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John O. Barner
(M. S. Thesis)

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ABSTRACT

A differential calorimeter suitable for measurement of high temperature heats of solid state transformations was designed and tested. The heats of transformation of SiO_2, K_2SO_4, Na_2SO_4-III, and FeS were measured and were found to be in general agreement with published values. Increase in heat content measurements were found to be 30 - 40% high due to unequal vertical heat losses from the two sample cells of the differential calorimeter. Recommendations for further studies are made.

I. INTRODUCTION

In recent years an acute lack of thermodynamic data for ceramic materials has become evident. The type of thermodynamic data desired include: 1) heat content and heat capacity data, 2) heats of crystallographic transformations, 3) heats of reaction, and 4) heats of melting.

The basic equation all heat content calorimeters utilize is:

$$H_T = H_o + \int_o^T c_p dT \tag{1}$$

where

H_T = heat content at temp. T

H_o = the internal energy at 0°K

$\int_o^T c_p dT$ = increase in heat content due to the heat capacity.

Because the heat content data above 298°K are usually of the most value, Eq. (1) is generally modified to:

$$H_T = H_{298} + \int_{298}^T c_p dT \tag{2}$$

where

$$H_{298} = H_o + \int_o^{298} c_p dT$$

Therefore,

$$H_T - H_{298} = \int_{298}^T c_p dT \tag{3}$$

But empirically,

$$c_p = a + 2bT - cT^{-2} \tag{4}$$

Therefore, Eq. (3) takes the empirical form:

$$H_T - H_{298} = aT + bT^2 + cT^{-1} + d. \tag{5}$$

The simplest and most common method for measurement of increase in heat content,[1,2] $H_T - H_{298}$, is the method of mixtures (dropping method). This method employs a furnace to heat a specimen to a known temperature and a heat sink of a mixture of a solid and liquid of the same composition. The sink is commonly a mixture of liquid water and ice. The dropped sample is allowed to come to equilibrium with the sink contents. As heat is liberated by the sample, part of the ice is melted. A corresponding change in volume accompanies the melting of the ice. The total amount of heat liberated can then be found by correlating the measured change in volume with the heat of melting of ice. To determine the heat content over a range of temperatures requires many individual runs.

Drop calorimeters are also used for the measurement of heats of crystallographic transformation.[1,2] In order to evaluate the heat of transformation, it is necessary to subtract two large heat content terms to yield a small heat of transformation. This subtraction is inherently inaccurate. For example, $H_{848} - H_{298}$ for α quartz is 8170 cal/mole; $H_{848} - H_{298}$ of the inverted quartz is 8460 cal/mole. The heat of transformation is, therefore, $H_\beta - H_\alpha = 290$ cal/mole. A one-percent inaccuracy in the measurement of either H_α or H_β would be approximately ± 80 to 85 cal. This small error would result in approximately a ±28% error in the reported value of the heat of transformation.

Several types of calorimeters have been devised for the measurements of heats of reaction.[1] These methods include the bomb calorimeter, the solution calorimeter, and direct adiabatic or isothermal calorimeters. The bomb calorimeter employs the heat capacity and temperature rise of

the sink material plus a known heat leakage rate to evaluate the heat of a reaction. The solution calorimeter evaluates the heats of solution of the products and the reactants of a reaction by dissolving each separately in an acid or liquid metal. The sum of the heats of solution of the reactants is subtracted from that of the products to yield the heat of reaction. A problem associated with solution calorimeters is that of obtaining high solution rates. In general, ceramics are quite resistant to acid solution.

The direct methods involve measuring the heat of reaction at the reaction temperature under adiabatic or isothermal conditions.[1]

Heats of melting are generally[1, 2] measured by drop calorimetry methods. The same problems which apply for measurements of heats of crystallographic transformation are present when heats of melting are being determined.

Attempts to apply the qualitative method used by ceramists for mineral identification, differential thermal analysis, to the measurements of heats of crystallographic transformation, heats of reaction, and heats of melting have been made by several investigators.[3, 4] In general, the validity of the results is questionable due to inherent variable characteristics of the method. These characteristics include selection of the proper area under the DTA curve to evaluate the reaction heat, calibrating of the apparatus, and variable properties of the materials selected for the standard and unknown samples.

Because the described calorimetry methods are generally time consuming and in some cases inaccurate, a quick and accurate method of obtaining heat contents, heats of crystallographic transformation, and possibly heats of reaction and heats of melting is desirable.

II. DIFFERENTIAL CALORIMETRIC METHODS

A. Differential Thermal Analysis

Differential thermal analysis is a qualitative experimental technique used primarily for identification of solid materials.[3, 4] The apparatus usually consists of a metal sample holder with two identical sample holes. A controlled furnace is used for heating the samples. A method for determining the differential temperature between the center of the standard sample (usually α-Al_2O_3) and the center of the unknown sample is employed. The differential temperature is plotted as a function of the temperature of the sample. The resulting curve has a characteristic shape for different materials and can, therefore, be used for qualitative analysis.

The heat of formation of the spinel Al_2FeO_4 from its component oxides was measured by Fischer and Lorenz[5] by a modified DTA method. A nickel cylinder was bored out and fitted with Al_2O_3 sleeves. One tube was packed with Al_2O_3, the other with an FeO - Al_2O_3 powdered mixture. Twenty Pt/Pt - 10% Rh thermocouples, connected in series, were wound on the two sleeves such that the odd junctions were in contact with one tube and the even junctions in contact with the other tube. The block was heated with a platinum-wound furnace. Heat effects sensed by the thermocouples were measured by a galvanometer. Heat effects of 70 to 200 cal extending over several hours were measured with an accuracy of ±15%.

Attempts to convert qualitative DTA to quantitative DTA have been made by several investigators.[3, 4] Attempts to correlate various areas under the peak produced in the differential temperature vs temperature plot have been made. No agreement as to where the base line should be constructed has been made. Calibration of the DTA apparatus is difficult

because of the inherent variables in the materials and techniques employed. These variables include: 1) bulk sample size and shape, 2) variable and unreproducible heating rates, and 3) differences in thermal diffusivities of the samples. Such thermal diffusivity differences can be caused by differences in the thermal conductivity, packed density, or heat capacity. These in turn are a function of the material, particle size, particle shape, particle distribution, and the entrapped gases.

In order to obtain a standard method for determining quantitative heats of crystallographic transformation, heats of reaction and heat of melting, accurate control or evaluation of all these variables would have to be made. Control or evaluation of all variables would be exceedingly difficult if not impossible.

B. Differential Calorimetry

Boas[6] and co-workers measured the energy stored in deformed copper rods by a differential method. Their apparatus consisted of two hollow cylindrical samples, one cold-worked, the other annealed. The samples were fitted with individual internally mounted heaters. The heaters supplied the heat necessary to keep the samples at the same temperature and also above the environmental temperature. The environment was heated by a controlled furnace. The differential power necessary to keep the differential temperature at zero was plotted as a function of time. Integration of the resulting curve yielded the heat necessary to maintain the temperature of the undeformed sample at the temperature of the deformed sample. The stored energy in the deformed sample is liberated by recovery and recrystallization. The experiments were made in vacuo.

The apparatus was capable of measuring, with an accuracy of 15%, a difference of 0.1 cal/g. The accuracy of the total heat measured was within ±1/2%.

The calorimeter to be described is based on the Boas calorimeter with suitable modifications to convert the design from a thermal conducting metal sample to an insulating ceramic sample.

III. DIFFERENTIAL CALORIMETER DESIGN CONSIDERATIONS FOR CERAMIC MATERIALS

The primary problem to be considered when converting Boas and co-workers differential calorimeter is the difference in thermal diffusivities of metals and ceramics. Metals in general have high thermal conductivities. Ceramic materials have low thermal conductivities. Metallic materials contain little or no porosity. Ceramic powders have variable packed densities which are generally considerably less than theoretical densities. Therefore, metals have high thermal diffusivities and ceramics low thermal diffusivities. This difference gives rise to a large thermal gradient across ceramic samples when they are heated. Conversely, the temperature gradient across like metal samples is considerably smaller.

When modifying the Boas calorimeter, sample cells to contain the powdered ceramic material are needed. The temperature of the portion of the cells which can be influenced by the environmental temperature (the outer surfaces) is the temperature which has to be controlled. The heat supplied by the heat source to control the temperature of the sample should flow through the sample so that the temperature-sensing device on the outer surface will be sensitive to rate of heat absorbed by the material. Therefore, a large temperature gradient together with slow

heat transfer is present in a ceramic sample. These two facts give rise to poor control of the outer surface temperatures. Because the poor control must be minimized, the geometry of the sample should be narrow in the direction of primary heat flow. If possible, it is desirable to have the ceramic sample at least partially heated from all sides so that the gradient will be further reduced.

IV. EXPERIMENTAL PROCEDURE

A. Design of the Differential Calorimeter

Because it was desirable to partially heat the sample from all sides and keep the sample dimensions narrow in the direction of primary heat flow, metallic concentric tubes with base plates were selected for the sample cells (Plate C and Fig. 4, Appendix A). The cells were mounted vertically on a central tube to minimize radiation transfer between them. The upper cell contained the unknown sample. The lower cell was empty so that the increase in heat content could be measured directly. Individual heaters were wound on the tube. Differential and monitoring thermocouples were mounted in buckets on the outer surface of the cells. A controlled furnace to heat the environment was provided. The cell temperature was always higher than that of the environment to prevent immeasurable heating from the environment. The apparatus was kept as symmetrical as possible to prevent unequal heat losses. Controlled atmosphere and vacuum facilities were provided.

The differential power necessary to maintain the cells at the same temperature was recorded as a function of time. Subsequent integration of this curve yielded the heat under consideration as the temperature was increased.

Plates A, B, and C show various views of the apparatus. A more detailed description of the apparatus can be found in Appendix A.

B. Sample Materials

The sample materials were -100-mesh powders. The materials investigated were SiO_2, K_2SO_4, Na_2SO_4 form III, and FeS. The SiO_2 was a commercial grade quartz powder. DTA investigations of the material revealed no extraneous reactions. X-ray analysis also showed only α quartz (Appendix B).

The K_2SO_4 was a sample obtained from K.K. Kelley of the U.S. Bureau of Mines. X-ray examination confirmed the sample to be the orthorhombic form with lattice parameters (a_o = 5.772Å, b_o = 0.722Å, c_o = 7.483Å) form of K_2SO_4 (Appendix B).

The Na_2SO_4-III was also obtained from K.K. Kelley. X-ray examination showed only the metastable form III Na_2SO_4 to be present (Appendix B).

X-ray examination of the technical grade FeS showed no extraneous lines (Appendix B).

The K_2SO_4 and Na_2SO_4-III were diluted with calcined α-Al_2O_3 so that the heats of transition involved would be of a controllable amount. The FeS and SiO_2 were undiluted.

For each material about 15 g to 20 g of sample were weighed and packed into the upper cell of the calorimeter.

C. Experimental Method

At the start of an experiment the chosen sample material of known weight was packed into the upper sample cell. The cell was placed in the

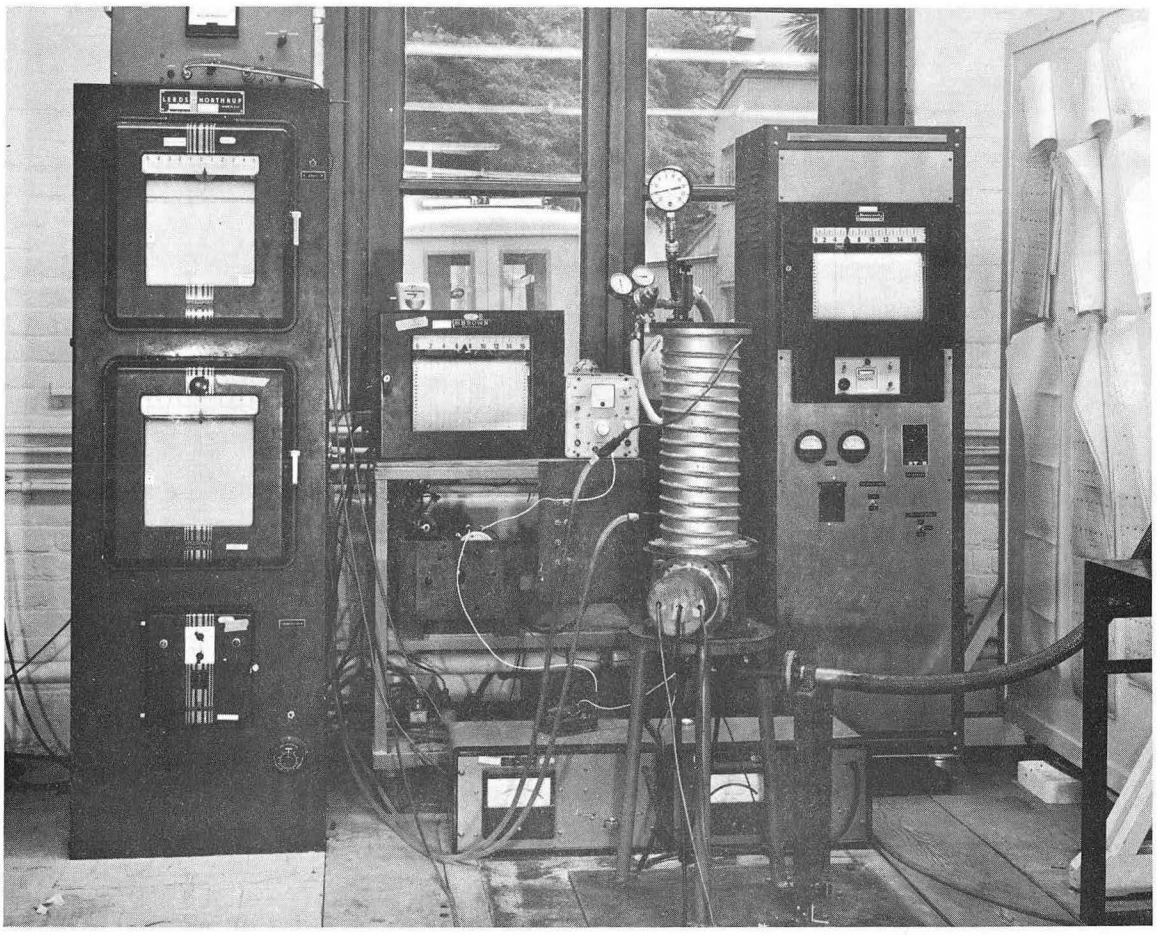

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PLATE A

OVERALL VIEW OF THE APPARATUS

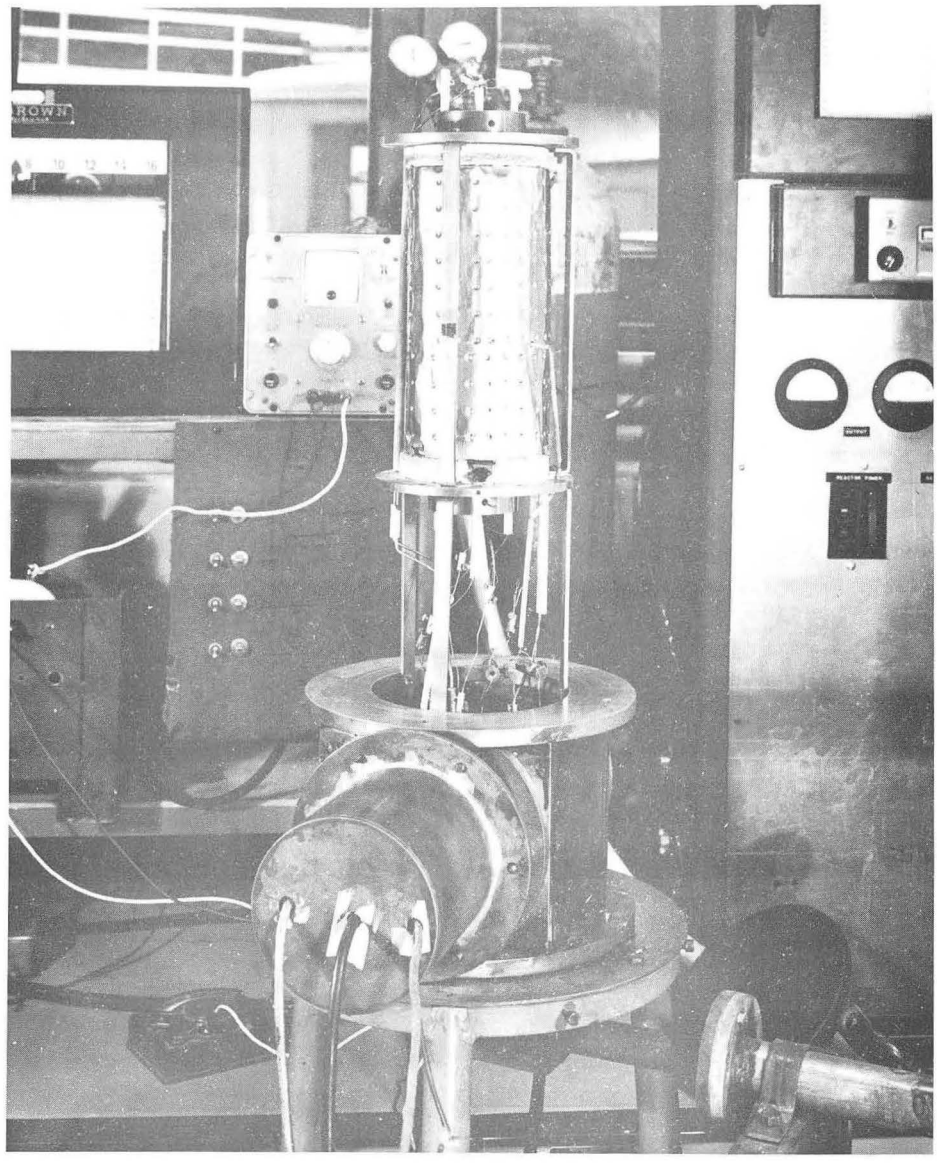

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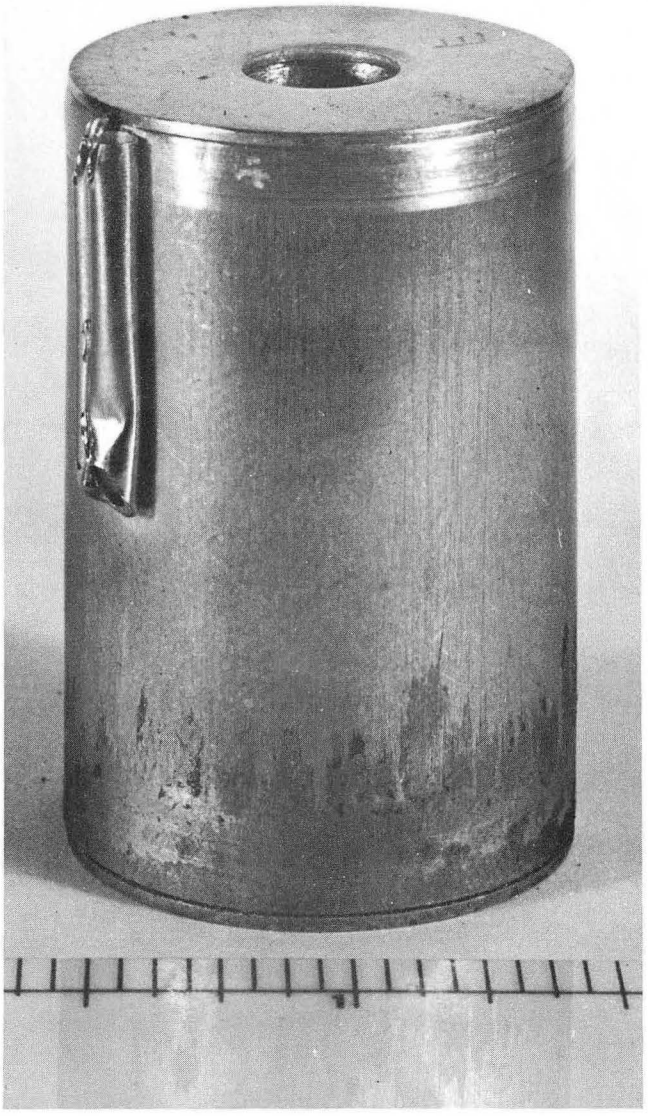
PLATE B

THE FURNACE ASSEMBLY



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calorimeter. The vacuum chamber was evacuated and flushed three times with helium gas. On the final flush the pressure was reduced to -20 in of mercury. All support equipment (i.e., recorders, controllers, wattmeters, etc.) were energized, standardized, and allowed to stabilize. The dc power and ac power were then turned on and the system allowed to equilibrate at the selected starting temperature.

After the differential temperature and differential power recorders were plotting straight lines, indicating equilibrium in the calorimeter, the environmental temperature was increased at either one or two mv per h by the furnace controller. In the present series of experiments the highest temperature required was about 1250°K. During the experiment the power inputs to the two small dc cell heating elements were controlled so that the differential temperature was within ±0.1°K. During the heating cycle the differential power required to maintain zero differential temperature was recorded as a function of time (Fig. 1). Cell temperatures were measured at arbitrary times during the run. These temperatures (T_2 and T_4, Fig. 1) were used to check the base line points of differential power required for subsequent equilibrium measurements at these temperatures. At the maximum temperature of each run (T_5) the calorimeter was allowed to come to equilibrium. By connecting the two end points (T_1 and T_5) and the in-run equilibrium points (T_2 and T_4) with straight lines, the base equilibrium line is obtained for the calorimeter at various temperatures in the heating interval. The closed figure (Fig. 1) obtained by joining the base lines and the experimental differential power curve represents the increase in heat content of the material within the temperature range investigated. If no reactions were present in that temperature interval, the

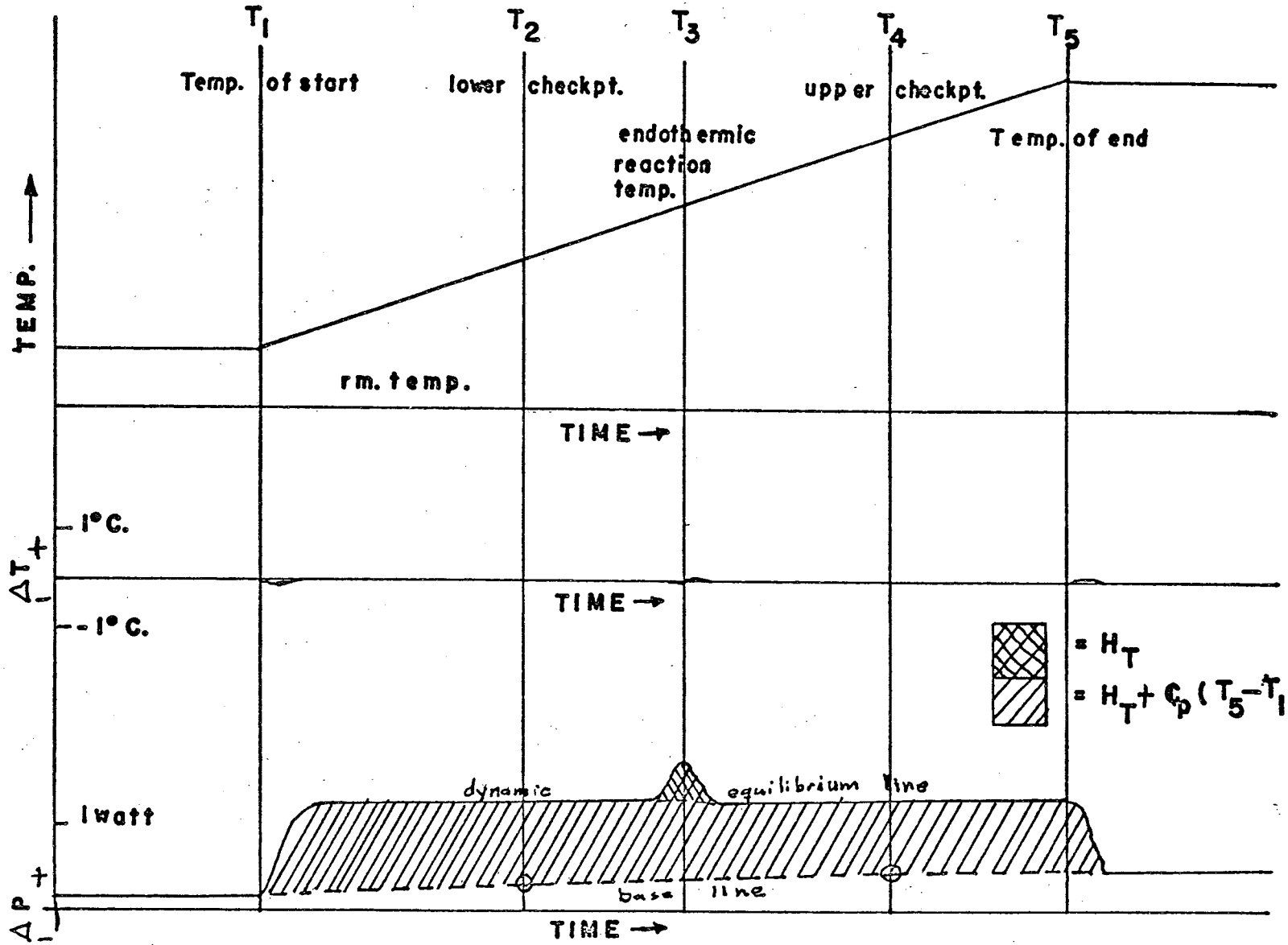


FIG. Ia

FIG. Ib

FIG. Ic

FIGURE 1

TYPICAL TEMPERATURE, DIFFERENTIAL TEMPERATURE AND POWER CURVES

heat observed was the product of the heat capacity times the temperature difference. If reactions are present in the interval, the observed heat is the sum of the reaction heat and the heat capacity -- differential temperature product.

The heat of reaction is found by drawing a straight line between the two lines observed before and after the reaction. This straight line is justified as a good approximation by the fact that before and after the reaction the lines are fairly straight and very close to the same value of differential power; also, due to the temperature gradient existing across the sample, only a small amount of material is undergoing reaction at any one increment of time. The heat capacity of the non-reacting sample should, therefore, be fairly close to an average of the products of the weights times the heat capacities of the product and reactant. This straight line is a good approximation of this average.

The type of curves recorded during the heating of a material undergoing an endothermic reaction is shown in Fig. 1. Figure 1a represents the cell temperature; Fig. 1b is typical of the differential temperature during the heating of the material; Fig. 1c represents a typical differential power curve.

The temperature of the cells was always higher than the temperature of the surroundings. Therefore, the heat transfer was always from the cells to the surrounding environment. Since the two cells were made of the same material and had the same geometry, the assumption was made that their rates of heat loss were equivalent.

Integration of the enclosed area in Fig. 1c yields the change in heat content of the material between the experimental temperatures. The

integration was done with a polar planimeter. The accuracy of integration is ±2%.

V. RESULTS

A. Heats of Crystallographic Transformation

Initial calibration runs with SiO_2 resulted in an average value of 198 cal/mole for the α quartz to β quartz inversion. Eight runs were made. The lowest value measured was 188 cal/mole while the highest was 203 cal/mole. The published value[2] for the α quartz to β quartz inversion is 290 cal/mole. The difference in the measured heat of transformation when compared to the published value is -31.9% (Table I).

The measured heat of transformation of K_2SO_4 at 856°K was 2309 cal/mole. Eight runs were made. Six runs resulted in measured values of 2309 cal/mole. A low value of 2250 cal/mole and a high value of 2380 cal/mole were also measured. The published value[2] for the heat of the K_2SO_4 transformation is 2140 cal/mole. The difference in the measured and published value was +7.9%.

One run was made with Na_2SO_4-III. The measured value for the heat of transformation at 514°K was 1780 cal/mole. The transformation is an irreversible endothermic reaction. Enough sample was available for only one run. The published value[2] for the heat of the transformation is 1790 cal/mole. The deviation of the measured value from the published value is -0.5%. It was observed that the reaction temperature was approximately 39°K above the published 514°K reaction temperature.

The measured value for endothermic transformation in FeS at 598°K was 154 cal/mole. Four runs were made. All runs resulted in the

Table I. Measured heats of transformation.

Material	Average meas. H_T, cal/mole	No. runs	Published H_T, cal/mole	Percent difference	Measured $T_{reaction}$	Published $T_{reaction}$
SiO_2, 14.2 g	198 cal/mole	8	290 cal/mole	-31.9%	848°K	848°K
K_2SO_4*	2309 cal/mole	8	2140 cal/mole	+ 7.9%	856°K	856°K
Na_2SO_4-III**	1780 cal/mole	1	1790 cal/mole	- 0.5%	≈553°K***	514°K
FeS, 40.01 g	154 cal/mole	4	120 cal/mole	-29.2%	598°K	598°K

* 5.26 g K_2SO_4 diluted by 12.63 g Al_2O_3.

** 4.19 g Na_2SO_4-III diluted by 10.0 g Al_2O_3.

*** Note reaction temperature deviation.

measured value of 154 cal/mole. The published value[2] for the transformation is 120 cal/mole. The difference was +29.2%.

During all measurements the temperature differential between the cells varied by less than ±0.1°C.

At various power levels to the cells and various heating rates the results are uneffected. (Table II). K_2SO_4 and FeS were heated at both 2 mv/h and 1 mv/h. At both heating rates the measured values were 2307 cal/mole and 154 cal/mole for K_2SO_4 and FeS, respectively. SiO_2 was heated by heat sources of 4.25 V, 6.25 V, and 8.25 V. At 4.25 V, poor control of differential temperature resulted in no measurement of the heat of transformation. Seven runs at 6.25 V resulted in a measured value of 198 cal/mole and one run at 8.25 V resulted in a value of 199 cal/mole.

B. Heat Content Measurements

Table III shows selected values for some typical measured values of the increase in heat content of some of the materials tested. SiO_2 was heated at 2 mv/h from 521°K to 1084°K. The measured increase in heat content was 3140 cal/sample weight. The calculated value from published data[2] was 2255 cal/sample weight. The deviation of the measured value from the calculated value represents a difference of +39.2%.

A 5.26 g K_2SO_4 and 12.63 g Al_2O_3 mixture was heated at both 1 mv/h and 2 mv/h. When the mixture was heated at 1 mv/h over the temperature range 694°K to 1040°K, the measured increase in heat content was 2070 cal/sample weight. The calculated value[2] for the increase in heat content was 1722 cal/sample weight; the deviation represents a difference of +20.2%.

Table II. Heating rates and power level vs results

Material	No. runs	Heating rate	Result	No. runs	Power level to full cell at room temp.	Result
SiO_2, 14.2 g	8	2 mv/h	198 cal/mole	7	6.25 V, 1 amp	198 cal/mole
				1	8.25 V, 1 amp	199 cal/mole
K_2SO_4, 5.26 g + Al_2O_3, 12.63 g	7	2 mv/h	2309 cal/mole	8	6.25 V, 1 amp	2309 cal/mole
	1	1 mv/h	2309 cal/mole			
FeS, 40.01 g	2	2 mv/h	154 cal/mole	4	6.25 V, 1 amp	154 cal/mole
	2	1 mv/h	154 cal/mole			

Table III. Heat content measurement results.

	Material	Heating rate	T_2	T_1	$H_{T_2} - H_{T_1}$ measured	$H_{T_2} - H_{T_1}$ calculated	Difference
1)	SiO_2, 14.2 g	2 mv/h	1084°K	521°K	3140 cal/sam.	2255 cal/sam.	+39.2%
2)	K_2SO_4, 5.26 g; Al_2O_3, 12.63 g	1 mv/h	1040°K	694°K	2070 cal/sam.	1722 cal/sam.	+20.2%
3)		2 mv/h	1047°K	694°K	2390 cal/sam.	1786 cal/sam.	+33.8%
4)		2 mv/h	987°K	609°K	2680 cal/sam.	1839 cal/sam.	+45.5%

When the same sample was heated at 2 mv/h over a similar temperature range, 694°K to 1047°K, the measured heat content increase was 2390 cal/sample weight. The calculated value[2] is 1786 cal/sample weight. The observed difference was +33.8%.

The same K_2SO_4 and Al_2O_3 mixture was heated at 2 mv/h over a lower temperature range, 609°K to 987°K. The measured heat content increase was 2680 cal/sample weight. The calculated[2] value was 1839 cal/sample weight. The deviation represents a difference of +45.5%.

The differences of increase in heat content were consistently in the range +30% to +45%.

It was observed that as the temperature of the calorimeter increased, the ΔP between the base line and the recorded value generally decreased. In other words, as the temperature increased, the percent error in the heat energy required to maintain "dynamic equilibrium", decreased. Qualitatively, this observation may be seen by comparing results No. 3 and No. 4. Result No. 4 is over a low temperature range, while result No. 3 is over a higher range. The increase in heat content over the lower temperature range is 11.7% higher than for the higher range.

Comparison of results No. 2 and No. 3 also show that a low heating rate improves the accuracy of the heat content measurements. However, rates below 1 mv/h had no observable effect on improving the accuracy.

VI. DISCUSSION OF RESULTS

A. Heat Content Measurements

Since the observed differences in the measurement of the heat contents were appreciable, a series of experiments was conducted to find the cause. It was observed that at all temperatures, where the calorimeter was allowed to equilibrate thermally, the full cell required more heat to maintain the equilibrium. Two experiments were, therefore, conducted at different power settings to find the temperature vs ΔP of equilibrium curves. The results of runs made at constant 6.25 V and constant 8.25 V to the full cell are shown in Fig. 2.

At both 6.25 V and 8.25 V, ΔP is increasingly temperature dependent. Therefore, the full cell is not only losing heat faster than the empty cell but its rate is increasing. Comparison of the two curves also shows that at 8.25 V the rate of heat loss from the full cell is higher than at 6.25 V. An adequate explanation for both these phenomena may be found in the asymmetry of the cell complex.

Figure 3 shows a diagram of the cell complex with its possible methods of heat transfer. At any equilibrium temperature, T_1, the power necessary to keep the outside of the full cell at T_1, is given by $P_F = \sum E_{loss} = E_1 + E_2$, where E_1 radiation loss from the cell surface and E_2 equals the conduction losses up the support tube. Likewise, the power necessary to keep the empty cell at $T_1^{\dagger}$, equals $P_E = E_1^{\dagger} + E_2^{\dagger}$. $T_1 = T_1^{\dagger}$. The bulk of the heat flow in both cells is assumed to be through the cell contents and not through the metal end caps. The heat transfer in the lower cell is by radiation; therefore, the inside wall temperature, $T_2^{\dagger}$, is only slightly higher than $T_1^{\dagger}$ and the temperature gradient from inside to outside is

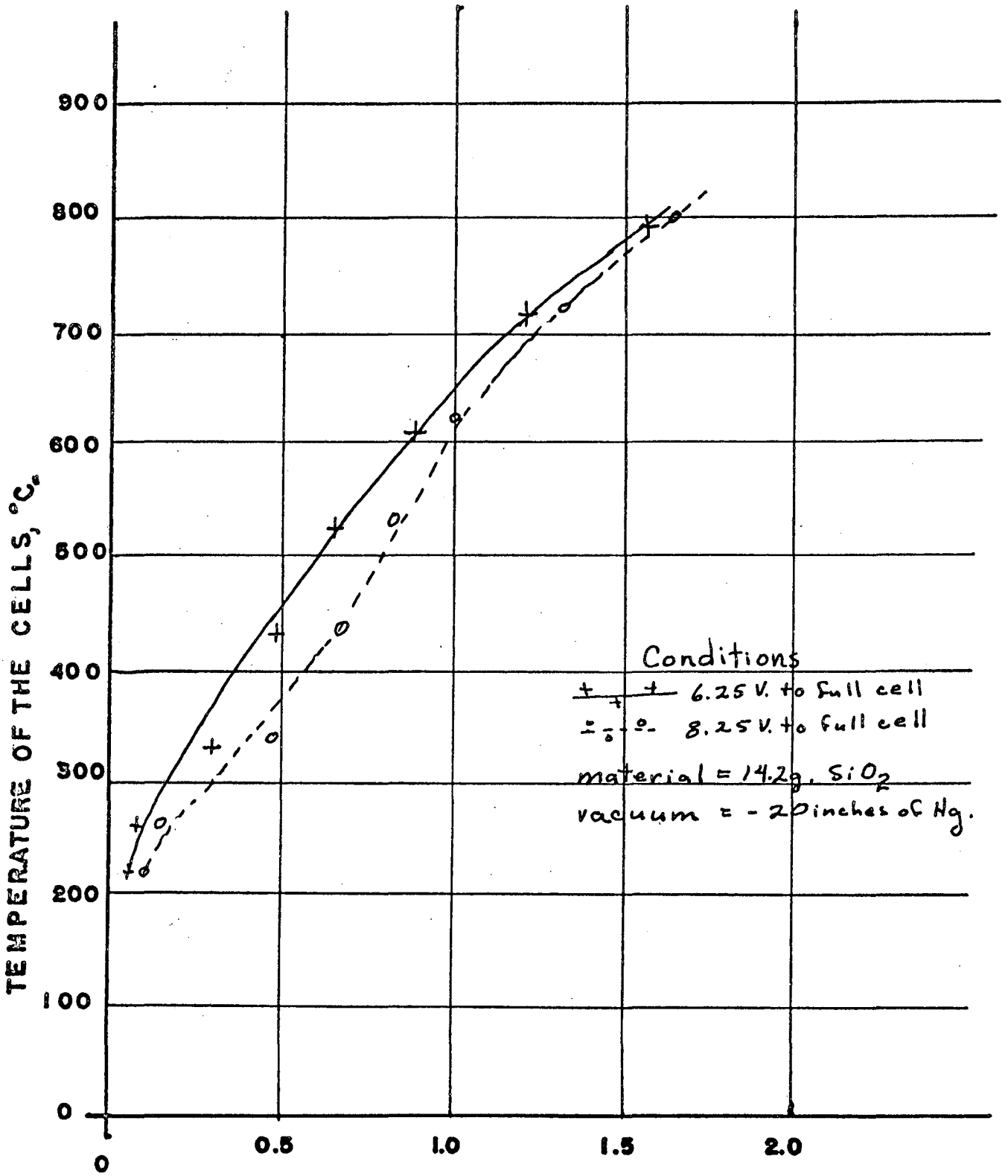
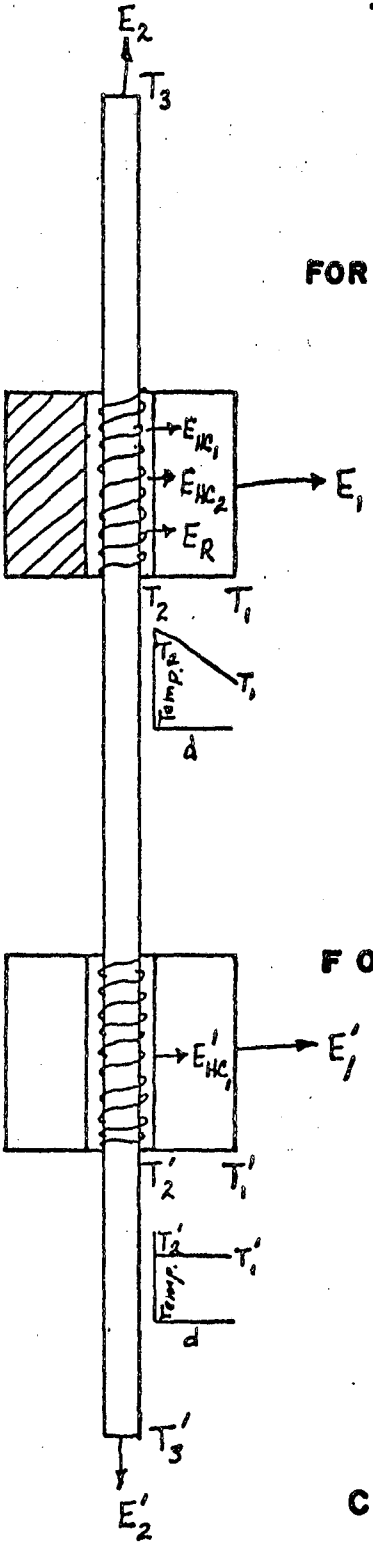


FIGURE 2

ΔP VS. TEMPERATURE

$T_1 = T_1'$, $T_2 \gg T_1 = T_1'$, $T_2' \gg T_1' = T_1$,

$T_3 \approx T_3' \ll T_2 > T_2'$, $E_1 = E_1'$



FOR FULL CELL.

1.) AT EQUILIBRIUM, $P_F = E_1 + E_2$

2.) DURING DYNAMIC EQUILIBRIUM,

$$P_F = E_1 + E_2 + E_{HC_1} + E_{HC_2}$$

where,

E_{HC_1} = heat cap. effect of cell metal

E_{HC_2} = heat cap. effect of sample

3.) DURING A REATION,

$$P_F = E_1 + E_2 + E_{HC_1} + E_{HC_2} + E_R, \text{ where } E_R = H_T$$

FOR EMPTY CELL.

1.) AT EQUILIBRIUM, $P_E = E_1' + E_2'$

2.) DURING DYNAMIC EQUILIBRIUM,

$$P_E = E_1' + E_2' + E_{HC_1}'$$

FIGURE 3

CELL HEAT LOSS DIAGRAM

small, $T_2' \geq T_1'$. However, in the full cell the heat transfer is primarily by conduction through an insulating material. There is, therefore, a reasonably large temperature gradient from the inside of the cell to the outside, $T_2 >> T_1$. The temperature of the heat sinks for the ends of the support rods are at approximately the same temperature, T_3 and T_3' and much less than the cell temperature, $T_3 \approx T_3' << T_1$. Therefore, the vertical gradients, which determine the conduction losses, are $T_2 - T_3$ for the full cell and $T_2' - T_3'$ for the empty cell. Because $T_2 - T_3$ is greater than $T_2' - T_3'$, the vertical conduction losses from the full cell are greater than from the empty cell; therefore, more power is required by the full cell to maintain equilibrium.

Conversely, when more power is applied to both cells, it is observed that the losses from the upper cell are greater. This observation supports the hypothesis.

As the equilibrium temperature of the calorimeter increases, the efficiency of radiation transfer in the lower cell increases. Meanwhile, the heat transfer of the full upper cell does not increase at the same rate as the improving radiation transfer in the lower cell. The result is that the ratio of full cell vertical conduction loss to empty cell vertical conduction loss is amplified even more; hence, as the temperature increases the full cell requires even more power to maintain equilibrium.

During the heating of the calorimeter, or "dynamic equilibrium", the power required by the upper full cell equals $P_F = E_1 + E_2 + E_{HC_1} + E_{HC_2}$. E_{HC_1} equals the heat capacity effect of the cell and E_{HC_2} equals the heat capacity effect of the sample. Likewise, $P_E = E_2' + E_1' + E_{HC_1}'$. The E_1/E_1' ratio equals 1. Since the upper cell now requires

even more power to maintain dynamic equilibrium due to the heat sink of its contents, $T_2 - T_1$ is even greater than when at equilibrium. Thus, the E_2/E_2' ratio becomes larger than when at equilibrium. The net effect is that heat content measurements result in high values compared to published values.

As pointed out in the results, as the temperature increased the ΔP between the equilibrium base line and the recorded "dynamic equilibrium" line decreased. Obviously, as the heat transfer by radiation becomes more efficient at higher temperatures the E_1/E_2 ratio decreases. Hence, even though there is an error due to E_2 during heating, the net measured ΔP decreased and the calorimeter records a more correct value of heat content as the temperature increases. In other words, as the dynamic equilibrium line remains constant, the equilibrium base line value approaches the dynamic equilibrium.

B. Heats of Transformation

For those materials of low H_T (i.e., SiO_2 and FeS) the measured heat of transformation varied by ±30%. If the published values[2] of $H_{T_{reaction}} - H_{298}$ are allowed to vary by ±1%, the measured H_T's for SiO_2 and FeS are within experimental error. For those materials of higher H_T (K_2SO_4 and Na_2SO_4-III) the published value[2] of the heat of transformation should be more accurate even if $H_{T\ reaction} - H_{298}$ varies by ±1%. The percentage error for these materials was considerably smaller and within acceptable limits.

Even though the magnitude of the heat content error is larger than the heat of transformation, the accuracy of the heat of transformation results can be seen by the following explanation. During a

transformation the temperature of the empty cell is changed to match that of the full cell. A new term is added to P_F so that $P_F = E_1 + E_2 + E_{HC_1} + E_{HC_2} + E_R$. E_R equals the heat absorbed during an endothermic reaction (in the case of an exothermic reaction E_R would be negative). No term is added to P_E. For comparative purposes let $T_2' - T_3 = 300°C$ and $T_2 - T_3 = 320°C$. Thus, the driving force for E_2 is 6.67% greater than for E_2'. If there is a 3°C retardation in $T_2' - T_3$ and $T_2 - T_3$ during the reaction, the driving force difference is 6.73%. In other words, the expected error would be 0.9% which is within the limits of the integration and measurability of the method. Therefore, the results should be correct within the ±2% limits.

The measured values for the α-β quartz transformation in SiO_2 and transformation at 598°K in FeS are believed to be more accurate than the reported values in the literature.[4]

VII. CONCLUSIONS

The initial design of a differential calorimeter for measurement of high temperature heats of solid state transformation has been completed. The apparatus was tested by measuring the heats of transformation of SiO_2 (198 cal/mole), K_2SO_4 (2309 cal/mole), Na_2SO_4-III (1780 cal/mole), and FeS (154 cal/mole).

Heat content measurements on these materials resulted in values 30 - 45% too high when compared to published values.[2] These deviations were due to unequal vertical heat losses from the sample cells of the calorimeter.

Recommendations for a refined differential calorimeter capable of measuring both heats of transformation and heat contents and possibly heats of reaction and heats of melting may be found in Appendix C.

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APPENDICES

A. Experimental Design

1. Design of the Differential Calorimeter

Two concentric metal sleeves fitted with base plates served as sample cells, 1a and 1b in Fig. 4. They are positioned by Morganite (Al_2O_3) sleeves, 2a, 2b, 2c, centered on a four-hole thermocouple rod, 3. The cell material was either nickel or platinum. The selection of which set of cells to use was determined by the operating temperature of the calorimeter. The cells are 1-1/2 in high by slightly less than 1 in diameter with a 3/8 in tube forming the inner wall. They are fitted with both removable tops and bottoms. Each cell will hold about 15 to 20 g of powdered sample. It was originally intended that one sample cell would be filled with an unknown material and the other with a standard material, Al_2O_3. Subsequent experimentation revealed that better differential temperature control upon heating could be achieved by leaving the standard cell empty. Quicker thermal response (the reason for the better control) allows the running of the experiments at low gas pressures. Therefore, the heating and cooling effects of convection currents are reduced. In addition, faster heating rates may be employed.

The central support tube is threaded at appropriate and vertically symmetrical positions to allow a winding of 8 mil platinum wire. These windings are the individual heating elements with which the cell temperatures are controlled. The leads to the windings are fed through, in the appropriate direction, the internal holes of the rod to the outside of the furnace assembly. These leads are made of 20 mil platinum wire to reduce heating effects in the lead wires. Once out of the furnace assembly

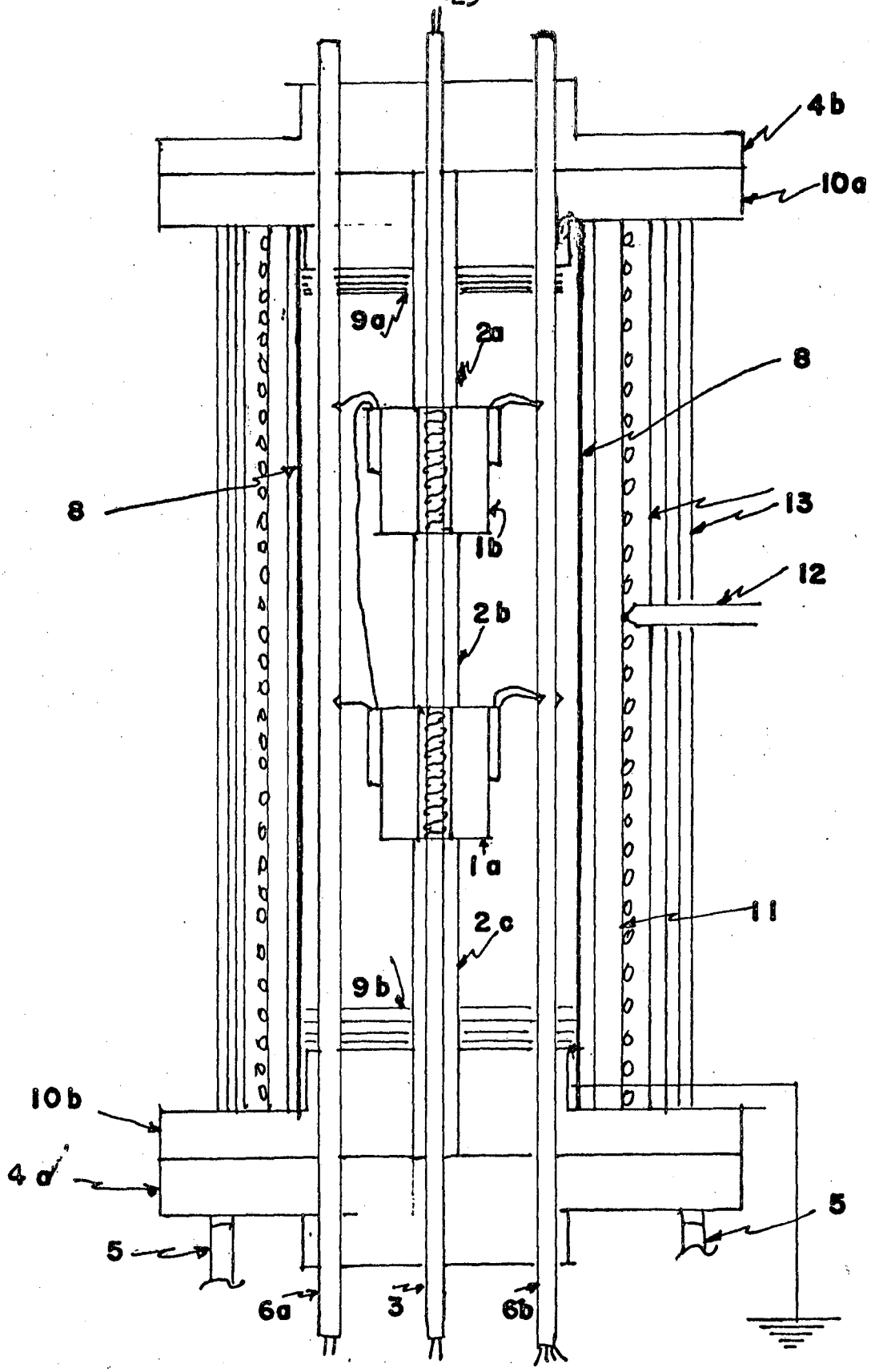


FIGURE 4

FURNACE ASSEMBLY

the platinum leads connect to heavy gage copper wires. The copper wires are fed out of the vacuum chamber through glass-to-metal sealed feed-throughs.

The central support tube, 3, is supported by a stainless steel plate, 4a, through which several holes equipped with Allen screws have been drilled. These holes accommodate several ceramic tubes to be described later in addition to the central support tube. The support plate is attached to three stainless steel rods, 5, in Fig. 4, which are bolted to the brass vacuum chamber base (Fig. 5). Stainless steel was selected for the support plate because this plate achieves a temperature at which brass would de-zinc in vacuum. The support plate serves as a foundation for the entire furnace assembly. A similar plate, 4b, is mounted on top of the furnace assembly by three more stainless steel rods. They are attached to the lower support plate, 4a, to complete the rigidity and symmetry of the assembly. Two holes drilled symmetrically about the central rod hole on a diameter chord of the base plates hold two four hole thermocouple tubes, 6a and 6b. Through these tubes are fed the differential and monitoring thermocouples. The thermocouple junctions are insulated with 1/16 in o.d. two-hole insulating tubes. These tubes are inserted into small metal buckets mounted on the outside of each of the individual sample cells. The internal furnace assembly (i.e., cells, central tube, and thermocouple tubes) is entirely surrounded by nickel shields. In the horizontal direction the shield is a cylindrical tube, 8. This shield acts as a high temperature shield for ac and dc strays. The shield is grounded. In the vertical direction the shields are groups of radiation shields, 9a and 9b, backed up by formed insulating refractory

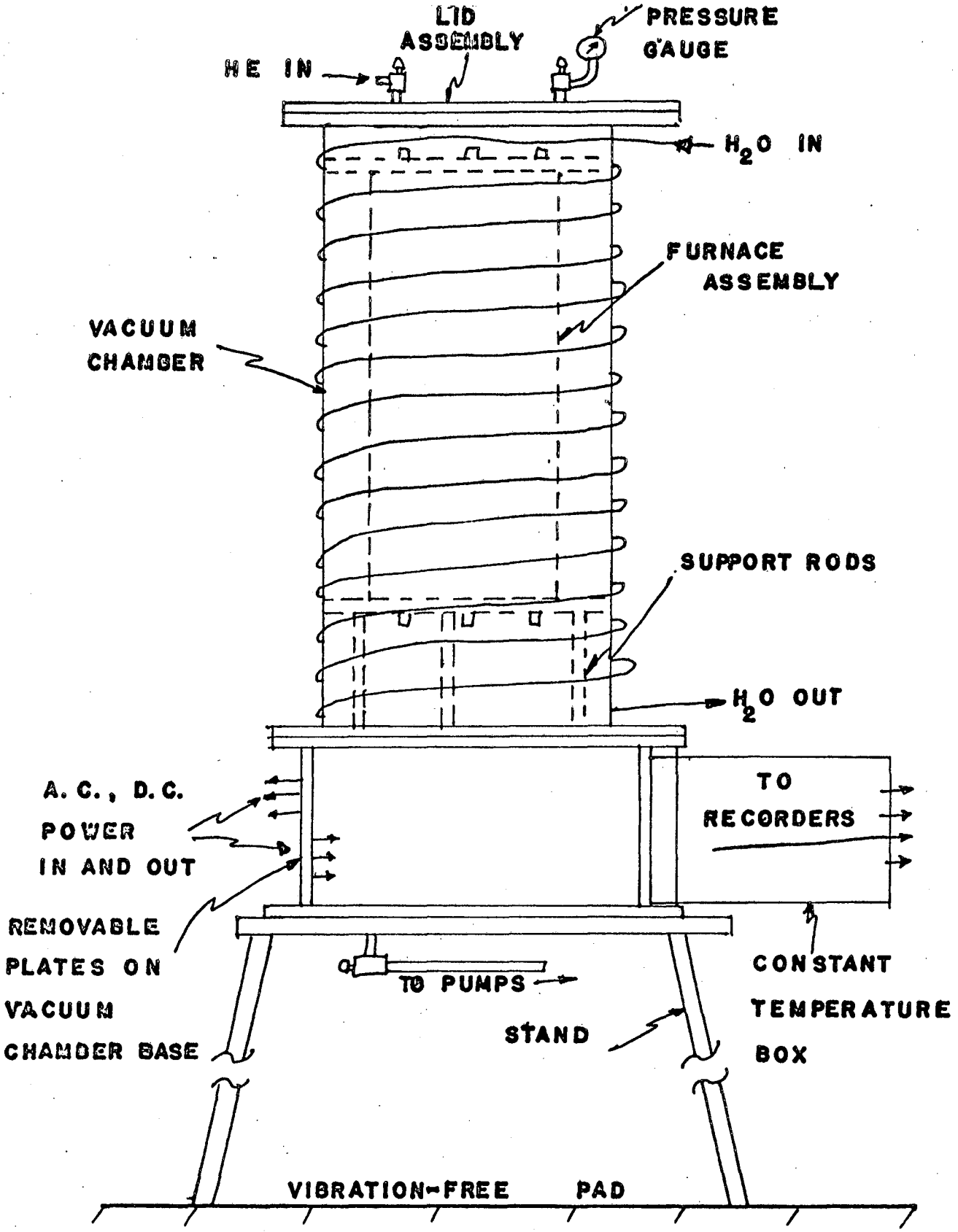


FIGURE 5

VACUUM CHAMBER ASSEMBLY

brick, 10a and 10b. The shields and brick retard heat losses in the vertical direction and reduce the vertical temperature gradients. The internal shield is enclosed by a threaded 3 in i.d. Alundum core, 11, on which Kanthal A-1 resistance wire is wound. A furnace program control thermocouple, 12, is mounted on the outside of the core. Since the thermocouple is in close proximity to the winding, it is very sensitive to the ac power changes made to control the programming of the environmental temperature. If the thermocouple were mounted in the cell chamber or next to the shield, the time lag and damping due to the passage of varying amounts of heat through the Alundum core would cause cycling of the environmental temperature surrounding the cells; the cycling environmental temperature would influence the rate of heat loss from the cells, causing cycling of their temperature also. The Alundum core is enclosed by a set of nickel radiation shields, 13, to minimize radial heat losses.

The furnace and interior cell assembly is enclosed in a water-cooled steel jacket which rests on the vacuum chamber base. The jacket is flanged and fitted with rubber O-rings to insure a vacuum tight system. A lid assembly containing ports with vacuum valves completes the vacuum chamber. The ports are connected to a vac-pressure gage and the facilities for supplying a controlled atmosphere. The vacuum chamber base is fitted with a port, vacuum valve, and access to vacuum pumps. Thus, heavy gases, not initially pumped out, can be displaced to the bottom of the chamber and pumped out leaving virtually a low pressure inert helium atmosphere. The vacuum chamber base is also equipped with two removable O-ring sealed brass plates. Through one plate all

ac and dc power leads are fed to the outside of the vacuum chamber. Through the other plate all thermocouple leads are fed. All leads are fed through the plates by means of glass-to-metal sealed feed-throughs.

All thermocouple junctions with lead wires, except the differential thermocouple, are made in the cold lower part of the vacuum chamber to facilitate dismantling of the equipment. The differential thermocouple leads are fed out of the chamber and make their junctions with the lead wire on a multiple junction board in a constant temperature box. The constant temperature box is mounted on the outside of the vacuum chamber base. This box reduces fluctuations in the differential emf due to convection currents in the ambient room atmosphere. All other thermocouple leads also made junctions on the multiple junction board in the constant temperature box to facilitate removal of the lead wires.

The entire vacuum assembly is mounted on a three-legged stand which is bolted securely to a vibration free pad. The pad is independent of the foundation of the building.

It was noted during the construction of the calorimeter that at low pressures and above 700°C surface conduction effects across the refractory between the dc individual heater windings and the differential thermocouple caused differential temperature errors. Introduction of one atmosphere of helium nullified this condition. But, heating of the upper cell by convection introduced large errors in the measured heat content measurements. A vacuum of 20 in of mercury with the remaining atmosphere being helium minimized both difficulties.

2. Control and Recording Equipment

a. The Differential Temperature Circuit (Fig. 6)

The differential temperature between the two cells is measured with a Pt-10% Rh/Pt/Pt-10% Rh differential thermocouple mounted in buckets attached to the outsides of the sample cells. The junctions of the thermocouples are in mechanical contact with the sample cells. The Pt-10% Rh legs are fed out of the cell chamber and down separate holes of a porcelain thermocouple tube. The junctions with the lead wires are made in the constant temperature box which is filled with room temperature air. The resulting differential emf is fed into a Leeds and Northrup dc microvolt amplifier, where it is amplified 20X. The resulting amplified differential emf is then fed to a Leeds and Northrup recorder used in conjunction with a Leeds and Northrup PAT controller. The entire circuit is ungrounded.

b. The dc Power Circuit (Fig. 7)

The output from the Leeds and Northrup controller controls the differential power supplied to the individual cells. The power supply is a Power Designs, Inc. transistorized dc power supply. It is variable from 0 to 20 V and will handle 0 to 5 amps. The individual sample heaters are connected in parallel with the control resistor in the leg which supplied power to the empty (most thermally responsive) cell. The control resistor is a 0 to 9 ohm Ohmite tapered resistor. It is connected so that the taper allows a nearly differential power change per step. The voltage across the filled cell is constant; thus, power input is only a function of the resistance change with temperature of the Pt winding. The power to the empty cell is controlled by the controller, set to keep the temperature of the two cells identical.

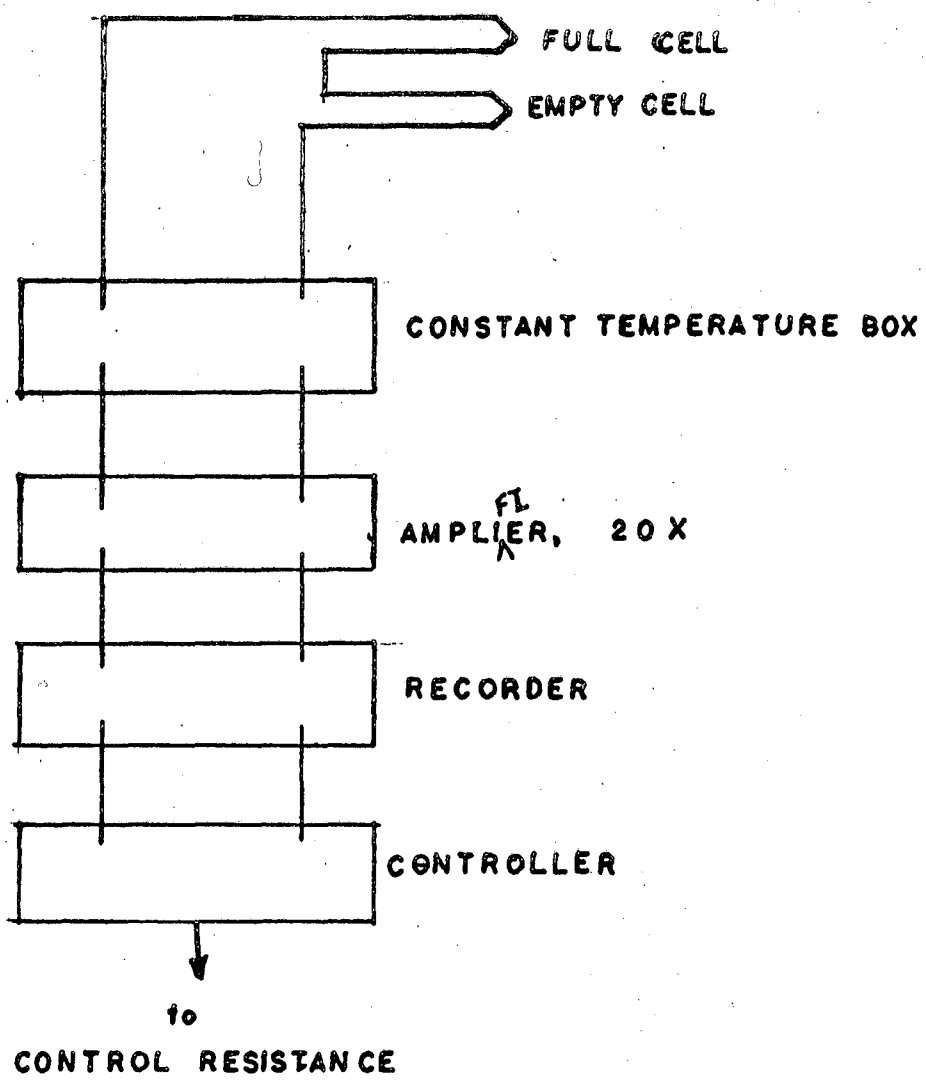
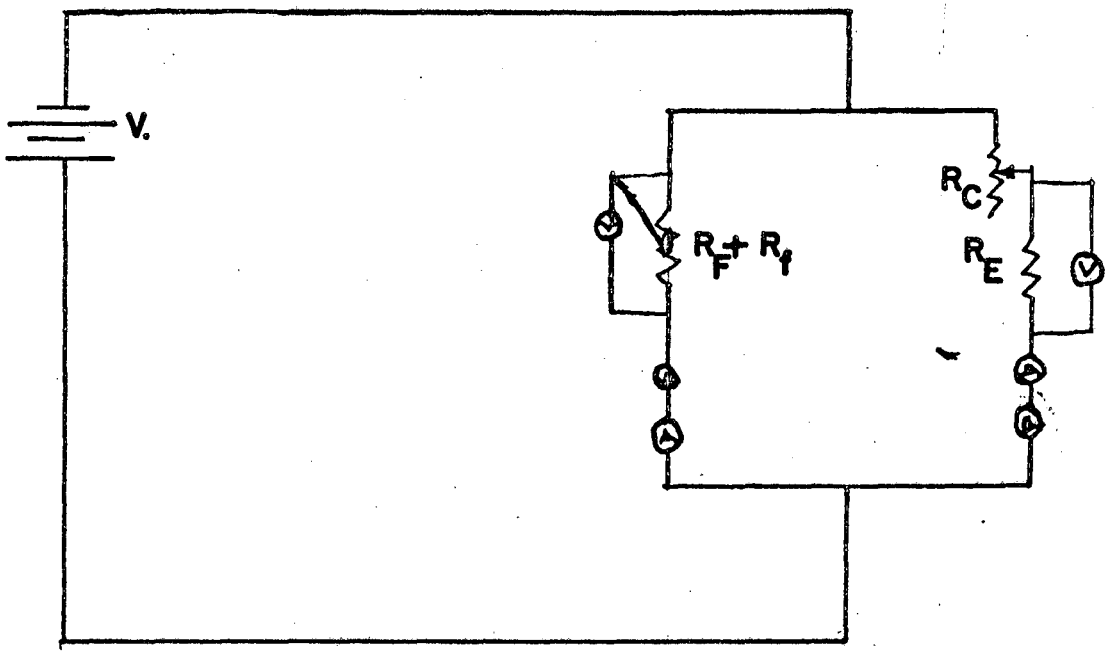


FIGURE 6

DIFFERENTIAL TEMPERATURE CIRCUIT



V = d.c. POWER SUPPLY, 7.75 V.

R_F = UNKNOWN SAMPLE HEATER = 3.5 Ω

R_E = EMPTY SAMPLE HEATER = 3.5 Ω

R_f = UNKNOWN SAMPLE VOLTAGE REGULATOR = 0 → 2 Ω

R_C = CONTROL RESISTOR = 0 → 9 Ω

FIGURE 7

D. C. POWER CIRCUIT

c. The Differential Power Recording Circuit (Fig. 8)

The differential power is measured by two Weston Inductronic Product resolver amplifiers. These devices are accurate wattmeters which put out an amplified potential proportional to the product of the input dc potential and the input current. Their outputs are bucked against one another; hence, the net output is the difference between their inputs. The net result is a measure of the differential power input to the two sample cells. The wattmeters were calibrated over the range of inputs used and were found to respond linearly to a linear variance of power input. They are very sensitive to vibration and are, therefore, mounted on the vibration-free pad. A 1000 ohm potentiometer is connected across the output of the wattmeters and an appropriate fraction of the potential drop across it is fed to a Leeds and Northrup recorder. The resulting differential power vs time plot is then integrated using a K.E. polar planimeter to yield the net heat involved during the heating of the unknown sample.

d. The Monitoring Thermocouple Circuit (Fig. 9)

A Pt/Pt-10% Rh thermocouple is mounted in a bucket directly across each cell from the differential thermocouple. The couples are electrically insulated from the sample cell to prevent feed-through of any signal from their recorder to the differential thermocouple circuit. The couple leads follow a path down a four-hole thermocouple tube to their appropriate lead wires. The two Pt leads are connected to the same junction. Three lead wires, therefore, continue from the vacuum chamber through the constant temperature box to a Brown potentiometer type two channel recorder. The temperatures of each cell are monitored

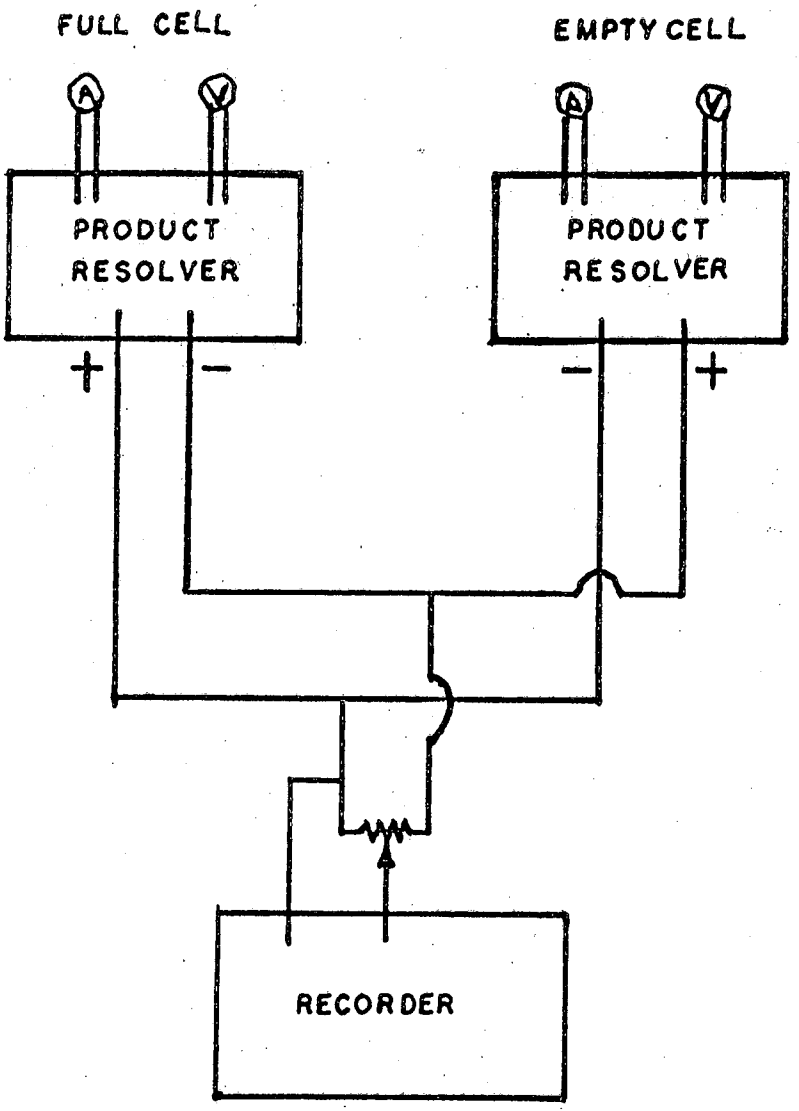


FIGURE 8

DIFFERENTIAL POWER RECORDING CIRCUIT

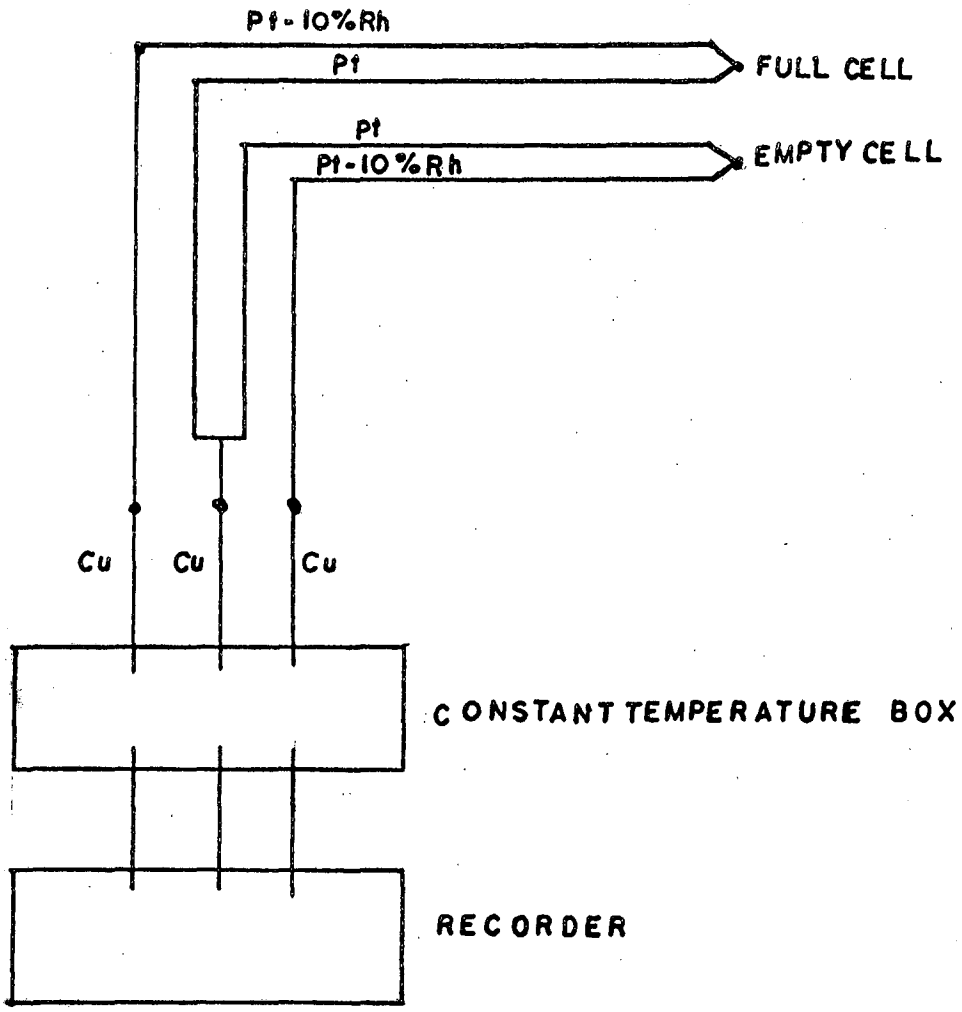


FIGURE 9

TEMPERATURE MONITERING CIRCUIT

on the recorder. This recording acts as checks of the reaction temperatures, cell temperatures, and validity of the output of the differential thermocouple.

e. The Furnace Control Circuit (Fig. 10)

The temperature of the environmental heating furnace is monitored by a Pt/Pt-10% Rh thermocouple mounted on the outside of the furnace core. This thermocouple is very sensitive to the power changes made to control the furnace. The output of this thermocouple is fed to a Brown Electronik 0 - 1600°C recorder. The control set-point of the recorder can be driven up or down at variable rates by the use of an interrupter. The error signal from the recorder is fed to a Brown electro-volt controller which is used in conjunction with a magnetic amplifier. The signal from the magnetic amplifier changes the power output of a 5 kva saturable core reactor. The reactor, operating off a 220 V line, supplies the power to the environmental temperature controlling furnace.

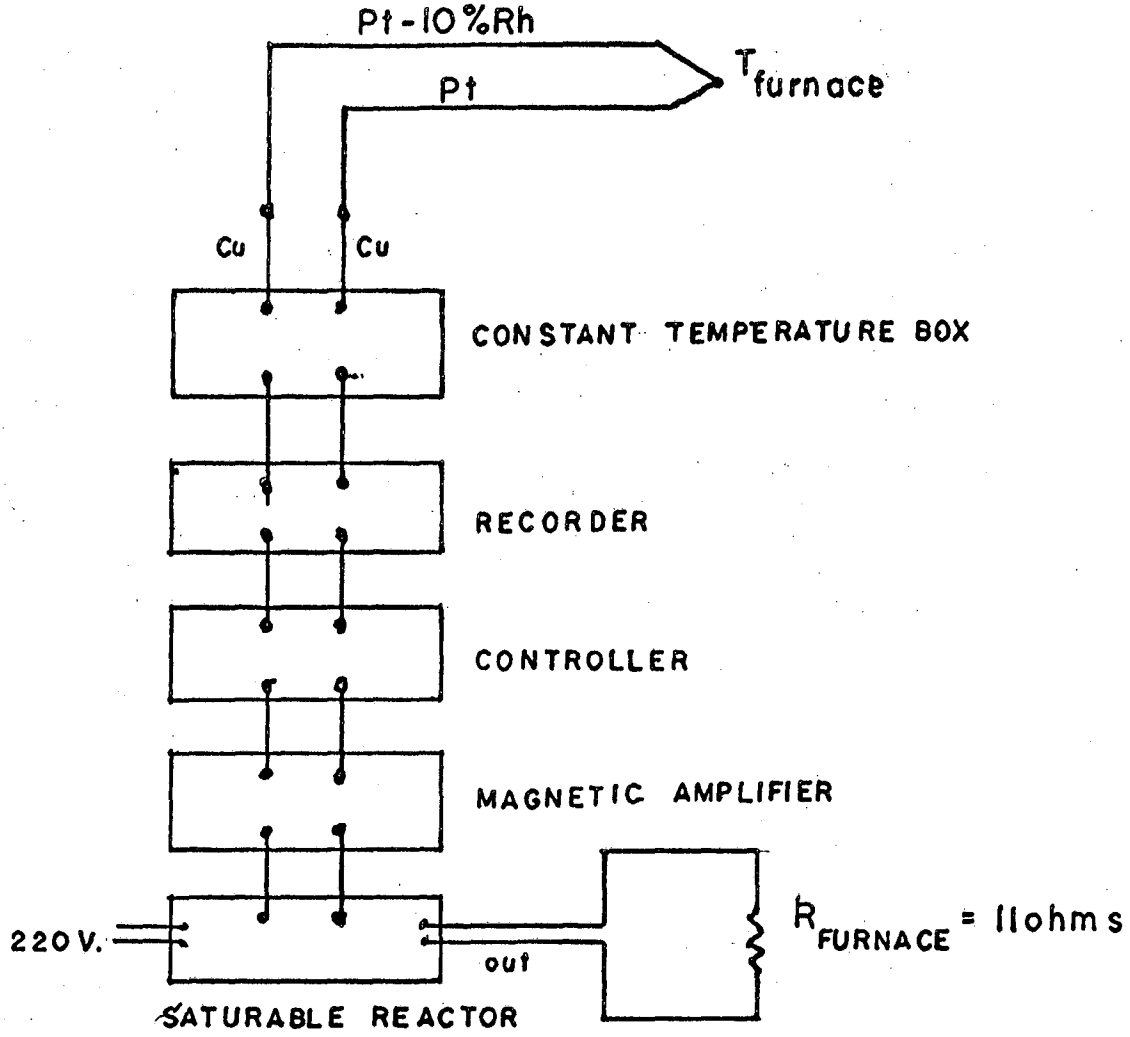


FIGURE 10

FURNACE CONTROL CIRCUIT

B. X-Ray Analysis of the Samples[7]

K_2SO_4

ASTM No. 5-0613		Observed	
5.03	- 8	4.98	- w
4.176	-28	4.15	- s
4.16	-23	4.15	- s
3.743	-18	3.74	- m
3.503	- 6	3.48	- m
3.384	-13	3.37	- m
3.140	- 9	3.13	- w
3.062	- 8	3.06	- w
3.001	-77	2.99	-vs
2.903	-100	2.98	-vs
2.886	-53	2.88	-vs
2.665	- 7	2.66	- w
2.602	- 2	2.60	- w
2.518	-13	2.51	- m
2.499	-15	2.49	- m
2.422	-25	2.41	- m
2.386	-13	2.38	- m
2.374	-17	2.37	- m
2.230	-19	2.23	- m
2.206	-14	2.20	- m
2.101	- 6	2.10	- w
2.089	-25	2.08	- m
2.082	-25	2.08	- m
2.002	- 7	1.996	- w
1.964	- 4	1.96	- w
1.945	- 7	1.94	- w
etc.		etc.	

FeS

4-0832			
2.98	-90	2.98	- s
2.93	-50	2.93	- m
2.67	-90	2.67	- m
2.52	-30	--	--
2.15	-30	2.14	- w
2.14	-50	2.14	- w
2.09	-100	2.09	-vs
1.95	-50	1.95	- m
1.92	-60	1.92	- w
1.75	-60	1.75	- w
1.72	-90	1.72	- m
etc.		etc.	

Na_2SO_4-III

ASTM No. 8-31		Observed	
4.74	-60	4.77	- s
4.47	-30	4.48	- w
3.91	-90	3.93	- s
3.76	-90	3.77	-vs
3.48	-80	3.48	- m
2.80	-100	2.81	-vs
2.63	-90	2.64	-vs
2.46	-10	2.466	- w
2.37	-80	2.38	- m
2.23	-30	2.24	- w
2.18	-20	2.18	-vw
2.12	-40	2.132	- m
2.10	-30	2.10	- m
2.08	-40	2.09	- m
2.06	-30	2.065	- m
1.958	-80	1.963	- m
1.877	-60	1.883	- m
1.764	-30	1.767	-vw
1.738	-80	1.738	- m
1.691	-30	1.691	- w

SiO_2(α quartz)

4-0490			
4.26	-35	4.27	- s
3.343	-100	3.35	-vs
2.458	-12	2.46	- m
2.282	-12	2.28	- m
2.237	- 6	2.24	- m
2.128	- 9	2.13	- m
1.980	- 6	1.98	- w
1.817	-17	1.82	- m
1.801	- 1	--	--
1.672	- 7	1.67	- w
1.659	- 3	1.66	- w
1.608	- 1	--	--
1.541	-15	1.54	- m
1.453	- 3	1.45	- w
1.418	- 1	--	--
1.382	- 7	1.38	- m
1.375	-11	1.375	- m
1.372	- 9	1.372	- m
1.288	- 3	1.289	- w
1.256	- 1	1.256	- w
etc.		etc.	

C. Recommendations for Further Work

A differential calorimeter which would accurately measure both heat contents and heats of transformation and possible heats of reaction and heats of melting would be a logical extension of this work. The primary problem causing inaccuracies has been shown to be unequal heat losses from the cells. It has also been shown that conduction losses rather than the radiation losses are the cause. Therefore, the conduction losses must be minimized.

The suggested design to minimize the conduction losses would incorporate the use of two concentric spheres as the sample cells. The sample containing part of the cell would be the volume between the two spheres. The difference in radii between the two spheres should be as small as practicable. Ribs of metal between the spheres would provide high conducting areas so that the sample might be partially heated from directions other than from that direction of primary heat flow (inside toward the outside). The small difference in radii would minimize the temperature gradient through the sample material. The cells would be suspended by their heating coil leads and the coils would be mounted internally. The cells would be small when compared to the preferably spherical or cubical furnace chamber. The thermocouples would be mounted externally. One cell would remain empty and the other would contain the sample material. This configuration would allow direct measurement of the increase in heat content and heat capacity data.

The secondary problem of ac and dc strays could be eliminated by use of a well shielded low voltage, high amperage environmental heating source. The reduction of voltage would reduce the driving force for

the ac strays. Extreme care should be taken to keep all surfaces free of carbon and oxide films.

Temperature limitations could be minimized by proper selection of materials.

The suggested modifications should result in a differential calorimeter capable of measuring heats of crystallographic transformations, heat contents, and possibly heats of reaction and heats of melting.

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