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A HIGH-TEMPERATURE CALORIMETER SYSTEM
FOR USE WITH MATERIALS CONTAINING PLUTONIUM

by

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ABSTRACT

A high-temperature calorimeter system has been constructed to conduct enthalpy increment studies on radioactive materials at temperatures to 3600°K. Samples are heated by induction and dropped by a condenser-discharge technique into a modified commercial adiabatic calorimeter. Sample temperatures are measured by an automatic optical pyrometer, and calorimeter temperatures are obtained by quartz thermometry. Other features of the system and its overall operation are discussed. Performance and capabilities of the system are demonstrated by measurements of the enthalpy of solid tungsten, solid and liquid uranium dioxide, and solid and liquid uranium-plutonium dioxide.

I. INTRODUCTION

A drop calorimeter has been constructed to carry out enthalpy increment studies at temperatures to 3600°K with plutonium-containing materials. Because of the extreme toxicity of plutonium, special precautions are required. In brief, a large aluminum enclosure (a "walk-in" hood) was constructed around an existing calorimeter system, and provisions were added for remote operation. Samples are heated by induction¹ and dropped into a modified commercial adiabatic calorimeter. The experimental temperature is limited by the melting point of container materials and by the compatibility of the container and its contents. Several high-temperature drop calorimeters have been described in the literature,¹⁻⁵ but none has been used at temperatures as high as those in the present work.

For convenience we have divided the description of the equipment into sections such as the hood construction, the vacuum system, and so on. A detailed description of the procedure during an experiment follows and should give an integrated view of the equipment.

II. DESCRIPTION OF EQUIPMENT

A. Walk-in Hood

An overall schematic view of the high-temperature drop-calorimeter system is shown in Fig. 1. This system is enclosed in a 10 x 7 x 8-ft-high aluminum walk-in hood. Figure 2 is a photograph of the calorimeter system

Fig. 1. Schematic View of High-temperature Drop-calorimeter System. ANL Neg. No. 308-172 Rev. 3.

Fig. 2. Calorimeter System inside Walk-in Hood

inside the walk-in hood. The front face of the hood is fitted with two 4-ft-wide overlapping sliding doors, each of which has a 3-ft-square Lucite window. The window in the door nearest the equipment is fitted with two neoprene, arm-length gloves.

In the side wall of the hood nearest the equipment is an additional Lucite window (23 x 16 in.). To the right of this window are two neoprene gloves mounted in the hood wall. These gloves are needed for making manipulations during an experiment. A window (23 x 16 in.) is mounted above the pyrometer housing located on the side wall opposite the prism view port of the drop tube. To the right of this window are mounted two more neoprene gloves to provide access to components inside the hood. Two Lucite windows on top of the hood permit good lighting by means of two 4-ft, double fluorescent fixtures.

The flooring in the hood was painted with a liquid-tile paint. All seams along the flooring and the aluminum sides of the hood, plus all visible

cracks and openings, were sealed with a silicone-rubber adhesive. The interior of the hood is maintained at a slightly negative pressure, even when one of the sliding doors is two-thirds open.

B. Vacuum System

The calorimeter roughing vacuum is obtained from a Welch No. 1405 Duo-Seal, 300-rpm, 0.05- μ m vacuum pump. In addition, the vacuum system has a 6-in. NCR Model NHS6 oil diffusion pump attached to a Granville-Phillips liquid-nitrogen baffle. The maximum pumping speed for this diffusion pump is 1500 liters/sec for air. Several hand valves, a large 6-in. hand gate valve above the liquid-nitrogen baffle, plus an electric gate valve in the drop-tube line between the prism adaptor assembly and the calorimeter are incorporated throughout the system to regulate, control, and give versatility to the various sections. A Helicoid pressure gauge, two Veeco thermocouple gauges, and a Veeco ionization gauge measure the pressure at specific sections.

The stainless steel furnace chamber (12 in. in diameter, 26 in. high) connects to the vacuum line through an 8.5-in. dia stainless steel elbow. A separate vacuum line connects to the calorimeter drop-tube section below the electric gate valve and provides greater versatility to the entire calorimeter system. Figures 1 and 2 show many of the above-mentioned components.

C. Induction-heating System

Power for the induction coil is supplied from outside the aluminum hood by a 25-kW, 250-kHz Ther-Monic generator coupled to an iron-core rf transformer. The generator, rf-transformer core and secondary outside the hood, and the work coil, the water-cooled flange, the water-cooled furnace chamber, and the water cooling for the oil-diffusion pump inside the hood are cooled with once-through laboratory water contained in sealed water lines. Various water lines are controlled by solenoid valves, and safety water-pressure switches were added in the event of insufficient cooling to essential parts of the system.

Inside the induction coil, which is located in the furnace chamber, is a 60-mil-wall, 1-in.-ID tungsten heat shield. This heat shield, which is slotted to make it a nonsusceptor, is essential for obtaining the higher sample temperatures. It also improves temperature uniformity and eliminates the possibility of the sample capsule touching and thus shorting the rf coil. The coil, mounted on an 8-in. flange that connects to the furnace chamber, is easily removable for periodic cleaning and, if necessary, for repairs.

D. Capsule-mounting and -drop System

The sample capsule is suspended in the work coil by a 10-mil tungsten wire wrapped around a 10-mil tungsten horizontal suspension wire. The ends of the horizontal suspension wire are crimped into pieces of 1/8-in. copper tubing, and these tubes are clamped between two massive copper electrodes fixed in an x-y motion device. This device, shown in Fig. 3, allows adjustment of the lateral position of the heated capsule from outside the vacuum chamber by means of a rotary feedthrough and a flexible cable linked to controls outside the aluminum hood. The copper electrodes are connected by flexible copper straps to a connector and feedthrough on the furnace chamber. A power cable attaches to this feedthrough and passes through the aluminum hood to a 1250-J (5-kV, 100- μ F) condenser bank. When it is desired to release the capsule, the condenser bank is discharged through the horizontal suspension wire causing the wire to vaporize rapidly. Very reliable and precise release of the capsule is achieved in this manner.

Fig. 3. Schematic Diagram of Capsule-positioning Device. ANL Neg. No. 308-1280.

E. Capsule-observation and Temperature-measurement System

Sample temperatures are measured with a Pyrometer Instrument Company automatic optical pyrometer operated in conjunction with a digital voltmeter. The pyrometer, a disappearing-filament-type pyrometer with automatic matching, is located inside the pyrometer box, which is just below the furnace chamber and opposite the prism adaptor assembly. The box is supported and permanently attached and sealed to the aluminum hood. The dimensions of the box are 20 x 21 x 13 in. deep. The back face is constructed of Lucite and thus provides for clear observation of the many important components of the equipment.

The pyrometer sights horizontally through an optically flat window on one of the four side arms of a prism and view-port assembly. This prism and view-port assembly attaches to the underside of the furnace chamber and forms part of the vertical drop tube through which the sample will fall on command into the calorimeter receiver.

Opposite the side arm containing the pyrometer window is a side arm with an attached flange containing a rotary, push-pull feedthrough bearing the prism-holder assembly. The prism is pushed in and out of the drop-tube area from outside the aluminum hood by means of a metal rod located beside the pyrometer box and penetrating the hood wall. This rod is connected to the feedthrough shaft and is shielded inside a copper tube to prevent radioactive contamination from reaching the outside of the hood. A miniature right-angle gear and flexible cable assembly connects to the end of the feedthrough shaft and permits control of the rotary motion of the viewing prism from outside the hood. With proper positioning of the prism, the sample capsule can be seen through the pyrometer for observation purposes as well as temperature measurements.

At right angles to the side arm with the pyrometer window and the side arm that contains the feedthrough bearing the prism-holder assembly are two additional side arms on this prism and view-port assembly. Each side arm has a flange with an attached optically flat viewing window. Opposite one viewing window is mounted a calibrated lamp for pyrometer calibration. Pyrometer calibrations and prism and window temperature corrections are carried out in the conventional manner⁶ using tungsten-strip lamp calibrated by the National Physical Laboratory, Teddington, England. An important feature of this prism and view-port assembly is that the pyrometer and related optics can be calibrated during the experiment while the sample is being heated or is already at a predetermined temperature.

Near the bottom of the furnace chamber and above the drop-tube opening is a three-position shutter operated through a rotary feedthrough manipulated from outside the hood by a flexible cable. The three positions for this shutter are as follows:

1. Open position--provides a clear path to the prism and sample capsule for temperature measurements and for dropping the sample capsule after the prism is removed from the drop-tube area.
2. Closed position--covers the drop-tube opening with a tantalum radiation shield and protects the prism from tungsten deposition.
3. Window position--allows a replaceable glass window to cover the drop tube and thereby permits the alignment and positioning of the capsule during heating. This shutter position also protects the prism from tungsten deposition at the higher capsule temperatures.

F. Calorimeter

The calorimeter is a modified Parr Instrument Company, Series 1230, adiabatic calorimeter with automatic jacket control. Other authors⁵ have used a similar calorimeter with good results. The calorimeter jacket cover and calorimeter cover are attached to the drop tube, which contains a radiation trap. This trap is a gold-plated copper disc, which can be operated manually from outside the calorimeter and from outside the hood. The receiver is attached below the radiation trap and is lined with tungsten.

Thermistor probes are supplied with the calorimeter and used to operate a hot- and cold-water supply system to maintain the calorimeter jacket temperature equal to the calorimeter bucket temperature. For actual measurements of the calorimeter temperatures, a Hewlett Packard Dymec Quartz Thermometer, Model No. 2801A, is used.

Electrical calibration of the calorimeter is performed over the same temperature change as that of each experimental drop. The energy equivalent of the calorimeter is measured by means of a small electric heater mounted on the radiation-shield housing inside the calorimeter bucket. Typically, a series of 19 electrical calibrations gave an energy equivalent of 2473 cal/°C with a standard deviation of 1 cal/°C.

G. Recirculating Water System

The recirculating hot- and cold-water system, located inside the walk-in hood, is used to control the temperature of the jacket of the Parr calorimeter. This water system, shown schematically in Fig. 4, consists of heat exchangers, water pumps, and various valves. The hot-water supply is heated by two thermostatically controlled immersion heaters. The cold-water supply is obtained (1) from a heat exchanger consisting of a sealed pipe with laboratory cold water passing through the pipe and around a coil of the cold-water supply line, and (2) from a Parr Instrument Company water cooler, Model DP5P, designed specifically for this type of calorimeter.

Fig. 4. Schematic Diagram of Recirculating Water System inside Walk-in Hood

H. Sample Capsules

1. Single-walled Capsules

Single-walled tungsten sample capsules, one of which is shown in Fig. 5, are used in the studies to a maximum temperature of 3050°K. A cap is electron-beam-welded onto the capsule after the sample has been placed inside. The single-walled capsules for the uranium oxide studies were welded at ANL, and the capsules for the plutonium-containing oxide studies were welded at Battelle Memorial Institute (Columbus, Ohio). The capsules were leak-checked after filling and welding, and no loose contamination was detectable on the outside of the capsules containing the plutonium samples.

Fig. 5. Single-walled Tungsten Sample Capsule

2. Double-walled Capsules

The double-walled tungsten capsules, one of which is shown in Fig. 6, have previously been used successfully for the liquid uranium oxide studies between 3000 and 3523°K and are presently being used for the molten

Fig. 6. Double-walled Tungsten Sample Capsule

uranium-plutonium oxide studies.

Basically, the double-walled capsule is the single-walled capsule electron-beam-welded inside another capsule. The double wall reduces radiant heat losses during the drop and improves temperature uniformity of the capsule at the higher temperatures. Thin tungsten radiation shields are added to the top stem of the capsule cap for additional heat shielding.

I. Fire Potential and Safety Protection of the Equipment

The apparatus and equipment inside the aluminum hood is constructed entirely of metal, except for the Viton and neoprene gaskets, insulating material around wires and cables to the various components, a small amount of plastic tubing, neoprene-reinforced water lines, glass view-port windows, and a Lucite cover over the water reservoir. The sample-capsule heating is performed entirely in vacuum; therefore, the fire potential of the experimental apparatus is minimal.

Safety devices have been incorporated in case there is insufficient cooling to various components. Electronic switches are also installed to require the proper experimental procedure to be followed before the sample capsule can be dropped.

Radiation-monitoring probes are located outside the hood. One probe can be swung and extended inside the hood if necessary. A representative from Radiation Safety is always present whenever an experimenter is required to enter the hood. Protective clothing, such as a one-piece paper suit, plastic boots and covers, gloves, and a plastic hood are worn by the experimenter before entering the hood. The plastic hood is attached by plastic tubing to filtered supplied air. The air supply continuously flows and maintains a positive pressure under the head hood. This system gives the experimenter easy breathing, improved visibility, good maneuverability, and alpha-radiation protection. A photograph of a "suited" experimenter (D. F. Fischer) is shown in Fig. 7.

One of the most important features of this high-temperature calorimeter system for use with radioactive materials is that once the "suited" experimenter has installed the sample capsule into the furnace chamber and

made the appropriate equipment connections, he leaves the interior of the hood. All other necessary manipulations and maneuvers required to do the experiment are accomplished from outside the walk-in hood.

Fig. 7. "Suited" Experimenter Prepared to Leave Walk-in Hood

III. EXPERIMENTAL PROCEDURE

Before an experiment is set up inside the walk-in hood, two experimenters must be present in addition to a representative from Radiation Safety. One experimenter is "suited" to enter the hood, and the other experimenter assists outside the hood.

The "suited" experimenter has his feet and part of his legs covered with plastic bags securely taped to the trousers below the knees. Two plastic shoe covers are worn over the plastic bag on each shoe. A zippered paper suit is worn over the usual work clothes. The hands are covered with

surgical gloves, and the cuffs of the gloves are taped securely over the sleeve of the paper suit. A second pair of surgical gloves covers the first pair. If a condition exists that is likely to cause the surgical gloves to be punctured, a third pair of heavier gloves is worn. A plastic hood is worn over the head, and its tabs are taped onto the paper suit. This hood has a plastic hose molded to the back to which a supplied-breathing-air line is attached. The airflow through the plastic hood is continuous at approximately 7 cfm. The breathing air is supplied from a 1-hp portable air compressor with appropriate line filters. A breathing air cylinder is used in a backup system in case of an emergency. Figure 7 is a picture of a "suited" experimenter prepared to leave the walk-in hood.

The following operating procedure is used for the experiments performed with the high-temperature calorimeter system shown in Fig. 2.

A. A beam-welded-closed tungsten capsule containing plutonium material and having no loose contamination on its exterior is weighed on a Mettler balance outside the walk-in hood.

B. The experimenter enters the hood with the sample capsule and performs the following functions:

1. Sample installation:
 - a. Removes the condenser-discharge drop-system electrode assembly (shown in Fig. 1) from the furnace chamber.
 - b. Installs the horizontal sample-support wire between the electrodes.
 - c. Attaches and positions the vertical sample-support wire from the sample capsule to the horizontal sample-support wire.
 - d. Reinstalls the condenser-discharge drop-system electrode assembly in the furnace chamber.
 - e. Aligns the sample by observing up through the drop-tube opening when the gate valve and upper shelter are opened and by giving directions to the experimenter outside the hood to adjust the x and y motion block shown in Fig. 3.
 - f. Replaces the furnace-chamber cover.
 - g. Closes upper shutter but leaves gate valve open.

2. Calorimeter preparation:

- a. Pours a measured amount of distilled water into the calorimeter bucket and installs bucket in the calorimeter jacket.
- b. Places and positions the receiver in the calorimeter bucket.
- c. Slides and positions the calorimeter, which is mounted on a metal sled with Teflon runners, under the drop tube and connects the drop-tube flanges. Figures 1 and 2 illustrate and show the relative positions and locations.
- d. Closes the lower shutter of the calorimeter and installs the lower shutter arm that enables the manipulation of this shutter from outside the hood.
- e. Checks the microswitch for the lower shutter light and safety circuit.
- f. Reconnects the electrical circuit for the water pump in the calorimeter jacket.
- g. Reconnects the electrical leads to the heater mounted on the radiation-shield housing inside the calorimeter and used for the electrical calibration of the calorimeter.
- h. Closes the calorimeter-jacket drain valve.
- i. Checks for proper water level in the reservoir for the recirculating-water system for the calorimeter jacket. (A schematic diagram of the recirculating-water system is shown in Fig. 5.)

3. System evacuation:

- a. Checks to see that both gas-bleed-in valves in the vacuum system are closed.
- b. Starts the rough pumping to the furnace chamber, drop tube, and calorimeter receiving tube.
- c. Opens the system to the diffusion pump after the pressure in the system is $<100 \mu\text{m}$. (The diffusion-pump heater and water-coolant lines were energized earlier.)

4. Departure from hood:

- a. Moves to the exit door of the hood (see Fig. 7).
- b. Surveys gloves with the mounted probe previously moved inside the door opening.
- c. Has the representative from Radiation Safety perform a complete body survey before attempting to leave the hood.
- d. Removes one outer shoe cover and steps onto a plastic sheet just outside the hood; then removes the cover from the other foot.
- e. Obtains another complete radiation survey just outside the hood next to the opened doorway.
- f. Removes the plastic hood, remaining shoe cover, and bags, gloves, and suit.
- g. Obtains a final radiation survey.
- h. Steps off plastic sheet and wraps the disposable materials in the plastic sheet for disposal into a dry-active-waste container.
- i. Closes the hood door.
- j. Surveys the surrounding floor area for radioactivity.

C. In the continuation of this experiment, no one should be required to enter the hood until the end of the experiment when the sample is to be removed for weighing.

D. The liquid-nitrogen level in the diffusion-pump cold trap is checked and replenished if necessary through the transfer of liquid nitrogen from a liquid-nitrogen Dewar and filling system outside the hood. A filled diffusion-pump cold trap will easily last overnight. A sample capsule is usually evacuated overnight.

E. After the system pressure is down to at least 1×10^{-6} Torr, the following steps are taken:

1. The recirculatory hot- and cold-water systems and water pump are activated and adjusted.
2. The calorimeter controller is adjusted for good calorimeter water-jacket-temperature control. (In a typical experiment, the calorimeter and its jacket water temperatures are adjusted to 0.000°C temperature difference.)

3. The power supplies for the test lamp, digital voltmeter, quartz-thermometer readout, and optical pyrometer are turned on.

4. A pyrometer standardization check is made with the test lamp inside the hood.

5. The following water-coolant lines to the various components are turned on:

a. Bell jar.

b. Induction coil.

c. Rf feedthrough.

d. Rf-transformer core.

e. Rf-transformer secondary.

f. The various components inside the Ther-Monic generator cabinet.

6. The Ther-Monic generator is activated, and the capsule is now ready to be heated.

F. The following steps are performed during the heating of the capsule:

1. The generator power is set and held for approximately 10 min at a setting to heat the sample to a temperature between 500 and 600°C.

2. The pressure in the system is watched closely during the heatup to be certain that it does not exceed 5×10^{-5} Torr.

3. By means of controls outside the hood, the prism is positioned in the drop tube and adjusted for sighting the capsule or the test lamp for pyrometer calibration checks during the capsule heatup.

4. The upper shutter, located in the bottom portion of the furnace chamber and shown in Fig. 1, has three basic positions:

a. Open--for making accurate temperature measurements and for dropping the capsule.

b. Closed--for providing radiation heat shielding between the prism and the capsule, and for protecting the prism from tungsten deposition.

c. Window--for permitting capsule observations (through a glass window between the prism and the capsule) for alignment and rough temperature measurements.

5. Once the approximate desired temperature is reached, the power setting and capsule temperature are held constant for a minimum of 20 min before the final capsule temperature is recorded. (Experiments using 60-min heating times have shown 20 min to be adequate.)

6. During the 20-min holding period, the capacitor-discharge condenser bank is energized to a ready condition.

7. After the final capsule temperature reading has been recorded, the top shutter closed, and the prism moved out of the drop-tube area, the following steps are performed:

a. The calorimeter-bucket temperature is recorded.

b. The lower calorimeter-drop-tube shutter and upper shutter are opened.

c. A check is made to see that the four pilot-safety lights for the various shutter positions are lit. (If one of the lights is not lit, a drop cannot be made.)

d. The condenser bank is fired to vaporize the capsule support wire and permit the hot capsule to free-fall into the calorimeter receiver.

e. The lower shutter, upper shutter, and gate valve are closed immediately.

f. The power to the capacitor-discharge bank is turned off.

g. The controls to the generator are lowered and turned off.

h. The prism is repositioned into the drop tube, and an alignment is made through the pyrometer for a calibration check with the test lamp.

i. Three minutes after the capsule drop, 60 Torr of helium is introduced into the receiver for improvement of heat transfer.

j. When the calorimeter-bucket temperature has come to equilibrium in approximately 20-30 min after the capsule drop, the temperature of the calorimeter bucket is recorded.

8. The calorimeter and calorimeter jacket are cooled to the temperature before the drop, and a calorimeter calibration is performed.

9. After the calorimeter calibration, all the equipment is shut down and turned off.

10. The representative from Radiation Safety is recalled, and an experimenter is "suited" to reenter the hood to perform the following functions:

a. Slowly bleed hood air back into the furnace chamber and calorimeter.

b. Detach the flange between the calorimeter and the drop tube.

c. Survey the calorimeter receiver tube for alpha contamination.

(1) If contamination is not detected,

(a) remove the sample capsule with tongs,

(b) survey the capsule, and

(c) place the capsule in a clean, preweighed container for capsule removal from the hood and weighing.

(2) If contamination is detected,

(a) carefully remove the sample capsule with tongs,

(b) place the capsule in a clean, preweighed container for capsule removal from the hood and weighing,

(c) remove all loose alpha contamination from the receiver and the drop tube,

(d) survey the surrounding area in the hood,

(e) carefully remove the cover from the furnace chamber and check for alpha contamination (if detected, all loose contamination is removed),

(f) lift out the condenser-discharge drop-system-electrode assembly, survey, and clean it if necessary, and

(g) leave the hood and discard the protective gear with the surveillance from the representative from Radiation Safety as previously explained in Sect. III.B.4.

11. The container with the capsule is weighed and later removed to the Alpha Facility for various analyses.

12. The numerous calculations with the data obtained during the experiment are performed.

This basically completes a cycle of operation with the high-temperature drop-calorimeter system and related equipment in enthalpy measurements of uranium-plutonium oxides.

IV. EXPERIMENTAL RESULTS

A. Solid Tungsten

As part of the testing of this high-temperature calorimeter system for use with radioactive sample materials, some measurements were made of the enthalpy of tungsten at high temperature. Four successive drops were made in the range 3110-3568°K. Deviations of the results from previous data reported by Leibowitz *et al.*⁷ varied from +0.85 to -0.63% with a mean deviation of 0.57%. This is considered to be satisfactory agreement.

B. Uranium Dioxide

Three experiments were performed at approximately 3000°K to check the enthalpy values for solid uranium dioxide reported previously by

Leibowitz *et al.*⁸ The three data points are plotted in Fig. 8 along with data of Leibowitz *et al.*⁸ and Hein and Flagella.⁹

An additional liquid uranium dioxide datum point was obtained at 3523°K and is shown in Fig. 8 to be in agreement with the other liquid-uranium dioxide data reported by Leibowitz *et al.*¹⁰

C. Uranium-Plutonium Dioxide

Fig. 8. Enthalpy of UO_2 to 3523°K. ANL
Neg. No. 308-2174 Rev. 2.

Measurements of the enthalpy of solid uranium-plutonium dioxide between 2348 and 3005°K have been completed, and the results will be published elsewhere. The enthalpy of liquid uranium-plutonium dioxide is being measured.

V. CONCLUSION

This high-temperature calorimeter system has proven to be very reliable for enthalpy increment studies with plutonium-containing materials. Much emphasis in the design and construction of this system has been given to the safety of the experimenters as well as to other personnel working in nearby areas.

The cost of putting this experiment into a walk-in hood was considerably less than if the equipment were constructed in a glovebox-type complex. Furthermore, the ease of doing an experiment with radioactive materials in this system is an important advantage.

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