Examination of errors that occur
when using a gas-filled calorimeter.

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Abstract

Measurement of a reaction between D_2 gas and a material using a calorimeter that is calibrated using H_2 will show erroneous excess power production at temperatures above ambient if all energy present in the calorimeter is not totally measured, a requirement very difficult to accomplish. This insidious error is explored using a stable Seebeck calorimeter.

Introduction

Exposure of certain powders to D_2 gas has been proposed to generate energy by a novel nuclear process. Verification of this claim requires use of an accurate calorimeter, a method to determine how much gas reacts with the sample, and a correlation between energy production and helium increase in the D_2 gas. Such a system has been constructed and will be described in other papers. This paper addresses an important source of error this study has revealed.

A useful calorimeter must meet several requirements including: 1. be calibrated over a range of power and sample temperature; 2. be stable over a long time; 3. have applied electric energy used for calibration released near where the anomalous heat is generated so as to avoid errors that temperature gradients would generate: 4. have a minimum energy loss or gain from the sample that bypasses detection.

The effect of #4 when using a conventional calibration based on H_2 is explored in this paper. This is a major source of error in such measurements and can appear to indicate stable excess energy when the behavior of D_2 is referenced to H_2 even though no excess is actually produced. This error is universal to all types of calorimeters used in this manner because it is caused by the difference in thermal conductivity between D_2 and H_2.

Apparatus

The present design is a Seebeck-type calorimeter (Fig. 1) in which the copper sample container is cemented to a TEC through which most energy is caused to pass. The sample (3-5 g) is contained within an aluminum foil cup that is placed in the copper cell. A resistor (~20 ohm), placed in the powder, heats the sample and provides a means to calibrate the calorimeter using electric power generated exactly where the novel energy is expected to originate. The aluminum cup containing the sample sits on a 100 ohm Pt RTD that measures sample temperature. A silvered vacuum-Dewar surrounds the cell and reduces heat loss from the cell through the surrounding gas. Consequently, heat can leave mostly by passing through the thermoelectric converter (TEC) and be removed from the system by flowing constant-temperature water (27±0.02° C). The system is attached to a source of vacuum (<1x10^{-7} torr) and to sources of D_2 or H_2 gas.
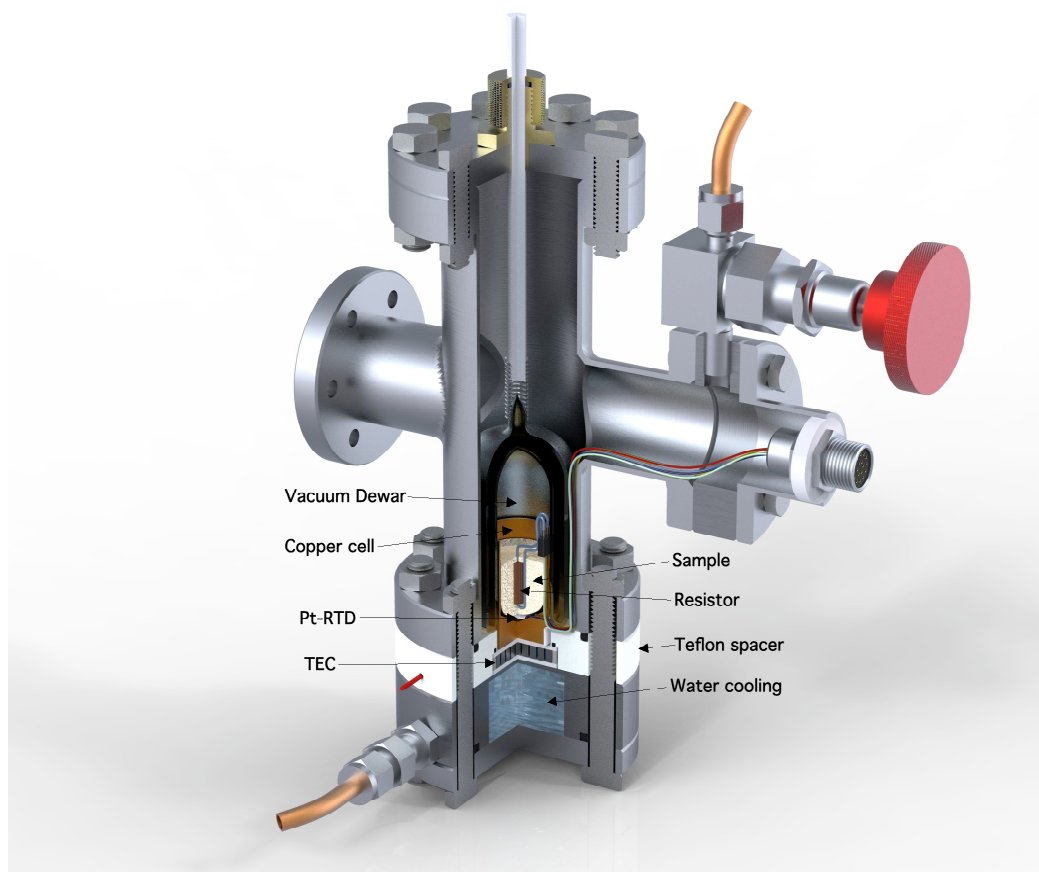
FIGURE 1. Exploded view of the calorimeter.

Figure 2 shows the copper cell in which the RTD can be seen. The resistor is plugged into a socket on the rim of the copper cup, which allows it to be removed when the sample is changed. Applied voltage is measured at this socket. The Dewar is shown in its place over the cell in Fig. 3. The seal between the Dewar and the Teflon is not gas-tight, allowing the sample to experience the surrounding gas pressure. The Teflon spacer provides a degree of thermal isolation for the cell and allows a gas tight seal at the top surface of the TEC. Consequently, the body of the TEC is not exposed to the gas used in the calorimeter. The completed assembly is shown in Fig. 4 and the entire apparatus is shown in Fig. 5.

The upper temperature limit is determined by the ability of the resistor to tolerate the temperature. A ceramic high-temperature type resistor is presently used allowing temperature in excess of 200° C to be maintained. The calorimeter requires about 120 minutes to achieve steady-state conditions after applied power is changed.

FIGURE 2. Cell assembly with aluminum-foil sample holder and resistor. The resistor has since been changed to a high temperature ceramic type. The RTD used to measure sample temperature is visible at the bottom of the copper cell. Gravity maintains contact between the aluminum cup and the RTD.

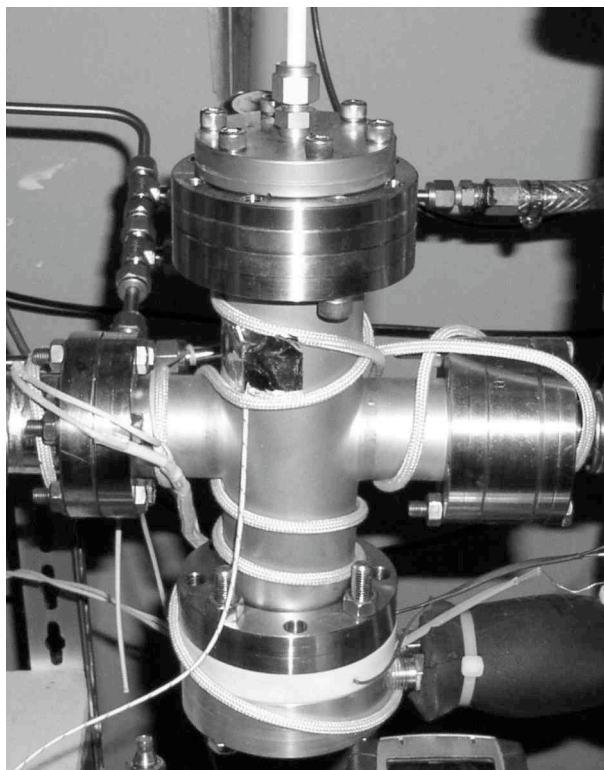FIGURE 3. Cell assembly covered by the vacuum Dewar.

FIGURE 4. Calorimeter assembly shown attached to the vacuum system and the source of cooling water.
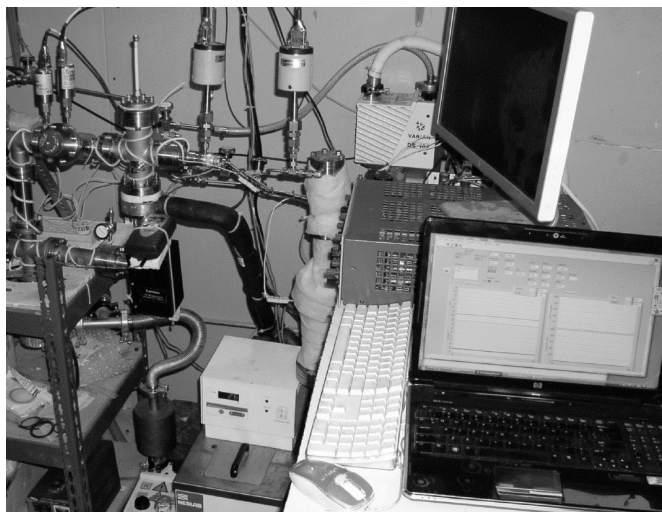

FIGURE 5. Completed apparatus shown with the Dewar in the up position. Power is applied to the heating tapes to maintain the wall at constant temperature (26°). The two pressure gauges (0-1000 mm) are visible to the right of the calorimeter. A 0-15 V DC power supply provides power to the resistor. Measurements are made using a National Instruments DA system and Labview.

The study starts by placing D_2, H_2 (~650 mm), air or vacuum in the calorimeter in sequence with the cell empty of sample. Measured electric power up to 8 watts is applied to the resistor in steps to achieve a series of temperatures between room temperature and 218° C. The resulting TEC voltage and cell temperature were measured when a relatively poor vacuum was in the Dewar owing to a leak and again when a good vacuum was restored (<5x10^{-7} torr). The resulting relationship between applied power and TEC voltage is plotted in Figs. 6 and 7. Each measurement is compared to the least-squares equation used to fit the respective data set and the difference is plotted as a function of sample temperature in Fig. 8 for the poor vacuum and in Fig. 9 for the good vacuum conditions. Almost all points are within a range of ±0.010 W around zero, which gives the maximum random variation in each measurement. If the results using H_2 are subtracted from those using D_2, as would be done if H_2 had been used to calibrate the calorimeter, an apparent excess energy is revealed that increases with sample temperature. This apparent excess is not real.

While the Dewar prevents most heat from leaving the cell, some loss is expected owing to gas conduction. As a result, the behavior is not the same for all gases. The amount of loss can be calculated by comparing the behavior of various gases to vacuum, which is expected to allow no gas conduction and very little energy loss. The amount of loss compared to vacuum is calculated and compared to the known thermal conductivities of the gases in Fig. 10. This comparison shows a 14% power loss at about 200° when H_2 or D_2 is used with a poor vacuum in the Dewar and about 10% loss when a good vacuum is used. As thermal isolation provided by the Dewar increases, the difference between H_2 and D_2 is expected to decrease. This decrease is apparently not linear in this calorimeter because the 14% and 10% loss conditions have essentially the same error between H_2 and D_2 (Figs. 8, 9, and 10).
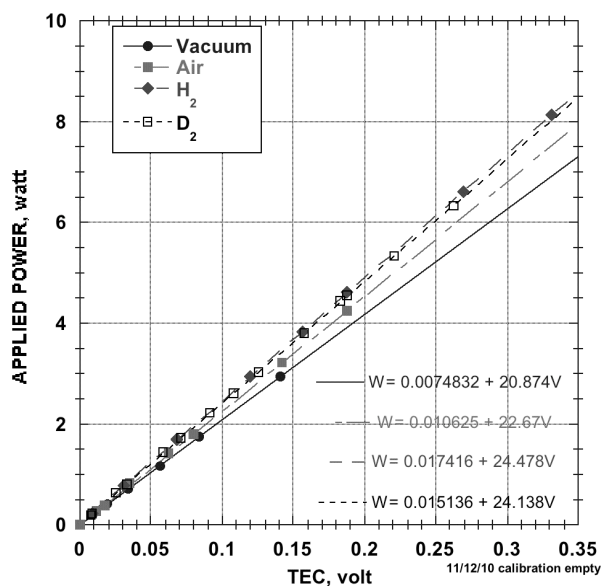

FIGURE 6. Relationship between applied power and the voltage generated by the thermoelectric converter (TEC) when a poor vacuum was present in the Dewar, thereby allowing greater loss of energy from the heated cell.
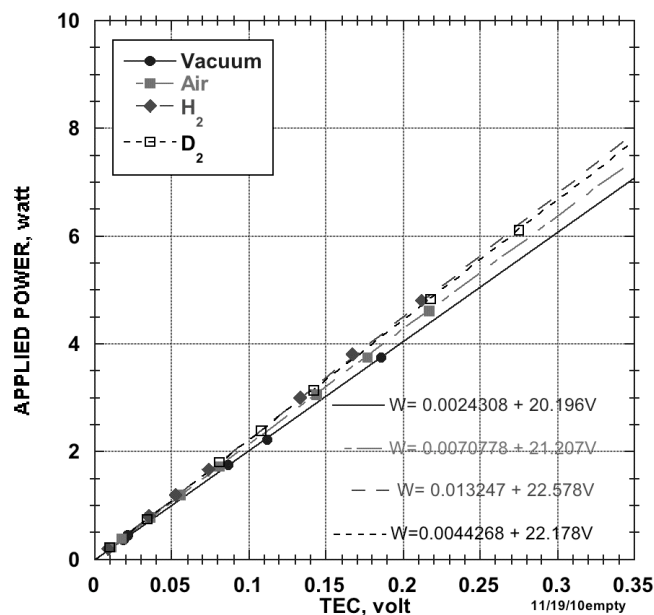
FIGURE 7. Relationship between applied power and the voltage generated by the thermoelectric converter (TEC) when a good vacuum was present in the Dewar.

Sample temperature at the same applied power is also strongly affected by the thermal conductivity of the gas, as shown in Fig. 11. In this case, the conduction through the gas moves heat to the TEC and away from the RTD. This is an example of the behavior expected when temperature is measured within a system and it alone is used to determine whether extra energy is made. In this case, a one watt error at 200° would be expected based on a H_2 calibration. Consequently, sample temperature cannot be used as an accurate measurement of excess energy. Using a vacuum and noting the large change in the relationship between sample temperature and applied power can reveal the existence of this error type.
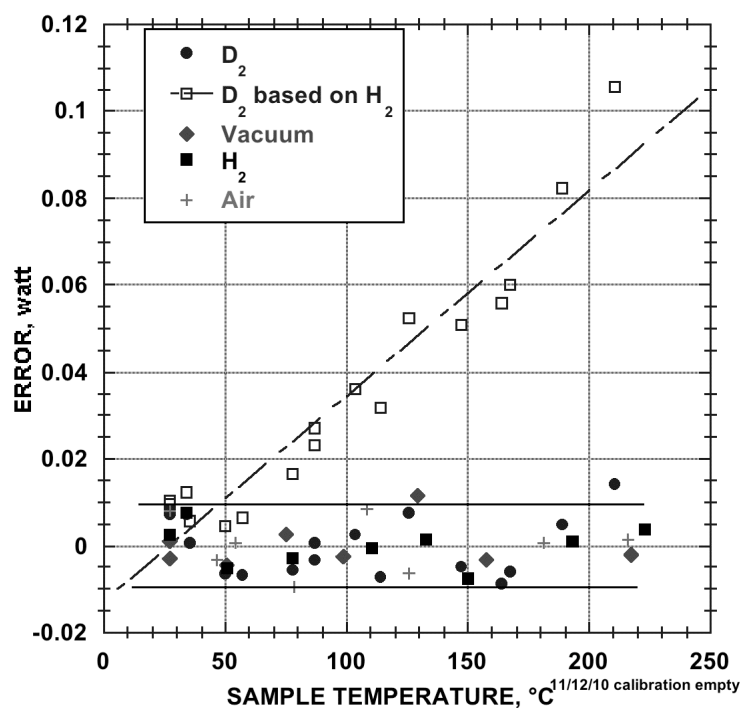
FIGURE 8. Difference between each data point and the least-squares equation applied to each data set for poor vacuum conditions in the Dewar. The curve is shown that would result if the equation obtained from H_2 were applied to D_2.
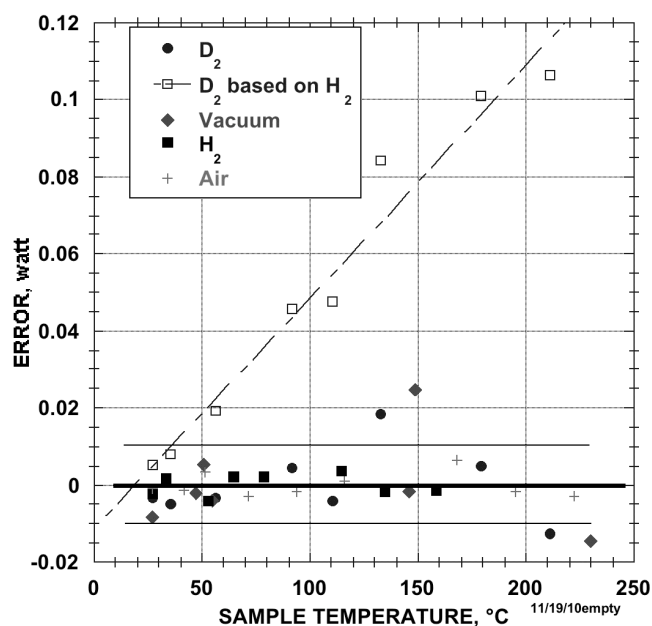

FIGURE 9. Difference between each data point and the least-squares equation applied to each data set for good vacuum conditions in the Dewar. The curve is shown that would result if the equation obtained from H_2 were applied to D_2.
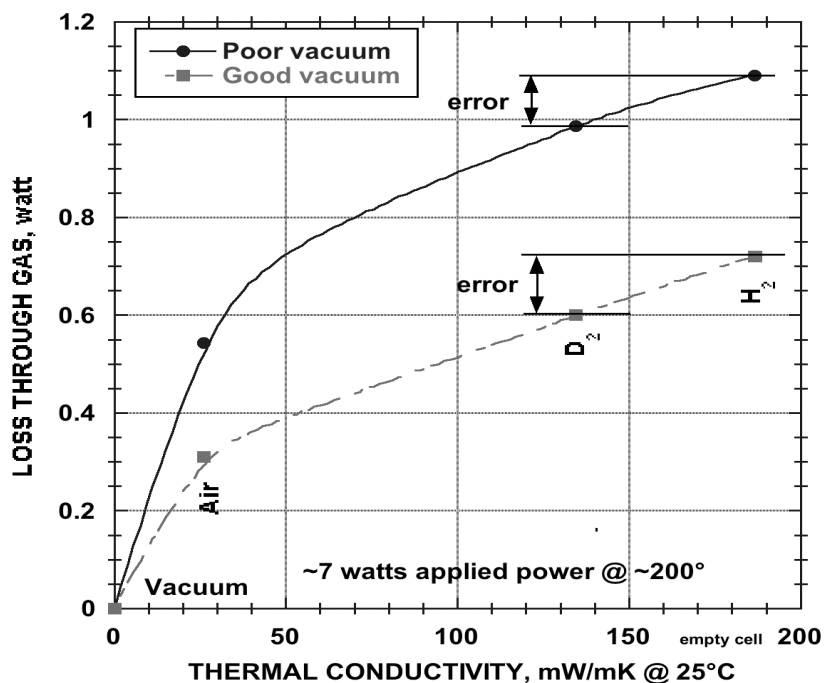
FIGURE 10. Comparison between the amount of power lost at about 200° when various gases are in the cell at pressures between 600-700 mm and the Dewar has different thermal isolation ability. The behavior is not sensitive to pressure.
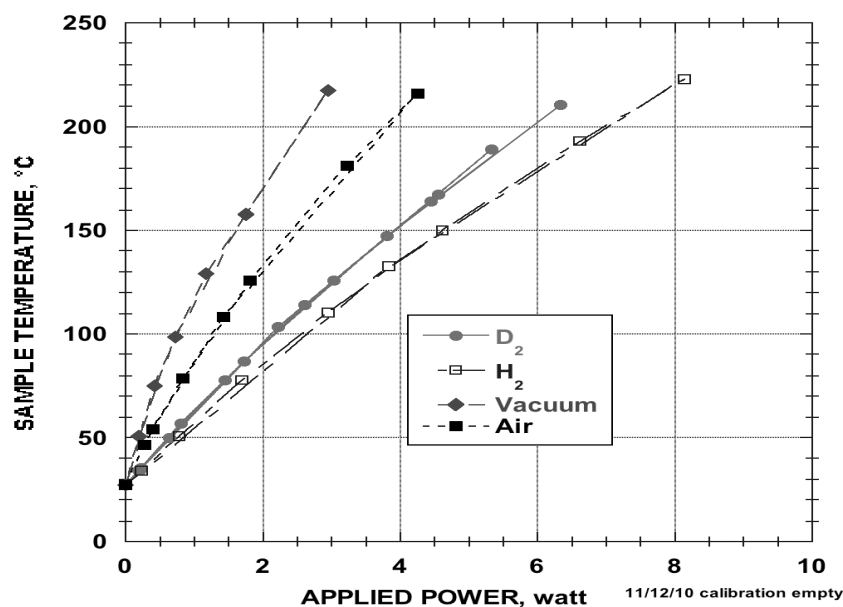

FIGURE 11. Sample temperature as a function of applied power for various gases. The relationship between the various conditions is directly related to the thermal conductivity in the gas-space. More power is required to achieve the same temperature when H_2 is used compared to vacuum because more energy is lost from the cell-system without heating the RTD when H_2 is used. In this case, much of the loss is through the TEC.

Discussion

The accuracy of a calorimeter in which gas is present is sensitive to the thermal conductivity of this gas because energy can move through the gas from where is being created and be lost before the amount can be measured. If such a calorimeter is calibrated using a different gas than the one being studied, i.e. using H_2 calibration while studying the effect of D_2, an apparent excess energy will be found that is produced only by the difference in thermal conductivity of these two gases. In this case, H_2 removes heat more effectively than does D_2, which means D_2 appears to generate excess energy equal to the difference in loss when H_2 is used as the reference gas.

Although the present design is basically a Seebeck type, the power is actually proportional to the temperature difference across the TEC thickness. This temperature could be measured several different ways and each will show the same kind of error. In other words, the same error will result regardless of how temperature is measured if heat is allowed to escape from the calorimeter before its value is measured. Even a flow-type calorimeter will show a difference between H_2 and D_2 if all heat generated in the cell by any means is not captured by the water.

The present design uses a Dewar to prevent significant loss. If this loss changes with time, the error based on a H_2 calibration will grow and this error will have all the expected characteristics of an increase in excess energy. On the other hand, if the device had been calibrated with D_2 before the unknown sample was inserted, any real excess would appear to decrease as the loss of heat increased. This is a more conservative situation than the former one. The amount of error produced by this unknown heat loss can be determined by comparing the slope of watt vs TEC volt (or degrees if a temperature is measured) when a vacuum is used to that obtained when H_2 is used. To the extent that these slopes differ, heat is being lost and the any apparent excess power is highly questionable. Nevertheless, error can be reduced using the following procedure.

1. Calibrate the calorimeter while empty of sample or containing an inert material using both D_2 and H_2.
2. Place the unknown material in the cell and compare the behavior to the H_2 calibration. If no change is observed, the calibration based on D_2 can be accepted as being unchanged. If a change in behavior based on H_2 is detected, the D_2 calibration can be corrected.
3. Examine the unknown material using the corrected D_2 calibration. At no time is the H_2 calibration used to directly calculate excess energy.

The error is linearly proportional to the difference between the sample temperature and the environment. As a result, the apparent excess increases from zero at room temperature and becomes larger as temperature is increased. Such a behavior would not be expected from a true energy generated by the sample because room temperature has no special significance to the nuclear reaction. True excess would be expected to increase in a nonlinear way from an arbitrary temperature. In addition, a true energy will be very sensitive to the conditions previously experienced by the sample Therefore, a stable and linear behavior that starts to increase as temperature is raised above room temperature must be viewed with suspicion, as this study demonstrates.

Conclusion

A significant error can occur in calorimeters that measure energy produced by a reaction involving D_2 when the calibration is based on H_2. This error can be misinterpreted as excess energy because it increases with temperature and appears to go away when the D_2 is removed and replaced by H_2. Application of proper procedures can eliminate the error.