies indicate that there is very little solid solubility in the alloy compounds investigated (10,15), it will be assumed that these compounds are completely ordered.

Thus, the equation used to estimate the entropy of fusion per g-atom for a compound A_aB_b , where A and B are metals, is

$$\Delta S_{fus}(A_aB_b) = \frac{1}{a+b} \left[\frac{a\Delta H_{fus}(A)}{T_{fus}(A)} + \frac{b\Delta H_{fus}(B)}{T_{fus}(B)} \right] - R(N_A \ln N_A + N_B \ln N_B). \quad (40)$$

The heat of fusion can then be estimated by rearranging Equation 41 to read

$$\begin{aligned}\Delta H_{\text{fus}} &= T_{\text{fus}} \Delta S_{\text{fus}} \quad (\text{cal/g-atom}) \\ &= (a + b) T_{\text{fus}} \Delta S_{\text{fus}} \quad (\text{cal/mole}).\end{aligned}\tag{41}$$

It is more difficult to predict the entropy of fusion of an inorganic compound such as ThCl_4 . A value of 3.0 cal/deg/g-atom was used, as suggested by Kubaschewski and Evans (13), for the entropy of fusion of thorium tetrachloride.

The results of the estimated heats of fusion and a comparison with the experimentally determined values are given in Table 4.

Table 4. Estimated and experimental values for the heats of fusion of MgZn_2 , CaMg_2 , CeZn , and ThCl_4

Compound	ΔT_{fus}	ΔS_{fus}	ΔH_{fus}	ΔH_{fus}	Deviation	
	$^{\circ}\text{K}$	(est) cal/deg/ g-atom	(est) cal/mole	(expt) cal/mole	cal	%
MgZn_2	863	3.74	9,682	9,687	5	+0.1
CaMg_2	987	3.43	10,156	11,744	+1588	+15.6
CeZn	1098	3.26	7,158	6,684	-294	-4.2
ThCl_4	1043	3.0	15,645	14,690	-955	-6.1

As can be seen, the estimated values lie very close to the experimental values except for CaMg_2 .

Very little information can be found in the literature on the heats of fusion of the compounds investigated. The only one found was the value of 10,200 cal/mole for the heat of fusion of MgZn_2 at its melting temperature (13). The value determined in this work is 9,687 cal/mole.

B. Heat of Formation

A difficulty arises during Run I for each heat of reaction experiment. Generally speaking, the reaction will not start until one of the pure reactants begins to melt, since diffusion in the solid state is negligibly slow. The initiation of reaction is accompanied by a sudden temperature rise of the sample for an exothermic reaction. Thus, for a time, the sample is hotter than the adiabatic ball because the adiabatic control section cannot respond fast enough and there is a net heat leak out from the sample. This causes the measured quantity, q_1 , to be larger than it actually should be, resulting in a less negative ΔH^0 .

An experiment was performed to determine how much heat was lost during reaction. The output of the differential thermocouple was monitored over a period of time for Run I of sample MgZn_2 IV. Figure 13 shows a plot of $(T_{\text{sample}} - T_{\text{ball}})$

vs. time. The time is taken to be zero at the beginning of the reaction, the melting point of zinc (419°C , 692°K). Only radiative heat transfer will be considered because the run was made under vacuum. The rate of heat transfer between the sample and adiabatic ball, at temperatures T_1 and T_2 respectively, due to radiation is given by the following equation (16):

$$\frac{dq}{dt} = \sigma \epsilon_1 A_1 (T_1^4 - T_2^4) \quad (42)$$

σ = Stefan-Boltzman const. = 1.36×10^{-12} cal/cm²/sec/deg⁴

ϵ_1 = emissivity of hotter body (crucible) = 0.49 (max)

A_1 = area of hotter body = 36.5 cm²

T_1 = temperature of hotter body

T_2 = temperature of colder body.

Equation 42 does not exactly describe the rate of heat flow because: complicating geometric factors are not considered, the emissivity is taken as its maximum value for tantalum, and the effect of the platinum radiation shield is not taken into account. Therefore, the above equation describes a maximum value for the rate of heat loss, the actual value being somewhat less. Thus, it is possible to assess an upper limit to the error caused by the sudden liberation of heat at

the commencement of reaction.

A plot of sample temperature minus adiabatic ball temperature is shown in Figure 13. The reaction began at time, $t = 0$. By knowing the temperature of the sample, T_1 , as a function of time, it was possible to determine the temperature of the ball as a function of time also. The values of the rate of heat loss at different times were evaluated and plotted in Figure 14. Mathematically,

$$\int_{t=0}^{t=t_1} \frac{dq}{dt} dt = q . \quad (43)$$

This integration was performed graphically by measuring the area under the curve of Figure 14 with a planimeter. A value of 153 calories was found for the maximum heat lost due to radiation. The platinum radiation shield which surrounds the sample decreases this heat loss approximately by a factor of two, as shown in the appendix of this thesis. Also, under the non-steady state conditions prevailing in the apparatus, the net heat loss should be further diminished. So, the maximum amount of heat lost during a reaction, less than 75 calories, is negligibly small when compared with ΔH^0 .

The estimation of the heat of formation or reaction is very difficult. Several methods are given by Kubaschewski

Fig. 13.

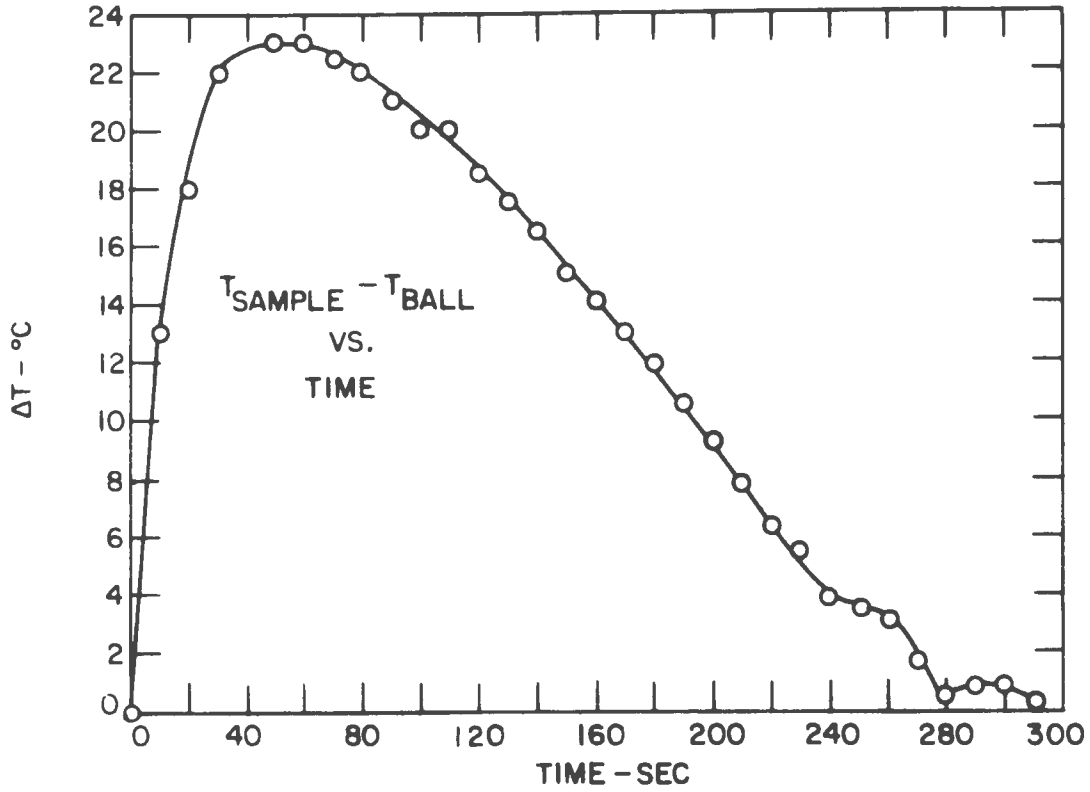
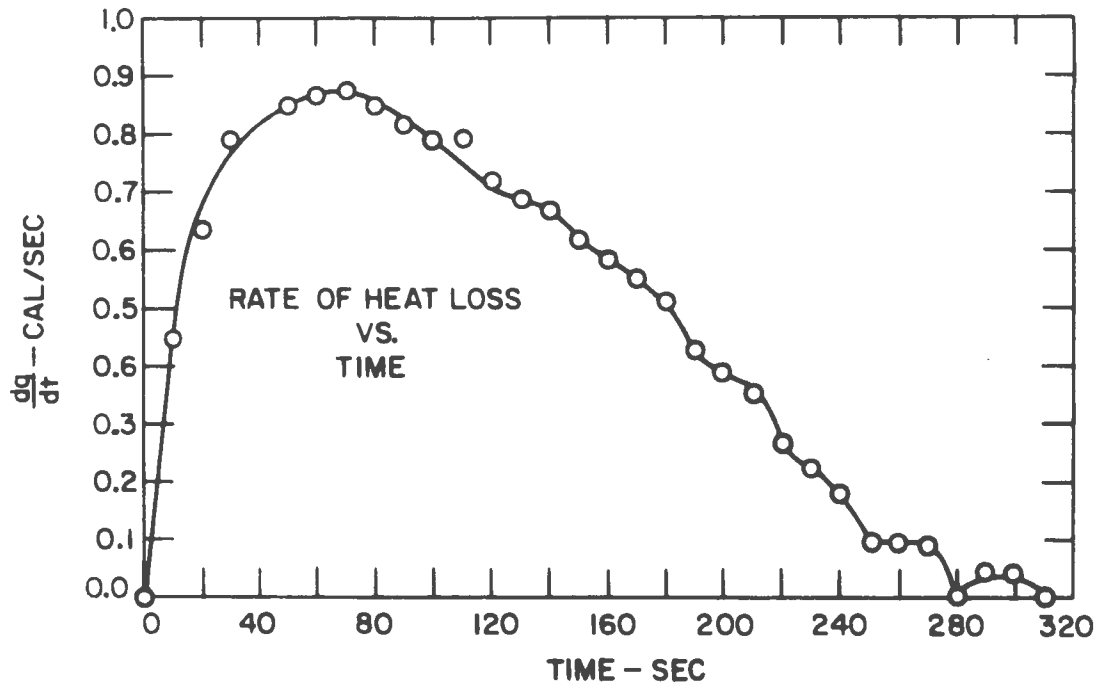
Fig. 13. Difference in temperature of the sample and adiabatic ball as a function of time during the formation of MgZn_2 from the elements.

Fig. 14.

Fig. 14. Rate of heat loss as a function of time calculated from the Stefan-Boltzman law during the formation of MgZn_2 from the elements.

and Evans (13), but their application to the compounds studied in this work seems to be very limited. For this reason, no attempt was made to estimate the heats of formation of MgZn_2 , CaMg_2 , and CeZn . There are, however, values for the heats of formation of these alloys presented in the literature. Table 5 gives this information.

Table 5. Comparison of the results of this work with the literature values for the heats of formation of MgZn_2 , CaMg_2 , and CeZn

Compound	Reference	ΔH_T° kcal/g-atom	T $^{\circ}\text{K}$
MgZn_2	13	-4.2	298
	17	-5.18	863
	17	-4.46	623
	12	-4.42	863
	12	-4.32	623
	this work	-4.30	863
	this work	-3.10	623
CaMg_2	18	-3.87	523
	19	-3.14	298
	20	-2.3	298
	this work	-3.12	523
CeZn	16	-9.8	773
	this work	-10.6	623

SUMMARY

One of the primary purposes of this investigation was to adapt the Rigaku Denki adiabatic calorimeter to the determination of the heats of transformation and reaction of metals, alloys, and metallic compounds. The author believes that this purpose has been fulfilled. The unit is both fast and accurate. Up to three determinations can be made per day on the heat of fusion of a material, and the results of this work compare favorably with estimated quantities and experimentally determined values reported by other investigators. The operative range of the unit is about 100-900°C.

Construction of a functional high-temperature adiabatic calorimeter is quite difficult. At temperatures above 500°C the effect of sporadic, stray currents becomes such that control of the system is seriously hampered. This problem is particularly frustrating since the heat leak rate caused by a temperature difference of the sample and its surroundings is a function of the fourth power of the absolute temperature.

Much of the work in this investigation was directed toward the improvement of the calorimeter. The sporadic currents were excluded from the system by proper grounding and electrical arranging of the sample chamber components. Even

though control appeared to be good after the stray currents were eliminated, it was noted that the calorimeter was still not adiabatic. There was detected a net heat flow from the surroundings to the sample. This problem was finally solved by the insertion of a small, variable emf source into the differential thermocouple circuit, making it possible to control the net rate of heat exchange between the sample and its surroundings, and actually to make it zero or negligibly small.

The Rigaku Denki apparatus, as modified in this work, is quite well suited to the measurement of enthalpies of fusion and transformation. It is possible to adjust the variable emf source (bucking pot) such that there is negligible heat transfer between the sample and surroundings, and thus directly measure the heat required to transform a substance.

Measurements were made on the heats of fusion of MgZn_2 , CaMg_2 , CeZn , and ThCl_4 . The respective heats of fusion were: 9,687 cal/mole, 7,826 cal/mole, 6,684 cal/mole and 14,690 cal/mole. In all these determinations, the scatter of the measurements was less than ± 3 pct. Previous work on the heats of fusion of pure elements by the author and E. R. Stevens indicated that the results were not biased in a specific direction when compared with other experimentally

determined values. Therefore, it is assumed that the major part of the error is caused by random deviations. For this reason, the average values of the heats of fusion should be accurate to ± 2 pct.

The heat of transformation of ThCl_4 at 406°C was measured and found to be 1,198 cal/mole.

The heats of formation of MgZn_2 , CaMg_2 , and CeZn were determined. The values obtained were, respectively: -4.30 kcal/g-atom at 863°K , -3.12 kcal/g-atom at 523°K , and -10.6 kcal/g-atom at 623°K . Literature values for these compounds are, respectively: -4.42 kcal/g-atom at 863°K , -3.87 kcal/g-atom at 523°K , and -9.8 kcal/g-atom at 773°K . The values obtained in this work are generally lower than the experimental values of other investigators, but in fairly good agreement. The method of adiabatic calorimetry directly measures the heat of formation of a compound whereas the results presented by other investigators were obtained by indirect means. The bucking pot was not used during the heat of formation experiments because it was not possible to accurately know the zero-pot-setting vs. temperature curve for each sample setup. Since without a bucking pot there was observed a net heat leak into the sample from its surroundings and the time to

transverse the temperature span of T_I to T_F is greater in Run II, the measured heats of formation should be less negative than the actual values. Thus, the magnitudes of the measured values are probably 0-10 pct less than the true values.

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APPENDIX

The sample becomes hotter than the adiabatic ball during an exothermic reaction. This results in heat being radiated from the sample until the adiabatic control section can adjust the ball temperature to be the same as the sample temperature. In Chapter III it was shown that the maximum amount of heat lost was about 150 calories for the reaction run of sample MgZn₂ IV. It is desired to approximate the effect of the radiation shield in order to see if such a heat loss drastically affects the experimental results.

A modified version of the Stefan-Boltzman law of radiative heat transfer (16), as previously mentioned in Chapter V, is

$$\dot{q} = \sigma A_H \epsilon_H (T_H^4 - T_C^4) \quad (1A)$$

where the subscript "H" refers to the hotter body, or emitter, and the subscript "C" refers to the colder body.

Assume that the sample is hotter than the adiabatic ball and that at steady state conditions it emits a quantity of heat per unit time of Δq_S . This heat flows through the platinum radiation shield, and thus the heat radiated by the shield to the adiabatic ball per unit time, Δq_R , is equal to Δq_S . The thermal emission rates of the shield and sample are also

the same,

$$\dot{q}_S = \dot{q}_R \quad (2A)$$

From Equation 1A it follows that

$$\sigma A_S \epsilon_S (T_S^4 - T_R^4) = \sigma A_R \epsilon_R (T_R^4 - T_B^4) \quad (3A)$$

where the subscript "B" refers to the adiabatic ball, "R" to the platinum radiation shield, and "S" to the sample. The values of the constants in Equation 3A are as follows:

$$A_S = 36.5 \text{ cm}^2$$

$$A_R = 66.0 \text{ cm}^2$$

$$\epsilon_S = 0.49$$

$$\epsilon_R = 0.30$$

$$A_S \epsilon_S = 18.3$$

$$A_R \epsilon_R = 19.8 .$$

Thus, for the purposes of obtaining an approximation, it can be stated quite clearly that

$$\sigma A_S \epsilon_S = \sigma A_R \epsilon_R . \quad (4A)$$

This simplifies Equation 3A to

$$T_S^4 - T_R^4 = T_R^4 - T_B^4 \quad (5A)$$

or, by transposing some terms,

$$T_R^4 = \frac{1}{2} T_S^4 + \frac{1}{2} T_B^4 \quad (6A)$$

If no radiation shield were used, the rate of heat transfer between the sample and adiabatic ball due to radiation would be, by Equation 1A,

$$\dot{q}_{NR} = \sigma \epsilon_S A_S (T_S^4 - T_B^4) \quad (7A)$$

where the subscript "NR" indicates no radiation shield present.

But, with the radiation shield in place, the heat transfer rate is

$$q_R = \sigma \epsilon_S A_S (T_S^4 - T_R^4) \quad (8A)$$

Substituting Equation 6A into Equation 8A, one obtains

$$\dot{q}_R = \sigma \epsilon_S A_S (\frac{1}{2}T_S^4 - \frac{1}{2}T_B^4) = \frac{1}{2}\sigma \epsilon_S A_S (T_S^4 - T_S^4) = \frac{1}{2}\dot{q}_{NR} \quad (9A)$$

So it has been mathematically shown that the platinum radiation shield diminishes the radiative heat transfer between the sample and adiabatic ball approximately by a factor of two for the steady state condition. Experimentally, a non-steady state condition prevails. This would tend to reduce further the heat lost due to radiation since the heat capacity of the platinum radiation shield causes its temperature to lag that of the sample. Applying these results to the reaction run of $MgZn_2$ indicates that a negligible amount of heat, somewhat less than 75 calories, was lost by the sample to its surroundings.