DESIGN, CONSTRUCTION, AND CALIBRATION OF A HIGH-TEMPERATURE
CALORIMETER; HIGH-TEMPERATURE THERMODYNAMIC PROPERTIES
OF SELECTED INORGANIC COMPOUNDS

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INTRODUCTION

Thermodynamics has become an important, if not essential, tool in the science of extractive metallurgy. The application of thermodynamics to metallurgical processes is becoming more commonplace as valid thermo-dynamic data are being gathered by various investigators. The present work was initiated to provide an apparatus whereby some of these much-needed thermodynamic data may be obtained and to measure the high-temperature heat contents of yttrium metal, tungsten hexachloride, and iron pentacarbonyl.

The usefulness and need of thermodynamic data may be illustrated if the general development of metallurgical processes is considered. The development of metallurgical processes may be divided into periods: first, the discovery of a basic reaction which results in the production of a desired product from available raw materials; second, a long period of process refinement by mechanical development during which little or no attention is given to the reaction; finally, a period of careful study of the chemical reaction itself.

In 1930 Dean (9) wrote concerning the steel industry: "The reaction of carbon with iron ore to produce pig iron and the subsequent refinements of the pig iron by an oxidation reaction is very old. Development in modern times has been almost entirely mechanical, the development of the blast

furnace, the Bessemer process, the Siemens process, and even the Aston process for wrought iron being mechanical improvements almost entirely."

Dean was of the opinion at the time he wrote the preceding that the science of metallurgy was entering the phase where the chemical reactions, themselves, were being considered. The question as to how far a given reaction could be made to proceed was being asked. It seemed as though mechanical processes had been improved to the point where they had approached the limit to which the basic reactions could be pushed, and the determination of this limit or equilibrium condition became of prime interest.

Since 1930 and in particular since World War II many metals of little previous interest or knowledge have become of major concern. The advent of the nuclear and aerospace industries, in particular, have given rise to the study of these "exotic" materials. Such metals as zirconium, hafnium, titanium, columbium, tantalum and many of their compounds are now in demand and their production is important to national security.

The need for these "new" materials is so acute that the development by phases of their production is no longer practical. In addition to determining a reaction whereby a desired product may be produced it is necessary to ask such questions as: under what conditions is this reaction most likely to proceed? Is there another reaction whereby the product may be obtained which would be easier to control and/or result in a better product yield?

The determination of equilibria or end points of chemical reactions by direct means is fraught with difficulty. The reason for this is that mechanical difficulties must be overcome which too often become the limiting factors even in the laboratory and, therefore, the actual limit to which the reaction may be carried cannot be obtained. There are, further, so many reactions of metallurgical materials that to survey each individually is an undertaking of such immensity as to make this course of action virtually impossible.

The thermodynamic viewpoint offers hope at this juncture. Knowing the thermodynamic properties of metallurgical materials the equilibrium of these materials under a given set of conditions may be calculated with reasonable accuracy. The practical or economic interest in a proposed chemical reaction is naturally dependent upon the equilibrium yield of a desired product. The use of thermodynamic data to calculate this equilibrium value rather than attempt each proposed reaction in the laboratory can result in great savings of both time and money.

Metallurgy is rapidly adopting the thermodynamic viewpoint and studies of thermodynamic properties of important metallurgical materials have been increased manyfold in recent years.

The measurement of thermodynamic properties of metallurgical materials is not an easy experimental task. These measurements however do not introduce mechanical difficulties. Furthermore, the number of

measurements necessary is reduced to the number of metallurgically important compounds rather than the almost unlimited number of reactions into which they may enter.

The compilation and evaluation of the data resulting from this work is also a major undertaking. A number of compilations of thermodynamic data have been made, notably those of Kelley (23), Stull and Sinke (43), Brewer (4), and Rossini (38), to mention a few. These compilations are invaluable to the worker in the field who has little time to adequately scan the literature for thermodynamic data and evaluate the values thus obtained.

Compilations such as these are, however, in constant need of revision due to the large amount of work currently in progress. Thermodynamic data are constantly being determined for previously uninvestigated substances as well as to check and improve upon values previously reported in the literature. Past and present workers in the field of metallurgical thermodynamics have by no means exhausted the field. Thermodynamic analyses of proposed metallurgical reactions are still handicapped by the lack of dependable experimental data.

Thermodynamics as applied to metallurgical processes may involve the use of one or more thermodynamic properties of the substances concerned with the particular process. The specific thermodynamic property investigated in this work was enthalpy. The heat evolved or absorbed by a system undergoing a temperature change at constant pressure is equal to the change

in enthalpy of the system. The enthalpy is a property or point function of a

system and, hence, is independent of the path by which the heat transfer

process takes place. Thus when undergoing a change in state, the amount

of heat absorbed or evolved by a metallurgical process may be calculated

from values of enthalpy at the initial and final states. Since one always

considers the change in enthalpy the absolute values of this quantity are

arbitrarily chosen above some reference temperature. The present conven-

tion in metallurgical thermodynamics is to use 25°C. or 298.15°K. as this

base temperature. Enthalpy values measured at temperatures above 25°C.

are designated "high-temperature" values. The symbol used for high-

temperature enthalpy is $H_T - H_{298.15}$. Units of enthalpy to be used in this

work are calories per gram mole.

Specific heats are obtained from enthalpy values by the defining

relationship $C_p = \left(\dfrac{\partial H}{\partial T}\right)_p$. This procedure is no disadvantage in most thermo-

dynamic calculations since enthalpy is more fundamental in this connection

than is specific heat.

Conversion of data to a specific heat basis is usually unnecessary

and may be omitted.

The means of mathematically representing high-temperature

enthalpy data has been discussed at length by Maier and Kelley (30). Their

suggested equation is of the form $H_T - H_{298.15} = aT + bT^2 + cT^{-1} + d$,

where T is the absolute temperature and a, b, c, and d, are constants

determined from experimental data. An expression for specific heat may be readily obtained from this equation by differentiation giving $C_p = a + 2bT - cT^{-2}$. The equation of Maier and Kelley does not always represent the best form in which experimental data may be represented, but for the sake of consistency among various investigators this form is in general use in the field.

There are three general classes of experimental methods used for determining high-temperature enthalpies and specific heats. They are: (1) methods depending on heating or cooling rates, (2) methods of direct determination of true specific heats, and (3) the method of mixtures or the "dropping method."

Methods depending on heating or cooling rates usually involve the comparison of these rates for substances being investigated with the corresponding rate for a substance of known specific heat, under supposed identical conditions. The reason for the relatively few precise results obtained by this method has been largely due to differences in thermal conductivity between the substance investigated and the standard substance and due to imperfectly reproducible heating or cooling conditions. Reproducibility is particularly important at high temperatures where small changes in geometry may seriously alter the rate at which radiant energy is received.

Methods for directly obtaining true specific heats involve the measurements of the quantity of heat required to raise the temperature of a known mass of substance by a relatively small amount. In order to obtain accurate

results from this method it is imperative to evaluate accurately heat inter-
change with the surroundings. Failure to do this has precluded accurate
measurements using this method, particularly at higher temperatures. One
of the more successful attempts to measure specific heats by this method has
been reported by Seekamp (30). White (48), in discussing the difficulties in-
volved in some methods of this type concluded by stating: "This account of
our investigations shows many points which could be made much clearer by
further experiment. The very number of these is a strong reason for not
continuing further. For even after a good deal more had been done still more
would seem desirable. One reason for the present work was to test the
probable value of the furnace calorimeter for certain very delicate deter-
mination of specific heats. The conclusion reached was that the dropping
method is more promising."

The method of mixtures has been widely and frequently employed.
This method consists of heating a substance under investigation in a furnace
to an accurately controlled and measured temperature then dropping it into a
calorimeter operating at or near room temperature. This method determines
the change in enthalpy of the substance between the temperature of the furnace
and that of the calorimeter.

There are two disadvantages of the method of mixtures that should
be mentioned:

1. The method is sometimes inadequate for obtaining heats of

transition particularly if the heat of transition is small. The heat of transition is obtained by measuring two relatively large quantities of heat, one for the higher and one for the lower-temperature modification and subtracting the latter of these from the former. Any error in the large quantities of heat then appears as error in the relatively small difference. These errors may be negligible in comparison to the large values but may represent too great an inaccuracy when applied to the small difference.

2. It may happen that the substance being investigated changes state upon heating and does not revert to its original state when cooled in the calorimeter. In discussing this possiblity Kelley (23) states, "while this is sometimes a nuisance, it is inconceivable that the careful experimenter would be misled by such behavior."

The method of mixture does, however, possess some distinct advantages, notably:

1. It is direct and reasonably rapid.

2. The results are quite reproducible, since conditions of data measurement may be repeated without an undue amount of difficulty.

3. There are no extraneous assumptions involved.

Many workers in the field have sought methods for measuring enthalpies or specific heats which would overcome the previously mentioned disadvantages inherent in the method of mixtures. To date, however, no such method has been devised that is widely applicable both as to the type of

substance investigated and to the temperature range of measurement. The method of mixtures remains the most used and most fruitful source of accurate thermodynamic data.

There are three types of calorimeters in use employing the method of mixtures. The calorimeter may be of the water type as described by White (47) or of the metal-block type described by Jaeger and Rosenbohm (19) Southard (41), and Kelley, Naylor, and Shomate (22); or of the ice type as described by Ginnings and Corruccini (15), Leake and Turkdogan (28), and Furukawa, et al. (13). These types of calorimeters all measure the amount of heat evolved as a substance cools from the furnace temperature to the calorimeter temperature.

In the water type the sample cools by transferring its heat to a known amount of liquid water. The temperature change of the water is then indicative of the enthalpy of the sample. Possible difficulties using a calorimeter of this type are: (1) rapid heat transfer to the water could result in vaporization which would obviously introduce errors; (2) the temperature of the water changes constantly making accurate determination of the calorimeter temperature difficult; and (3) costly instrumentation is required to accurately measure the relatively small temperature change of the water.

In the metal block type the sample cools by transferring heat to a relatively massive block of a good conducting metal such as copper. This method possesses some disadvantage also, notably: (1) the temperature of

the metal block changes as it receives heat making determination of the calorimeter temperature difficult; (2) costly instrumentation is required to measure accurately the relatively small temperature change of the block, and (3) the metal block being massive with respect to the dropped sample, will possess temperature gradients throughout its cross section making any temperature measurement of the block definitely dependent upon the location at which such measurements are taken.

The ice type involves heat transfer from the dropped sample to ice enclosed in a constant volume chamber. The effect of this heat transfer is the melting of a portion of the ice. A pool of mercury in the bottom of the constant volume chamber is connected to an external reservoir of mercury by a small tube. As the ice changes phase from solid to liquid its volume decreases. Mercury is then drawn into the chamber from the external reservoir to compensate for the change in volume of the ice. The amount of mercury drawn into the constant volume chamber is, then, directly proportional to the amount of heat transferred to the ice from the capsule and sample. Advantages of the ice calorimeter are: (1) the temperature of the calorimeter remains constant, and (2) the only instrumentation required is a balance to measure the weight change of the external mercury reservoir.

The determination of accurate thermodynamic values is dependent upon the use of a pure substance for investigation – the experimental data being no better than the substance upon which measurements are performed.

The thermodynamic investigations described herein were performed at the Albany Metallurgy Research Center of the U. S. Bureau of Mines under a cooperative agreement between the Bureau of Mines and Oregon State University. The Albany center of the Bureau has as one of its major objectives the preparation of inorganic compounds in as pure as possible form. As a consequence the station has available certain elements and compounds in as pure form as is presently available. The construction and operation of one or more calorimeters to measure the thermodynamic properties of these substances was a natural consequence of work already in progress at this site. It is expected that the thermodynamic investigations thus made will assist metallurgists both at the Bureau of Mines and elsewhere in future research concerning those substances investigated.

DESCRIPTION OF EQUIPMENT

The equipment used to determine high-temperature enthalpy data included an ice calorimeter with which enthalpy values were measured; a high temperature furnace and related temperature controls used to heat the sample to a predetermined temperature prior to its drop into the calorimeter; and temperature measuring equipment to establish the temperature of the sample while in the furnace.

Calorimeter

The ice calorimeter used in this work is shown schematically in figure 1. Its principal components, along with the mercury accounting system, are labeled in order to aid the following description of the equipment.

The central tube of the calorimeter (19) was fabricated of 1/16 inch thick copper, tapering from 7/8 inch O.D. at the top to 5/8 inch at the bottom. The tapered portion of this tube was 8 inches long, the taper then being 1/32 inch per inch of tube length. Twenty-two circular discs 2 inches in diameter were cut from 0.032 inch copper sheet. These discs were then silver soldered to the periphery of the central tube at intervals of 3/8 inch. Initial attempts at freezing an ice mantle encountered difficulty in forming ice of sufficient thickness around the bottom fin. For this reason the bottom fin was cut to an outside diameter of 1-1/4 inches. After this alteration an ice mantle of nearly uniform thickness was obtained with relative ease.

1. Mercury reservoir
2. Scale
3. Capillary arm
4. Mercury accounting system
5. Removable beaker
6. Three-way valve
7. Mercury line
8. Ice canister
9. Brass flange
10. Wax impregnated gauze
11. Spacer ring
12. O-ring seal
13. Brass clamping collar
14. Ice mantle
15. Water
16. Mercury
17. Outer glass vessel
18. Inner glass vessel
19. Central calorimeter tube
20. Nylon sleeve
21. Upper calorimeter tube
22. Radiation gate
23. Water feed line

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FIGURE I.- Ice Calorimeter.

The purpose of the fins was twofold. First they increased the effective heat transfer area between the capsule and ice mantle. Once the portion of the ice mantle next to the calorimeter tube melted leaving a layer of water in this area the mantle would have a tendency to slide or change its position with respect to the calorimeter tube. The second purpose of the fins was to prevent this from happening.

Extending 1/2 inch above the tapered portion of the central calorimeter tube was a straight threaded section of 7/8 inch outside diameter. A nylon sleeve (20) joined the lower calorimeter tube to the supporting upper tube (21). Nylon was used for the sleeve construction because of its chemical inertness, its "memory" or ability to resume its original shape when mechanically deformed, and its relatively low thermal conductivity. All metal parts above the nylon sleeve were also fabricated from materials possessing lower thermal conductivities than copper to minimize the conduction of heat away from the ice mantle.

The upper calorimeter tube was made of brass and had brass flanges soldered to it for the purpose of holding two glass vessels in place. The inner glass vessel (18) was formed from pyrex tubing of 75 millimeters outside diameter, 2.4 millimeters wall thickness and was 12 inches long. This inner vessel enclosed the lower calorimeter tube and contained distilled water (15), the ice mantle (14), and mercury pool (16). This portion of the calorimeter will be referred to hereafter as the mantle chamber.

Concentric with the inner vessel was a 14-1/2 inch long outer glass vessel (17) formed from pyrex tubing of 100 millimeters outside diameter and 2.4 millimeters wall thickness. The space between the two vessels contained air which insulated the mantle from the surrounding ice bath.

The upper 3/4 inch of each glass vessel was wound with gauze (10) which was thoroughly impregnated with picene wax which bonded the gauze to the glass surface. The glass vessels were held firmly to the flanges by threaded clamping collars (13) and neoprene "O-ring" gaskets (12) which gripped the wax-impregnated gauze. The "O-rings", in addition to gripping the gauze to hold the vessels in place, also afforded a seal around each of the glass vessels. This sealing arrangement was quite simple and could be broken easily for quick disassembly of the unit. A detailed view of these seals is shown in figure 1.

Directly above the upper calorimeter tube was a 1/2-inch thick copper disc (22), 5 inches in diameter, enclosed in a brass housing. This disc will be referred to hereafter as the radiation gate. This gate minimized radiant energy interchange between the furnace and the calorimeter well. The gate and its housing are illustrated in figure 2. A peg attached to the housing extended into a slot in the gate. The contact of this peg with either end of the slot limited the rotation of the gate mechanism to a circular arc of approximately 45 degrees. Prior to dropping the sample the gate was maintained in the closed position; the gate was opened during the
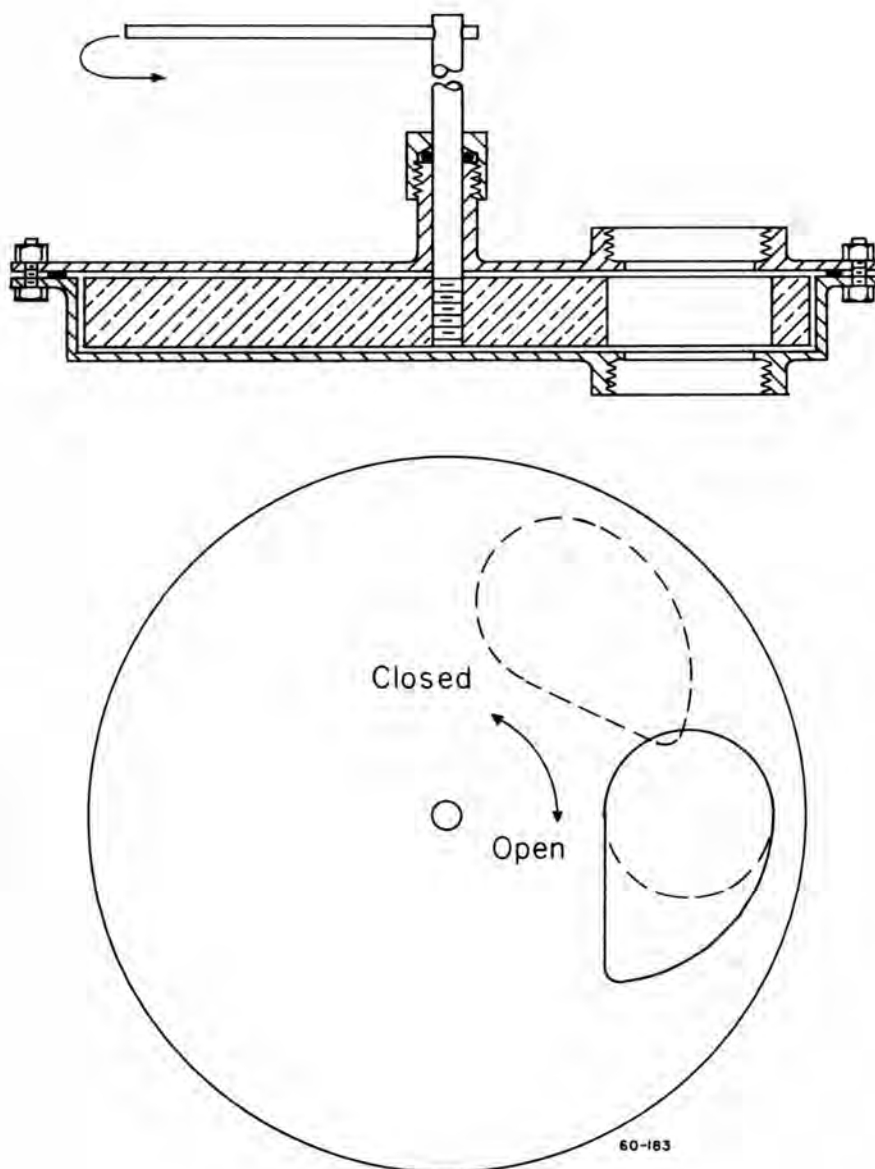
FIGURE 2.- Radiation Gate.

dropping period to allow the capsule to pass from the furnace into the calorimeter well and then the gate was reclosed. In the closed position the opening was only large enough to accommodate the suspension wire which held the sample container. A stop insured that the gate closed to the same size opening for each sample drop and that the suspension wire was not sheared off. The gate was silver plated on both sides to decrease its emissivity thereby minimizing radiant energy transfer. The gate and its housing, together with the calorimeter components previously discussed, were positioned in a bath of crushed ice and water to maintain the temperature gradient in all directions essentially zero. A 1-1/8 inch diameter steel tube extended 8-3/4 inches above the gate housing to within 1/16 inch of the central tube of the furnace.

A stainless steel tube (7) of 1/8-inch outside diameter extended from the mercury pool in the mantle chamber up through the ice cannister (8) and thence to the glass mercury accounting system (4). This tube afforded the passage by which the mercury left or entered the mantle chamber as the ice mantle was frozen or melted. The tube was coiled three times in the ice cannister to provide sufficient contact between the mercury and ice, thus insuring that any mercury entering the calorimeter was at $0°$C.

Furnace

The furnace used to heat the sample and enclosing capsule to a desired temperature is illustrated in figure 3. The furnace was mounted vertically on bearings (12) which permitted its rotation at the time of a sample drop to a position directly above the calorimeter tube.

The furnace core consisted of two concentric alundum cylinders. The inner cylinder (9) of 1-1/2 inch outside diameter and 24 inches in length was ground to fit snugly inside the outside cylinder (8). Specially ground grooves, 1/16 inch in depth with 3/8 inch pitch were ground bifilarly into the outside surface of the inner cylinder to position the heating element wire (7). The heating element consisted of 48 feet of number 20 B and S gage platinum -10 percent rhodium wire. The outer alundum cylinder had an inside diameter of 1-1/2 inch, an outside diameter of 2 inches and was 24 inches long. The ends of the furnace tube were supported in specially designed alundum blocks. The entire furnace core was separated from the furnace shell (4) by 4 inches of powdered alumina insulation (6).

The control thermocouple (11) was a single-junction, platinum and platinum 13 percent rhodium element. The junction was located directly adjacent to the heating element midway between the ends of the furnace tube. The elements of the control thermocouple were enclosed in a 3/16 inch ceramic protection tube which extended out to the shell of the furnace.

1 . Aluminum plunger

2 . Pt–10% Rh suspension wire

3 . Indicating thermocouple

4 . Furnace

5 . Air space

6 . Insulation

7 . Pt–10% Rh heating element

8 . Outer furnace tube

9 . Inner furnace tube

10 . Pt–10% Rh capsule containing sample

11 . Control thermocouple

12 . Ball bearings

13 . Ceramic plug

14 . Counterweight

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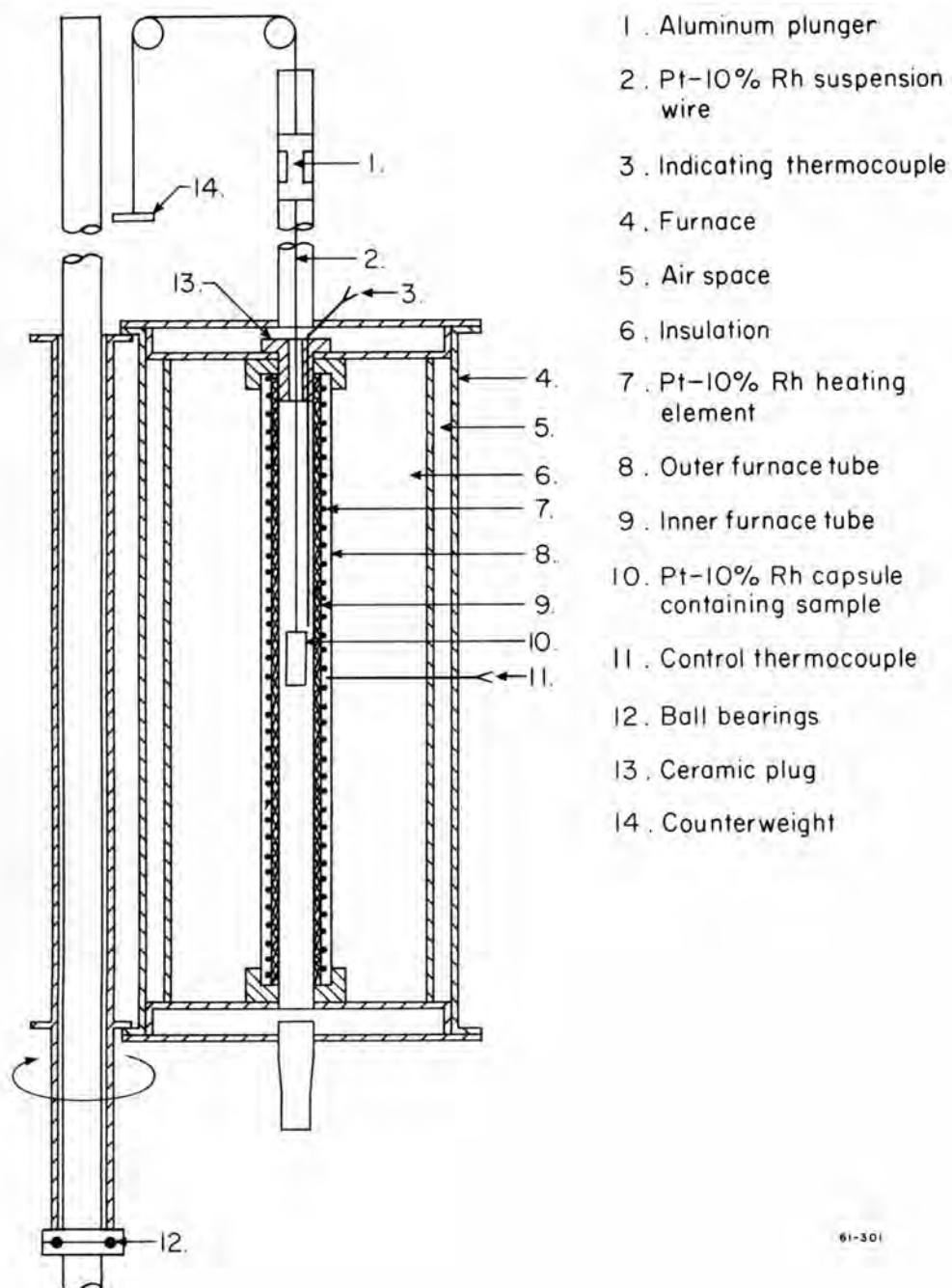
FIGURE 3.-Furnace and Associated Equipment.

These elements were connected to terminals on the furnace shell and thermocouple lead wire led from these terminals to the panel-mounted temperature control unit. In the control unit the signal from the control thermocouple was compared with the set-point temperature which had been previously set by the operator. After comparing the two signals, the unit applied a D.C. voltage to a magnetic amplifier where this signal was amplified and applied to the core of a saturable-core reactor. The primary side of the reactor was connected to a 110 volt, 60 cycle outlet. The power from the secondary side of the reactor to the primary furnace element was controlled by the D. C. potential applied to the core of the reactor. This D. C. potential varied in proportion to the magnitude of the difference between the set-point and furnace temperatures. Utilizing this control, the furnace temperature as measured by a separate thermocouple was maintained to within one-half of 1°C. over the entire operating range from 400 to 1600°K.

Readings of thermocouple E.M.F. values taken at 1 inch intervals throughout the length of the furnace indicated an essentially isothermal zone in the middle three inches of the furnace. Temperature variation in this zone was less than 1°C. Figure 4 shows the temperature profiles obtained by traverses at different temperature readings of the indicating thermocouple. These data are presented in table I. The different profiles clearly show the isothermal zone but also indicate that this isothermal zone moves

TABLE 1. - Furnace temperature profile data
center winding only

Indicating TC: Start	6.530	7.640	8.719	9.879	11.067	12.251
: End	6.530	7.643	8.720	9.882	11.065	12.257
Temperature	1000	1100	1200	1300	1400	1500

Distance from bottom
of heating element, in
inches

0	0.382	0.455	0.523	0.598	0.677	0.751
1	0.542	0.745	0.916	1.193	1.421	1.667
2	1.185	1.559	1.958	2.414	2.975	4.278
3	2.269	2.928	3.635	4.490	5.682	7.512
4	3.361	4.215	5.107	6.271	7.311	8.900
5	4.216	5.185	6.185	7.096	8.345	9.827
6	4.827	5.872	6.933	7.923	9.110	10.539
7	5.230	6.343	7.477	8.555	9.626	11.160
8	5.552	6.720	7.863	9.061	10.210	11.430
9	5.825	7.003	8.160	9.419	10.575	11.779
10	6.061	7.225	8.395	9.600	10.781	12.046
11	6.257	7.422	8.584	9.838	11.011	12.163
12	6.398	7.575	8.728	9.896	11.063	12.264
13	6.494	7.650	8.788	9.903	11.084	12.267
14	6.536	7.668	8.788	9.901	11.079	12.261
15	6.530	7.640	8.720	9.877	11.065	12.258
16	6.486	7.558	8.594	9.826	11.030	12.229
17	6.387	7.422	8.419	9.602	10.832	12.031
18	6.226	7.240	8.173	9.315	10.327	11.655
19	6.003	6.958	7.856	8.963	10.199	11.337
20	5.689	6.607	7.454	8.584	9.628	10.853
21	5.284	6.128	6.916	7.996	9.073	10.283
22	4.760	5.536	6.245	7.235	8.335	9.518
23	4.132	4.766	5.437	6.341	7.384	8.551
24	3.376	3.904	4.421	5.156	6.003	7.127

TABLE I. - Furnace temperature profile data
center winding only

Indicating TC: Start	0.847	1.669	2.566	3.483	4.500	5.503
End	0.847	1.667	2.566	3.482	4.521	5.539
Temperature	400	500	600	700	800	900

Distance from bottom
of heating element, in
inches.

0	0.161	0.184	0.216	0.243	0.297	0.344
1	0.173	0.202	0.249	0.299	0.415	0.519
2	0.195	0.346	0.511	0.606	0.789	1.007
3	0.202	0.538	0.652	1.097	1.444	1.846
4	0.283	0.614	0.901	1.620	2.147	2.742
5	0.341	0.797	1.173	2.047	2.793	3.459
6	0.410	0.902	1.341	2.392	3.167	3.974
7	0.512	1.083	1.588	2.623	3.508	4.361
8	0.576	1.134	1.772	2.806	3.737	4.647
9	0.654	1.280	1.903	2.972	3.925	4.885
10	0.685	1.386	2.087	3.116	4.107	5.103
11	0.748	1.444	2.212	3.248	4.259	5.280
12	0.800	1.529	2.396	3.354	4.388	5.413
13	0.819	1.598	2.494	3.431	4.470	5.500
14	0.845	1.667	2.561	3.467	4.513	5.541
15	0.845	1.668	2.567	3.483	4.521	5.541
16	0.844	1.667	2.563	3.473	4.500	5.503
17	0.839	1.607	2.474	3.431	4.433	5.413
18	0.831	1.597	2.429	3.354	4.320	5.268
19	0.825	1.533	2.383	3.234	4.163	5.076
20	0.818	1.509	2.244	3.057	3.942	4.797
21	0.810	1.462	2.110	2.856	3.656	4.446
22	0.803	1.324	1.875	2.555	3.296	4.002
23	0.799	1.269	1.647	2.242	2.853	3.480
24	0.764	1.090	1.527	1.931	2.338	2.841
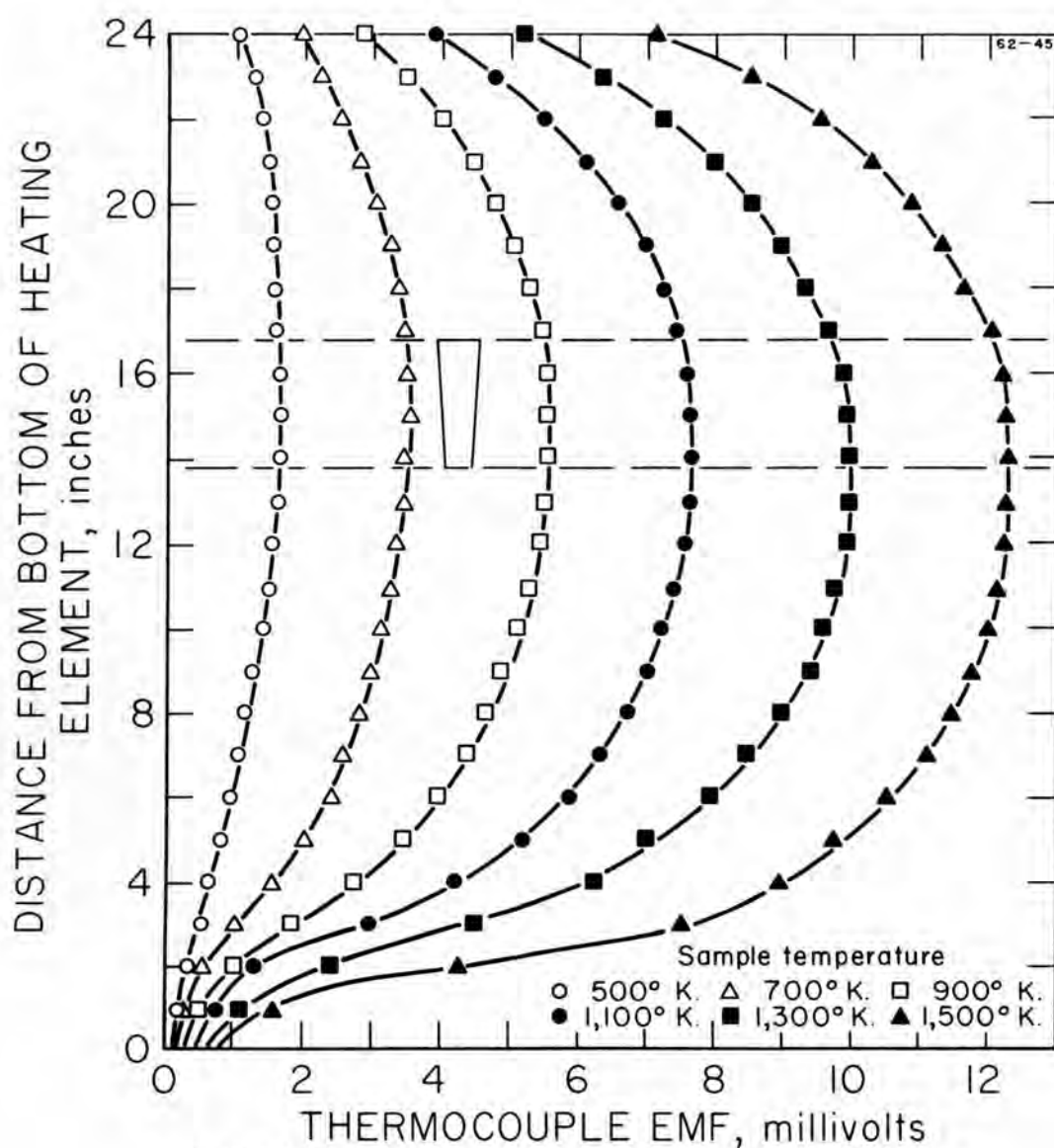
FIGURE 4.-Furnace Temperature Profiles
Without Supplementary Windings.

laterally downward in the furnace as the temperature is increased. To counteract this effect supplementary windings of platinum -10 percent rhodium were wound at each end of the furnace tube. These supplementary windings were connected in series and were connected to a powerstat for control. Manual control of the power applied to these supplementary windings produced a flatter temperature profile as indicated in figure 5. The temperature profile shown in figure 5 obtained when the supplementary windings were used in conjunction with the primary furnace element shows the presence of a longer isothermal zone in the portion of the furnace where the capsule was suspended.

A steel tube of 1 inch inside diameter extended 4 feet above the furnace. The internal surface of this tube was ground to a close tolerance to accomodate a 2 inch long aluminum plunger (1). A 24 gage platinum -10 percent rhodium suspension wire (2) connected the plunger to the sample capsule (10). This wire passed through a small hole in a ceramic plug (13) in the top of the furnace. The plunger was connected by a nylon cord to an external counterweight (14). This arrangement insured a continual connection with the capsule thus enabling the operator to extract it easily from the calorimeter tube after a drop. The counterweight was made of soft iron and was in the field of a small solenoid when the capsule was in its proper position inside the furnace. A switch in the field circuit for the solenoid was mounted in front of the calorimeter housing. This arrangement provided
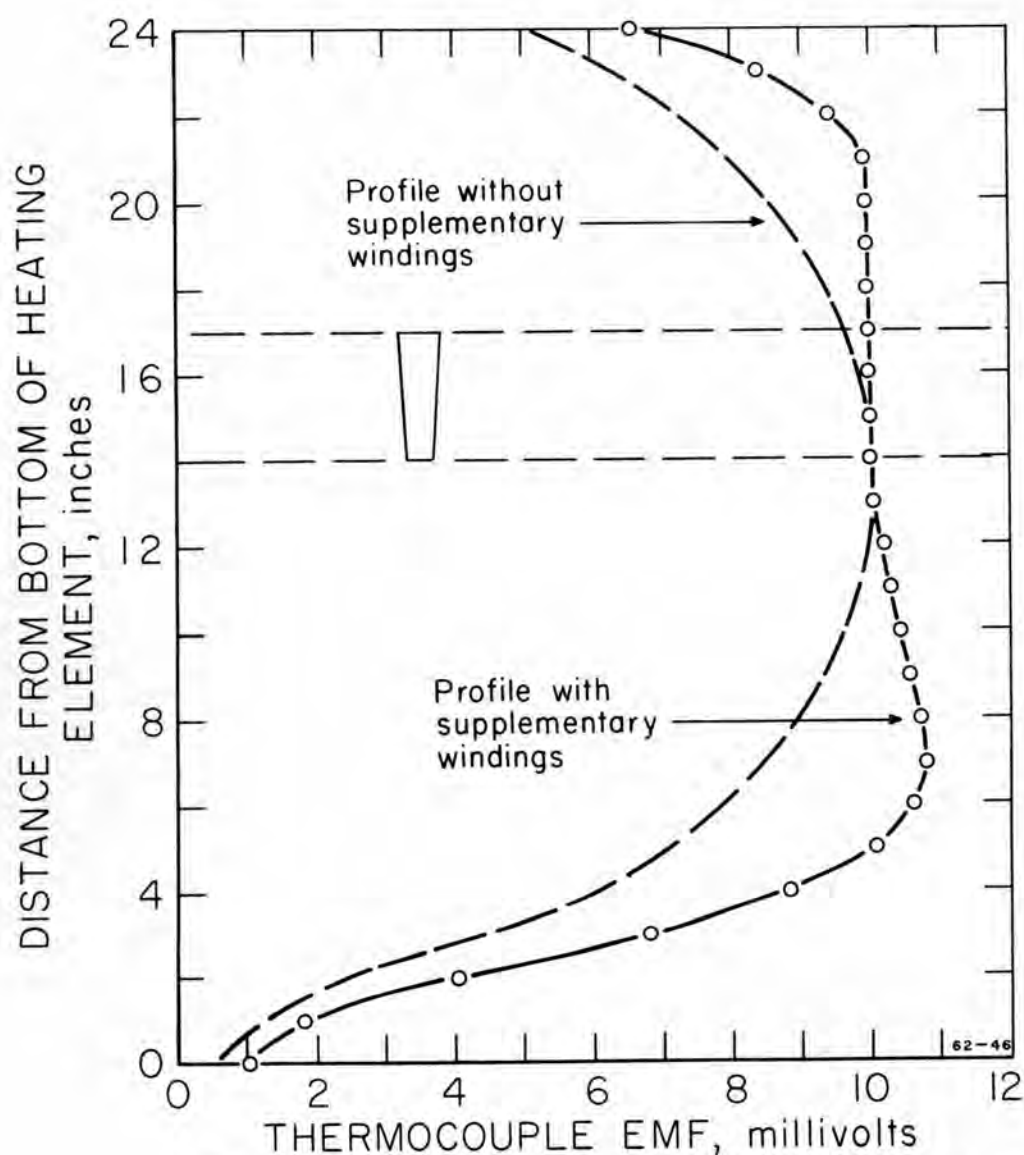
FIGURE 5.-Furnace Temperature Profile at
1,300° K. Sample Temperature With
Supplementary windings.

a means whereby the switch could be thrown by the operator to allow the capsule to drop from the furnace into the calorimeter in conjunction with the opening of the radiation gate, allowing the gate to remain open for identical periods of time during each run.

The close fit between the aluminum plunger and steel tube provided a braking action as the plunger descended in the tube. As the plunger fell, air in the bottom of the tube was compressed and forced to escape through the small space between the plunger and the tube wall. This air cushion allowed the capsule to settle more slowly into the calorimeter than if it were in free fall. The length of time for the capsule to traverse the distance from its place of suspension in the furnace to the bottom of the calorimeter tube was measured to be 3.0 ± 0.1 seconds.

Temperature Measurement Equipment

The temperature of the capsule and enclosed sample when in the furnace was measured by a single-junction thermocouple (3, fig. 3) of platinum and platinum -10% rhodium, the hot-junction of which was located one millimeter above the top of the capsule. This thermocouple will be referred to hereafter as the indicating thermocouple. The thermocouple elements were enclosed in a 3/16-inch ceramic protection tube which was mounted vertically in the refractory plug (13 fig. 3) in the top of the furnace tube. An ice-bath cold junction was used for reference temperature compensation. The indicating thermocouple was calibrated initially by

comparison with a National Bureau of Standards certified platinum -10 percent rhodium thermocouple. After each 30 hours of operation above 1000° C the thermocouple was recalibrated at the gold point. A Rubicon portable potentiometer was used to measure the thermocouple e.m.f.

The entire apparatus is shown pictorially in figure 6. In this view one may observe the furnace control panel on the left, the calorimeter and furnace on the center and the mercury system to the right. The furnace is rotated away from the calorimeter in this figure to allow a better view of the calorimeter.

The apparatus is shown in figure 7 while in operation. In this view the furnace is in position directly above the calorimeter. Clearly shown in this view are the stainless-steel radiation shield between the furnace and the calorimeter, the crushed ice surrounding the calorimeter, and the styro-foam insulation around the outside of the ice bath. The operator is shown reading the temperature of the capsule in the furnace using a portable potentiometer.
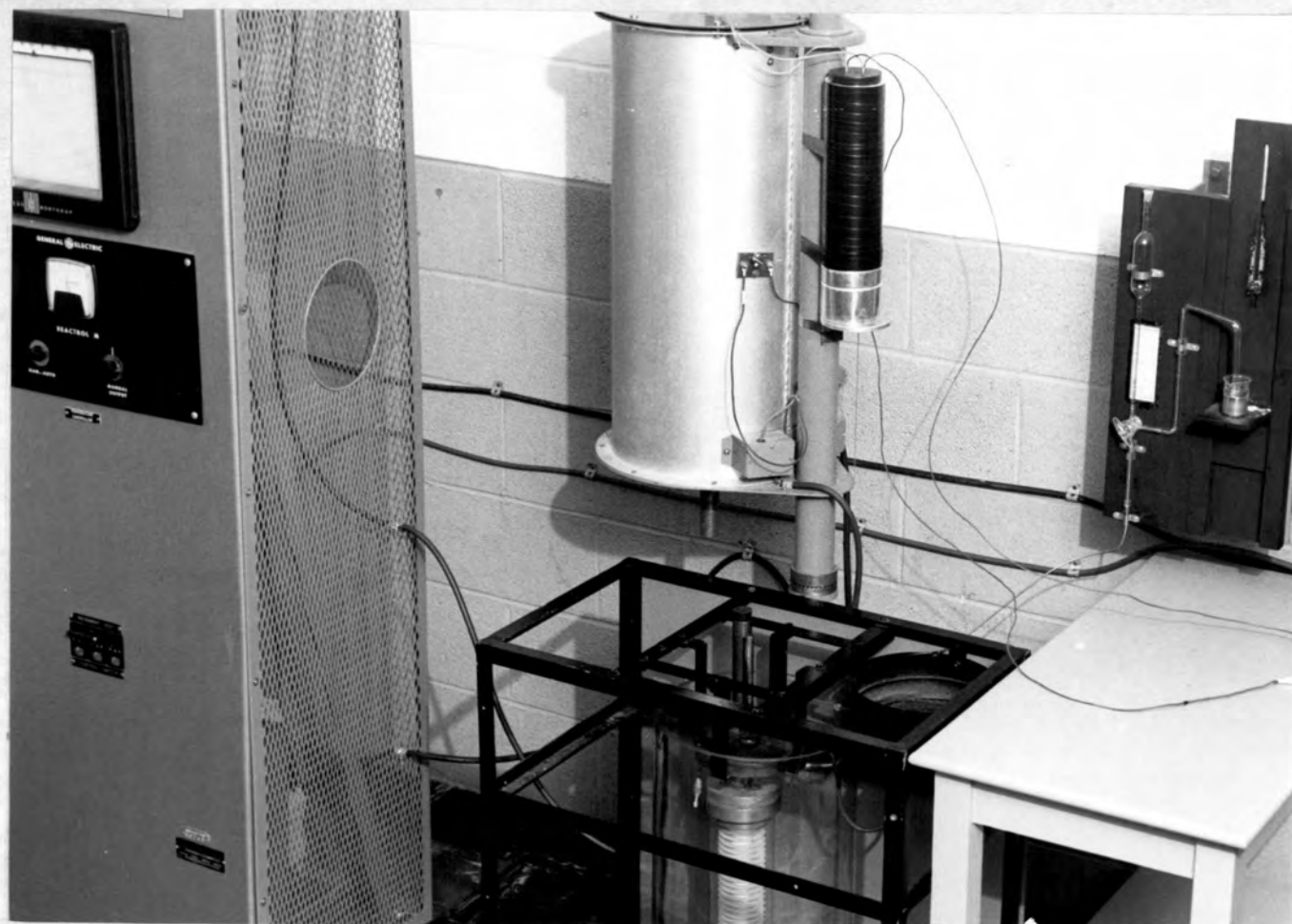
FIGURE 6.-Enthalpy Determination Apparatus

FIGURE 7.–Enthalpy Determination Apparatus in Operation

OPERATING PROCEDURE

In the following section the operational procedure for the ice calorimeter and its associated equipment is described. Portions of equipment operation that are described in detail are: filling the mantle chamber, freezing the ice mantle, and an account of data determination including the evaluation of the heat-leak rate. In the following description of operational procedure, the numbers following each item of equipment mentioned refer to the labeling in figure 1.

Filling the Mantle Chamber

Following assembly of the calorimeter, distilled water that had been de-aerated by boiling was introduced into the mantle chamber. This was accomplished by applying suction at the end of the tube (23) leading out the top of the mantle chamber, thus pulling water in through the accounting system (4). The chamber was completely filled with water by this process. An ice mantle was then frozen around the central tube which, due to the increased volume of the ice formed, forced some of the remaining water back out of the accounting system. A beaker of mercury (5) was then placed at the outlet of the accounting system as shown in figure 1 and mercury was sucked into the mantle chamber as well as into the accounting system as the ice mantle melted. The chamber was carefully observed during the filling operation to insure

that no air bubbles were present. The contents of the mantle chamber required no further alteration during the operation of the calorimeter.

Freezing the Ice Mantle

The initial step in determining a single enthalpy value involved freezing the ice mantle around the central tube and fins. The ice mantle was frozen by inserting inside the calorimeter tube another, closely fitting copper tube, which was filled with a dry ice-acetone mixture. Two copper tubes were used, one to freeze the lower portion of the mantle and the other to freeze the upper portion. The mantle chamber was observed visually during the freezing operation in order to better control the type of mantle frozen. The mantle was frozen thick enough to avoid the creation of holes during the period of heat transfer. If a hole had been produced in the ice mantle, heat could have been transferred directly out into the water surrounding the mantle. The method of evaluating the amount of heat transferred involved using mercury from the accounting system to replace the change in volume as the ice was melted. Any additional heat sink would lead to erroneous results. The freezing of a too thick mantle decreased the sensitivity in measuring the heat transfer and increased the possibility of breaking the glass vessel enclosing the mantle chamber. An optimum shape of the ice mantle was determined by

experience and an attempt was made to secure the optimum shape each time an ice mantle was frozen. The lower portion of the ice mantle where most of the heat was absorbed was first frozen to the desired thickness; the freezing of the upper portion was then accomplished. The thickness of the ice mantle at any position was controlled by the level of the dry ice-acetone mixture in the inserted tube and by the length of time of freezing. Immediately following the formation of the ice mantle a crushed ice-water mixture was added to the outer bath which completely surrounded the calorimeter and radiation gate. Ice was also added to the ice cannister at this time.

Heat Leak Rate Determination

High temperature enthalpy values were obtained by measuring the weight of mercury displaced as a portion of the ice mantle surrounding the central calorimeter tube was melted. Melting of the ice mantle was a result of the hot capsule and enclosed sample transferring heat to the ice mantle by virtue of the existing temperature difference. The decrease in volume as a portion of the ice mantle melted caused mercury to be drawn in from the external mercury reservoir beaker (5) which was weighed before and after the sample drop. The weight of mercury drawn into the calorimeter was then indicative of the enthalpy of the sample and capsule at the temperature to which they were heated prior to being dropped into the central calorimeter tube.

The weight of displaced mercury determined in this manner could be converted directly into enthalpy units provided all of the mercury drawn into the calorimeter was a result of heat transferred from the sample and capsule to the ice mantle. This, however, was not the case. A small amount of heat was observed to reach the mantle chamber despite attempts to insulate it from the surroundings. The weight of mercury drawn into the calorimeter had to be corrected to account for this extraneous heat or "heat leak".

The initial technique used for heat-leak evaluation involved measuring the time for the mercury level in the capillary arm (3) of the mercury accounting system (4) to fall a prescribed distance as measured by the scale (2) behind the capillary arm. This procedure was followed when the three-way valve (6) was positioned so that mercury drawn into the calorimeter as a result of any heat leak was supplied by the capillary arm. The heat-leak rate was measured in this manner before and after the sample drop and an average value applied to the time interval between weighings of the mercury reservoir beaker.

All such heat-leak rate determinations were accomplished with the furnace rotated into the drop position above the calorimeter. A stainless steel radiation shield was placed between the furnace and calorimeter to minimize radiant energy interchange between the two.

The furnace was maintained at the operating temperature during all heat-leak rate evaluations. This made conditions for the heat-leak rate determination identical to those for the subsequent sample drop and enthalpy measurement.

Data obtained using the technique for heat-leak evaluation were quite consistent as long as the weight of mercury displaced due to heat leak was a small percentage of the total weight of mercury displaced. Determinations made at low temperatures such as those for iron carbonyl initially showed a slight amount of scatter. It was thought that since extremely small total amounts of displaced mercury were involved that any errors involved in the heat leak evaluation could account for the small inconsistencies present. Room temperature fluctuations were also observed to affect the consistency of the data, further indicating a possible error in heat-leak determination.

A new method of heat-leak evaluation was devised to overcome these problems. A typical datum determination is plotted in figure 8 and the measured values corresponding to this plot are presented in table 2. The mercury reservoir beaker was weighed at 5 minute intervals before and after the sample drop. The time between weighings was measured by a stopwatch. Table 2 gives the weight of the beaker and contained mercury at regular time intervals from the start of the run.
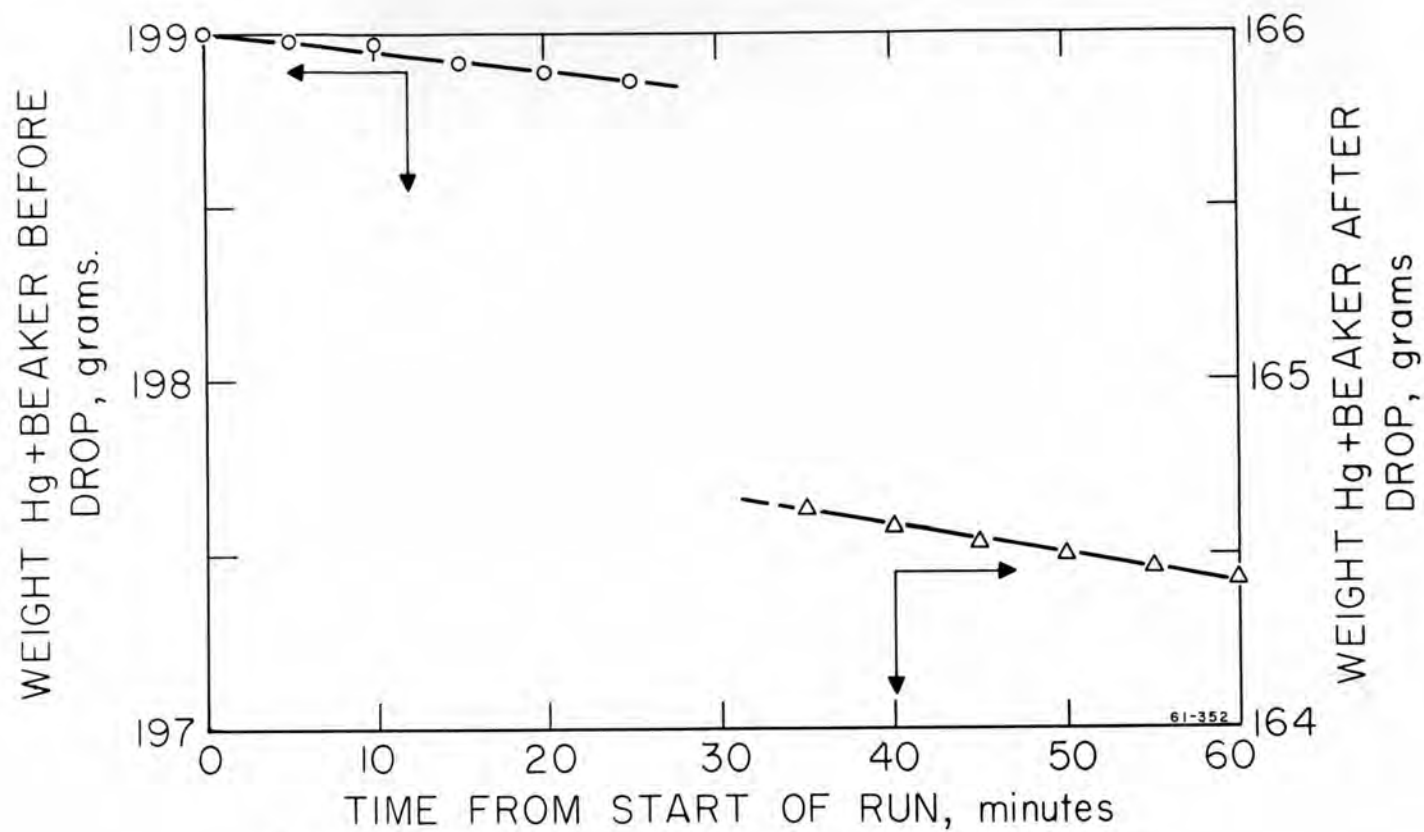
FIGURE 8.- Enthalpy Determination for Yttrium
Metal at 1,200° K.

TABLE 2. - Enthalpy determination of yttrium metal

Temperature * 8.735 MV, 926.9° C., 1200.0° K

Time from start of weighing, minutes	Wt. beaker + mercury, grams
0	199.0115
5	198.9840
10	198.9773
15	198.9148
20	198.8947
25	198.8692
28	sample dropped into calorimeter
35	164.6362
40	164.5833
45	164.5357
50	164.5011
55	164.4710
60	164.4286

*Temperature measurement by a calibrated Pt-10% Rh thermocouple with ice-bath reference temperature compensation.

At each of the five minute intervals the three-way valve of the mercury accounting system was positioned so that the mercury drawn into the calorimeter was supplied by the capilliary arm. This allowed a continuous supply of mercury to the calorimeter while the mercury reservoir beaker was removed for weighing. When the mercury reservoir was replaced after weighing the three-way valve was positioned so that the beaker once more supplied mercury to the calorimeter. Care was taken to be sure that the mercury level in the capilliary arm of the mercury accounting system was the same each time the beaker was removed for weighing. This was done to insure that the mercury level in the system remained the same and that all mercury drawn into the system from the beaker was accounted for accurately.

A plot such as that illustrated in figure 8 was made concurrently with the weighings. When the weight of mercury and beaker became a linear function of time indicating a constant heat-leak rate the sample was dropped into the central calorimeter tube. Approximately 10 minutes after the final weighing prior to the sample drop periodic weighings of the mercury reservoir were begun again. When the weight again became a linear function of time the run was terminated. This complete process took approximately 1 hour.

The first weighing of the mercury reservoir beaker following the sample drop was made seven minutes after the drop took place. Subsequent weight values at five-minute intervals fell on a straight line through the second weight value indicating that the sample and capsule were in thermal equilibrium with the ice mantle within twelve minutes of the time of the drop.

The slope of the upper line in figure 8, which was the heat-leak rate prior to the drop, was calculated to be 0.9486×10^{-4} grams of mercury displaced per second. The heat-leak rate following the drop was calculated to be 1.2892×10^{-4} grams of mercury displaced per second. The quantity to be determined from these values was the weight of mercury displaced due to heat leak in the ten minute interval between weighings during which the sample was dropped into the calorimeter.

The initial heat-leak rate of 0.9486×10^{-4} grams per second was applied to the three minute period before dropping the sample and capsule. The weight of mercury displaced due to heat leak during this three minute interval was 0.0171 grams. The second heat leak rate of 1.2892×10^{-4} grams per second was applied over the last twelve minutes of this interval resulting in a displacement of 0.0928 grams of mercury during this time interval. The sum of these two values, 0.1099 grams was then the calculated amount of mercury displaced

during the drop interval due to heat leak and will be referred to henceforth as the heat-leak correction.

The total weight of mercury displaced during the drop interval was the difference between the weight at the beginning of the interval and the weight taken fifteen minutes later. This value was 34.2859 grams. Subtracting the heat-leak correction from this value gave as a result 34.1760 grams of mercury displaced by the hot capsule and sample due to their combined enthalpies at 1200.0° K.

The second method of heat leak evaluation applied a heat-leak correction over a fifteen-minute interval instead of the hour or more as was done initially. This shorter time interval caused the heat-leak correction to be a much smaller value in proportion to the total weight of displaced mercury. This as well as the fact that differences in heat-leak values before and after the sample drop were accurately accounted for made this method the more preferable of the two. All yttrium metal, iron pentacarbonyl and tungsten hexachloride data were obtained using the newer method. Subsequent work with this apparatus will also employ the newer method.

The heat-leak correction was in all cases small, but the accurate determinations of and accounting for this effect was necessary for precise experimental results.

EVALUATION OF THE CALIBRATION FACTOR

A calibration factor for the ice calorimeter was required before high-temperature enthalpy values could be determined experimentally. This involved establishing the calibration factor, K, which related the weight of mercury drawn into the calorimeter to the number of calories of heat absorbed. A U. S. Bureau of Standards sample of calorimetry grade aluminum oxide was used in verifying the calibration factor.

Bunsen's original equation (6) for the theoretical calibration factor of an ice calorimeter was expressed as:

$$K = \frac{L_f}{(V_i - V_w)D_m}$$

where: K is the calibration factor

L_f is the heat of fusion of ice

V_i is the specific volume of ice

V_w is the specific volume of water

D_m is the density of mercury

Using the following values for a temperature of 0° C. reported in the International Critical Tables:

L_f = 333.6 $\pm$ 0.33 international joules per gram of ice

V_i = 1.09014 $\pm$ 0.006 milliliters per gram of ice

V_w = 1.00013 milliliters per gram of water

D_m = 13.5955 grams per milliliter of mercury

The calibration factor, K, was found to be between 268.75 and 272.35 international joules per gram of mercury.

The implication from Bunsen's equation is that the calibration factor of an ice calorimeter is a constant regardless of the specific form of calorimeter used. The equation is, however, in terms of the physical properties of water, ice and mercury at 0° C., the freezing point of water at standard atmospheric pressure. These physical properties, even of the most pure substances, are not known exactly as indicated by the variable values listed in the International Critical Tables. It was this uncertainty that required an experimental verification of the calibration factor with Bunsen's equation as a guide.

Leake and Turkdogan (28) using an electrical calibration technique determined a calibration factor for an ice calorimeter to be 270.54 ± 0.17 absolute joules per gram of mercury. Furukawa (13), also by an electrical calibration, evaluated an average calibration factor of 270.48 ± 0.03 absolute joules per gram of mercury. This latter value, falling within the range predicted from Bunsen's equation and also within the limits of precision of the work of Leake and Turkdogan, was the value chosen to apply in the present work.

In calibrating the calorimeter described in this report, a known weight of calorimetry grade aluminum oxide was enclosed in a platinum, 10 percent rhodium capsule.

The capsule was 3 inches in length, tapering from a diameter of 19/32 inch at the top to 1/2 inch at the bottom. This taper was made to conform with the inside dimensions of the central calorimeter tube in order to provide the most effective contact between the two surfaces, thus resulting in effective heat transfer. The top of the capsule was also made from platinum, 10 percent rhodium and was fabricated in the form of a small cup. The top fitted down inside the capsule approximately 1/4 inch. After filling the capsule with the aluminum oxide sample the lid was fused to the capsule using a tungsten arc while under an argon atmosphere. A small hangar fused to the top of the capsule provided the means by which the capsule was attached to the suspension wire.

The sample and capsule were heated to an established temperature and then dropped into the calorimeter following the operational procedure previously discussed. The weight of mercury displaced as a result of each drop is reported in table 3.

The data in table 4 are sufficient to determine the weight of mercury displaced by platinum -10 percent rhodium from the ice point up to 1600° K. The equation expressing the weight of mercury displaced in the calorimeter as a function of the absolute temperature is:

$$W = 4.8507 \times 10^{-4}T + 4.4116 \times 10^{-8}T^2 + 4.9418 \ (1/T) - 0.1537$$

where: W = weight of mercury displaced in grams per gram of PT - 10% Rh

T = absolute temperature in degrees Kelvin

TABLE 3. – Weight of mercury displaced due to
heated sample and container

Temperature, °K.	Mercury displaced, grams
407.7	9.1515
612.3	26.3367
720.0	36.1932
805.1	44.1148
912.5	54.7868
981.6	60.4829
1,103.5	73.0192
1,157.2	78.2737
1,193.0	81.8869
1,277.0	90.3705
1,355.9	99.1076
1,499.6	112.6319

Similar experimental values were determined for the empty capsule. These
values are reported in table 4.

TABLE 4. – Weight of mercury displaced by empty
platinum –10 percent rhodium capsule

Temperature, °K.	Mercury displaced, grams
533.1	4.8108
703.3	8.1935
889.5	11.9272
1,019.6	14.7667
1,223.3	19.3139
1,399.0	23.2291
1,592.3	27.6728

Using this equation it was possible to determine the weight of mercury displaced by the platinum -10 percent rhodium capsule at each of the temperatures of table 3. Subtracting each value thus obtained from the total weight of mercury displaced by the capsule and the aluminum oxide sample gave as a result the weight of mercury displaced by the aluminum oxide sample alone. The values thus obtained are tabulated in the second column of table 5.

The weights of mercury displaced by the sample were converted to units of calories per mole of aluminum oxide using the calibration factor of 270.48 international joules or, its equivalent 64.646 calories per gram of displaced mercury reported, by Furukawa. These values are in the third column of table 5.

Since 298.15° K. is generally used as a reference temperature, the calculated enthalpy values with respect to 273.15° K were adjusted to enthalpies above 298.15° K. The average specific heat for aluminum oxide reported by Kelley was used for changing the reference temperature base. These values are in column 4 in table 5.

The experimentally determined enthalpy values for the calorimetry grade aluminum oxide reported in table 5 are illustrated in figure 9. These values have been superimposed on the solid line representing Furukawa's established $H_T - H_{298.15}$ data for aluminum oxide. The agreement between the measured and established values of enthalpy is apparent. The average deviation between the data of Furukawa and the results of this work are 0.13%.
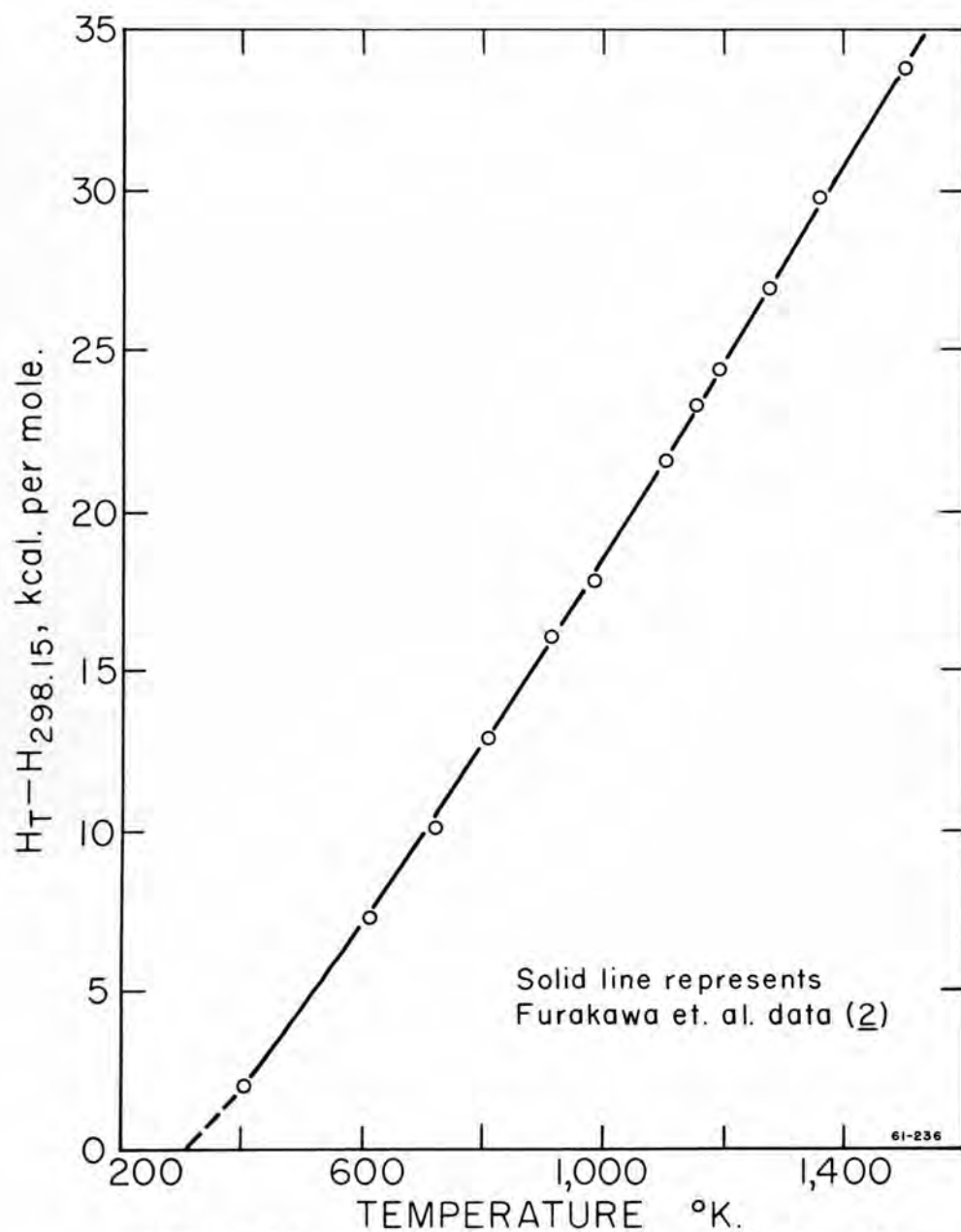
FIGURE 9.–Enthalpy of Aluminum Oxide Above 298.15° K.

Solid line represents
Furakawa et. al. data (2)

61-236

TABLE 5. - Enthalpy determination of Al_2O_3

Temperature, °K.	Mercury displaced by Al_2O_3 sample, grams	$H_T - H_{273.15}$ calories/mole	$H_T - H_{298.15}$ calories/mole
407.7	6.7265	2,650	2,200
612.3	19.9267	7,850	7,400
720.0	27.5936	10,870	10,420
805.1	33.7487	13,290	12,840
912.5	42.1492	16,620	16,170
981.6	46.3600	18,260	17,810
1,103.5	56.2326	22,150	21,700
1,157.2	60.2963	23,750	23,300
1,193.0	63.1099	24,860	24,410
1,277.0	69.6992	27,450	27,000
1,355.9	76.6343	30,190	29,740
1,499.6	86.8203	34,200	33,750

SAMPLE PREPARATION AND PROTECTION

The samples of yttrium metal, iron pentacarbonyl, and tungsten hexachloride used in this work were required to be of high-purity. Precautions were necessary to insure these substances remained pure during the course of investigation. A description of the preparation of these substances follows along with the chemical and spectrographic analyses obtained for each substance prepared. Also included is a description of the process by which these substances were sealed within protective capsules to prevent their exposure, thereby maintaining their purity.

Sample Preparation

The sample of yttrium metal used in this work was prepared by the metallic reduction of yttrium trichloride as described by Block, et al. (3). The distilled chloride was reduced by heating it with lithium metal in a molybdenum crucible inside an argon-filled retort. By-product alkali metal chlorides and excess alkali metal reductant were separated from the resulting yttrium sponge by heating for several hours under a high vacuum in the same retort used in the reduction step. Spectrographic analysis of the resulting metal follows in table 6. Only those elements actually detected are included.

TABLE 6. – Spectrographic Analysis of Yttrium Metal

Element	Amount Present, parts per million	Element	Amount Present, parts per million
Al	<10	Mo	100
B	40	Na	40
Ba	+40	Nb	+100
Ca	+40	Ni	1000
Cd	+20	Pb	+50
Co	<10	Si	10
Cr	<100	Sn	+5
Cu	30	Sr	+100
Fe	100	Ti	+50
K	+1	V	60
Li	+1	Zn	+100
Mg	5	Y	over 10%
Mn	+10		

+ = not detected at this level
< = detected but less than amount indicated

The spectrographic analysis for yttrium metal indicated the major impurity to be nickel. The total amount of detected impurities was 1485 parts per million indicating a sample purity of approximately 99.85%.

The sample of iron pentacarbonyl upon which measurements were made was secured from Antara Chemicals, a subsidiary of General Analine and Film Corporation. The supplier of this compound guaranteed its purity at greater than 99.9%. It was used without any further treatment.

The sample of tungsten hexachloride used was prepared by the direct chlorination of tungsten metal bar ends that were obtained from Wah Chang Corporation. This direct chlorination was performed in pyrex glass

equipment. The chloride prepared in this manner was distilled in pyrex glass. The temperature was raised slowly to allow the lower-boiling oxychlorides to vaporize first. When the gases given off displayed the deep purple color characteristic of tungsten hexachloride they were allowed to condense. A spectrographic analysis of the crystalline tungsten hexachloride thus collected follows in table 7. Only those impurities actually detected are included.

TABLE 7. - <u>Spectrographic Analysis of Tungsten Hexachloride</u>

Element	Amount Present, parts per million	Element	Amount Present, parts per million
Al	10	Mo	+500
B	<10	Ni	+10
Ba	+50	Pb	+500
Co	+10	Si	10
Cr	+50	Ti	+10
Cu	<10	V	+10
Fe	50	W	Above 10%
Mg	<10	Zn	+500
Mn	+10		

+ = not detected at this level
< = detected but less than amount indicated

Chemical analysis of this same sample of tungsten hexachloride indicated the presence of 0.017% carbon, 0.001% nickel, 54.5% chlorine, and 45.4% tungsten. These percentages of tungsten and chlorine are within 0.9% of the stoichiometric values of 53.64% and 46.35% respectively. From the analyses described the purity of the tungsten hexachloride sample used was greater than 99.828%.

Loading the Capsules

The enthalpy measurements performed in this work required that the materials being measured were completely enclosed and sealed from the atmosphere so that, at the relatively high temperatures of operation, these materials would not oxidize, hydrolyze, or change in composition in any manner by exposure to elements that would promote such changes. Each of the materials measured was, therefore, enclosed in capsules under a blanket of argon gas.

The samples of yttrium metal and tungsten hexachloride were enclosed in platinum-10 percent rhodium capsules of identical design to those used in the previously described calibration measurements performed on aluminum oxide. These materials were transferred to the capsules within a glove box that had been previously evacuated to 20 microns pressure and then backfilled with argon gas. While still in this inert atmosphere, caps were placed on the capsule and the capsules sealed by arc welding. After removal from the glove box the weld was examined for holes under a microscope.

The weight of sample enclosed inside a capsule in this manner was determined by first weighing the capsule and cap prior to their insertion into the glove box; this weight was then subtracted from the weight of the capsule, cap, and sample after the sealing operation just described was accomplished.

Possible errors resulting from the procedure are: outgassing of the sample during the welding operation due to vaporization of the sample by the high temperature of the arc, and, loss of capsule material by vaporization during the welding operation.

The first of these, vaporization of the sample, could have two deleterious effects. First, at high temperatures the sample could decompose resulting in an impure material for subsequent measurements, therefore, meaningless data. Second, outgassing could cause inclusions or holes in the weld and an imperfect seal on the sample.

Outgassing of the sample was observed in early attempts at capsule welding. This was overcome by performing the welding operation in a water-cooled copper holder. By circulating water through the shell of the copper holder the heat generated from the arc was dissipated and the sample, therefore, did not reach a temperature sufficiently high to vaporize it in significant amounts. When cooling the capsule in this manner none of the sample was observed to vaporize and outgassing during the welding operation ceased to be a problem.

Loss of capsule material during the welding operation could have resulted in inaccurate determinations of the sample weight. Such an inaccuracy would have led to erroneous results since all enthalpy values were calculated on a per mole basis. Visual observation of the welding operation indicated good flow characterisitcs of the melt and no apparent material

vaporization. From these observations and the relatively short time required to weld the capsule (less than one minute in each case), the error due to loss of capsule material in the welding operation was concluded to be negligible.

An early attempt to seal iron pentacarbonyl in these same platinum-10 percent rhodium capsules was unsuccessful. Iron pentacarbonyl, being a liquid at room temperatures, had a relatively high vapor pressure at room temperature. Its vapor pressure when exposed to the arc in the sealing operation was excessive even when the water cooling was used. From this experience it was concluded that capsules of a different design would have to be fabricated.

The capsule material chosen to enclose the iron pentacarbonyl samples was silver. Silver was chosen because of its heat conduction characteristics, its ability to be cold worked, and its relative low cost compared with other materials possessing suitable characteristics.

The silver capsules were fabricated from one-half inch inside diameter tubing with 0.040-inch wall thickness and flat stock of the same 0.040 inch thickness. A special punch and die were fabricated to give the silver tubing the proper taper so that it would conform to the inside of the central calorimeter tube for good heat transfer. The top and bottom of the capsule were cut from the flat silver sheet, and the bottom arc welded in

place. A 1/8-inch hole was drilled in the center of the top piece and a 1 1/2-inch long piece of silver tubing, 1/8 inch outside diameter and 0.049 inch wall thickness was inserted in this hole and arc welded in place. When this was accomplished the top piece was welded to the capsule completing the fabrication of the silver capsules.

Prior to loading, the silver capsules were leak checked by submerging them in water while subjected to a pressure of 40 lb/in^2 of helium. Only one of the five capsules fabricated showed a leak under these conditions and this one was not used in any measurements.

After leak checking the silver capsules were evacuated through the small tube extending from the top and then backfilled with argon gas. This operation was performed 4 times before the tygon filling tube was clamped shut. The capsules and iron pentacarbonyl sample were placed into the glove box for subsequent evacuation of the box and back filling with argon gas.

The liquid iron pentacarbonyl sample was loaded into the silver capsules using a hypodermic syringe. The hypodermic needle was inserted in the small tube extending from the top of the capsule and the iron carbonyl sample then injected into the capsule until it came to within approximately 1/2-inch of the top of the small tube. The hypodermic was then withdrawn and the end of the small silver tube clamped shut to seal the sample within the capsule. No contamination of the sample occurred during the filling operation since the liquid sample entering the capsule displaced argon gas

with which the capsule had been filled previously. There was also no

problem with sample vapor since no arc welding was necessary to seal the

capsule.

The small silver tube extending from the top of the capsule also

provided a means of attaching the capsule to the suspension wire so that the

capsule could be easily extracted from the calorimeter following a drop.

RESULTS

In this section the experimental results, obtained using the equipment and procedures previously described, are presented. High-temperature enthalpy data were obtained for the encapsulating materials platinum – 10 percent rhodium and silver and these values are included along with those for yttrium metal, iron pentacarbonyl, and tungsten hexachloride.

The thermodynamic property entropy is also useful in certain types of calculations. The entropy change with temperature may be calculated from the enthalpy data obtained in these measurements. The means of determining entropy values as well as the results obtained from the described calculations are also included.

Enthalpy of Capsules

The operating temperatures reached in this work as well as the characteristics of the materials used required that the samples of yttrium metal, iron pentacarbonyl, and tungsten hexachloride be sealed in protecting capsules for all measurements. As a result, all direct measurements of weights of mercury displaced included that displaced due to the enthalpy of the capsule at the prevailing temperature as well as that due to the sample, which was the quantity of interest.

This required that the weight of mercury displaced or the enthalpy of the capsule material as a function of temperature be known. No such

values were reported for platinum -10 percent rhodium, hence measure -
ments were necessary to determine the appropriate quantities for this alloy.
The results of these measurements are included in table 3, page 43. The
equation expressing the weight of mercury displaced in the calorimeter by
platinum -10 percent rhodium as a function of the absolute temperature is:

$$W = 4.8507 \times 10^{-4}T + 4.4116 \times 10^{-8}T^2 + 4.9418 (1/T) - 0.1537$$

where W = weight of mercury displaced in grams

per gram of Pt + 10% Rh

T = absolute temperature in degrees Kelvin.

Data are available for the enthalpy of metallic silver at various
temperatures. It was decided, however, to measure the enthalpy of an
empty silver capsule to insure good results for the iron pentacarbonyl
enclosed in the silver capsules and also to check further the reliability of
the ice calorimeter. Such data were obtained for an empty silver capsule,
measurement being taken at 100 degree intervals between 400° K. and 1200° K.
The results of these measurements are presented in table 8.

TABLE 8. - <u>Enthalpy of metallic silver above 273.15° K.</u>
(measured values)

Temperature, °K	Weight mercury displaced, grams	$H_T - H_{273.15}$ calories/mole
399.2	4.5177	760.4
500.4	8.2313	1385.4
601.3	12.0446	2027.3
699.6	15.8476	2667.4
800.4	19.9262	3349.2
899.5	23.8327	4006.1
999.9	28.0468	4720.4
1100.5	32.5528	5474.2
1198.3	37.2222	6251.9

A least-squares analysis of these data gave the following equation

for the enthalpy of the silver metal as a function of absolute temperature:

$$H_T - H_{273.15} = 5.00T + 1.15 \times 10^{-3}T^2 - 1405$$

where: $H_T - H_{273.15}$ = enthalpy of metallic silver

above 273.15° K in calories per mole

T = absolute temperature in degrees Kelvin

when converted to the conventional reference temperature of 298.15° K. the

resulting equation was: $H_T - H_{298.15} = 5.00T + 1.15 \times 10^{-3}T^2 - 1592$

where: $H_T - H_{298.15}$ = enthalpy of metallic silver above 298.15° K. in

calories per mole

T = absolute temperature in degrees Kelvin.

A comparison of the values obtained using the latter equation with

those reported by Kelley (23) are presented in table 9.

TABLE 9. - Enthalpies of Metallic Silver from this work and
as reported by Kelley (23), above 298.15° K.

Temperature, °K.	$H_T - H_{298.15}$ cal/mole this work	$H_T - H_{298.15}$ cal/mole Kelley	Percent difference
400	602	615	-2.11
500	1206	1240	-2.90
600	1832	1885	-2.81
700	2482	2535	-2.09
800	3154	3195	-1.28
900	3850	3880	-0.77
1000	4568	4585	-0.37
1100	5310	5310	0.0
1200	6074	6060	+0.23

The comparisons in table 9 verify the purity of the silver capsule

material at least as to reproducibility of standard enthalpy values and also

further substantiate the use of the ice calorimeter as a source of accurate

enthalpy data. A plot of the measured enthalpy data for metallic silver

corrected to a base temperature of 298.15° K. is presented in figure 10.

Experimental Data

Experimental measurements were performed on the three

materials: yttrium metal, iron pentacarbonyl, and tungsten hexachloride.

The results of the measurements of these materials are presented in tables
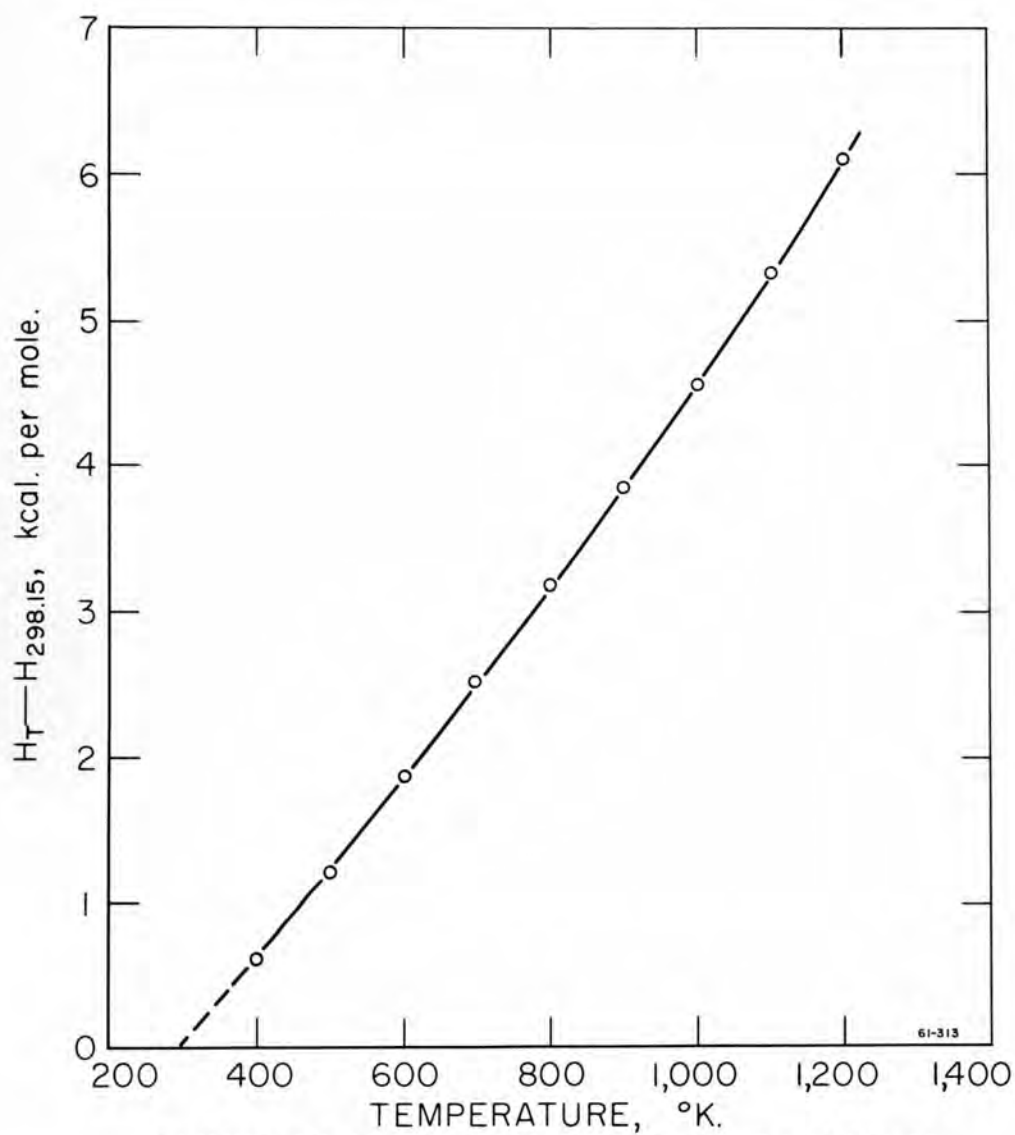
10, 11, and 12 respectively.

FIGURE 10.-High Temperature Enthalpy of Silver.

TABLE 10 - <u>Enthalpy of Yttrium Metal Above 273.15° K</u>
(measured values)

T, °K.	$H_T - H_{273.15}$ cal/mole	T, °K.	$H_T - H_{273.15}$ cal/mole
400.8	901.8	897.8	4317.8
500.6	1574.4	999.2	5108.3
600.8	2208.4	1100.8	5942.0
699.3	2879.7	1200.0	6775.7
798.7	3557.0	1300.6	8084.9

$H_T - H_{273.15} = 1.2041\,T + 3.393 \times 10^{-3}T^2 - 0.4176 \times 10^6 T^{-1} + 944.6$

$H_T - H_{298.15} = 1.2041\,T + 3.393 \times 10^{-3}\,T^2 - 0.4176 \times 10^6\,T^{-1} + 739.9$
(cal/mole (298–1300° K)

$C_p = 1.2041 + 6.786 \times 10^{-3}\,T + 0.4176 \times 10^6\,T^{-2}$ cal/mole deg.

TABLE 11 - <u>Enthalpy of Iron Pentacarbonyl Above 273.15° K.</u>

T, °K.	$H_T - H_{273.15}$ cal/mole	T, °K.	$H_T - H_{273.15}$ cal/mole
301.8	1559.3	345.0	3981.7
306.0	1839.6	355.0	4644.1
315.5	2247.0	365.0	5091.6
319.3	2562.2	375.0	5650.4
329.3	3018.7	387.0	6332.0
339.3	3751.9		

$H_T - H_{273.15} = 5.5636 \times 10^{-2}\,T - 15.1975$ K cal/mole

$H_T - H_{298.15} = 5.5636 \times 10^{-2}\,T - 16.588$ K cal/mole
(298° – 378° K)

$C_p = 5.5636 \times 10^{-2}$ K cal/mole–deg.

TABLE 12 – <u>Enthalpy of Tungsten Hexachloride Above 273.15° K</u>
(measured values)

Temperature, °K.	$H_T - H_{273.15}$ cal/mole	Temperature, °K.	$H_T - H_{273.15}$ cal/mole
406.8	6,328	544.3	17,042
427.1	7,625	547.6	17,138
449.3	8,800	553.2 (β)	17,267
474.7	9,794	560.1 (ℓ)	19,281
498.0	11,515	573.9	20,027
502.4 (α)	11,865	584.3	20,411
507.8 (β)	15,397	598.5	21,304
512.9	15,587	602.9	21,560
538.9	16,641		

WCl_6, (α) (c)

$$H_T - H_{273.15} = 16.452\ T + 4.4663 \times 10^{-2}T^2 - 7,808\ \text{cal/mole}$$

$$H_T - H_{298.15} = 16.452\ T + 4.4663 \times 10^{-2}\ T^2 - 8,872\ \text{cal/mole}$$
$$(298° - 504°\ K)$$

$$C_p = 16.452 - 8.9326 \times 10^{-2}T\ \text{cal/mole deg.}$$

WCl_6, (β) (c)

$$H_T - H_{273.15} = 42.877\ T - 6,390\ \text{cal/mole}$$

$$H_T - H_{298.15} = 42.877\ T - 7,453\ \text{cal/mole}$$
$$(504° - 556°\ K)$$

$$C_p = 42.877\ \text{cal/mole-deg.}$$

WCl_6 (ℓ)

$$H_T - H_{273.15} = 52.804\ T - 10,319\ \text{cal/mole}$$

$$H_T - H_{298.15} = 52.804\ T - 11,382\ \text{cal/mole}$$
$$(556 - 610°\ K)$$

$$C_p = 52.804\ \text{cal/mole-deg.}$$

Included below each of these tables are equations for enthalpy above 273.15° K, enthalpy above 298.15° K, and specific heat. The units for $H_T - H_{273.15}$ and $H_T - H_{298.15}$ are calories per mole. The units for C_p are calories per mole-degree Kelvin. All temperatures are in degrees Kelvin.

The three sets of equations presented for tungsten hexachloride are for the three different phases of that substance encountered: the two crystalline states denoted (α) and (β) and the liquid phase denoted (ℓ).

The temperature range for which each set of equations is valid is included parenthetically below each $H_T - H_{298.15}$ expression.

The experimental data obtained for each substance corrected to a base temperature of 298.15° K are represented graphically in figures 11, 12, and 13.

Calculation of Entropy Increments Above 298.15° K.

The thermodynamic function, entropy, is defined by the relation:

$$ds = \frac{d\,Q_{REV.}}{T}$$

For a constant pressure heat transfer such as occurs in the calorimeter:

$$d\,Q = d\ (\Delta H)$$
$$= d\ (H_T - H_{298.15})$$

Thus entropy may be evaluated from the expression:

$$\int_{298.15}^{T} ds = \int_{298.15}^{T} d\,\frac{(H_T - H_{298.15})}{T}$$
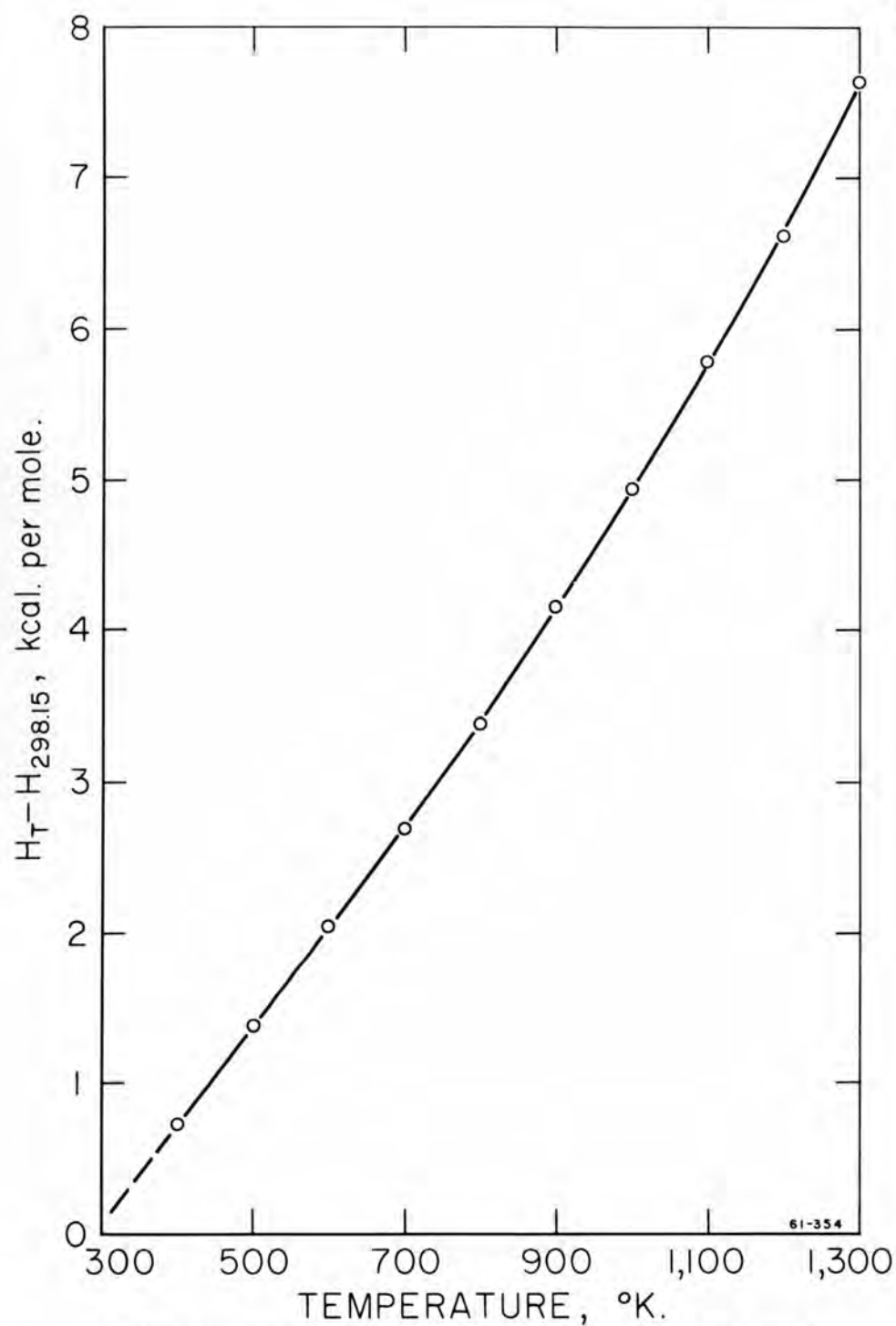
FIGURE 11.-High Temperature Enthalpy of
Yttrium Metal.
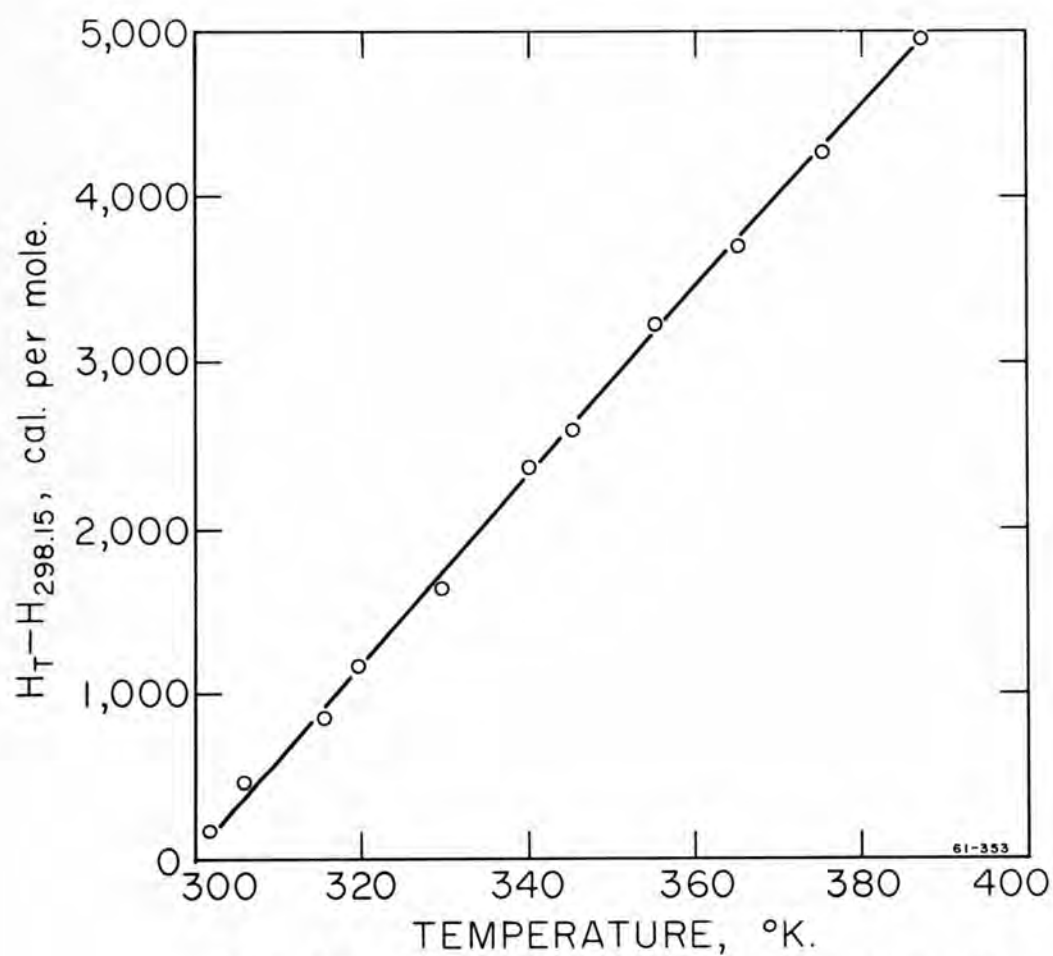
FIGURE 12.–High Temperature Enthalpy of
Iron Pentacarbonyl.
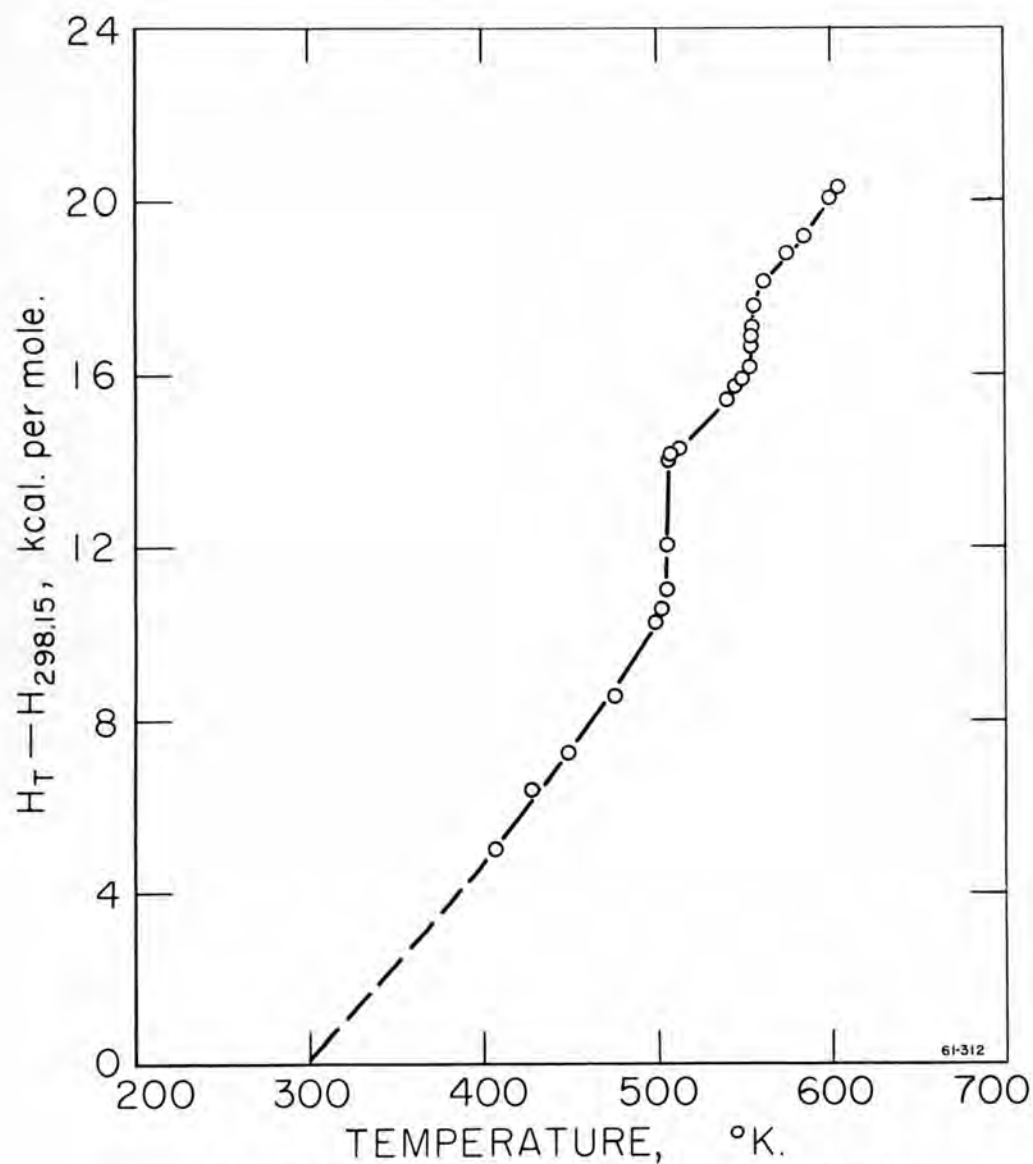
FIGURE 13.-High Temperature Enthalpy
of Tungsten Hexachloride.

This expression may be integrated by parts to give:

$$S_T - S_{298.15} = \frac{H_T - H_{298.15}}{T} + \int_{298.15}^{T} \frac{(H_T - H_{298.15})d\,T}{T^2}$$

The integrated term may be evaluated directly from smooth data. The integral may be evaluated by graphically integrating a plot of $\frac{H_T - H_{298.15}}{T^2}$ against T.

The procedure just described was used to evaluate the entropy increments for each of the substances measured. Tabulated results of this procedure are included for yttrium metal, iron pentacarbonyl, and tungsten hexachloride in tables 13, 14, and 15 respectively. The resulting entropy increments are also tabulated along with smoothed enthalpy values as functions of absolute temperature for each of the three substances measured in tables 16, 17, and 18.

TABLE 13 – Calculation of Entropy Increments of Yttrium Metal Above 298.15° K.

Temperature, °K.	$H_T - H_{298.15}$ cal/mole	$\dfrac{H_T - H_{298.15}}{T}$ cal/deg. mole	$\dfrac{H_T - H_{298.15}}{T}$ cal/deg.^{2} mole	$\displaystyle\int_{298.15}^{T} \dfrac{H_T - H_{298.15}}{T^2}\,dT$ cal/deg. mole	$S_T - S_{298.15}$ cal/deg mole
400	720.5	1.80125	0.0045031	0.28113	3.08
500	1355.1	2.71020	0.0054204	0.78588	3.496
600	1987.9	3.31317	0.0055219	1.33554	4.648
700	2648.8	3.7840	0.0054057	1.88192	5.666
800	3352.6	4.19075	0.0052384	2.41413	6.660
900	4107.9	4.56433	0.0050715	2.96962	7.493
1000	4919.4	4.9194	0.0049194	3.42916	8.349
1100	5790.3	5.26391	0.0047854	3.91440	9.178
1200	6722.7	5.60225	0.0046685	4.38709	9.989
1300	7718.2	5.93708	0.0045670	4.84886	10.786

TABLE 14 – Calculation of Entropy Increments of Iron Pentacarbonyl
Above 298.15° K.

Temperature, °K.	$H_T-H_{298.15}$ cal/mole	$\dfrac{H_T-H_{298.15}}{T}$ cal/deg mole	$\dfrac{H_T-H_{298.15}}{T}$ cal/deg.^{2} mole	$\displaystyle\int_{298.15}^{T}\dfrac{H_T-H_{298.15}}{T^2}dT$ cal/deg. mole	$S_T-S_{298.15}$ cal/deg. mole
300	107	0.35666	0.001189	0.00185	0.35851
310	656	2.11613	0.0068262	0.03658	2.15271
320	1211	3.78438	0.11826	0.12984	3.91422
330	1770	5.36364	0.016253	0.27024	5.63388
340	2328	6.84706	0.020138	0.45220	7.29926
350	2891	8.2600	0.02360	0.67089	8.93089
360	3438	9.5500	0.026528	0.92153	10.47153
370	4005	10.82432	0.029255	1.20045	12.02477
380	4549	11.97105	0.031503	1.50424	13.47529

TABLE 15 – Calculation of Entropy Increments of Tungsten Hexachloride
Above 298.15° K

Temperature, °K.	$H_T-H_{298.15}$ cal/mole	$\dfrac{H_T-H_{298.15}}{T}$ cal/deg. mole	$\dfrac{H_T-H_{298.15}}{T}$ cal/deg.^{2} mole	$\displaystyle\int_{298.15}^{T} \dfrac{H_T-H_{298.15}}{T^2}\,dT$ cal/deg. mole	$S_T-S_{298.15}$ cal/deg. mole
400	4,855	12.1375	0.030344	1.74947	13.887
420	5,917	14.0881	0.033543	2.38834	16.4764
440	7,014	15.9409	0.036229	3.08606	19.027
460	8,147	17.7109	0.038502	3.83337	21.5443
480	9,316	19.4083	0.040434	4.62273	24.0310
500	10,520	21.0400	0.042080	5.44787	26.4879
504 (α)	10,765	21.3591	0.042379	5.61679	26.9758
504 (β)	14,147	28.0694	0.055693	5.61679	33.6861
510	14,414	28.2627	0.055417	5.95012	34.2128
520	14,843	28.5442	0.054893	6.50167	35.0459
530	15,271	28.8132	0.054365	7.04796	35.8612
540	15,700	29.0741	0.053841	7.58899	36.6631
550	16,129	29.3255	0.053319	8.12479	37.4505
556 (β)	16,386	29.4712	0.053006	8.44377	37.9150
556 (ℓ)	17,977	32.3327	0.058152	8.44377	40.7765
560	18,188	32.4786	0.057998	8.67607	41.1547
570	18,716	32.8351	0.057605	9.28408	42.0892
580	19,244	33.1793	0.057206	9.82814	43.0074
590	19,772	33.5119	0.056800	10.39817	43.9101
600	20,300	33.8333	0.056389	10.96412	44.7974
610	20,828	34.1443	0.555974	11.52594	45.6702

TABLE 16. - Enthalpy and Entropy for Yttrium Metal Above 298.15° K.
(smooth values)

Temperature, °K.	$H_T-H_{298.15}$ cal/mole	$S_T - S_{298.15}$ cal/deg. mole	Temperature, °K.	$H_T-H_{298.15}$ cal/mole	$S_T-S_{298.15}$ cal/deg. mole
400	720	2.08	900	4110	7.49
500	1360	3.50	1000	4920	8.35
600	1990	4.65	1100	5790	9.18
700	2650	5.67	1200	6720	9.99
800	3350	6.66	1300	7720	10.79

TABLE 17. - Enthalpy and Entropy for Iron Pentacarbonyl Above 298.15° K
(smooth values)

Temperature, °K.	$H_T-H_{298.15}$ cal/mole	$S_T - S_{298.15}$ cal/deg. mole	Temperature, °K.	$H_T-H_{298.15}$ cal/mole	$S_T-S_{298.15}$ cal/deg. mole
300	103	0.34	350	2880	8.92
310	659	2.14	360	3440	10.46
320	1220	3.90	370	4000	12.02
330	1770	5.62	380	4550	13.47
340	2330	7.29			

TABLE 18 – Enthalpy and Entropy for Tungsten Hexachloride Above 298.15° K
(smooth values)

Temperature, °K.	$H_T - H_{298.15}$ cal/mole	$S_T - S_{298.15}$ cal/mole, deg.	Temperature, °K.	$H_T - H_{298.15}$ cal/mole	$S_T - S_{298.15}$ cal/mole, deg.
400	4,860	13.89	530	15,270	35.85
420	5,920	16.48	540	15,700	36.66
440	7,010	19.03	550	16,130	37.45
460	8,150	21.54	556 (β)	16,390	37.92
480	9,320	24.03	556 (ℓ)	17,980	40.78
500	10,520	26.49	560	18,190	41.15
504 (α)	10,770	26.98	570	18,720	42.09
504 (β)	14,150	33.69	580	19,240	43.01
510	14,410	34.21	590	19,770	43.91
520	14,840	35.05	600	20,300	44.80

DISCUSSION OF RESULTS

The ice calorimeter herein described, along with its associated equipment, is capable of producing valid high-temperature enthalpy data with high precision. This was verified by the close agreement between enthalpy values for a National Bureau of Standards sample of calorimetry grade aluminum oxide measured with this equipment and the standard enthalpy values for that compound. Equipment precision was further substantiated by extremely close agreement between measured and established enthalpy values for metallic silver.

The analyzed purities of the samples upon which enthalpy measurements were performed were as follows: yttrium metal, 99.85%; iron pentacarbonyl, 99.9%; and tungsten hexachloride 99.825%. Enthalpy values reported for substances of purity such as these may be safely used in thermodynamic calculations. These enthalpy values represent the enthalpies of the pure substances very well.

Enthalpy measurements of yttrium metal were limited to 1300°K and below due to the formation of a low-melting eutectic of yttrium and the platinum -10 percent rhodium capsule material somewhere between 1300 and 1400°K. The melting point of yttrium, 1773°K (3) could, therefore, not be reached with the capsules available.

The reported boiling point of iron pentacarbonyl is 378°K (29). Due to the constant volume of the capsule enclosing this compound the data for iron pentacarbonyl do not show a sharp discontinuity at the boiling point. The equations included for iron pentacarbonyl are, therefore, not recommended for use above 378°K.

Enthalpy data for tungsten hexachloride show distinct phase transformations at 504°K and 556°K. Similar results were reported by Ketelaar et. al. (25) from vapor pressure measurements. Ketelaar reported a solid-state transformation at 500°K with an associated enthalpy of transformation of 3.4 kilocalories per mole. The results of this work show close agreement with those of Ketelaar. The solid-state transformation was encountered at 504°K with an associated enthalpy change of 3.38 kilocalories per mole. The lower temperature modification of tungsten hexachloride is denoted (α) in this work, and the higher temperature modification by the symbol (β).

Ketelaar reported the melting point of tungsten hexachloride to be at 557°K. with an enthalpy of fusion of 2.3 kilocalories per mole. The melting point was encountered at 556°K in this work. The associated enthalpy of fusion was measured to be 1.59 kilocalories per mole, a difference of 0.71 kilocalories per mole from the results of Ketelaar. The value obtained from the present work is believed to be the better of the two due to the more direct method of enthalpy determination and the excellent reproducibility of data in the temperature region near 556°K. as shown in figure 13.

The boiling point of tungsten hexachloride was reported to be 609.7°K. by Ketelaar. As in the case of iron pentacarbonyl already discussed, no discontinuity in the experimental data was encountered at the boiling point. The data and equations for tungsten hexachloride in the liquid phase are not recommended for use above 610°K.

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