

DETERMINATION OF HEAT OF COMBUSTION OF BIOFUELS.

Instructors

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(some parts of the text were translated into English by mgr Agnieszka Krogul)

LITERATURE:

1. R. T. Morrison, R. N. Boyd: *Chemia organiczna*, tom 2 (rozdz. 33: Tłuszcze) PWN, Warszawa 1985. (in Polish) or R. T. Morrison, R. N. Boyd: *Organic Chemistry*, vol. 2.(in English).
2. S. Bredsznajder, W. Kawecki, J. Leyko, R. Marcinkowski: *Podstawy ogólne technologii chemicznej*, PWN Warszawa 1973. (in Polish)
3. S. E. Manahan: *Environmental Chemistry*, Brooks/ Cole Publishing Company, 1984.
4. H. Koneczny: *Podstawy technologii chemicznej*, (rozdz. V: Paliwa i ich przerób), PWN, Warszawa 1973. (in Polish)
5. R. Bogoczek, E. Kociotek-Balawejder: *Technologia chemiczna organiczna*, rozdz. 2, WAE, Wrocław 1992. (in Polish)
6. *Spalanie i paliwa* praca zbiorowa pod red. J. Kordylewskiego, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2005. (in Polish)
7. J. Ciborowski: *Inżynieria chemiczna. Inżynieria procesowa*, WNT, 1973. (in Polish)

ATTENTION: Student are obliged to search information on the presented subjects from additional sources (physical chemistry and thermochemistry textbooks from the library, internet sources etc.)

Requirements

Definitions: energy and conversion of energy, fuels, biofuels (bioethanol, biodiesel), heat / thermal capacity, calorimetric constant, combustion, diffusion, fats and vegetable oils, fatty acids and their esters, triglycerides (triacylglycerols), FAME (fatty acid methyl esters), physical and chemical properties of fats.

1. Combustible materials (flammable substances). Fuels – definition and classification. Combustion processes, chain reactions, heat of combustion and calorific value, explosions, explosion limit, spark-ignition engine, compression-ignition engine (Diesel engine, diesel). Cetane Number, Octane Number.
2. Basic concepts and definitions of thermodynamics and thermochemistry: functions of state, thermodynamic functions, heat, work, laws of thermodynamic and thermochemistry (Hess's law, Kirchoff's law).
3. Heat transfer and mechanisms of heat exchange (heat conduction, convection, thermal radiation).
4. Calorimeters: definition, design, the calorimeter constant (heat capacity of calorimeter), typical calorimetric plot of temperature versus time.
5. Knowledge on the procedures of analysis of biofuels and analysis of combustion products, described in this manual.

INTRODUCTION – THEORY

The definition of a fuel is wide – it includes **any substance which, through physical and chemical changes provides significant amounts of heat, which is used for technical and households (like domestic heating) purposes**. Such definition is much broader than the older one, according to which fuels were "solid / liquid / gaseous organic substances able to react with oxygen to form carbon dioxide and water vapour releasing large amounts of heat". Fuels are a source of energy in the sense that chemical energy is converted into heat energy as a result of chemical processes.

Based on the criterion of fuel origin, fuels can be divided into two main groups:

- a) natural fuels (hard coal = coal, brown coal = lignite, petroleum, natural gas, peat, biomass, wood),
- b) synthetic fuels which result from less or more complicated transformation of natural fuels (e.g. coke, petrol) or from chemical synthesis of high-energy substances (e.g. rocket propellant - nitromethane, a mixture of hydrogen peroxide and methanol) as well as nuclear fuel.

Taking into account other criteria we can distinguish, depending on the state of matter: solid and fluid (liquid and gaseous) fuels or, depending on the origin, fossil fuels and biofuels. Depending on the application, we can distinguish fuel for heat production and fuel for transportation, and depending on the calorific value¹ we can divide fuels into low-calorie and high-calorie fuels (low energy and high energy fuels).

In most cases fuels are combustible substances it means the substances capable to exothermic reaction with air after the initiation (ignition). For commonly used fuels we use parameters which allow to compare the amount of energy that can be released by this reaction. **The calorific value** is a measure of the amount of heat obtained by combustion of unit of mass (or volume) of fuel. The calorific value of organic substances containing carbon, hydrogen, sulfur and oxygen is described by the following empirical equation:

$$W_u = 33900C + 121000\left(H_2 - \frac{O_2}{8}\right) + 10500S - 2500\left(W + \frac{9}{8}O_2\right) \quad \left[\frac{\text{kJ}}{\text{kg}}\right]$$

where: C , H_2 , O_2 , S are mass participation of these elements, respectively, and W is contents of water (humidity of material).

When combustion is total and the reaction products are brought into the standard state (at constant volume), the heat obtained in this process is called the **heat of combustion**. The process should be **total** (stoichiometric, without loss of substance, no evaporation) and **complete** (to the thermodynamically most stable product). In thermochemistry the heat is measured in [kJ / mol] units and in energetics a basic unit is [kJ / kg]. Measurements of heat of combustion is carried out in a bomb calorimeter.

The heat of combustion is called the **upper calorific value**, since it corresponds to the total heat produced from the fuel. In combustion processes taking place in furnaces and engines water vapor is produced, which is not condensed. Mostly it is "entrained" with the other flue gases, which prevents the use of energy released during its condensation. Therefore, to evaluate the quantity of the resulting heat another parameter is more appropriate a **lower calorific value**. This is the amount of heat (expressed in kJ / kg) released by complete combustion of unit mass of fuel in a bomb calorimeter, when the combustion products cool off to the initial fuel temperature (at constant volume), but assuming that water is not condensed.

An example of the solid fuel is wood. The dry weight of wood contains about 50% carbon, 6.3% hydrogen and 44.2% oxygen. During the combustion of wood we obtain relatively small (0.3-1%) amount of ash. Wood is classified as **biomass** and it is reproducible energy resource, unlike fossil

¹ In physics and energetics a term *calorific value* is used whereas a term *caloric value* is in use in medicine.

fuels, which are admittedly of plant origin, but the process of their formation is so long that you can not talk about the reproducibility of fossil fuels in the biological sense. **Solid fossil fuels** are peat, brown coal (lignite), hard coal and anthracite. The calorific value of peat is within 18 000 to 25 500 kJ / kg range. Hard coal called anthracite, which includes the least of volatile substances and the most of elemental carbon, has the highest energy value (37 000 kJ / kg). As a result of combustion of fossil fuels ash (slag) - consisting of Al₂O₃, SiO₂, Fe₂O₃, CaO, MgO - is produced.

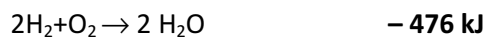
Fluid fossil fuel are mainly petroleum (calorific value is an average 44 000 kJ / kg) and natural gas, of which calorific value is the most varied - depending on:

- deposits associated with petroleum (so-called wet natural gas and dry),
- contents of individual hydrocarbons (CH₄ to C₅H₁₂ fractions),
- amount of nitrogen and hydrogen sulfide.

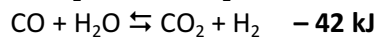
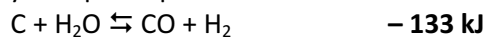
Combustion in the presence of oxygen from the air (79% N₂ + 21% O₂, disregarding the content of water and CO₂) may proceed with an excess of oxygen or deficit of oxygen. It should be also remembered that the fuel can react with oxygen-containing substances (eg. H₂O, CO₂), which are externally supplied or which are produced during combustion. Combustion with oxygen insufficiency (lack of oxygen) is described by the equations:



however, with enough amount of oxygen:



Oxygen-carrying substances may also participate in the combustion reaction:



Combustion (for heat production) should be carried out with enough amount of air, but introducing too much excess of air is not preferred because it decreases the temperature of the exhaust gases. Reduction of the amount of exhaust gases (flue gases, exhausts) can be achieved by the use of oxygen-enriched air.

Combustion processes of gaseous, fluid and solid fuels undergo in different ways. Mixing the gaseous fuel with air and combustion at the burner nozzle is a process that occurs in the **kinetic zone** and thus it depends on the rate of chemical reaction. In contrast, when the combustible gas is mixed with air in the reaction zone (furnace) – the process of mixing will be the reaction rate limiting factor and combustion process will take place in the **diffusion zone**.

The advantages of gaseous fuels include: ease of transport (pipelines), the ease of bringing gas to the furnace (combustion chambers), the formation of gaseous products of combustion process without solid or liquid residues, the ability to pre-heat the fuel, resulting in a higher temperature of exhausts (i.e. the formation of larger temperature gradient during heat exchange).

Combustion of fluid fuels is associated with conducting a process in a biphasic system fuel / air. Appropriate mixing of the reactants is to spray the fuel in the combustion chamber (the liquid particles of formed aerosol pass rapidly into a state of steam). This process depends on temperature, particle fragmentation, type of fuel. During combustion process no solid or liquid residues are formed.

Solid fuels burn in multiphase system – apart from the gas-solid phase boundary, a combustible gas fraction can be released at high temperatures. The combustion process **occurs at the interface (phase boundary)**, so, development of the surface and the way of mixing fuel with air is very important. In contrast to the combustion of liquids and gases, products of solid fuel combustion are not only gases but also residues such as ash and slag.

Combustion of solid fuels can be arranged in several ways. Fuel can be burnt on a movable or stationary fire grate and air can be supplied from below. The air goes through a layer of fuel and combustion occurs in a manner dependent on the fuel particle size, method of their arrangement, air velocity, fuel capacity for sintering, the amount and method of removal of generated ash. It is hard to keep a smooth combustion of solid fuel. The second method of the combustion of solid fuels involves the use of pulverized coal in specially constructed cyclone furnaces, where the effective mixing of dust from the air takes place. Large development of the surface makes this method rapid, complete and efficient. Dust generated during the combustion is blown from the combustion chamber and separated from the exhausting gases in cyclones, filters and electrofilters.

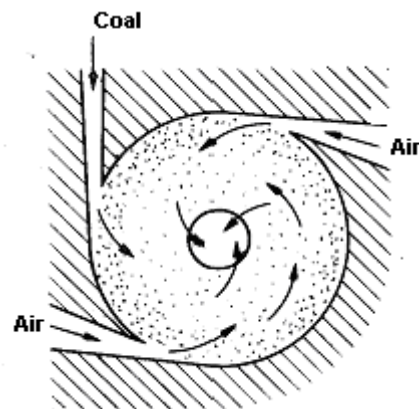


Figure 1. Scheme of the cyclone furnace for combustion of solid fuels (by S. Bredsznajder, R. Kawecki, J. Leyko, R. Marcinkowski: *General fundamentals of chemical technology*, OWN Warsaw 1973).

Ash produced after combustion of solid fuels is a residue of: (i) inorganic compounds contained in the fuel, (ii) the ingredients of plants of which coal was formed (about 1% of fuel) or (iii) geological contamination introduced into the coal (which may be up to 30% of total weight). The ash contains Al_2O_3 , SiO_2 , Fe_2O_3 , CaO , MgO and small amounts of other inorganic substances. Melting or sintering of ash, accompanied by combustion, is very unfavorable process leading to the slag formation which flood and block fire grate.

Combustion

Combustion is a dynamic (non-equilibrium, depending on the time) oxidation process involving the atoms, molecules, radicals that are in one phase or at the phase boundary. The rapid exothermic reactions cause the release of energy also in the form of light (flames, glowing, sparks) or the formation of gradients that are the reason of heat and mass flow (the flow of chemical individuals), thus, the flames are moving in uncoordinated ways.

If the amount of combustible gas in a mixture with air (oxygen) gradually increases, a minimum value is reached above that a mixture becomes combustible. This minimum fuel content is called the **lower combustion limit**. If the contents of gaseous fuel is further increased, then upper a certain value of the mixing it will be inflammable. This is the **upper combustion limit**. These parameters are strongly dependent on the temperature - the higher temperature of the mixture, the bigger is difference between upper and lower limits. For some mixtures, within the lower and upper combustion limit we can distinguish the areas of explosion - when the rate of flame spread reaches a detonation (explosion) rate. This problem will be discussed later.

The flames (formed during combustion of stoichiometric mixtures of air with the generally used fuel) reach temperature 2000 K. When the composition of mixture changes reaching the limits of flammability, flame temperature drops to 1400 K.

Table 1. Combustion temperatures of selected gases.

Gas (fuel)	Oxidant	Fuel participation /% vol.	Temperature / °C
H ₂	air	31.6	2045
H ₂	O ₂	78	2660
CO	air	20	1650
methane	air	10	1875
ethane	air	58	1895
propane	air	4,15	1925
butane	air	3,2	1895
acetylene	air	9	2325
acetylene	O ₂	33	3007
ammonia	air	21	1700
CO+ N ₂	air	47,3	1675
CH ₄ +N ₂	air	17,5	1725
9CH ₄ + H ₂	air	10,5	1880

Combustion have to be initiated with ignition. This might be **spontaneous ignition**,² when the amount of heat provided or dissipated inside the system is greater than allowed to discharge the heat. The second type of ignition is the **spark ignition** when the flame is initiated in one place (e.g. by a spark), and from this place it is spreading to the rest of the system.

Heating of combustible liquids, including liquid fuels (even at temperatures below the boiling point) leads to increased evaporation of the liquid, and, if they are non-volatile it can lead to secretion of volatile and flammable substances derived from their decomposition. **Flash point**³ is the lowest temperature at which the tested substance (heated in a specific way), emits a sufficient amount of gaseous products to produce with air a mixture which can be ignited being close the flame (i.e. as a result of the ignition point). If under the same conditions ignited vapour burns without external source of flame for at least 3 seconds, then this temperature is called **temperature of burning**.⁴ Temperature of combustion is usually about 20-60 °C higher than the ignition temperature.

Explosions

When the rapid exothermic reaction occurs in a limited space and when as a result of this reaction gaseous products are produced, the pressure suddenly (which is uncontrolled) jumps (increases) and this is called explosion. The amount of heat discharged is less than the amount of heat generated, resulting in an increase of temperature and, according to the Arrhenius kinetic equation, we observe acceleration of the reaction. Self-accelerating reaction will take place faster and faster until one of the reactants runs out. For mixtures of air (or oxygen) with hydrogen, hydrocarbons, vapors of sulfur, phosphorus, carbon disulfide and other organic solvents, such a process has a radical chain mechanism.

Whether the mixture is explosive, depends on the type of substance, mixture composition, temperature and pressure. **Explosion limits** (combustibility, ignition) are characteristic features of combustible mixtures:

² Also called spontaneous ignition or autoignition.

³ Ignition temperature.

⁴ Fire point, temperature of combustion.

- **lower explosive limit (LEL)** is the lowest concentration of fuel in the mixture of air / oxygen / oxidizing agent, when the mixture is still capable to produce a flash fire; below that concentration no ignition is possible with any initiating factor.
- **upper explosive limit (UEL)** is the highest concentration of fuel in the mixture of air / oxygen / oxidizing agent when the mixture is still capable to produce a flash fire; above that concentration ignition or spread of flame is not possible.

Outside these limiting concentrations an ignition of mixture does not occur even if the ignition source has an infinitely large energy. Limits of explosion expressed in concentrations are identical with the ignition limits, however, limits of explosion are dependent on the pressure and temperature, so we can talk about the temperature and pressure limits of explosion. Figure 2 presents chart of ability of hydrogen / air mixtures to explode. The parameters of susceptibility to explode for selected combustible gases and organic solvents are presented in Tables 2 and 3.

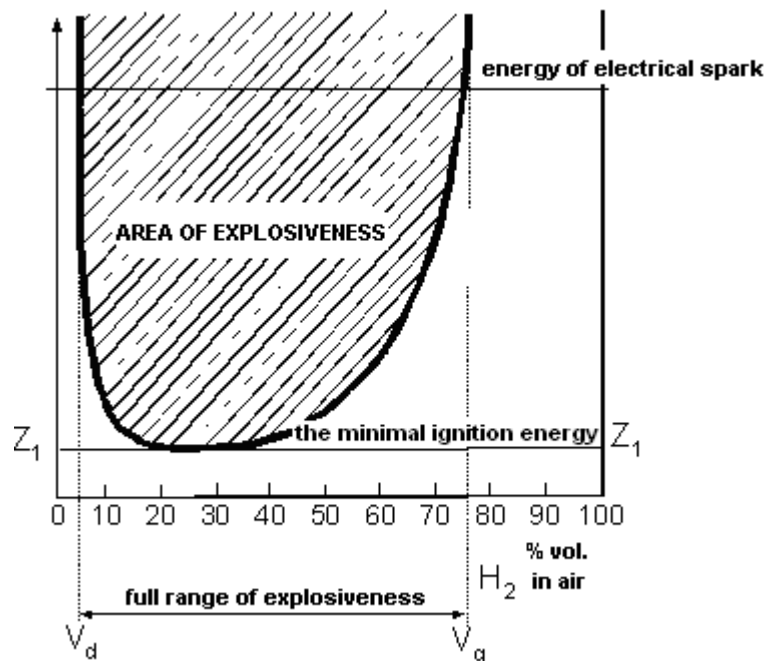


Figure 2. Dependence of ignition energy on the composition of hydrogen - air mixture: Z_1 - the minimal ignition energy, $E_{\min} = 0.019$ mJ, V_d - lower explosion limit, V_g - upper explosion limit.

Table 2. Values of lower (LEL) and upper (UEL) explosive limits for mixtures of combustible gases with air or oxygen.

Gas	% gas content in the air		% gas content in the oxygen	
	LEL	UEL	LEL	UEL
Hydrogen	4,1	74,2	4,0	94,0
Carbon monoxide	12,5	74,2	15,5	94,0
Methane	5,3	14,0	5,1	61,0
Ethane	3,2	12,5	3,0	66,0
Propane	2,4	9,5	2,3	55,0
Butane	1,9	8,4	1,8	48,0
Acetylene	2,5	80,0	2,5	98,0
Coke oven gas ^a	5,6	31,0	---	---
Water gas ^b	6,2	72,0	---	---
Natural gas ^c	4,5	17,0	---	---
Town gas ^d	35,0	74,0	---	---

^a Industrial fuel obtained by heating of coal at a temperature above 1000 ° C in a specially constructed furnace, in the absence of oxygen. ^b Combustible gas formed during the reaction of coal or natural gas with steam in the presence of suitable catalysts. It is a mixture of carbon monoxide and hydrogen (it also contains a few percent of carbon dioxide, nitrogen and hydrocarbons). ^c Fossil fuel of organic origin which is collected in the crust of the Earth. ^d Other names: city gas, gasworks gas.

Table 3. Parameters characterizing selected organic solvents.

	Ignition temperature (flash point) °C	LEL*	UEL*	minimum temp. of autoignition °C	maximum pressure of explosion kPa	Explosiveness Group
ethanol	11	3,1	20	425	634	IIA
methanol	11	5,5	36,5	470	625	IIA
acetone	-19	2,1	13	540	772	IIA
isopropanol	12	2,0	12	400		IIA
dichloromethane		13	18	660		IIA
methyloamine	-17,8	4,9	20,7	430		IIA
toluene	4	1,3	7	570	566	IIA
ethyl eter	-40	1,6	48	160	801	IIB
ethyl acetate	-4	2,2	11,5	460	752	IIA
dioxane	12	2	22	180		IIB

* Values of lower (LEL) and upper (UEL) explosion limits.

When the combustion is performed in order to obtain heat - a process is carried out in furnaces or boilers. Then, the thermal energy can be converted into mechanical work e.g. in steam turbines. A more direct and more effective way to convert chemical energy into mechanical work is the use of internal combustion engines (more specifically, heat engines with internal combustion). In

reciprocating engines⁵ the energy is converted into the work of piston or pistons moving in a cylinder (cylinders). This movement is converted into the torque of the crankshaft.

In **spark-ignition engines** (Figure 3) combustion is initiated by a spark of the spark plug. Fuels used in this type of engines may be natural gas, light fractions of petroleum (liquid gas, petrol, leaded petrol) as well as flammable and volatile organic substances (e.g. methanol, ethanol). Spark engines have light constructions and simple design and they easily receive high speed, high power gain, and they are easy to start.

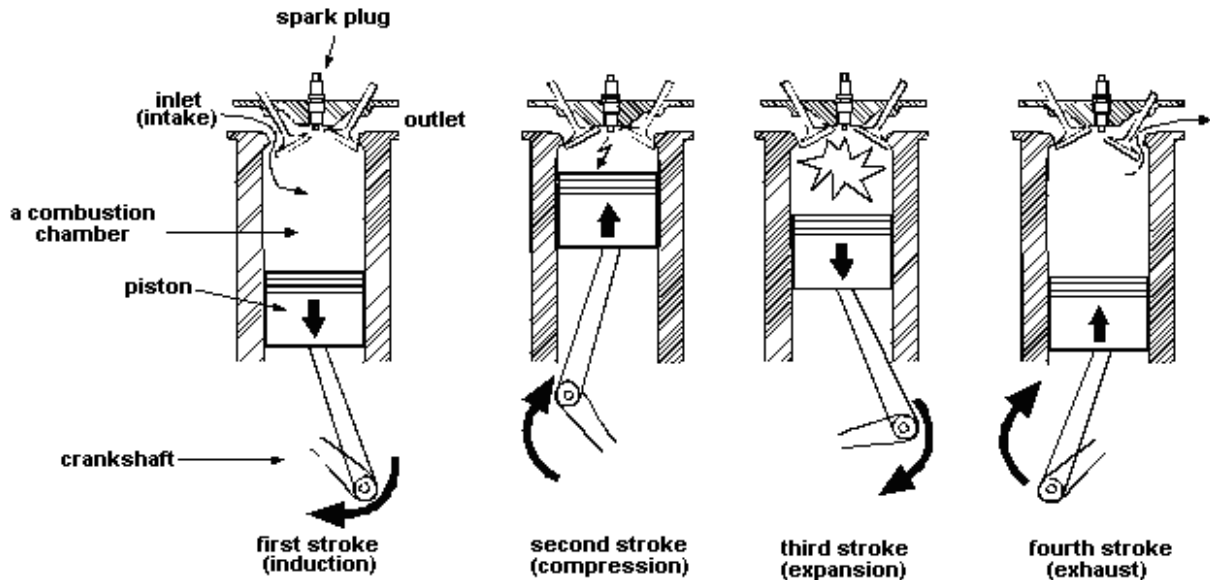


Figure 3 Scheme of four-stroke engine (four-cycle engine) with spark ignition.

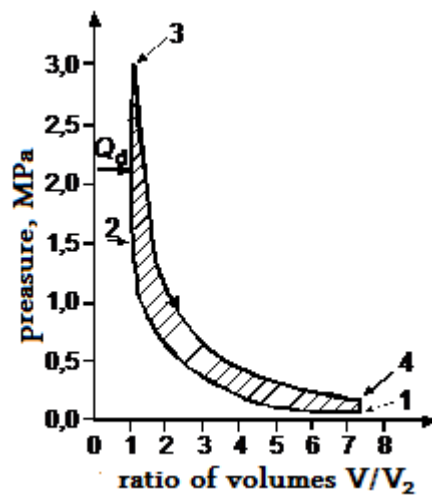


Figure 4. Spark-ignition engine cycle (according to *Combustion and fuels* edited by J. Kordylewski, Publishing House of Wrocław University of Technology, Wrocław, 2005).

optional material

⁵ A reciprocating engine (or a piston engine) is a heat engine using one or more reciprocating pistons to convert pressure into a rotating motion.

Motor efficiency, η , refers to the amount of useful work dW that we can get from a definite quantity of supplied heat, dQ_h . Since the useful work ($dW = -pdv$) is the difference between the heat absorbed ($dQ_h < 0$) and heat discharged ($dQ_c > 0$), we have:

$$\eta = \frac{-dW}{-dQ_h} = \frac{-dQ_h - dQ_c}{-dQ_h} = 1 - \frac{dQ_c}{-dQ_h} = 1 + \frac{dQ_c}{dQ_h}$$

The efficiency of reciprocating combustion spark-ignition engine is given by:

$$\eta = 1 - \varepsilon^{1-\kappa}$$

where ε is the compression ratio (the ratio of cylinder volume to the harmful volume V_1/V_2 , see Figure 4, position 1 and 2) and $\kappa = C_p / C_v$. Compression ratio in combustion engines is in the 8:1 to 11:1 range, but above 8.5:1 the combustion with engine knocking may occur (on the course of explosive), leading to the destruction of the piston, rings and bearings.

Engine knocking combustion⁶ is due to self-ignition of the mixture, and this effect is strongest for the stoichiometric mixture of fuel and air. A measure of resistance to detonative combustion of the motor fuel for spark-ignition engines is the **octane number (ON)**. This parameter is equal to the percentage of isooctane (2,2,4-trimethylpentane) in a mixture of *n*-heptane / isooctane, which produces the same number of knocks in the tested engine as in analyzed fuel. ON for motor fuels is between 80-98 and this ON value is obtained by addition of **anti-knock** agents, in the past the organic lead compounds were used like tetraethyl lead. Today in lead-free petrol (lead-free gasoline) some alcohols like methanol, ethanol, and *tert*-butanol are used and some ethers (methyl *tert*-butyl ether or methyl *tert*-amyl ether), and their amount, regulated by standards, may reach 10%. Role of anti-knock agents is suppression of uncontrolled combustion by introducing radicals into the system, which in non-explosive way initiate the combustion process at a lower temperature, and at the same time they recombine with an excess of radicals generated during spontaneous ignition.

Spark engines have some disadvantages (less efficiency and less durability) if compared to **diesel engines (compression-ignition engines)**. Diesel engines are also internal combustion engines with piston, but the ignition of fuel-air mixture occurs as a result of increasing temperature exceeding the flash point. Diagram of the diesel engine is shown in Figure 5A.

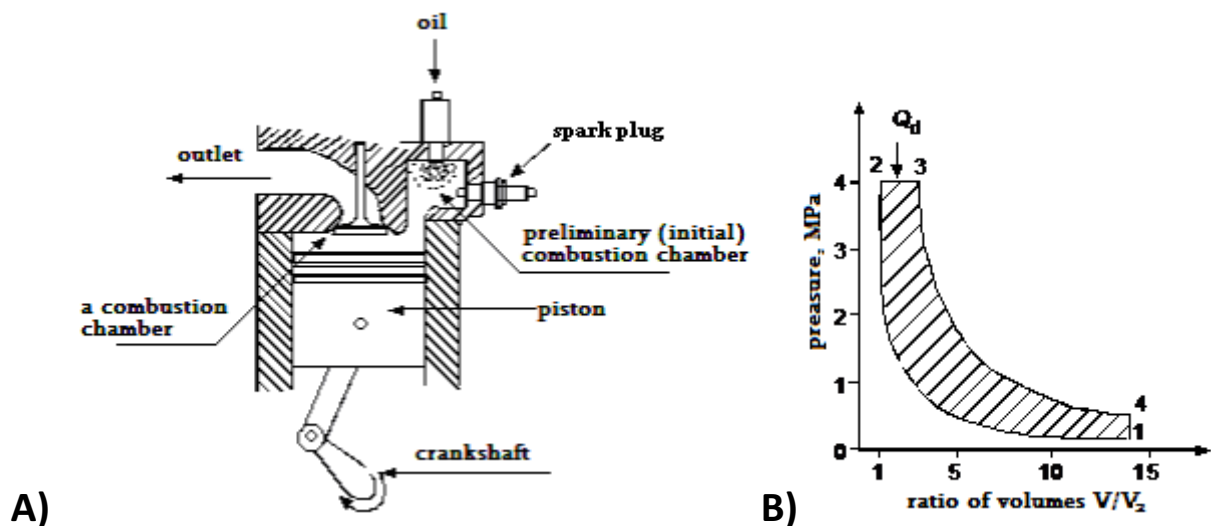


Figure 5. A) Scheme of the self-ignition engine, and B) Diesel engine cycle (according to *Combustion and fuels* edited by J. Kordylewski, Publishing House of Wroclaw University of Technology, Wroclaw 2005).

⁶ Also called knock, detonation, spark knock, pinging or pinking.

In this engine, the air is sucked and compressed and during the compression process a temperature strongly increases. Compression ratio ϵ in diesel engines ranges from 14:1 to 23:1. After the piston reaches the top position, it is followed by injection, spraying and immediate evaporation of fuel, which in contact with hot air is ignited. The piston moves down and when reaches lowest point (dead position), the exhaust valve opens and exhausts fly out of the cylinder.

The efficiency of a diesel engine is described by the formula:

$$\eta = 1 - \frac{\epsilon^{1-\kappa} \phi^{\kappa} - 1}{\kappa \phi - 1}$$

where ϕ is a degree of engine load (volumes ratio V_3/V_2 , see Figure 5B, volume corresponding to positions 3 and 2). The diesel engine works with a greater compression ratio (ϵ) than the spark-ignition engine, so its efficiency is higher than the efficiency of the spark-ignition engine. Other advantages of diesel engines are lower failure (break-down) and greater durability of the engine, achieving greater power and bigger torque. The disadvantages of diesel engines compared to the spark-ignition engines are higher production costs, the greater mass of diesel engines, higher emissions of nitrogen oxides and solid particles, and some difficulties with start at lower temperatures.

Due to different mechanism of action and the conditions in spark-ignition engine and diesel, we use different fuels. Instead of gasoline the higher fractions of crude oil (petroleum) are used – diesel fuel and heavy oil (black oil, mazout). The basic parameter characterizing the fuel for diesel engines is **the capacity for spontaneous combustion - the Cetane Number, CN**. CN is determined by comparing the time of ignition of reference fuel and analyzed diesel fuel. The reference fuel is a mixture of cetane (hexadecane, $C_{16}H_{34}$, for which CN = 100) - which possesses a very short time of ignition - and α -methyl-naphthalene. Pure cetane has CN = 100, while a mixture of cetane and α -methyl-naphthalene (1:1) has CN = 50. Unbranched (straight) saturated hydrocarbons (paraffins) are characterized by a cetane number from 70 to 110, worse properties are observed for branched paraffinic hydrocarbons ($20 < CN < 70$), and CN for aromatic hydrocarbons is from 0 to 60. Generally, light fractions of petroleum have low cetane number comparing to higher fractions (but their low content is beneficial for starting a diesel engine). The minimum CN value, according to the Polish Norms, equals 51. In addition to CN, other properties are also important i.e. lubricating properties of fuel (oil) for diesel engines.

BIOFUELS

Since the time of energy crisis in 1970's the energy sources alternative to fossil fuels (petroleum, natural gas and coal) have been strongly demanded and are still being searched. The amounts of fossil fuels estimated on the basis of all previously known supplies is presented in Table 1.

Table 4. World supplies of fossil fuels (based on S. E. Manahan: Environmental Chemistry, Brooks/ Cole Publishing Company, 1984).

Fuel name	Estimated amount	Energy value
shale oil	30×10^{12} liters	$0,32 \times 10^{15}$ kWh
tar-sand oil	48×10^{12} liters	$0,51 \times 10^{15}$ kWh
liquid petroleum	32×10^{14} liters	$3,25 \times 10^{15}$ kWh
natural gas	$2,8 \times 10^{14}$ m ³	$2,9 \times 10^{15}$ kWh
coal and lignite	$7,6 \times 10^{12}$ tons	$55,9 \times 10^{15}$ kWh

Fossil fuels are called non-renewable energy sources, which means that their amount is still decreasing because of intensive exploitation. Rising prices of fuel and climate changes associated

with intensive use of fossil fuels are the reason for search for alternative energy sources, which currently are classified as:

- **hydroelectricity**
- **wind energy**
- **geothermal energy**
- **energy of tides (a kind of hydroenergy)**
- **solar energy**
- **photovoltaics**
- **biogas (from cogeneration processes)⁷**
- **biomass (from cogeneration processes)**
- **heat energy transformed by solar devices**
- **biofuels from vegetable oils**
- **biogas fuel from fermentation of whole plants**
- **new generations of biofuels**
- **passive utilization of solar energy**
- **new solar technologies.**

Energy exists in many forms, which can be transformed from one to another. Conversion of electricity in the light energy carried out in traditional light bulbs (with resistant wire inside) yields 5% while the remaining 95% is lost as transformed into heat. The efficiency of coal power plants (coal → steam → electricity) is about 40%. The efficiency of conversion of heat energy into mechanical energy, which occurs in steam turbines, is described according to the Carnot Cycle and the second law of thermodynamics as an inequality:

$$\eta = \frac{W}{Q} \leq \frac{T - T'}{T} = 1 - \frac{T'}{T}$$

thus, the efficiency depends on the initial (T) and final (T') temperature. A typical steam turbine engine works within the range of temperatures T = 810 K and T' = 330 K, so its maximum theoretical efficiency would be 59%. At the beginning of the twentieth century temperature of produced steam was 550 K, and the maximum efficiency was 40% (total efficiency was a few percent!). In modern power plants, using new, more durable construction materials, steam temperature reaches about 830 K. Heat losses and temperature fluctuations cause a further decline in the efficiency of conversion of heat into mechanical energy to 47% and taking into account the stage (step) of producing a hot, pressurized steam (chemical energy → steam) the total efficiency drops to 40%.

The efficiency of nuclear power plants is limited by the maximum achievable temperature (reactor core may not exceed a certain temperature, typically 620 K) and therefore the efficiency of conversion of nuclear energy in electricity is about 30%. Energy loss (60% in the conventional power plant and 70% in nuclear power plant) is dispersed, contributing to the heating up the atmosphere (it is called thermal pollution).

In the twentieth century, the efficiency of coal power plants has increased from 4 to 40%, and the replacement of steam locomotives by internal combustion (diesel engines) contributed to 4-fold increase in the efficiency of conversion of chemical energy into mechanical energy. Efficiency of conversion of several types of energy is presented in Table 5. Loss of energy is very large compared to the total energy production. This problem is related to production methods and ways of its conversion in devices used by people as well as access to various sources of energy and minimizing of pollution generated during the conversion process.

⁷ **Cogeneration** (also **combined heat and power, CHP**) is the use of a heat engine or a power station to simultaneously generate both electricity and useful heat.

Tabela 5. Examples of energy conversion.

ENERGY	światlna	chemical	thermal	mechanical	electric	kinetic
light	-	photosynthesis, W<0,6%			solar cell, W=10% light bulb, W=4%	
chemical	chemiluminescence	-	Home gas furnace, W=85%		batteries = storage cell	
thermal (heat)			-	Steam turbine	thermoelement (thermocouple), W=7% Electric heater W=100%	
mechanical				-	Power generator, W=98%	↑ Jet engine
electric			↑ Steam boiler, W=88%	Electric motor, W=60-90%	-	power generator in fly-wheel
kinetic						-

In accordance with EU directives (directive 30/2003/EC) participation of alternative fuels should systematically increase from 2% in 2005 to 5.75% in 2010 and 10% in 2020. The use of hydro, solar, tidal, wind and geothermal powers is dependent on geographical and geological conditions and is not always possible or profitable. Similarly, the application of advanced technologies in order to use the photovoltaic effect has not reached cost-effectiveness threshold that would allow to utilize these energy sources on a large scale. In the countries of the moderate climatic zone, biomass is basic and widely accessible energy source. The concept of biomass is defined in different ways. By **definition 1**, they are *biodegradable fractions of products, waste and residues from agro-food industry (including substances of plant and animal origin), from forestry and derivative industries, as well as the biodegradable fractions of municipal and industrial waste.* According to **definition 2** these are *all kinds of substances formed during biological and biochemical processes occurring in nature, being a potential source of energy for specific applications.*

Efficiency of solar energy conversion by plants is small, usually a fraction of a percent (in sugarcane conversion efficiency reaches a maximum value of 0.6%), however, in the natural environment the scale of biomass production is so great that it is potentially the largest source of energy.

The primary renewable resource is wood - a material that is 75% composed of polysaccharides, including cellulose, and many substances can be extracted from wood, among others tannins, pigments, terpenes, sugars, starch, pectin, resins, adhesives, hydrocarbons, carboxylic acids, steroids, ethers, fats and waxes. The wood is used on a large scale to produce a whole range of other useful products - boards, plywoods, chipboards, paper, methanol, cellophane, plastics, rayon, terpene oils. Methanol is called an alcohol timber because in the past most of this compound was obtained by pyrolysis of wood. In developing countries a combustion of wood is still the primary source of heat.

Fuels made from biomass are called biofuels. Like biomass, biofuels are among the renewable energy sources. The use of biofuels as additives to fossil fuels reduces petroleum consumption and contributes to a more favorable balance of carbon dioxide on a global scale,

because the carbon dioxide released during combustion derives from biomass which previously bounded the same amount of CO₂ in the process of photosynthesis. Furthermore, compared with the exploitation of fossil fuels, the use of biofuels reduces the amount of sulfur and nitrogen oxides emitted to the atmosphere. Although the group of solid biofuels includes such types of biomass as granulated or briquetted straw, industrial sawdust and other processed vegetable wastes, later we will focus on liquid and gaseous biofuels only.

Commonly used liquid biofuels are **bioethanol** in blends with gasoline, **biodiesel** containing methyl esters in blends with diesel, biomethanol (as a component or fuel derived from biomass), **bio-ETBE** derived from ethanol (ETBE: Ethyl tertiary-Butyl Ether), **bio-MTBE** obtained from methanol (MTBE: Methyl Tert-Butyl Ether) and **pure vegetable oils** meeting the requirements for their use in engines. The prefix bio- is introduced in order to put emphasis that a substance is derived from biomass. However, there is no chemical difference between, for example, synthetic ethanol and ethanol derived from biomass.

Examples of gaseous biofuels are **bio-gas**, **Bio-DME** (DME: Dimethyl Ether) and **bio-hydrogen** - all derived from biomass.

Cultivation of plants from which biofuels are made (especially biodiesel and bioethanol) covers more and more agricultural areas and may cause a reduction in food production, leading to an increase in prices of basic food products. Today, biofuels are equivalent to 1.5 million barrels of petroleum a day and their production becomes competitive relating to food production (according to the World Bank production of biofuel caused 75% of the dramatic increase in food prices that occurred in 2007-2008. Further development of the area of the food crops used for biofuels production might cause a serious global food deficiency. The use of edible plants (negative factor) or waste (positive factor) is the basis for biofuels division into I, II and III generation. Taking into account the impact of biofuel production on the materials management, the division is given below.

BIOFUELS OF FIRST GENERATION :

- ethanol formed in the fermentation process,
- vegetable oils obtained by conventional methods,
- biodiesel obtained by transesterification of oils,
- biodiesel obtained by transesterification of waste fats,
- bio-gas produced from agricultural wastes,
- Bio-ETBE derived from ethanol,
- bioMTBE obtained from methanol.

BIOFUELS OF SECOND GENERATION are biofuels produced on the basis of biomass and waste materials unsuitable for the food industry, forestry, etc. They include:

- bioethanol derived from lignocellulose (advanced hydrolysis and fermentation),
- synthetic biofuels obtained as a result of gasification / liquefaction of biomass,
- biodiesel obtained by refining of waste plant oils,
- bio-gas produced by gasification of lignocellulose,
- hydrogen generated by gasification or biological processes.

BIOFUELS OF THIRD GENERATION

- methanol obtained by gasification of lignocellulose,
- hydrogen generated by gasification of lignocellulose.

According to Polish regulations on bio-components in gasoline it is forbidden to add methanol. Ethanol may be added to the fuel to reach maximally 10% by volume and higher alcohols in an amount not greater than 0.1% v / v. Gasoline with 10% of ethanol emits about 2% less toxic substances and 10% less CO than gasoline with 10% methyl tert-butyl ether, however, up to 14%

more nitrogen oxides (NO_x) is evolved during combustion of gasoline/EtOH mixtures. Engine oils may contain maximally 5% vol. of added fatty acid esters.

BASIC THERMOCHEMISTRY

Every chemical process occurs with heat exchange, thus, determination of a heat evolved or absorbed during a reaction allows to follow the extend of that reaction. The area of science that studies heat effects in materials (including the heat-mechanics connections) is named thermodynamics, and chemical thermodynamics is a part of physical chemistry that covers heat effects connected with chemical reactions, phase transitions, and other chemical or physical processes accompanied by heat transfer. A word "calorimetry" derived from the Latin *calor* meaning heat, and the Greek *metry* meaning to measure, is the science of measuring the amount of heat and it is an integral part of thermochemistry. Processes and transitions can be endothermic (when a system absorbs the heat from the surrounding, $Q > 0$) or exothermic (when a system releases the heat from the surrounding, $Q < 0$):



Heat of reaction under constant volume (Q_v) is the amount of heat exchanged with surrounding when:

- (i) a process is carried out at **isochoric** ($v = \text{const}$) or **isothermal** ($T = \text{const}$) conditions,
- (ii) the heat is the only energy exchanged and the system does not exchange with surrounding any other form of energy,
- (iii) the process is carried out exactly for stoichiometric amounts of reactants,
- (iv) the process starts from pure substrates to give pure products.

Heat of reaction under constant pressure (Q_p) is the amount of heat exchanged with surrounding when:

- (i) process is carried out at **isobaric** ($p = \text{const}$) and **isothermal** ($T = \text{const}$) conditions,
 - (ii) the system exchanges energy as heat or/and as work
- and conditions (iii) and (iv) are the same as for previous definition of Q_v .

Therefore, during reaction:



the energy is transferred to/from surrounding as a heat or as a work of volume change or as other forms of work (electric work, radiation).

The heat of reaction under constant volume and heat of reaction under constant pressure are connected by the following relationship: $Q_p = Q_v - \Delta n$, where Δn denotes a change (increase or decrease) of gaseous reagents, and $\Delta n = \sum n_i(\text{products}) - \sum n_i(\text{substrates})$.

According to **the Hess's law** (published in 1840) when all processes are isochoric or all processes are isobaric, their summaric (total) heats Q_p or Q_v do not depend on the pathway or the number of processes but depend on initial and final state of the system. In other words, *the heat evolved or absorbed in a chemical process is the same whether the process takes place in one or in several steps*. As a consequence, we are able to apply thermodynamic equations as simple mathematical equations. Thus, unknown heat of a reaction can be calculated when we know the heats of all other reactions forming the chemical cycle.

The Kirchoff's law describes how the heat of reaction depends on temperature:

$$dQ_{p0} / dT = \sum n_i C_{pi} (\text{products}) - \sum n_i C_{pi} (\text{substrates}) = \Delta C_p$$

where n -number of moles, C_p , C_v -molar heat capacities (amount of heat needed to increase the temperature of one mole of a substance by one degree) under constant volume and constant pressure. After integration, two equations are obtained:

$$\text{for } p = \text{const:} \quad Q_{p2} = Q_{p1} + \int_{T_1}^{T_2} \Delta C_p \, dT \quad (\text{x2})$$

$$\text{dla } v = \text{const:} \quad Q_{v2} = Q_{v1} + \int_{T_1}^{T_2} \Delta C_v \, dT \quad (\text{x3})$$

Heat of formation of a compound is a heat of synthesis of 1 mole of substance under its standard state (constant pressure 1 atm, 298.15K) from simple substances (constituent elements) in their standard states. On the basis of the Hess's law we can calculate the heat of formation of a compound if we know the heat of combustion of that compound and the heats of combustion of the elements constituting that compound. For example, heat of formation of 1 mol of methane (CH₄) equals the difference of the combustion heat of CH₄ and the heats of combustion of 1 mole of elemental carbon and two moles of gaseous molecular hydrogen (in standard state).

A device used for measurements of heat effects during physical and chemical processes is named calorimeter. Calorimeters can be designed in a number of ways,⁸ but usually the most basic parts are: a temperature sensor (or heat sensor) and a calorimetric dish (calorimetric chamber), placed inside insulated container. Calorimetric chamber and temperature sensor are inner part of calorimeter whereas insulated container plays a role of protector against heat exchange between calorimeter and surroundings.

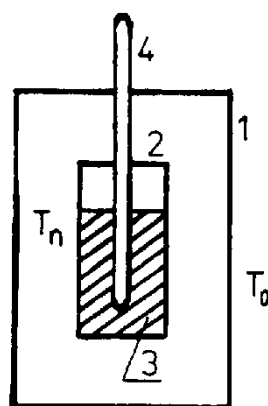


Figure 1. General (simplified) scheme of calorimeter. 1 – Protector/insulated container, 2 – calorimetric chamber, 3 - sampel, 4 – temperature sensor T_0 i T_n – temperature of container and chamber.

Calorimeters can be divided into several groups of instruments, depending on their design, mode of work, the kind of measured effect. For example: ice calorimeter (where heat of observed process is absorbed by ice/water system and on the basis of increasing volume of water the heat of process can be precisely measured), bomb calorimeter (applied for measurements of heat of combustion), Junkers calorimeter for measurements of calorific values of gaseous fuels, reaction calorimeters, flow calorimeters for measurements of heat effects during mixing and dissolving).

⁸ The following types of calorimeters can be distinguished: reaction calorimeters, heat flow calorimeters, heat balance calorimeters, bomb calorimeters, constant-pressure calorimeters, differential scanning calorimeters, isothermal titration calorimeters, X-ray microcalorimeters, heat-loss calorimeters and high-energy particle calorimeters, and others.

There is no universal rule of classification of calorimeters, and such a classification would be difficult because calorimetry, as a part of thermochemistry, has various sub-areas dedicated to different specific problems (static calorimetry, dynamic calorimetry, flow calorimetry etc.). The most common classification is based on three main groups. In **isothermal calorimeters** (as in Figure 1) temperature of insulator (T_0) and temperature of calorimetric chamber (T_n) remain constant when the observed process is carried out. In **adiabatic calorimeters** temperature of insulator (T_0) and temperature of calorimetric chamber (T_n) are equal each other but they are not constant ($T_0 = T_n \neq \text{const.}$). In both kinds of calorimeters the heat exchange is minimized because there is no temperature gradient between calorimetric chamber and insulated container and these kinds of calorimeters can be applied for measurements of small heat effects. Third group of calorimeters includes **non-isothermal and non-adiabatic calorimeters**, where $T_0 \neq T_n \neq \text{const.}$, i.e. a temperature is not constant and there are different temperatures of calorimetric chamber and protecting insulator. This is the most numerous and the most diverse group of calorimeters, including **diathermic calorimeters** ($T_0 = \text{const.}$, $T_n \neq T_0$). The general scheme of this type of calorimeter is shown in Figure 2.

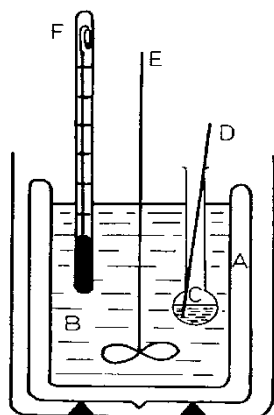


Figure 2 Diathermic calorimeter for liquid phase processes: A- insulation shield, B-calorimetric liquid, D- a baguette for breaking the ampoule, C- ampoule with the tested substance, E-stirrer, F - Beckman type thermometer.

In its simplest version of calorimeter a Dewar vessel filled with water can be used as a shield, with a stirrer and an accurate thermometer. Calorimetric chamber is a dish containing one of reactants and another reactant is separated with thin glass wall or the second reactant is inside another glass ampoule. The reaction starts when glass wall or ampoules are broken. In **flow calorimeters** one or both reacting solutions are pumped (continuously or periodically) to calorimetric chamber. When the heat of combustion is to be measured, the calorimetric chamber is a **bomb calorimeter** – a hermetic stainless steel chamber (called also “decomposition vessel”) working under high pressure.

Heat evolved during the process causes an increase of temperature of calorimetric chamber and is transferred outside to cause an increase of temperature of all parts of calorimeter. Each part of calorimeter has its own mass (m_i) and its own heat capacity (c_i). Heat absorbed by all these parts of calorimeter is the same as heat released during the studied process and can be expressed as $q = \sum m_i c_i \Delta T$. The sum: $\sum m_i c_i$ is constant and called a **calorimeter constant** or **heat capacity of the calorimeter, K**.

Calorimeter constant (heat capacity of the calorimeter, K) is the amount of a heat that is required to achieve a 1° increase of temperature of calorimetric system (including water). The calorimeter constant is usually presented in units of joules per degree Celsius ($J/^\circ\text{C}$) or joules per kelvin (J/K). Every calorimeter has a unique calorimeter constant. K can be determined by measurement of increase of temperature of calorimeter when a process of known heat is carried out (for example, for standard substance). Conditions of calibration (reference) experiment should be as close as possible to the conditions of experiments to be done with unknown samples. After K is determined, the amount of heat released during measured process can be calculated from simple equation: $q = K \Delta T$

Analytical signal recorded during the calorimetric experiment is named calorimetric plot or calorimetric curve and will be described in further part, in the section about calorimetric bomb and heats of combustion.

Heat exchange and mechanisms of heat transfer.

The temperature gradient is a driving force for heat flow from the high to the low temperature region. Heat transfer is classified into various mechanisms:

- heat conduction,
- convection,
- radiation,
- phase/change transfer.

Heat conduction occurs between two objects being in physical contact or, within one physical object, when energy is transferred as electron movement or oscillations of atoms within crystal lattice.

Convection is a transfer of energy due to fluid motion. **Free (natural) convection** means a process where fluid (gas, liquid) motion is accelerated by different densities caused by different temperatures of fluid. **Forced convection** is when the flow of fluid over the surface is accelerated by external forces (for example, stirrers and pumps) inducing the artificial convection current.

Thermal radiation occurs when electromagnetic waves are emitted as a consequence of thermal energy - random movements of atoms and molecules. Movement of charged particles (protons and electrons) causes the emission of radiation as one of the possible ways of energy escape from the system. Thermal radiation is located within microwaves, infrared and visible light depending on the temperature of the system. *This way of energy transfer can occur in vacuum.*

Phase-change transfer of heat is fourth mechanism of heat exchange and, more correctly, energy transfer, because in this mechanism the energy from intermolecular interactions (hydrogen bond) is converted into heat (and *vice versa*) during phase transition in the medium, for example, water-to-ice, water-to-steam, steam-to-water, or ice-to-water. The phase-transfer mechanism will not be described in this section.

Usually transfer of heat occurs through all three mechanisms, however, depending on the conditions, one mechanism dominates. Convection and conduction frequently occur simultaneously and such combined way is commonly called the heat transfer.

Steady heat transfer occurs when temperature gradient is constant within the system, thus, temperature gradient is constant with respect to time and **the rate of heat exchange** is calculated as heat to time ratio:

$$\dot{Q} = \frac{Q}{t} \quad (x4)$$

For unsteady conditions the ratio of exchanged heat to time is defined as differential equation:

$$\dot{Q} = \frac{dQ}{dt} \quad (x5)$$

Heat flux q is a heat rate per unit area [W/m^2] and can be expressed as:

$$q = \frac{\dot{Q}}{A} \quad (x6)$$

where A means area perpendicular to direction of heat flow. Unlike the rate of heat exchange (a scalar quantity) the heat flux is a vector quantity, and its direction is perpendicular to the surface of heat flow and direction of vector is from higher to lower temperature.

In agreement to Fourier's law for thermal conductivity in one dimension (x direction) a heat flux is proportional to temperature gradient and opposite to it in sign (therefore, a sign minus is included in the equation):

$$q = -\lambda \frac{dT}{dx} \quad (x7)$$

and the constant λ is thermal conductivity, expressed in units [W/m K]. Coefficient λ depends on the material and informs about ability of a given material to conduct the heat. The highest values of λ are observed for metals.

If the heat is transferred through homogeneous solid wall, integration of equation x7 gives:

$$q = \frac{\lambda}{x} (T_1 - T_2) \quad (\text{x8})$$

Heat flow during convective heat transfer (after some simplifying assumptions are undertaken) is described by Newton equation:

$$q = \alpha \Delta T \quad (\text{x9})$$

where:

α - heat transfer coefficient [W/m² K], and its magnitude depends on many factors: the way a fluid flows (laminar or turbulent), rate of the flow, viscosity and density of a fluid, thermal conductivity of the wall contacting with fluid, α is significantly bigger for the forced convection;

ΔT -difference in temperature between the solid surface and surrounding fluid area in [K] units.

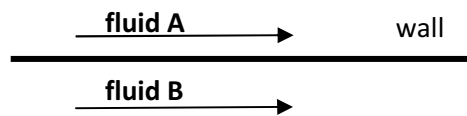
Heat flow for heat transferred during **thermal radiation** (from ideal black body) is described by Stefan-Boltzmann law:

$$q = \sigma_0 T^4 \quad (\text{x10})$$

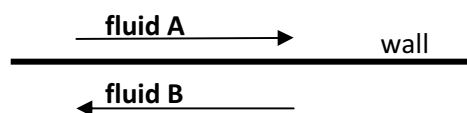
where constant of proportionality, σ_0 , is called Stefan-Boltzmann constant (5.672 10⁻⁸ W/m K), and T is temperature of radiating body, in kelvins.

Equipment designed for efficient heat transfer from one medium to another is called heat exchanger. A simplest example of laboratory heat exchanger with fluids separated by wall is glass condenser. There are many types of arrangement of flow, however, two of them have to be mentioned as very basic.

1. Concurrent flow, where both fluids flow in the same direction:

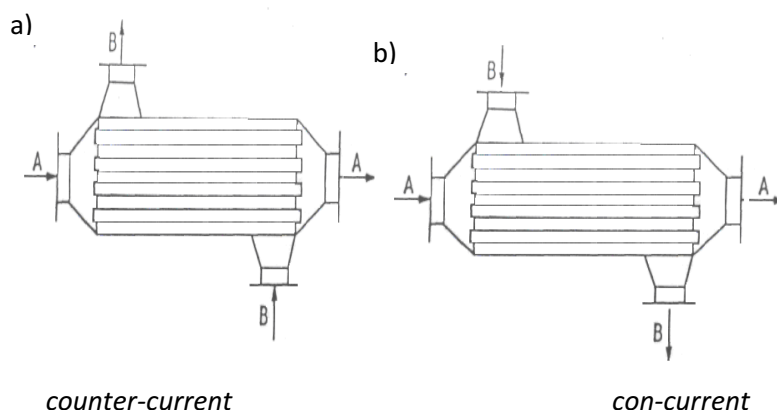


2. Counter-current flow where fluids flow in opposite directions:



Other arrangements are cross flow, spiral flow.

The counter-current flow arrangement is the most commonly applied method of heat transfer as more efficient than the con-current one. For counter-current method a smaller surface of heat exchange is required, temperature gradient is always enough to be a significant driving force for heat transfer, thus, smaller amounts of heating/cooling agent are needed for efficient heat exchange. Examples of heat exchangers are presented in the schemes below.



A driving force for heat transfer -temperature gradient – is changing through the whole distance of heat exchanger, regardless its counter-current or con-current arrangement. To calculate temperature gradient in flow systems a **log mean temperature difference (LMTD)** is used:

$$LMTD = \frac{(\Delta T_A - \Delta T_B)}{\ln \frac{(\Delta T_A)}{(\Delta T_B)}} \quad (\times 11)$$

where ΔT_A is the temperature difference between the two streams at the end A, and ΔT_B is the temperature difference between the two streams at the end B.

DETERMINATION OF HEAT OF COMBUSTION - OVERVIEW.

Combustion is conducted in calorimetric bomb (Berthelot-Mahler type) filled with high pressure oxygen. The calorimetric bomb is placed in water jacket (water calorimeter) and the increase in temperature of the calorimetric system is the measured analytical parameter. Compound to be burned (standard/reference material or measured sample) is placed in open calorimetric crucible. Measurements of temperature before and after combustion (the initial period and the end period) allow to determine the correction factors for heat exchange between calorimeter and surrounding. The heat of combustion is calculated on the basis of temperature increase, the calorimeter constant (heat capacity of the calorimeter) and mass of the sample.

Basic description of calorimetric experiment

Experiment is performed inside pressure calorimetric bomb under oxygen atmosphere (pressure ca. 30 bars) to obtain complete combustion of organic compound. Normally, solid substances can be burned directly in powder form, however, rapidly burning substances (for example benzoic acid) must not undergo combustion in loose form. These substances tend to squirt, and it would therefore not be possible to ensure complete combustion. In addition, it is possible the decomposition vessel could be damaged. Such substances are pressed into tablets before combustion with a special press. The sample (as a form of tablet) is placed inside the crucible. The substance must be weighed directly into the crucible with an accuracy of 0.1 mg. Distilled water or a solution must also be added to the decomposition vessel. The ignition is facilitated by the means of cotton thread connecting the tablet with ignition wire.

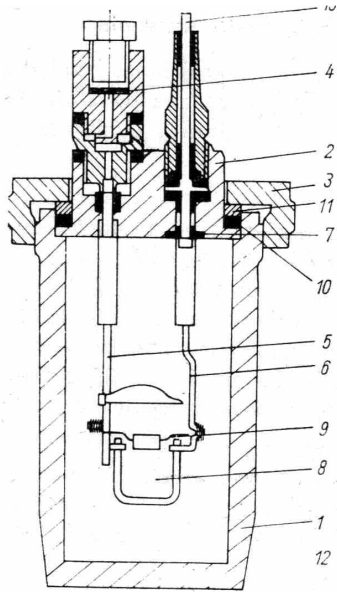


Figure 3. Scheme of calorimetric bomb vessel. (older version than used in the current experiment).

1 – main corps of the bomb, 2 – head, 3 – cap screw, 4 – inlet valve, 5,6 – electric connections (electrodes), 7 – electricity insulator, 8- crucible, 9 – ignition wire (in this version with a tablet), 10 – rubber gasket, 11 – metal ring, 12 – outlet valve (not shown on the scheme), 13 – connection to power.

(from: *Ćwiczenia Laboratoryjne z chemii fizycznej* translation from German, PWN Warszawa 1975.)

Connection to power causes the glowing of ignition wire and ignition of cotton thread, thus, the flame is transferred to the sample.

An example of calorimetric plot resulting from combustion experiment is presented in Figure 4. The measurement can be divided into three periods shown as three segments /sectors on the calorimetric plot. After the calorimetric vessel is charged with a sample and placed within calorimeter bath a few minutes is needed to thermally equilibrate the system. Then, the **initial period** of measurement starts and the changes of temperature are recorded to monitor the rate of heat exchange between calorimetric system and the surrounding. Usually this period takes five minutes and 5-10 values of temperature are recorded (30 or 60 second intervals). On Figure 4 this initial period is presented as segment from T_1 to T_3 . In the **main period** a combustion of the sample occurs (at T_3) and the energy is transferred to the whole calorimetric system (an increase of temperature can be seen on Fig. 4). Temperature increases until point T_4 is reached and the **final period** starts. During that period a temperature is still monitored and recorded in the same way as in the initial period. Duration of the final period is the same as duration of initial period – in both these time segments a rate of heat exchange between calorimeter and surrounding is monitored and recorded.

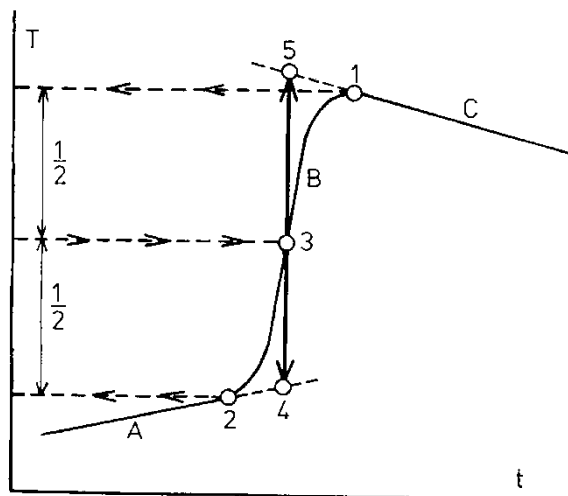


Figure 4. Plot of temperature (T) of calorimeter system versus time (t) of calorimetric experiment. Letters A, B, C denote periods: initial, main, and final, respectively.

A corrected increase of temperature, ΔT_{cal} , can be calculated from the equation:

$$\Delta T_{cal} = T_n - T_o + c \quad (x12)$$

where:

T_n – last value of temperature in the main period,

T_o - last value of temperature in the initial period

c – correction for heat exchange between calorimeter and surrounding.

Correcting factor c is calculated by Bunte's formula:

$$c = n_t [(\Delta i + \Delta f) + r \Delta f] \quad (x13)$$

where: n_t is a number of temperature points recorded per minute, Δi is a mean value of temperature increase (in K or °C) per one minute during the initial period, Δf is a mean value of temperature decrease (in K or °C) per one minute during the final period, r is number of temperature points recorded during the main period. Value of ΔT_{cal} is usually less than 3 degrees (precision of temperature measurement is usually 0.0001°C or less).

For analyzed process if ΔT is known, the amount of heat can be calculated from the heat balance and it is a sum of heat consumed (absorbed) by calorimeter and the heat exchanged with the surrounding. Therefore, the amount of heat measured with calorimeter is given by the equation:

$$Q_{measured} = -K \times \Delta T_{cal} \quad (x14)$$

where K – calorimetric constant (heat capacity of the calorimeter), ΔT_{cal} – change (increase/decrease) of temperature calculated with corrections (see eq. x13). Since combustion is exothermal process, the results will have negative sign, thus, in the formula x14 a minus is added before the $K\Delta T_{cal}$ expression. If the mass of the analyzed sample is known, the heat can be expressed in cal/g or J/g, however, the heat measured during experiment is a sum of heat from combustion of the sample and some extraneous energy generated during combustion of other materials present in the system (for example, combustion aids, igniters, sulfuric acid and nitric acid formed from molecular nitrogen). The heat of combustion of the cotton thread that ignites the sample and the electric energy needed for the ignition would result in distorted values of the measurement. This effect is taken into consideration in the calculation with a correction value. Almost all substances to be analyzed contain sulfur and nitrogen. Under the conditions that prevail during calorimetric measurements, sulfur and nitrogen undergo combustion and form SO_2 , SO_3 and NO_x .⁹ Sulfuric and nitric acid arise in combination with the water resulting from combustion and humidity. To obtain the standard gross calorific value, the effect of the heat of solution on the gross calorific value is corrected.

The calorimetric constant (heat capacity of the calorimeter) is calculated from equation:

$$K = \frac{Q_{st} \times m_{st} + c_1 + c_b + c_N}{\Delta T_{cal}} \quad (x15)$$

where:

Q_{st} is a heat of combustion of the standard substance used for calibration [cal/g or J/g],

m_{st} is a mass of the standard substance [g],

ΔT_{cal} – change of temperature monitored during experiment [°C or K],

c_1 - correction for heat released during combustion of steel wire (c_1 should be included when older type of calorimetric bomb is used, for platinum wire $c_1=0$),

c_b - correction for heat released during combustion of cotton thread,

c_N - correction for heat released during combustion of nitrogen to form HNO_3 .

Corrections c_b i c_N are calculated in the following ways:

⁹ Nitrogen oxides formed during ignition and combustion can catalyze the oxidation of SO_2 to SO_3 .

$c_b = 4200 \text{ [cal/g]} \times \text{mass of cotton thread [g]}$, (in the experiment the heat of combustion of cotton thread: $50 \text{ J} = 11.94 \text{ cal}$ has been determined by producer),

$$c_N = 1.43 \times v_{\text{NaOH}}$$

where 1,43 is a heat of formation of 1.00 mL of 0,1M nitric acid (in cal/mL) and v_{NaOH} is the volume (in milliliters) of 0.1 M NaOH used for titration of nitric acid formed during combustion.

ATTENTION: If the calculations are to be performed in joules, the 1.43 factor has to be recalculated into joules.

HEAT OF COMBUSTION OF BIOFUELS - - INSTRUCTION MANUAL

The purpose of this experiment is to determine heat of combustion and total calorific value of solid and liquid organic compounds (including fuels and biofuels). During the experiment, students will carry out a series of measurements in order to do:

- a) calibration of the calorimeter (determination of calorimetric constant, K),*
- b) determination of the heat of combustion of biofuel,*
- c) determination of the heat of combustion of other organic substance,*
- d) titration of combustion products – to calculate corrections for heats of combustion.*

As a result, students will be able to use the calorimeter apparatus (calorimetric bomb), they will calculate the heat of combustion and calorific value of organic materials as well as they will be able to compare the calorific values of fossil fuels with biofuels (biodiesel, FAME). After the experiment the students gain the ability to perform qualitative and quantitative description of the fuels and biofuels and ability to present resulting data and to critically assess the quality and applicability of (bio)fuels.

Equipment	lab glass and small equipment	safety equipment
Calorimeter IKA C2000	burette 1 item	latex gloves
decomposition vessel (bomb)	conical flasks 4 items	lab glasses
stainless steel crucible	squeeze bottle 2 items	
thermostatic bath	tweezers 1 item	
can with compressed O ₂	pipette 10 mL 1 item	
pressure regulator	disposal pipettes	
laboratory press	disposal syringes	
analytical balance		
computer + printer		

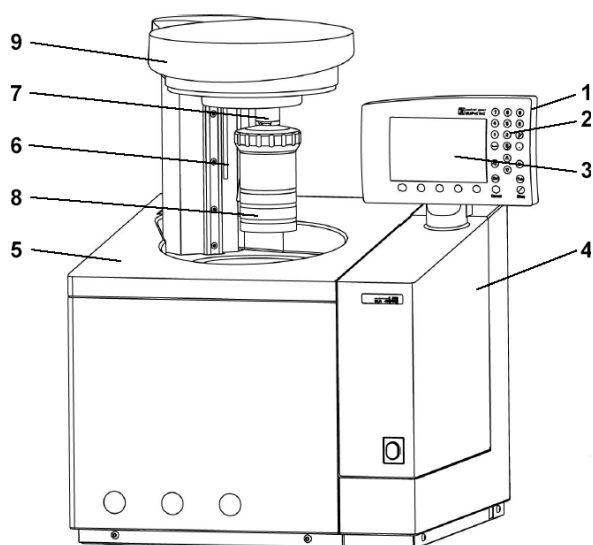


Figure 5. Scheme of IKA C2000 calorimetric system.

1. Control panel, 2. Keyboard, 3. Display, 4. Electronics unit, 5. Measuring cell. 6. Temperature sensor. 7. Oxygen filling device. 8. Decomposition vessel. 9. Measuring cell cover. Figure copied from original operating instruction for IKA C2000 basic calorimeter system.

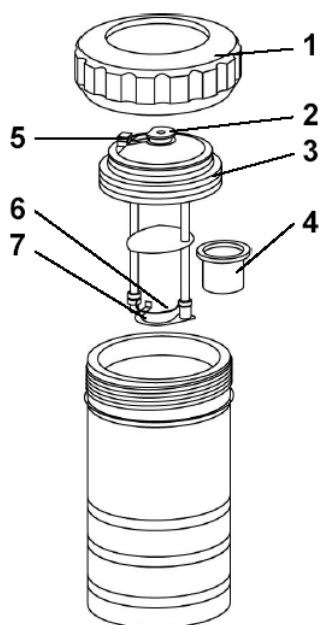


Figure 6.
Individual parts of the decomposition vessel.
1. Cap screw.
2. Oxygen valve.
3. Cover.
4. Crucible.
5. Electrical ignition contact.
6. Ignition wire.
7. Crucible holder.

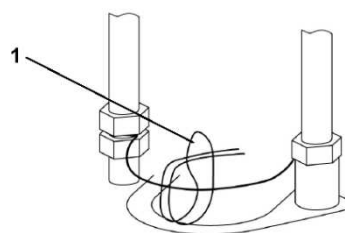


Figure 7.
Fastening a cotton thread (1) onto the ignition wire.



Figure 8.
Pressure reducer valve with manometers, mounted to pressure gas can with O₂.

Chemicals

a) benzoic acid is used as thermochemical standard during the experiment – its heat of combustion is 6324 cal/g (if weight is measured in air at temp. 20°C) or 6319 cal/g (if weight is measured in vacuum).

The standard should be of analytical grade characterized by the following parameters:

melting point		122°C
assay		99,90 %
ashes	no more than	0,02 %
chlorides	no more than	0,0005 %
sulfates	no more than	0,005 %
heavy metal ions		none
water	no more than	0,03%

b) cotton thread (heat of combustion 50 J)

c) 0.1 M solution of NaOH

d) 0.1 M solution of HCl

e) phenolphthalein, 1% in ethanol

f) biofuel (FAME)

Performing the measurement

1. Check the connection of the gas can with oxygen, turn on the main valve and check the oxygen pressure on the manometers.
2. Turn the chiller (thermostate) on and set up the working temperature as 20°C.
3. Turn the calorimeter on.
4. Turn on the computer and printer (chose CALWIN icon, option: isoperibol, „new measurement”)

Determination of calorimeter constant

Heat capacity of the calorimeter is determined by the means of standard material (benzoic acid, described in the previous section).

5. Preparation of the standard (reference) material: using laboratory (“two decimal place”) balance weigh about 0.6-0.9 g of benzoic acid (the amount of reference has to be adjusted to obtain 2-3°C increase of temperature during calorimetric measurement) and make tablet by the means of the laboratory press. All parts of pellet press and plates have to be clean (before use clean them with acetone or ethanol and make sure the parts are dry).
6. Using analytical balance weight **clean and dry** crucible from calorimetric vessel, record its weight with accuracy 0,0001 g (0,1 mg), remove it from the balance, place the tablet of standard compound (from point 5) inside the crucible and **weigh the total mass of the crucible with content**. Calculate the weight of standard, m_{st} .
7. Using pipette add 10,0 cm³ of distilled water to the calorimetric vessel.
8. Fasten a cotton thread around ignition wire (see Figure 7). Crucible with tablet within the crucible holder (Fig. 6) and align the cotton thread with a pair of tweezers so that it hangs down into the crucible and is immersed in the sample. This ensures that during the ignition process the burning thread will ignite the sample.
9. Close the decomposition vessel.¹⁰ Always hold the decomposition vessel securely on the top by the skew cap. Keep the vessel always in vertical position.
10. Guide the decomposition vessel into the filler head of the open measuring cell cover until it catches in place.
11. Input to the software (CALWIN) all information on the sample (weight, name of a file). Make certain that the desired operating mode is set. Press “start” button.
12. Filling with high pressure oxygen, stabilization of the calorimeter and measurements of temperature are carried out automatically. After the experiment is complete, the measuring cell cover opens. As soon as the message BOMB↑ appears on the small display, you can remove the decomposition vessel. Decompress the vessel with safe way using the venting button.
13. Open the vessel and check whether the sample underwent a complete combustion. If you notice a presence of unreacted compound -the determination should be cancelled and its result has to be rejected.
14. Transfer the water from the decomposition vessel to conical flask, use three or four additional portions of distilled water (from a squeeze bottle) to completely rinse out all the products generated during combustion and absorbed in water.
15. Clean the decomposition vessel with cover and crucible - they should be clean and dry before the next measurement.
16. Place the conical flask containing solution (from point 14) in water bath (95°C) for 5 minutes, then remove and cool it, add 10,00 cm³ of 0.1000 M NaOH, add two drops of 1% alcoholic solution of phenolphthalein and titrate excess of unreacted NaOH with 0.1000 M HCl.

¹⁰ You do not need to remove air from decomposition vessel. A presence of nitrogen is sometimes desired (when?) and the results are corrected on the basis of analysis of the amount of nitric acid generated during combustion.

Calculation of the calorimetric constant

17. Determine the increase of temperature ΔT_{cal} (using eq. X12) including correction factor according to equation X13. (an example of calculation of ΔT_{cal} : see example #1 in section entitled: Examples of calculations). Calculate the calorimeter constant on the basis of equation X15, taking the weight of the sample, correction for heat released by the cotton thread and correction for nitrogen combustion. (an example of calculation of K_f : see example #2 in section entitled: Examples of calculations).
18. Repeat points 5-17 twice. Each time calculate the K . Take arithmetic mean as the final result.

Determination of heat of combustion of biodiesel (FAME)

19. On analytical balance weight **clean and dry** crucible from calorimetric vessel, record its weight with accuracy 0,0001 g (0,1 mg), remove it from the balance, pour inside the crucible 0.5-0.8 cm³ of biofuel (Fatty Acid Methyl Esters), and **weigh the total mass of the crucible with content**. From the difference calculate the mass of the sample (m_s)
20. Determine the heat of combustion of the studied sample in the same way as for standard material (as described in points 7-16). Each time calculate ΔT_{cal} as it was described in point 17.
21. The heat of combustion of bio(fuel) Q_{fuel} can be calculated from modified equation X14 with appropriate corrections:

$$Q_{fuel} = \frac{K \times \Delta T_{cal} - c_b - c_N}{m_s} \quad [\text{cal/g}] \quad (\times 16)$$

where: K - calorimetric constant, ΔT_{cal} - temperature increase determined according to point # 20, m_s -mass of the sample, c_b -correction for heat released during cotton thread combustion, c_N - correction for heat released during combustion of nitrogen to form HNO₃ (including molecular nitrogen from air and nitrogen from the analyzed compound).

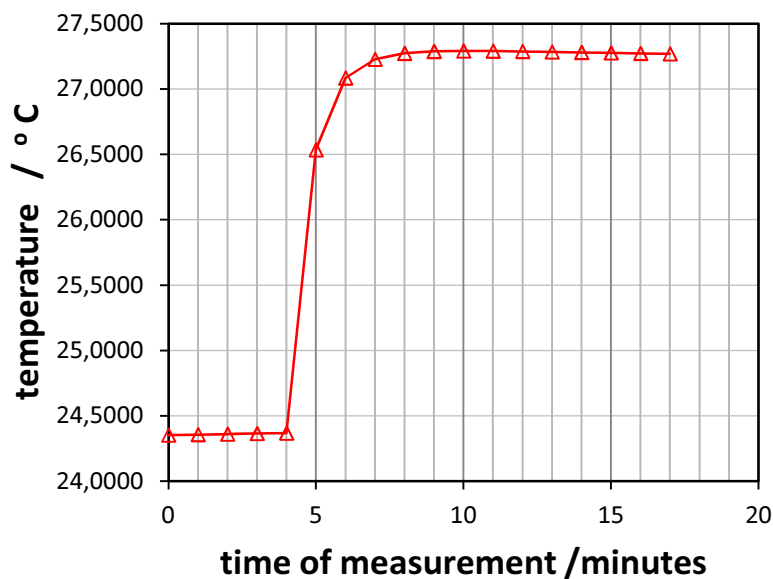
22. Repeat activities described in the points 19-21. Each time calculate Q_{fuel} . Take an arithmetic mean as the final result.
23. Calculate the error of determination.

Examples of calculations

Example 1 – Calculation of ΔT_{cal}

measured values:

initial period:		main period:		final period:	
time / min.	temp. °C	time / min.	temp. / °C	time / min.	temp. / °C
0	24,3527	0	26,5350	0	27,2845
1	24,3561	1	27,0851	1	27,2807
2	24,3599	2	27,2273	2	27,2769
3	24,3640	3	27,2737	3	27,2732
4	24,3681	4	27,2885	4	27,2694
		5	27,2919		
		6	27,2909		
		7	27,2881		



The increase of temperature ΔT_{cal} can be calculated from eqns. X12 and X13.

$$T_n = 27.2881^\circ\text{C},$$

$$T_o = 24.3681^\circ\text{C},$$

$$n_t = 1 \text{ value per minute},$$

$$\Delta i = (24.3681^\circ\text{C} - 24.3527^\circ\text{C}) / 4 \text{ min} = 0.0154^\circ\text{C}/\text{min}$$

$$\Delta f = (27.2694^\circ\text{C} - 27.2845^\circ\text{C}) / 4 \text{ min} = 0.0151^\circ\text{C}/\text{min}$$

$$r = 8$$

$$c = n_t [(\Delta i + \Delta f) + r \Delta f] = 1/\text{min} \times [0.0154^\circ\text{C}/\text{min} + 0.0151^\circ\text{C}/\text{min} + 8 \times 0.0151^\circ\text{C}/\text{min}] = 0.1513^\circ\text{C}$$

and

$$\Delta T_{cal} = 27.2881^\circ\text{C} - 24.3681^\circ\text{C} + 0.1513^\circ\text{C} = 3.0713^\circ\text{C}$$

error of ΔT_{cal} value denoted as $\Delta \Delta T_{cal}$ is a sum of all errors of individual components ($\Delta T_n, \Delta T_o, \Delta c$):

$$\Delta T_n = 0.0001^\circ\text{C}$$

$$\Delta T_o = 0.0001^\circ\text{C}$$

$$\Delta c = n_t [(\Delta \Delta p + \Delta \Delta k) + r \Delta \Delta k] = 1/\text{min} \times [0.0001^\circ\text{C}/\text{min} + 0.0001^\circ\text{C}/\text{min} + 8 \times 0.0001^\circ\text{C}/\text{min}] = 0.001^\circ\text{C}$$

therefore,

$$\Delta \Delta T_{cal} = 0.0012^\circ\text{C}$$

Example 2 – Calculation of the calorimetric constant

For calibration of calorimeter a reference material (1.0182 g of benzoic acid) was used, mass of cotton thread was 5.1 mg and the temperature increase was 2,4951°C. Post-reaction solution removed from the decomposition vessel was heated to remove CO₂ and then 10.00 mL of 0,1000 M NaOH was added. Excess of sodium hydroxide was titrated with 5.30 mL of 0,1000 M HCl (the phenolphthalein became colorless).

$$m_{st}=1,0182 \text{ g}$$

$$Q_{st} = 6.324 \text{ kcal/g}$$

$$\Delta T_{cal} = 2.4951 \text{ }^\circ\text{C}$$

$$m_b=0.0051 \text{ g}$$

$$V_{NaOH}=4.70 \text{ mL}$$

Thus, after applying the equation x15 the value of K is obtained:

$$K=[6324 \text{ cal g}^{-1} \times 1.0182 \text{ g} + 4200 \text{ cal g}^{-1} \times 0.0051 \text{ g} + 1.43 \text{ cal mL}^{-1} \times 4.70 \text{ mL}] / 2.4951^\circ\text{C} = 2592 \text{ cal/}^\circ\text{C}.$$

PLEASE NOTE: this example contains the data expressed in calories!

Example 3 – Calculation of error of determination of K

Parameters m_{st} , Q_{st} , ΔT_{cal} are the same as in example 2. Heat of combustion of the cotton thread is $50 \pm 1 \text{ J}$.

The individual parameters have the following maximal errors:

error of ΔT_{cal} determination is 0.0012°C ,

error of heat of cotton thread combustion $1 \text{ J} = 0.24 \text{ cal}$,

error of determination of heat of nitrogen combustion 0.05 cal/mL (assuming that error of titration is 0.01 mL and error of converting factor is 0.01 cal/mL).

$$K = (Q_{st} \times m_{st} + c_1 + c_b + c_N) / \Delta T_{cal} \quad [\text{cal/}^\circ\text{C}] \quad (\text{x15})$$

Applying the calculus, the error of a function of several variables can be calculated as a sum of its partial derivatives:

$$\Delta K = \pm \left[\left| \left(\frac{\partial K}{\partial Q_{st}} \right) \Delta Q_{st} \right| + \left| \left(\frac{\partial K}{\partial m_{st}} \right) \Delta m_{st} \right| + \left| \left(\frac{\partial K}{\partial c_b} \right) \Delta c_b \right| + \left| \left(\frac{\partial K}{\partial c_N} \right) \Delta c_N \right| + \left| \left(\frac{\partial K}{\partial \Delta T_{cal}} \right) \Delta \Delta T_{cal} \right| \right]$$

$$\Delta K = \pm \left[\left| \left(\frac{\partial K}{\partial Q_{st}} \right) \Delta Q_{st} \right| + \left| \left(\frac{\partial K}{\partial m_{st}} \right) \Delta m_{st} \right| + \left| \left(\frac{\partial K}{\partial c_b} \right) \Delta c_b \right| + \left| \left(\frac{\partial K}{\partial c_N} \right) \Delta c_N \right| + \left| \left(\frac{\partial K}{\partial \Delta T_{cal}} \right) \Delta \Delta T_{cal} \right| \right]$$

$$\left(\frac{\partial K}{\partial Q_{st}} \right) = \frac{m_{st}}{\Delta T_{cal}} = \frac{1,0182}{2,4951} = 0.41$$

$$\left(\frac{\partial K}{\partial m_{st}} \right) = \frac{Q_{st}}{\Delta T_{cal}} = \frac{6324}{2,4951} = 2534.56$$

$$\left(\frac{\partial K}{\partial c_b} \right) = \frac{1}{\Delta T_{cal}} = \frac{1}{2,4951} = 0.40$$

$$\left(\frac{\partial K}{\partial c_N} \right) = \frac{1}{\Delta T_{cal}} = \frac{1}{2,4951} = 0.40$$

$$\left(\frac{\partial K}{\partial \Delta T_{cal}} \right) = -\frac{Q_{st}m_{st} + c_b + c_N}{(\Delta T_{cal})^2} = -\frac{6324 \times 1.0182 + 11.9 + 6.721}{6.2255} = -1037.30$$

$$\Delta K = \pm [0.41 \times 1 + 2.3456 \times 0.0001 + 0.40 \times 0.24 + 0.40 \times 0.05 + 1037.30 \times 0.0012] \\ = 0.41 + 0.00 + 0.09 + 0.02 + 1.04 = \pm 1.52 \text{ cal/deg}$$

therefore, the result obtained in example 2 is: $K = 2592 \pm 2 \text{ cal/deg}$

Example 4 – Calculation of heat of combustion of (bio)fuel.

For the measurements the following substances were used: 0,7760 g of biofuel and cotton thread with previously determined heat of combustion as 60 J. Increase of temperature was determined as 3.4804°C.

Post-reaction solution removed from the decomposition vessel was heated to remove CO₂ and then, 10.00 mL of 0,1000 M NaOH was added. Excess of sodium hydroxide was titrated with 5.10 mL of 0,1000 M HCl (the phenolphtalein became colorless). Calorimetric constant is determined as, for example, $K=10845 \pm 9$ J/K.

$$m_s=0.7760 \text{ g}$$

$$K= 10845 \pm 9 \text{ J/K}$$

$$\Delta T_{cal}= 3.4804 \text{ K}$$

$$c_b= 60 \pm 1 \text{ J}$$

$$V_{NaOH}=4,90 \text{ mL (i.e. a result of subtraction: } 10.00 \text{ mL } -5.10 \text{ mL)}$$

Correction for heat of nitrogen combustion is 1.43 cal/mL (that is, 5.98 J/mL).

$$c_N=5.98 \text{ J mL}^{-1} \times 4.90 \text{ mL}=29.3 \text{ J}= 29 \pm 1 \text{ J}$$

$$Q_{fuel} = \frac{K \times \Delta T_{cal} - c_b - c_N}{m_s} = \frac{10845 \times 3.4804 - 60 - 29}{0.7760} = 48526 \text{ J/g}$$