DETERMINATION AND MEASURE OF HEAT CAPACITY AT CONSTANT VOLUME AND PRESSURE.

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ABSTRACT

This work examines the determination and measuring of heat capacity at constant volume and constant pressures. Determining the heat capacity at constant volume from experimental volumetric data. The proposed methodology uses the experimental (P-ρ-T) data for a ternary mixture of methane, ethane and propane measured over a range of temperatures from 140K to 500K and at a pressure of up to 200MPa. The heat capacity of most systems is not a constant. Rather, it depends on the state variables of the thermodynamic system under study. Different measurements of heat capacity can be peformed commonly at constant pressure and temperature. The values measured are usually subscripted by ρ and V to indicate the definition. Gases and liquids are typically measured at constant volume.

INTRODUCTION

Heat capacity is also known as thermal capacity. It is a physical property of matter. Heat capacity can be defined as the amount of heat to be supplied to an object to produce a unit change in its temperature. Heat capacity can also be defined as the ratio of heat absorbed by a material to the temperature

change. Heat capacity is measured using a calorimeter. A calorimeter is an object used for calorimetry, or the process of measuring the heat of chemical reactions or physical changes as well as heat capacity.

The SI units, heat capacity is expressed in units of joules per Kelvin (J/K). An objects heat capacity (denoted by symbol C) is defined as the ratio of the amount of heat energy transferred to an object to the resulting increase in temperature of the object.

$$C = \frac{Q}{\Delta T}$$

Heat capacity is an extensive property, so it scales with the size of the system. A sample containing twice the amount of substance as another sample requires the tranfer of twice as much heat (Q) to achieve the same change in temperature (ΔT).

The measurement of Heat Capacity.

From research, the heat capacity of most systems is not a constant. Rather, it depends on the state variables of the thermodynamic system under study. In particular, it depends on temperature itself, as well as on the pressure and the volume of the system, and the ways in which pressures and volumes have been allowed to change while the system has passed from one temperature to another. The reason for this is that pressure-volume work done to the system raises its temperature by a mechanism other than heating, while pressure-volume

work done by the system absorbs heat without raising the system's temperature.

The temperature dependence is why the definition a calorie is formally the energy needed to heat 1g of water from 14.5 to 15.5°C instead of generally by 1°C. Different measurements of heat capacity can therefore be performed, most commonly pressure and constant volume. The values thus measure are usually subscripted by V and p respectively to indicate the definition.

Gases and Liquids are typically also measured at constant volume. Measurements under constant pressure produce larger values than those at constant volume because the constant pressure values also include heat energy that is used to do work to expand the substance against the constant pressure as its temperature increases. This difference is particularly notable in gases where values under constant pressure are typically 30% to 67% greater than those at constant volume.

The relationship between thermodynamics and the definition of Heat Capacity:

The internal energy of a closed system changes either by adding heat to the system or by the system performing work. Recalling the first law of thermodynamics which states that energy can neither be created nor destroyed, it can only be altered in form. It is also known as the Law of Conservation of Energy:

$$dU = \delta Q - \delta W$$

For work as a result of an increase of the system volume,

We can rewrite the formula to:

$$dU = \delta Q - PdV$$

If heat is added at constant volume, then the second term of this relation vanishes and one readily obtains the formula shown below:

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V$$

where C_V defines the heat capacity at constant volume.

C_p is also a very important quantity is the heat capacity pressure. With the enthalpy of the system give by:

$$H = U + PV,$$

Therefore, the equation will change, the equation that we had for dU will change to

$$dH = \delta Q + VdP$$

So, at constant pressure we get the following equation below;

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P.$$

We have two equations now, at constant volume and also at constant pressure.

Constant volume: $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V$

since the pressure remains constant during the process, the calorimetry is used to determine the changes in enthalpy occuring in solution.

Experiment 1: Constant-pressure calorimeter.

Apparatus: (a) Two nested styrofoam cups
(b) A lid with two holes.
(c) Thermometer.

SET UP:

Step 1: Fill a beaker with approximately 150-200mL of water and place it on a hot plate set on high.
Step 2: Weigh one piece of aluminium and one piece of copper. Record these values in the data table.
Step 3: Drop both metals into the beaker.

Procedure:

1. Measure 10 grams of $CaCl_2$ and bring place it on your lab station.
2. Using the rubber band, attach the lid to the styrofoam calorimeter, flat side down.
3. Measure 75 mL of water H_2O and pour it into a calorimeter through the large hole
4. Put the temperature probe into the calorimeter through the small hole
5. Pour $CaCl_2$ into the calorimeter through the large hole and stir slowly with a glass rod.
6. Continue to stir until the temperature levels out, or stops changing

7- Record the initial temperature and the maximum temperature of water.
8. Calculate the amount of energy absorbed by the water
9. Determine how much energy was released per mole of $CaCl_2$

Figure : Coffe-cup calorimeter.

Ref: theory.labster.com.

(B) Constant-volume calorimeter.

It is an instrument that is used to measure the heat generated during changes that do not involve changes in volume.

Experiment 2:

In this technique, a sample of burning element or a compound is burned under constant volume in a device called a bomb calorimeter.

The amount of heat released in the reaction can be calculated using the equation $q = -C\Delta T$, where C is the heat capacity of the calorimeter and ΔT is the temperature change.

$$q = -C\Delta T$$

where : q - amount of heat
C - heat capacity
ΔT - temperature change.

Apparatuse for a Bomb calorimeter:

1. Steel bomb which contains the reactants.
2. Water bath in which the bomb is submerged.
3. Thermometer.
4. A motorized stirrer.
5. Wire for ignition.

Figure below shows the set-up of the experiment.

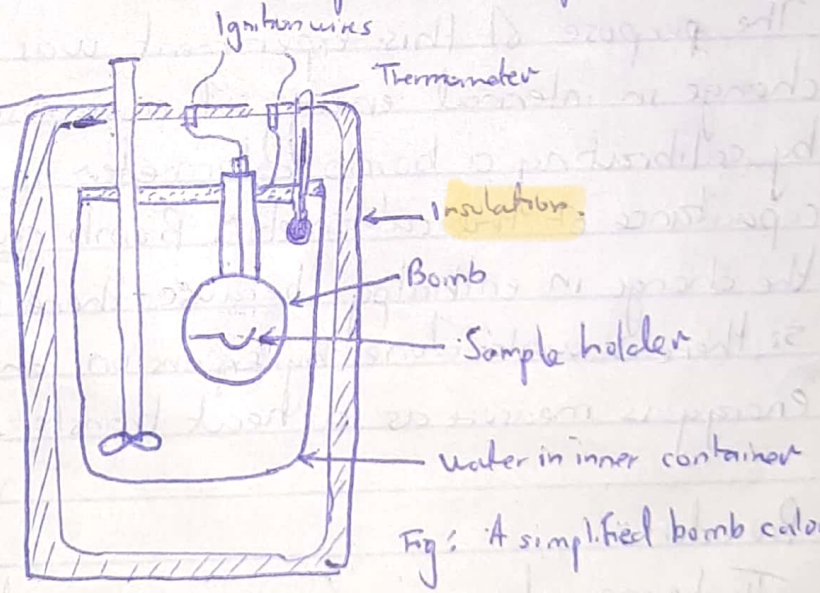

Fig: A simplified bomb calorimeter.

Determining the Heat of Reaction.

The amount of heat that the system gives up to its surrounding 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 through the combustion reaction.

$$q_{reaction} = -q_{calorimeter}$$

where $q_{calorimeter} = q_{bomb} + q_{water}$

If the constant volume calorimeter is set up the same way as same steel bomb and the same amount of water the the heat capacity of the calorimeter can be measured using the following formula:

$$q_{calorimeter} = (\text{heat capacity of calorimeter}) \times \Delta T$$

BOMB CALORIMETRY.

: ABSTRACT for the Constant volume calorimetry:

The purpose of this experiment was to determine the change in internal energy of a sucrose combustion system by calibrating a bomb calorimeter in order to find the heat capacitance of the calorimeter. Bomb calorimetry can measure the change in enthalpy because there is no change in volume so there is work done by expansion and any internal energy is measure as a heat transfer.

Procedure:
The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction.

The bomb calorimeter works in the same manner as a coffee cup calorimeter, with one big difference. In a coffee cup calorimeter, the reaction takes place in the water. In a bomb calorimeter, the reaction takes place in a sealed metal

container, which is the bomb vessel.

Experiment procedure and steps:

1. The given organic fuel is weighed accurately and transferred to stainless steel crucible of the bomb calorimeter.
2. The stainless steel bomb calorimeter containing fuel is immersed in copper calorimeter containing known quantity of water which is further surrounded by air and water jacket to prevent the entry of heat from outside.
3. Sufficient amount of oxygen is supplied to burn the fuel from the oxygen inlet of the bomb calorimeter.
4. Initial temperature of the water is noted.
5. The fuel is burnt by producing electric spark inside the bomb calorimeter.
6. The heat liberated is absorbed by water in copper calorimeter.
7. The final maximum temperature is measured.

Note: By measuring the rise in temperature of known quantity water, and knowing the specific heat of water, knowing the weight of chemical fuel and water equivalent of calorimeter, the GCV of fuel can be determined.
(GCV - Gross calorific value).

Observations:

1. Mass of chemical fuel taken = 'm' kg
2. Mass of water in calorimeter = 'w1' kg
3. Water equivalent of calorimeter = 'w2' kg
4. Initial temperature of water = 't1' °C
5. Final temperature of water = 't2' °C
6. Increase in temperature = (t2 - t1) °C

Calculations:

Heat liberated by 'm' kg of chemical fuel in a closed vessel
= Heat absorbed by (w1 + w2) kg of water in calorimeter
..... equation 1.

= m × GCV ... equation 2.

Heat absorbed by 1 kg of water to raise its temperature by 1°C = 'S' (Specific heat of water = 4.187 kJ/kg/°C.

Therefore. Heat absorbed by (w1+w2) kg of water to raise its temperature from t1°C to t2°C = (w1+w2) × (t2-t1) × S
..... equation 3.

Substituting equation 2 and 3 in 1:

m × GCV = (w1+w2) × (t2-t1) × S.

Conclusions :

Bomb calorimetry is generally used to measure the heat of combustion for organic materials. The pricple of operation is to saturate the material with oxygen, within a sealed container and ignite using a hot wire. The recorded enthalpy change is thus to sum of all bonds broken and bonds made converting thee organic solid into simple gaseous molecules. The constant pressure calorimeter measures the change in enthalpy of a reaction occuring in a liquid solution.

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