Constant Volume Calorimetry

Constant Volume Calorimetry, also known as bomb calorimetry, is used to measure the heat of a reaction while holding volume constant and resisting large amounts of pressure. Although these two aspects of bomb calorimetry make for accurate results, they also contribute to the difficulty of bomb calorimetry. In this module, the basic assembly of a bomb calorimeter will be addressed, as well as how bomb calorimetry relates to the heat of reaction and heat capacity and the calculations involved in regards to these two topics.

Introduction

Calorimetry is used to measure quantities of heat, and can be used to determine the heat of a reaction through experiments. Usually a coffee-cup calorimeter is used since it is simpler than a bomb calorimeter, but to measure the heat evolved in a combustion reaction, constant volume or bomb calorimetry is ideal. A constant volume calorimeter is also more accurate than a coffee-cup calorimeter, but it is more difficult to use since it requires a well-built reaction container that is able to withstand large amounts of pressure changes that happen in many chemical reactions.

Structure of the Constant Volume Calorimeter

In a constant volume calorimeter, the system is sealed or isolated from its surroundings, and this accounts for why its volume is fixed and there is no volume-pressure work done. A bomb calorimeter structure consists of the following:

- Steel bomb which contains the reactants
- Water bath in which the bomb is submerged
- Thermometer
- A motorized stirrer
- Wire for ignition

All of these components are contained within the double-walled outer part of the calorimeter. After the initial temperature of the water is measured, the heated wire inside the bomb starts the reaction. After combustion the final temperature of the water is measured, and then the change in temperature of the reactants can be calculated. Through the combustion reaction, the temperature rises due to the conversion from chemical energy to thermal energy that occurs through the reaction.

Determining Heat of Reaction

The amount of heat that the system gives up to its surroundings so that it can return to its initial temperature is the heat of reaction. The heat of reaction is just the negative of the thermal energy gained by the calorimeter and its contents ($q_{calorimeter}$) through the combustion reaction.

$$q_{rxn} = -q_{calorimeter} \ (where \ q_{calorimeter} = q_{bomb} + q_{water}) \qquad \textbf{(1)}$$

If the constant volume calorimeter is set up the same way as before, (same steel bomb, same amount of water, etc.) then the heat capacity of the calorimeter can be measured using the following formula:

$$q_{calorimeter} = \ heat \ capicity \ of \ calorimeter \ x \ \Delta T \qquad \textbf{(2)}$$

Heat capacity is defined as the amount of heat needed to increase the temperature of the entire calorimeter by 1 degree Celsius. The equation above can also be used to calculate q_{rxn} from $q_{calorimeter}$ calculated by equation **(2)**. The heat capacity of the calorimeter can be determined by conducting an experiment.

Example

1.150 g of sucrose goes through combustion in a bomb calorimeter. If the temperature rose from 23.42°C to 27.64°C and the heat capacity of the calorimeter is 4.90 kJ/°C, then determine the heat of combustion of sucrose, $C_{12}H_{22}O_{12}$, in kj per mole of $C_{12}H_{22}O_{12}$.

Given:

- mass of $C_{12}H_{22}O_{12}$: 1.150 g
- $T_{initial}$: 23.42°C
- T_{final}:27.64°C
- Heat of Capacity: 4.90 kJ/°C

Using equation **(2)** calculate $q_{calorimeter}$:

$q_{calorimeter}$ = (4.90 kJ/°C) x (27.64 - 23.42)°C = (4.90 x 4.22) kJ = 20.7 kJ

Plug into equation **(1)**:

$$q_{rxn} = -q_{calorimeter} = -20.7 \ kJ$$

But the question asks for kJ/mol $C_{12}H_{22}O_{12}$, so this needs to be converted:

$$q_{rxn} = \frac{-20.7\ kJ}{1.150\ g\ C_{12}H_{22}O_{12}} = \frac{-18.0\ kJ}{g\ C_{12}H_{22}O_{12}}$$

Per Mole $C_{12}H_{22}O_{12}$:

$$q_{rxn} = \frac{-18.0\ kJ}{g\ C_{12}H_{22}O_{12}}\ X\ \frac{342.3\ g\ C_{12}H_{22}O_{12}}{1\ mol\ C_{12}H_{22}O_{12}} = \frac{-6.16\ X\ 10^3\ kJ}{mol\ C_{12}H_{22}O_{12}}$$

Problems

1. After going through combustion in a bomb calorimeter a sample gives off **5435 cal**. The calorimeter experiences an increase of **4.27°C** in its temperature. Using this information, determine the heat capacity of the calorimeter in kJ/°C.
2. Referring to the example given above about the heat of combustion, calculate the temperature change that would occur in the combustion of**1.732 g** $C_{12}H_{22}O_{12}$ in a bomb calorimeter that had the heat capacity of **3.87 kJ/°C**.
3. Given the following data calculate the heat of combustion in kJ/mol of xylose, $C_5H_{10}O_5$(s), used in a bomb calorimetry experiment: mass of $C_5H_{10}O_5$(s) = **1.250 g,** heat capacity of calorimeter = **4.728 kJ/°C,** Initial Temperature of the calorimeter = **24.37°C,** Final Temperature of calorimeter = **28.29°C.**
4. Determine the heat capacity of the bomb calorimeter if **1.714 g** of naphthalene, $C_{10}H_8$(s), experiences an **8.44°C** increase in temperature after going through combustion. The heat of combustion of naphthalene is **-5156 kJ/mol** $C_{10}H_8$**.**
5. What is the heat capacity of the bomb calorimeter if a **1.232 g** sample of benzoic acid causes the temperature to increase by **5.14°C**? The heat of combustion of benzoic acid is **-26.42kJ/g**.

Answers to Practice Problems

1. Use equation **(2)** to calculate the heat of capacity:

$q_{calorimeter} = \ heat\ capicity\ of\ calorimeter\ x\ \Delta T$

5435 cal = heat capacity of calorimeter x 4.27°C

Heat capacity of calorimeter = (5435 cal/ 4.27°C) x (4.184 J/1 cal) x (1kJ/1000J) = 5.32 kJ/°C

2. The temperature should increase since bomb calorimetry releases heat in an exothermic combustion reaction.

Change in Temp = (1.732 g $C_{12}H_{22}O_{12}$) x (1 mol $C_{12}H_{22}O_{12}$/342.3 g $C_{12}H_{22}O_{12}$) x (6.61 x 10^3 kJ/ 1 mol $C_{12}H_{22}O_{12}$) x (1°C/3.87kJ) = 8.64°C

3. [(Heat Capacity x Change in Temperature)/mass] =[((4.728 kJ/°C) x(28.29 °C – 24.37 °C))/1.250 g] = 14.8 kJ/g xylose

q_{rxn} = (-14.8 kJ/g xylose) x (150.13 g xylose/ 1 mol xylose) = -2.22x10³ kJ/mol xylose

4. Heat Capacity = [(1.714 g $C_{10}H_8$) x (1 mol $C_{10}H_8$/128.2 g $C_{10}H_8$) x (5.156x10³ kJ/1 mol $C_{10}H_8$)]/8.44°C = 8.17 kJ/ °C

5. Heat Capacity = [(1.232 g benzoic acid) x (26.42 kJ/1 g benzoic acid)]/5.14°C = 6.31 kJ/ °C

Outside links

- http://www.youtube.com/watch?v=muD84mkjVGM
- http://en.wikipedia.org/wiki/Calorimeter

References

1. Petrucci, Ralph H. Herring, F Geoffrey. Madura, Jeffery D. Bissonnette, Carey. GENERAL CHEMISTRY Principles and Modern Applications.Custom Edition for Chem 2 UCD. Upper Saddle River, New Jersey; Pearson Canada, 2011.
2. Oxtoby, David W. Gillis, H.P. Campion, Alan. Principles of Modern Chemistry. Sixth Edition. Belmont, Ca; Thompson Learning, Inc., 2008.
3. http://www.chem.ufl.edu/~itl/2045/lectures/lec_9.html