

C2. Heat of Combustion of Liquid Combustibles

I. OBJECTIVE OF THE EXPERIMENT

Determine the heat of combustion of a combustible using calorimetry.

II. BACKGROUND THEORY

Most sources of energy available to man are in chemical form. They are chemical compounds that are unstable at high temperatures. When they are heated passed a certain point, chemical reactions occur (generally oxidation), and the combustible or its components decompose into more stable compounds. The thermodynamic variable that allows us to describe this process is the Gibbs function, defined by:

$$G = U - TS + YX \quad (1)$$

where U is the energy of the system; S its entropy, T its temperature, and Y and X determine a pair of conjugated variables. In the particular case where Y and X correspond to P and V (pressure and volume) the corresponding Gibbs function is called "free enthalpy" or "Gibbs free energy".

In this case, we are studying chemical reactions with a constant external pressure, which generally leads to simultaneous variations of U , S and PV . These reactions can spontaneously evolve as long as G decreases. The state is at an equilibrium when G reaches a minimum. According to Berthelot's law, the reaction that occurs is that which generates a maximal amount of heat Q . The amount of heat produced during the combustion is called *heat of combustion*. There exist several different methods to determine this value. The simplest one is by using heat-exchanging calorimeter.

CALORIMETRY

The experimental equipment is made up of a heat-exchanging calorimeter, which is a container designed to exchange heat between two fluids without losses. During the measure, a reference liquid (generally water) of given heat capacity c goes through the exchanger. In the exchanger, is a burner containing the liquid to study. The combustion energy ΔQ will increase the internal energy of the exchanger by ΔU_1 and that of the water flowing through it by ΔU_2 , which will increase the temperature of both of these. The first principle of thermodynamics allows us to write:

$$\Delta Q = \Delta U_1 + \Delta U_2 \quad (2)$$

In a stationary state, i.e. for a constant water throughput and for constant water temperatures going in and coming out of the calorimeter (T_0 and T_1 respectively), the internal energy of the exchanger remains constant. Therefore, in this state, $\Delta U_1 = 0$ the entire amount of heat produced by the burner is absorbed by the water passing through the exchanger.

Over a time interval Δt , we have:

$$\Delta U_1 = cD\Delta t(T_1 - T_0) = cM(T_1 - T_0) \quad (3)$$

where D is the cooling water throughput
 $M = D \cdot \Delta t$ is the amount of cooling water passing through the calorimeter over a time Δt .

Knowing c , M and $\Delta T = (T_1 - T_0)$, we can determine the heat ΔQ released by the combustion, and finally the heat of combustion H given by:

$$H = \frac{\Delta Q}{m} = \frac{cM \cdot \Delta T}{m} \quad (4)$$

where m is the amount of combustible burned over the time required for M to pass through the system

III. EXPERIMENTAL SETUP

The equipment is made up of the following elements (see fig. 1)):

- calorimeter (1)
- burner with reservoir (2)
- scale (3)

The cooling water passes through the tube (4), and enters the cylinder (5). The excess amount of water in the cylinder stabilizes the water level going in, and allows us to set the throughput of water through the calorimeter, by adjusting the valve (6). The excess water exits through the tube (7). The container of the burner is partially filled with the liquid to study. This combustible is consumed by the burner, which is placed in the cavity of the calorimeter, and transfers the heat released during combustion to the water. The thermometers (8) and (9) indicate the temperature T_0 and T_1 of the water entering and exiting the calorimeter. The mass of water M heated in the calorimeter flows through the valve (10), which allows for it to be collected in a measuring container (15). The burner containing the combustible is placed on a scale that allows us to determine the amount of combustible burned. Gases produced during combustion are released through the tube (12). The mass M_c of condensed water must carefully be collected through the tube (13).

Knowing M , m , M_c , T_0 and T_1 , we can determine the heat of combustion H of the combustible according to equation (5)

$$H = \frac{cM(T_1 - T_0) - \underbrace{M_c \cdot \Delta H}_{\text{Condensation heat}}}{m} \quad (5)$$

Knowing that: $\Delta H_{\text{vap}} = 40.6 \text{ kJ/mol} = 2257 \text{ kJ/kg}$



Figure 1: Overview of the different items

IV. EXPERIMENTS

Determine the heat of combustion of two different combustibles (butane/propane mix camping gas and ethanol). Determine H and its standard deviation for each combustible, and compare this value to the theoretical heat of combustion (see below)

Operating instructions

- Carefully open the faucet on the wall, while looking at the water level in the cylinder (5). The excess water flows out through the tube (7).
- Place the valve (10) in the \ominus position.
- Open the valve (6) to any position, and wait until the calorimeter fills up, which will be indicated by excess water flowing through (11).
- After filling up the calorimeter, place and light the burner (2) in the calorimeter's cavity, and place it on the scale (3). Make sure the flame stays in the center of the calorimeter. The temperature T_1 of the water exiting the calorimeter increases. Wait a few minutes for the temperatures to stabilize.
- Simultaneously measure M , m , M_c , T_0 and T_1 .
 - Place the container (15) on the scale (14) and write down M_0 , the mass of the empty container.
 - Place the valve (10) in the \ominus position. The heated water now flows into the container. At the same time, write down the mass indicated by the scale 3 (m_0).
 - After a certain amount of time, place the valve 10 back to the \ominus position. Write down the values indicated on the scales 3 (m_1) and 14 (M_1) and the thermal probes 8 and 9.
 - Knowing the mass of the burned combustible ($m_1 - m_0$), the mass of the heated water ($M_1 - M_0$) and the mass of the condensed water M_c , calculate the heat of combustion according to equation (5).
- Repeat step 5 for different positions of the valve (6) and different values of m ($m_1 - m_0$).
- Repeat steps 5 and 6 using the ethanol burner (16).

Theoretical determination of the heat of combustion

It is generally possible to determine the heat of combustion from the formation energies of the different components of the combustible. The difference gives the heat of the reaction, i.e. the amount of heat produced by the combustion (Hess Law)

Example: Heat of combustion of benzene C_6H_6 .



Heat of formation (see tables) :	49.1 kJ/mol	pour C_6H_6
	-393.5 kJ/mol	pour CO_2
	-241.8 kJ/mol	pour H_2O gaz
	0	pour O_2

(Formation energy of elements is zero)

therefore, the heat of the reaction is:

$$\Delta Q = -\Delta H_r = -(6 \cdot (-393.5 \text{ kJ/mol}) + 3 \cdot (-241.8 \text{ kJ/mol}) - 49.1 \text{ kJ/mol}) = 3135.6 \text{ kJ/mol}$$

and since one mole of benzene has a mass of 78g, we get:

Heat of combustion of benzene: $H = 40.2 \text{ MJ/kg}$