

Thermal Dynamics of Bomb Calorimeters

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EXECUTIVE SUMMARY

An analysis was performed to account for instrument dynamics and heat losses or gains at the boundaries on the heat measured in bomb calorimeters by different standard methods. The objective was to develop a general relationship between the measured temperature history and the heat released in a bomb calorimeter in a prolonged process during which the thermal dynamics of the calorimeter and heat losses to the environment could affect the result. An analytic expression was derived and tested by calculating the heat of combustion from the measured temperature history for the three common methods of bomb calorimetry: adiabatic, isoperibol, and static jacket. In each case, the analytic expression gave accurate heats of combustion by explicitly accounting for the instrument dynamics and heat losses at the boundaries without the need for empirical temperature corrections as in the standard methods. Therefore, the validated analytic result is useful for calculating the heat of an intermittent or prolonged process, such as electrical resistance heating and subsequent thermal runaway of lithium ion batteries, in a bomb calorimeter.

INTRODUCTION

The bomb calorimeter [1] is widely used to determine the combustion heat of foods and condensed fuels using standard methods [2–7]. These standard methods use elaborate piecewise corrections to account for non-adiabatic conditions (i.e., heat exchange with the surroundings during a test in which heat is released instantaneously, as an impulse) [8]. If heat is released intermittently or over an extended time period, it is not clear that the mathematics used in the standard methods to compute the heat of an impulsive process are correct. The three principle methods of bomb calorimetry (adiabatic, isoperibol, and static jacket) differ only in their boundary conditions. For each of these methods, the heat of an arbitrary process occurring in the pressure vessel should be calculable from the temperature history of the water bath. The present approach is to use a lumped heat transfer model of a standard bomb calorimeter to solve for the heat of an arbitrary process in terms of the temperature history of the calorimeter. Good agreement between the theoretical and measured calorimeter responses to a heat pulse (combustion) would validate the model and provide the heat transfer and thermal capacitance coefficients for the bomb calorimeter.

CALORIMETER MODEL

The thermal dynamics of bomb calorimeters are modeled using a lumped heat transfer analysis in which heat is released in a pressure vessel/bomb immersed in a stirred water bath that is surrounded by a static air space bounded by an insulated (static) jacket, a constant/controlled temperature jacket (isoperibol), or a changing temperature (adiabatic) jacket. A schematic diagram of a standard bomb calorimeter system used for combustion measurements [2–4] is shown in figure 1. The steel pressure vessel (bomb) containing the sample at a uniform temperature T_b is immersed in a stirred water bath at temperature T_w , where the temperature of the calorimeter system is measured and recorded as a function of time, t . The water bath is inserted into an enclosed jacket having temperature T_j that is either static ($T_j \approx T_\infty$), held at a constant temperature ($T_j \geq T_\infty = \text{constant}$), or matched to the water bath temperature to prevent heat escape ($T_j = T_w$). These three boundary conditions (methods) are referred to as static jacket, isoperibol, and adiabatic bomb calorimetry, respectively. When heat Q is generated inside the pressure vessel (bomb) during an experiment at rate $dQ/dt = Q'$, the rate of change of the bomb's internal energy is:

$$C_1 \frac{dT_b}{dt} = Q' - K_1(T_b - T_w) \quad (1)$$

The rate of internal energy change of the water bath is the difference between the heat transferred to the water bath from the bomb and the heat lost from the water bath to the surroundings through the air gap and jacket:

$$C_2 \frac{dT_w}{dt} = K_1(T_b - T_w) - K_2(T_w - T_j) \quad (2)$$

Temperature measurements are made in the water bath during the experiment, and the heat of the process is calculated from the temperature difference, $\theta_2 = T_w - T_j$. In the bomb calorimeter of

figure 1, depending on the method used, the water bath either: 1) retains all the heat of the process (adiabatic), 2) absorbs heat from the combustion process and jacket (isoperibol), or 3) absorbs heat from the combustion process and loses heat to the environment (static) jacket. The jacket temperature, T_j , which is a boundary condition, defines these three methods of bomb calorimetry. They are: $T_w < T_j$ (isoperibol); $T_w = T_j$ (adiabatic), $T_w > T_j$ (static jacket).

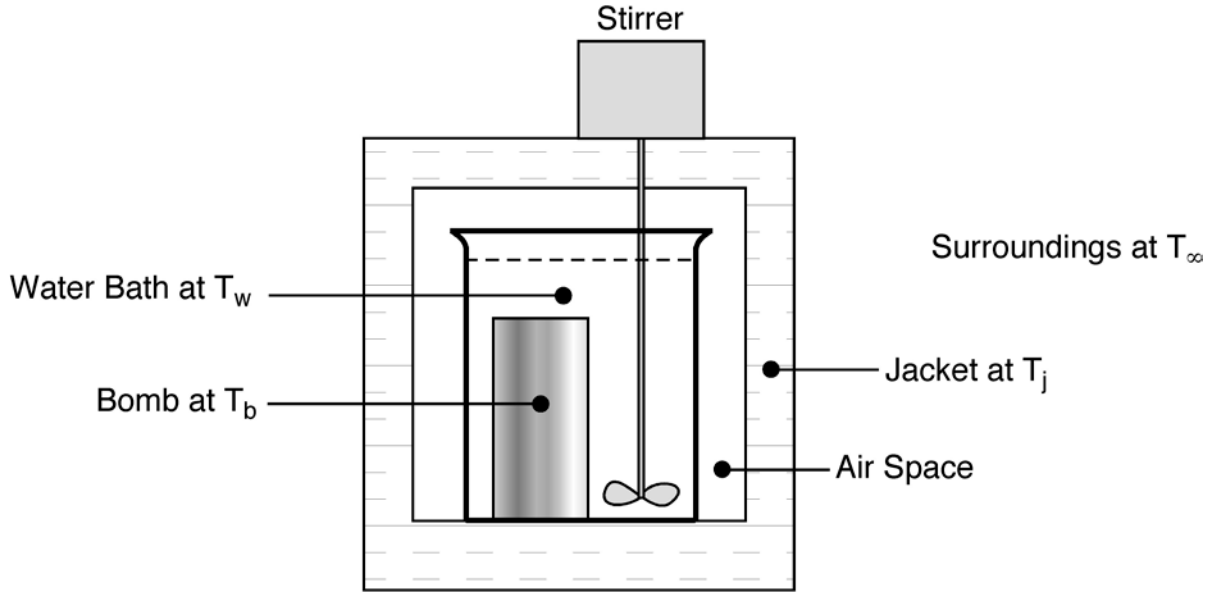


Figure 1. The bomb calorimeter system of lumped heat transfer analysis

HEAT RELEASED IN AN ARBITRARY PROCESS

To begin, define a temperature difference between the pressure vessel/bomb and the water bath, $\theta_1 = T_b - T_w$ and a characteristic time for the bomb, $\tau_1 = C_1/K_1$, such that equation 1 becomes:

$$\frac{d\theta_1}{dt} + \frac{\theta_1}{\tau_1} = \frac{Q'}{C_1} \quad (3)$$

The temperature difference between the water bath and the jacket is $\theta_2 = (T_w - T_j)$ and the characteristic time of the calorimeter system (bomb + water bath) is $\tau_2 = C_2/K_2$. With these definitions, equation 2 becomes:

$$\frac{d\theta_2}{dt} + \frac{\theta_2}{\tau_2} = \frac{K_1}{C_2} \theta_1 \quad (4)$$

Equations 3 and 4 are coupled differential equations that must be solved for the change in the measured bath temperature history, $T_w(t)$. The strategy is to solve equations 3 and 4 for the heat of an arbitrary process in terms of $\theta_2(t)$. Taking the Laplace transforms of equation 3, with superscripted bars indicating the transformed function and s indicating the transform variable:

$$s\bar{\theta}_1 - \theta_1(0) + \frac{\bar{\theta}_1}{\tau_1} = \frac{s\bar{Q}}{C_1} - Q(0) \quad (5)$$

Because $\theta_1(0) = T_b - T_w = Q(0) = 0$ at $t = 0$:

$$\bar{\theta}_1 = \frac{s\bar{Q}}{C_1} \left(\frac{\tau_1}{1 + s\tau_1} \right) \quad (6)$$

The Laplace transform of equation 4 is:

$$s\bar{\theta}_2 - \theta_2(0) + \frac{\bar{\theta}_2}{\tau_2} = \frac{K_1}{C_2} \bar{\theta}_1 \quad (7)$$

Substituting equation 6 for $\bar{\theta}_1$ into equation 7 and rearranging terms, the transformed equation for the heat of a process is:

$$\bar{Q} = K_2 \frac{\bar{\theta}_2}{s} + C_2 \left(1 + \tau_1 / \tau_2 \right) \bar{\theta}_2 + C_2 \tau_1 s \bar{\theta}_2 - C_2 \theta_2(0) \left(\frac{1}{s} + \tau_1 \right) \quad (8)$$

The inverse Laplace transform of equation 8, with x as the dummy time variable of integration, is:

$$Q(t) = K_2 \int_0^t \theta_2(x) dx + C_2 \left(1 + \frac{\tau_1}{\tau_2} \right) \theta_2(t) + C_2 \tau_1 \frac{d\theta_2(t)}{dt} - C_2 \theta_2(0) + C_2 \tau_1 \delta(0) \quad (9)$$

The last term in equation 9 contains the unit impulse, $\delta(t)$. For a heat pulse at $t = 0$:

$$\delta(0) = \begin{cases} 0 & t \neq 0 \\ \infty & t = 0 \end{cases}$$

If the initial condition is $T_b = T_w = T_0$ when the bomb is fired at $t = 0$, then, $\theta_2(t) = (T_w - T_j) = (T_w - T_0) - (T_j - T_0) = \Delta T - \theta_j$ and $\theta_2(0) = -\theta_j$. With these substitutions and with $\delta(0) = 0$, equation 9 becomes:

$$Q(t) = K_2 \int_0^t \Delta T(x) dx + C_2 \left(1 + \frac{\tau_1}{\tau_2} \right) \Delta T(t) + C_2 \tau_1 \frac{d\Delta T(t)}{dt} - K_2 \int_0^t \theta_j(x) dx - C_2 \tau_1 \frac{d\theta_j}{dt} - C_2 \left(1 + \frac{\tau_1}{\tau_2} \right) \theta_j + C_2 \theta_j \quad (10)$$

For constant θ_j and for $\tau_2 \gg \tau_1$ the last three terms vanish:

$$\begin{aligned}
Q(t) &= K_2 \int_0^t \Delta T(x) dx + C_2 \left(1 + \frac{\tau_1}{\tau_2} \right) \Delta T(t) + C_2 \tau_1 \frac{d\Delta T(t)}{dt} - K_2 \int_0^t \theta_j(x) dx \\
&= C_2 \left\{ \frac{1}{\tau_2} \int_0^t \Delta T(x) dx + \left(1 + \frac{\tau_1}{\tau_2} \right) \Delta T(t) + \tau_1 \frac{d\Delta T(t)}{dt} - \frac{1}{\tau_2} \int_0^t \theta_j(x) dx \right\} \\
&= C_2 f(t)
\end{aligned} \tag{11}$$

Equation 11 shows that the heat of any process in a bomb calorimeter is proportional to the thermal capacity of the calorimeter system, C_2 , and a function of time, $f(t)$. Equation 11 is useful for direct calculation of the heat of process (including combustion) in an adiabatic, isoperibol, or static jacket bomb calorimeter without resorting to complex temperature corrections [8–10] for non-adiabatic boundary conditions.

TEMPERATURE HISTORY FOR A HEAT PULSE (COMBUSTION)

When heat is generated rapidly in the calorimeter at time $t = 0$ (e.g., by combustion) such that the duration of heat generation is much shorter than τ_1 or τ_2 , the heat release rate Q' can be written in terms of the heat pulse of magnitude Q released at $t = 0$ using the unit impulse $\delta(t)$. Substituting $Q'(t) = Q\delta(t)$ into equation 3, taking Laplace transforms, and rearranging:

$$\bar{\theta}_1 = \frac{Q}{C_1} \left(\frac{\tau_1}{1 + s\tau_1} \right) + \theta_1(0) = \frac{Q}{C_1} \left(\frac{\tau_1}{1 + s\tau_1} \right) \tag{12}$$

Substituting equation 11 for $\bar{\theta}_1$ into equation 7, solving for $\bar{\theta}_2$ and taking the inverse Laplace transform of the result:

$$\theta_2(t) = \theta_2(0)e^{-t/\tau_2} + \frac{Q}{C_2(1 - \tau_1/\tau_2)} \left(e^{-t/\tau_2} - e^{-t/\tau_1} \right) \tag{13}$$

Substituting $\theta_2(0) = -\theta_j$ into equation 12 gives the temperature history of a bomb calorimeter for a heat pulse of magnitude Q released at $t = 0$:

$$\Delta T = \theta_j \left(1 - e^{-t/\tau_2} \right) + \frac{Q}{C_2(1 - \tau_1/\tau_2)} \left(e^{-t/\tau_2} - e^{-t/\tau_1} \right) \tag{14}$$

A fit of equation 14 to the measured temperature history $\Delta T(t)$ for a heat pulse of known magnitude Q allows the calorimeter constants τ_1 , τ_2 , and C_2 to be determined.

MODEL VALIDATION

ADIABATIC METHOD ($K_2 = 0$)

For the adiabatic calorimeter, no heat is lost to the surroundings. This is equivalent to setting $K_2 = 0$ and $\tau_2 = \infty$ in equations 11 and 14. Making these substitutions in equation 14 gives the temperature history for an adiabatic calorimeter:

$$\Delta T(t) = \frac{Q}{C_2} \left(1 - e^{-t/\tau_1}\right) \quad (15)$$

Equation 11 gives the heat of a process in an adiabatic bomb calorimeter in terms of the measured temperature rise of the bath when $K_2 = 0$ and $\tau_2 = \infty$:

$$Q(t) = C_2 \left(\Delta T + \tau_1 \frac{d\Delta T}{dt} \right) \quad (16)$$

When the bomb and water bath reach equilibrium, $d\Delta T/dt = 0$, and the total heat of the process is proportional to the steady-state (maximum) temperature rise:

$$Q = Q(\infty) = C_2 \Delta T(\infty) = C_2 \Delta T_{\max} \quad (17)$$

ISOPERIBOL METHOD ($\theta_j = \text{CONSTANT} > 0$)

In isoperibol bomb calorimetry, the jacket is maintained at a constant temperature that is above the bath temperature, so heat is added to the calorimeter before ($t < 0$), during ($t = 0$), and after ($t > 0$) firing. If the temperature rise of the water bath prior to firing (also called the initial period [8]) is measured, the rate of heat transfer from the jacket to the calorimeter is calculable from equation 14 with $Q = 0$. The result is:

$$\frac{T_j - T_0}{T_j - T_w} = e^{t/\tau_2} \quad (18)$$

Consequently, a plot of $\ln[(T_j - T_0)/(T_j - T_w)] = -\theta_j/\theta_2(t)$ versus $1/t$ has slope $1/\tau_2 = K_2/C_2$ from which K_2 can be determined if C_2 is known. Figure 2 shows such a plot for data obtained from the literature [11] and private communications [12] for an isoperibol bomb calorimeter. For this experiment, the reported [12] experimental parameters are $T_j = 25.58^\circ\text{C}$ (298.58K) and $Q_0 = 23,028$ J by benzoic acid combustion, and the calorimeter constants are: $C_2(1 + \tau_1/\tau_2) = 9965$ J/K. From this information and the slope of the plot in figure 2, $K_2 = (4.03 \times 10^{-5} \text{ s}^{-1})(9946 \text{ J/K}) = 0.40$ W/K, which is the reported value for the calorimeter [12].

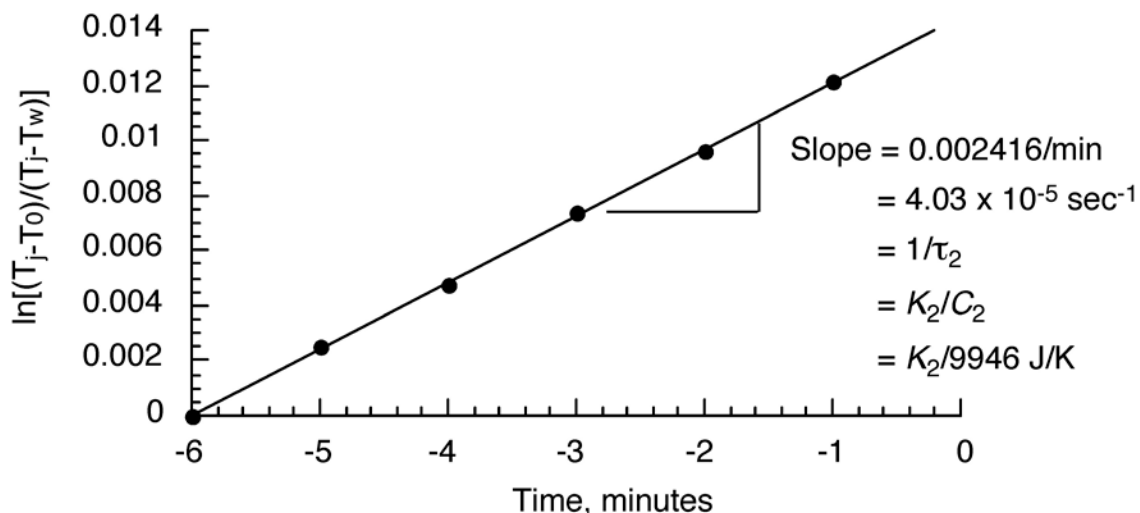


Figure 2. Plot of equation 18 used to obtain K_2 for isoperibol bomb calorimeter

Figure 3 is a plot of the temperature history of an isoperibol bomb calorimeter having $T_j = 25.58^\circ\text{C}$ (298.6K) [11] and the fit of these data to equation 14 for $Q_0 = 23,028$ J using $\tau_1 = 0.8$ minutes and $\tau_2 = 415$ minutes as fitting parameters from which $C_2(1 + \tau_1/\tau_2) = 9965$ J/K and $C_2 = (9965 \text{ J/K})/(1 + 0.8/415) = 9946$ J/K. These parameters are summarized in table 1.

Table 1. Heat of combustion (Q) and thermal constants of isoperibol bomb calorimeter

Q_0 (J)	θ_j ($^\circ\text{C}$)	θ_j (K)	C (J/K)	τ_1 (min)	τ_2 (min)	K_2 (W/K)	C_2 (J/K)
23,028	25.58	298.74	9964.6	0.8	415	0.40	9946

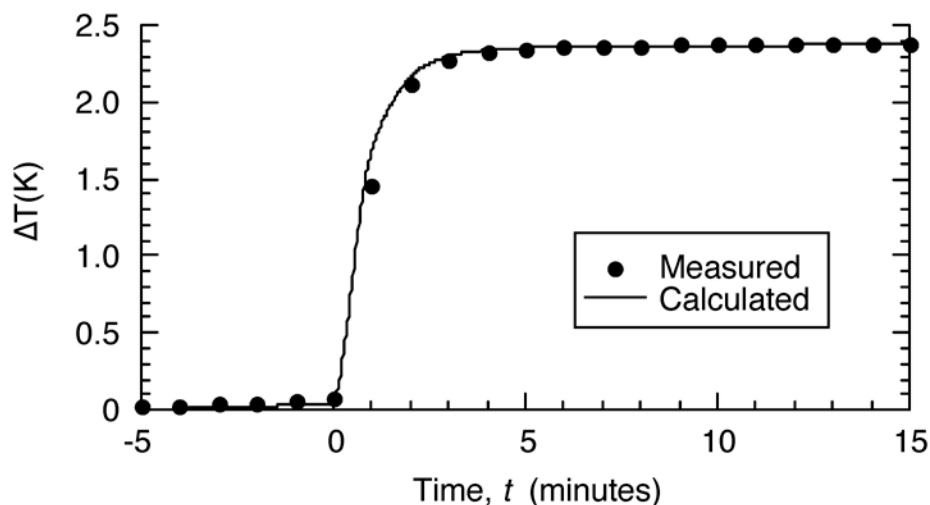


Figure 3. Measured (points) and calculated (line) temperature history for $Q_0 = 23,028$ J heat impulse in isoperibol calorimeter

In isoperibol calorimetry, the jacket temperature is held constant so $\theta_j = T_j - T_0$ is also a constant, and equation 11 becomes:

$$Q(t) = K_2 \int_0^t \Delta T(x) dx + C_2 \left(1 + \frac{\tau_1}{\tau_2} \right) \Delta T(t) + C_2 \tau_1 \frac{d\Delta T(t)}{dt} - K_2 \theta_j t \quad (19)$$

Figure 4 is a locally weighted least-squares fit of equation 19, evaluated for the temperature history in figure 3 and a benzoic acid heat of combustion $Q_0 = 23,028$ J. The steady-state value at $t > 7$ minutes is $\langle Q \rangle = 23,002 \pm 3$ J, which is within 0.1% of the reported Q_0 in table 1.

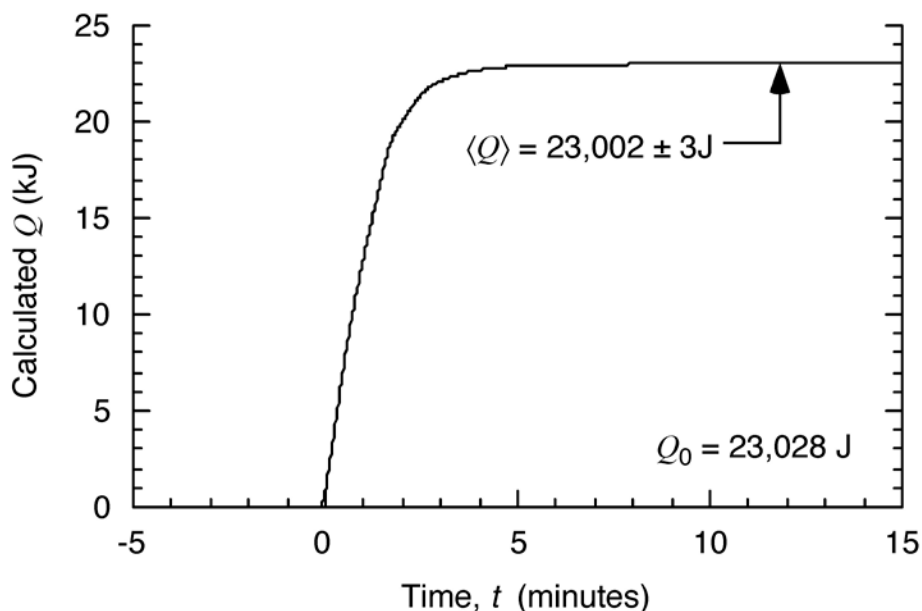


Figure 4. Measured temperature rise (points) and calculated heat (line) for benzoic acid combustion $Q_0 = 23,028$ J in isoperibol bomb calorimeter

STATIC JACKET CALORIMETER ($\theta_j \approx 0$)

A static jacket bomb calorimeter (Model 1341, Plain Jacket Oxygen Bomb Calorimeter, Parr Instrument Company, Moline, IL) was used in our laboratory for these experiments according to standard procedures [2-4]. The masses and heat capacities of the calorimeter system components are given in table 2. Benzoic acid ($Q_0 = 26.453$ kJ/g) from a commercial source was used for calibration and stored in a dessicator until use. Ambient (T_∞) and water bath temperatures (T_w) were logged continuously at 1 Hz for the duration of the experiment using a commercial data acquisition module and software (National Instruments, 11500 Mopac Expressway, Austin, TX 78759).

Table 2. Static jacket calorimeter component masses and heat capacities

Calorimeter Component	Mass (g)	Specific Heat, c (J/g-K)	Heat Capacity, C_i (J/K)
Combustion Bomb	2973	0.46	1368
Calorimeter Vessel	847	0.46	390
Bath Water	2000	4.18	8360
$C_2 = \Sigma C_i =$			10,118

Figure 5 is a plot of the measured temperature rise histories of the water bath $\Delta T(t)$ for benzoic acid combustions (including the fuse corrections), $Q_0 = 14,640$ J and $26,194$ J. The theoretical temperature rise history (equation 14 with $\theta_j = T_\infty - T_0$) was fit to the experimental data for each Q_0 , resulting in the solid line in figure 5 and the best-fit parameters in table 3. Note the similarity of the parametrically determined thermal response parameters in tables 1, 2, and 3 for bomb calorimeters from the same manufacturer. In tables 2 and 3, $C_1 = 1368$ J/K and $\tau_1 = 60$ s, so the heat transfer coefficient between the pressure vessel and the water bath is $K_1 = C_1/\tau_1 = 22.8$ W/K = 1.37 kJ/min-K, or approximately 500 W/m²-K, based on the surface area of the bomb.

Table 3. Best-fit thermal response parameters for static jacket bomb calorimeter

Q_0 (J)	ΔT_{\max} (°C)	C (J/K)	τ_1 (min)	τ_2 (min)	K_2 (W/K)	C_2 (J/K)
14,640	1.478	9905	1.0	550	0.300	9923
26,194	2.629	9963	1.0	550	0.303	9981
Average Values:		9934 ± 41	1.0	550	0.302	9952 ± 41

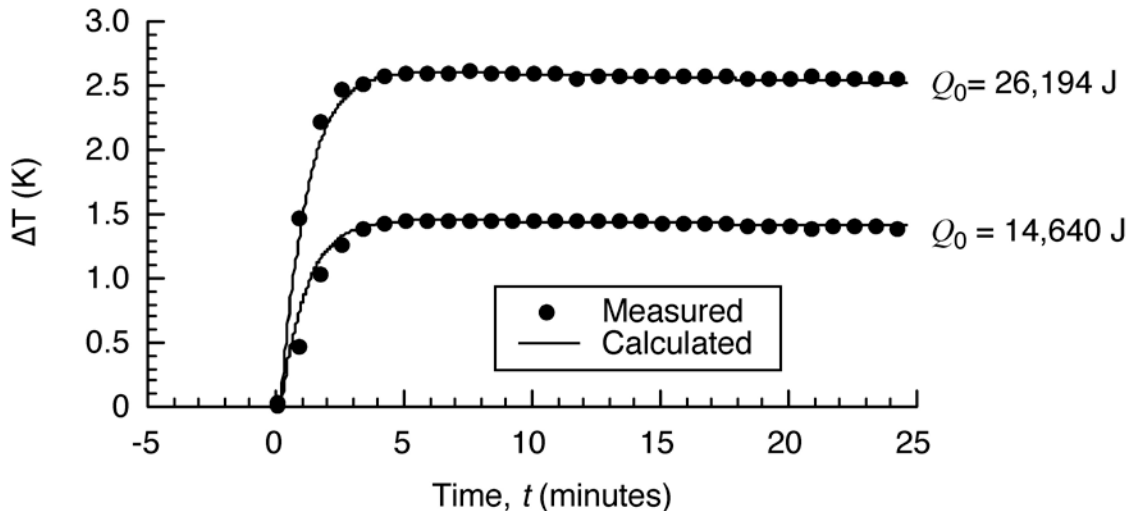


Figure 5. Measured and calculated temperature histories of water bath for Q in table 3

The static jacket bomb calorimeter can be classified as a ballistic calorimeter in that the temperature history for a heat pulse follows a ballistic trajectory, having a rising, maximum, and descending period [13]. As with the adiabatic and isoperibol methods of bomb calorimetry, the heat of a generalized process in a static jacket bomb calorimeter is calculable from the experimental data using equation 11, and the temperature history for a combustion experiment is given in equation 14. However, in this case, $T_j \approx T_\infty$, and the boundary condition is quasi-static, $\theta_j = T_\infty - T_0$.

Figure 6 is an expanded plot of the first several minutes of data in figure 5. The theoretical temperature histories calculated from equation 14 and the thermal response parameters in table 3 are shown as the solid lines through the experimental data points. The temperature in figure 6 reaches a maximum ΔT_{\max} in the static jacket bomb calorimeter at approximately 6 to 7 minutes after firing (i.e., $t_{\max} \approx 6-7$ minutes). The theoretical value of t_{\max} is obtained by substituting equation 14 into the integral term of equation 11, with $\theta_j \approx 0$ for the static jacket, and solving for the upper limit t_{\max} at ΔT_{\max} when $d\Delta T/dt = 0$. The result, which is evaluated using τ_1 and τ_2 from table 3, is:

$$t_{\max} = \frac{\tau_1 \tau_2}{\tau_2 - \tau_1} \ln \left[\frac{\tau_2}{\tau_1} \right] = 6.3 \text{ minutes} \quad (20)$$

This theoretical result, which is in excellent agreement with the data in figure 6, shows that the time to the maximum temperature rise for a combustion experiment in a static jacket bomb calorimeter, t_{\max} , depends only on the time constants τ_1 and τ_2 of the bomb and water bath, respectively. Substituting equation 20 for the upper limit of the integral term in equation 11 when $d\Delta T/dt = 0$ and $x = \tau_1/\tau_2$, shows:

$$Q = C_2 \left\{ 1 + x - \frac{x \ln[x]}{1-x} \right\} \Delta T_{\max} = C \Delta T_{\max} \quad (21)$$

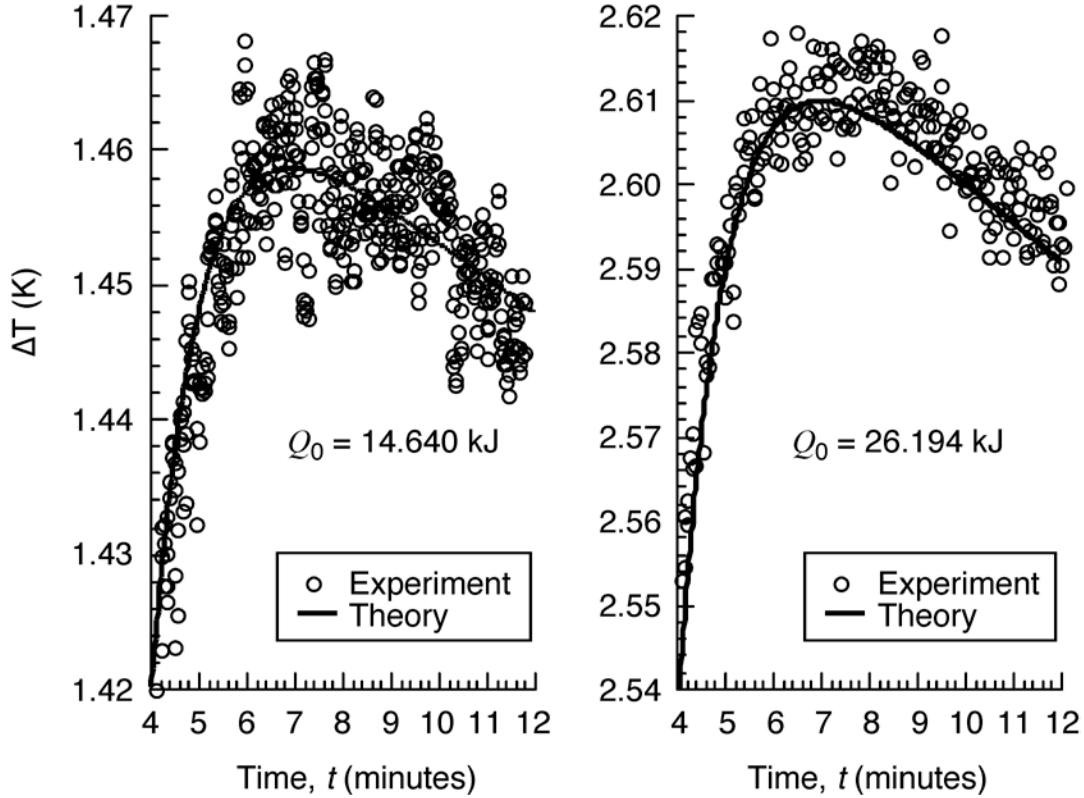


Figure 6. Temperature histories in the vicinity of ΔT_{\max} for Q_0 in table 3

Equation 21 shows that the energy equivalent of the calorimeter $C = Q/\Delta T_{\max}$ is a constant that depends only on the thermal response times of the bomb (τ_1) and water bath (τ_2). According to the present analysis, all thermal leakage and response time corrections for a static jacket bomb calorimeter are contained in the empirical proportionality constant C , and adjustments to ΔT_{\max} are unnecessary and inaccurate. Note that when $\tau_2 = \infty$ and $x = 0$, equation 21 is the adiabatic result, $Q = C_2 \Delta T_{\max}$.

In static jacket bomb calorimetry, the jacket temperature T_j approximates the time-average ambient temperature, $\langle T_\infty \rangle$. In this case, θ_j will be a small constant approaching zero, $\theta_{j,\infty} = T_j - T_0 \approx \langle T_\infty \rangle - T_0$, and equation 11 becomes:

$$Q(t) = K_2 \int_0^t \Delta T(x) dx + C_2 \left(1 + \frac{\tau_1}{\tau_2} \right) \Delta T(t) + C_2 \tau_1 \frac{d\Delta T(t)}{dt} - K_2 \theta_{j,\infty} t \quad (22)$$

Figure 7 is a locally weighted, least-squares fit of equation 22, evaluated for the data of figure 5 with the thermal parameters in table 3. The average plateau values between the vertical dashed lines in figure 7, $\langle Q \rangle = 14,632$ J and $\langle Q \rangle = 26,165$ J, are in excellent agreement with the nominal Q_0 in table 3 for the benzoic acid calibration experiments.

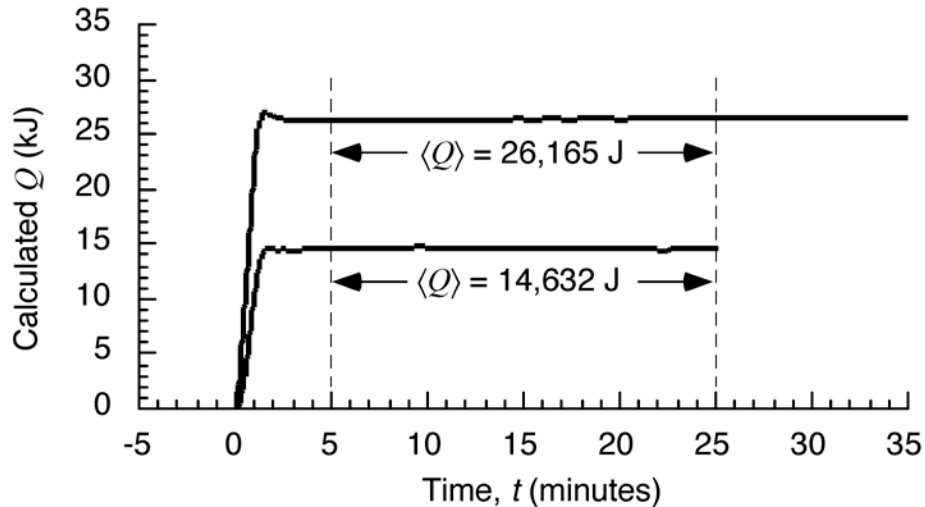


Figure 7. Calculated \bar{Q} using equation 21 and temperature histories of figure 5 compared to nominal values $Q_0 = 14.63$ kJ and $Q_0 = 26.165$ kJ in table 3

CONCLUSIONS

The heat released in an arbitrary process in a bomb calorimeter can be computed from the measured temperature history for three standard methods: adiabatic, isoperibol, and static jacket. For a heat impulse such as combustion, the heat released in adiabatic and static jacket calorimeters is proportional to the maximum temperature according to standard methods. For intermittent or protracted heat release histories, as occurs during electrical resistance heating and subsequent thermal runaway of lithium ion batteries, the heat released is directly calculable from the recorded temperature history using the present methodology without the need for semi-empirical corrections for non-adiabatic behavior.

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