A8 *Version 02.2019*

Calorimetric determination of the combustion enthalpy

1. The main purpose:

The main defined issue in this experiment is to determine the combustion enthalpy of two aromatic hydrocarbons (anthracene and salicylic acid) using an adiabatic bomb calorimeter.

2. Theory

The course of a chemical reaction in a closed system (with constant volume) is accompanied by a transfer of the reaction heat $\mathbf{q_v}$ from the reactor center to the surrounding area. When during the reaction no mechanical work $\delta\mathbf{w}=0$ has been applied or generated, the reaction heat released q_v equals simply the increase of the inner energy of the reactor, $\mathbf{\Delta U}$, $\mathbf{\Delta U= q_v}$. For reactions taking place under constant pressure the reaction heat $\mathbf{q_p}$ equals the difference in the enthalpy of the system, $\mathbf{\Delta H= q_p}$. For exothermic reactions ($\Delta H < 0$) proceeding under isothermal conditions ($\Delta T = 0$) the heat generated in the reactor become partly transferred to its environment ($q_p < 0$). For endothermic reactions ($\Delta H > 0$) proceeding under isothermal conditions ($\Delta T = 0$) the reactor takes the energy from its environment ($q_p > 0$). These relations enable to determine changes of the enthalpy due to the reaction simply by measuring the related temperature jump in the area surrounding the reactor.

When a reaction between two species A and B leads to several products, C, D…Z, according to a general reaction scheme: $\nu_a A + \nu_b B \rightarrow \nu_c C + \nu_d D + \dots \nu_r Z$, then due to Hess's rule the standard reaction enthalpy $\mathbf{\Delta_r H^o}$ can be calculated as a sum of standard formation enthalpies $\mathbf{\Delta_b H^o_i}$ for all species involved:

$\mathbf{\Delta_r H^o = \sum_i \nu_i \Delta_b H^o_i}$, where the stoichiometric coefficients v_i remain positive for products and negative for educts.

This general relation results from the independency of the enthalpy of the reaction path, (thermodynamically the enthalpy is a state function).

Numerous reactions cannot be performed under exact standard reaction conditions. For such a case the resulting reaction enthalpy can be calculated by the Kirchhoff's formula which relates the modified enthalpy $\mathbf{\Delta_r H}$ (T_2) to the temperature dependent molar heat capacity $\mathbf{C_{p,i}}$ (T) for all species involved:

$$\mathbf{\Delta_r H}(T_2) = \mathbf{\Delta_r H}(T_1) + \int_{T_1}^{T_2} \mathbf{\Delta_r C_p}(T)dT$$

where $\mathbf{\Delta_r C}_p = \sum_i \mathbf{\nu_i C_{p,i}}(T)$

The temperature dependency of the molar heat capacity $\mathbf{C_{p,i}}$ (T) for each species involved in the reaction can be usually approximated by the following expression: $\mathbf{C_{p,i}}(T) = a + b/T + c/T^2$ where a, b and c are empiric parameters

Following the general definition of the enthalpy: $H = U + pV$, the reaction enthalpy $\Delta_r H$ end the reaction energy $\Delta_r U$ are connected with each other via the relation:

$\mathbf{\Delta_r H = \Delta_r U + \Delta\nu_{gas} RT}$

For gas phase reactions $\mathbf{\Delta\nu_{gas}}$ means the related changes of the mole number.

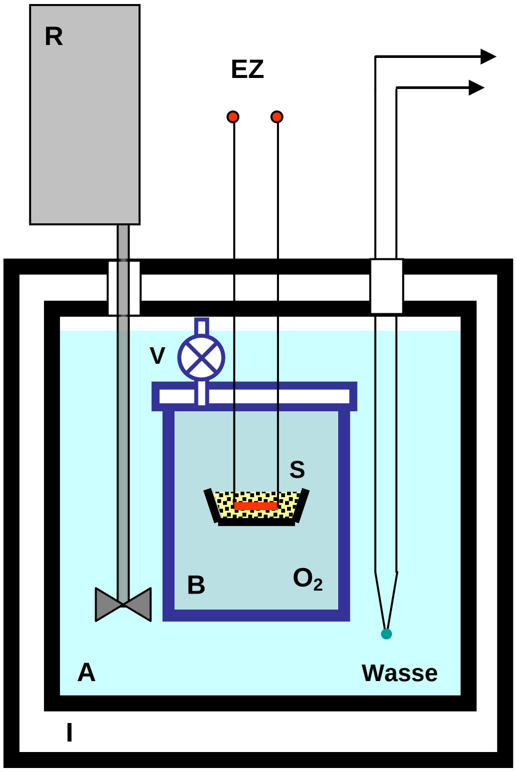
For reactions in solid and liquid phases it is possible to approximate: $\mathbf{\Delta_r H \approx \Delta_r U}$

The measurements of the reaction enthalpy will be performed in an *adiabatic bomb calorimeter*: a closed vessel (reactor) embedded in a water bath, both implemented into an isolating calorimeter. The related measurements are based on the relations explained above: $\mathbf{\Delta_r U = q_v}$ and $\mathbf{\Delta_r H = q_p}$. When the reaction heat released by an isolated reactor (marked by its heat capacity C) leads to a temperature increase ΔT then the related reaction heat q can be calculated as $q = C\Delta T$. Depending on the reaction conditions ($\Delta p=0$ or $\Delta V=0$) it is possible to determine $\mathbf{\Delta_r H}$ and $\mathbf{\Delta_r U}$: $\mathbf{\Delta_r H} = q_p = C\Delta T$ and $\mathbf{\Delta_r U} = q_v = C\Delta T$ (assuming that the heat capacity of the calorimeter is known). The characteristic parameter C can be determined by performing the full combustion of a certain amount of a standard substance with known combustion enthalpy (in our case benzoic acid, $C_7H_6O_2$).

3. Experiment

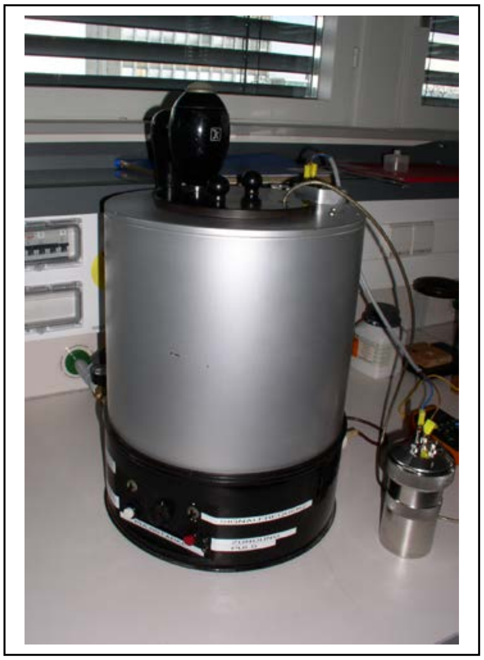
The measurement will be conducted in three stages using the same bomb calorimeter: (1) First, the heat capacity of the calorimeter C has to be determined by measuring the combustion heat for benzoic acid. This substance has been chosen because in the literature it exhibits a well documented value of the combustion heat, $\Delta_V U$ =3231.9 kJ/mol. (2) In the second stage the value C determined in the foregoing section will be exploited for precise measurement and calculation of the combustion heat of anthracene powder ($C_{14}H_{10}$). (3) Finally the same procedure will be repeated for determining the combustion heat of salicylic acid ($C_7H_6O_3$). In all three experiments the combustion of the hydrocarbons will be performed in closed steel vessel (reactor) filled with molecular oxygen up to 20 bar, i.e. the reaction proceeds at constant volume.

A. Experimental setup



Scheme of the apparatus
A – water bath, R – stirrer B – combustion vessel
S - pellet, EZ – electric ignition
V – valve, I – isolator, T – thermocouple

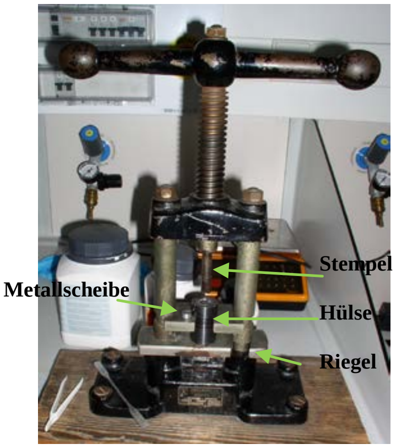
adiabatic bomb calorimeter



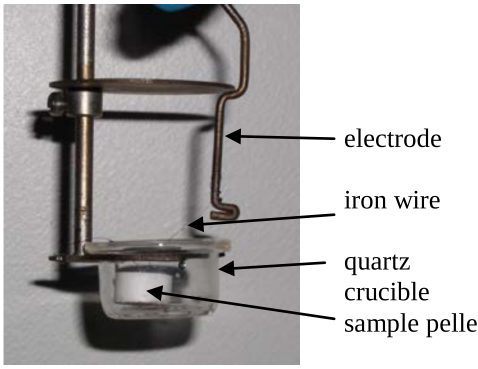
The adiabatic bomb calorimeter
(IKA-Werk Stauffen)

B. Preparation of the samples

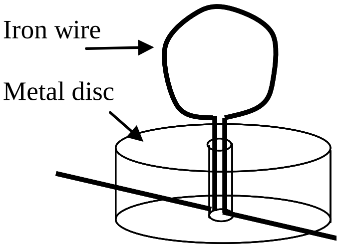
The substances used here for measurements: Benzoic acid, Anthracene und Salicylic acid are supplied as powders. Using a mechanical pressing device (see scheme below) the powder must be converted into solid pellets (pills).



Mechanical press setup



Sample holder inside of the metallic

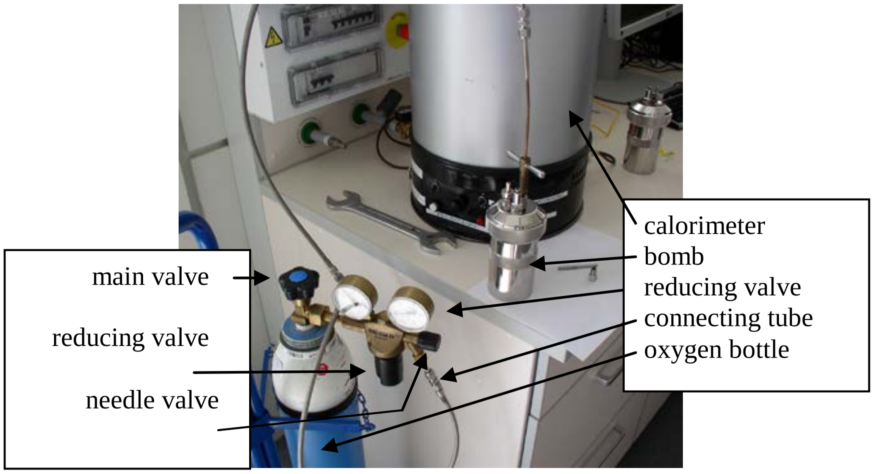


First, a 12 cm-long metal wire together with the quartz crucible should be weighted by an electronic balance (Sartorius AX6202). Then the metal wire should be mounted as ignitor into a metal disc (see the scheme above) and subsequently set from the bottom side into the sleeve of the pressing device. The sleeve (hull) with the metal disc in the bottom (as a plug) forms a small container which should be filled from the open end with the powder. (For each experiment the mass of the powder required to get convincing results should be approximately ~1 g). The powder will be pressed against the metal disc (and the iron wire inside) by rotating the main screw in the pressing device. A stabile sample pellet will be reached when rotating the screw up to fell a first mechanical resistance and subsequently move the screw further by a half turn. The lower locking bar in the pressing device should be moved by side and the pellet created can be released from the tube simply by moving down the pressing stamp. After separating the sample pellet (together with the embedded iron wire) from the metal disc the pellet will be weighted precisely with the electronic balance to determine the sample mass **m** (~1 g). The sample (powder pellet) placed in the quartz crucible has to be mounted in the holder connected with the top of the reactor bomb. The ends of the iron wire (ignitor wire) must be gently wrapped around the electrodes in order to close the electric circuit. Finally the cover of the bomb together with the sample installed will be strongly screwed down by hand. Now the reactor is closed but still not filled with oxygen.

In principle the bomb calorimeter consists of two parts only: the bomb reactor and the water bath. Both components commonly absorb the reaction heat released. The heat absorbed by the water bath scales with the mass of the bath, i.e. we have to set this value first. The clean and dry calorimeter tank (without foot spacer) should be placed on the coarse balance and filled with 2455g room-temperature water (related net water mass 1760 ± 1 g). At this water mass the bomb reactor embedded in the bath remains entirely covered by water without short-circuiting the electrical connectors (both electrode connectors have to be located above the water level). After completing the whole experiment the calorimeter tank has to be filled with water again (up to reaching the (tank + water)-mass of 2455g). The outer surface of the bomb has to be dried before being inserting into the calorimeter tank.

C. Preparation of the calorimeter

Next, the closed bomb has to be filled with oxygen gas (p=20 bar) prior to being positioned it in the water bath (water filled calorimeter tank). For this purpose the return valve in the bomb will be connected with the high-pressure gas bottle by means of a special flexible metal tube (see the image below).



Prior to opening the main valve on the gas bottle you have to check if the knob of the reducing valve is unscrewed. The needle valve (knurled screw in the top-right corner at the valve) should also be closed.

Now the main valve at the gas bottle can be opened slowly. The manometer at the left side indicates now the pressure inside the bottle to be usually in between 100 and 200 bar. Next, the pressure in the outgoing side can be settled at a level of 4 bar (simply by turning the knob on the reducing valve to the right). The connecting tube and the bomb itself can be now flushed by oxygen (removal of air from the reactor). This can be achieved by slowly opening the needle valve (left turning) and opening the purger at the bomb for several seconds. After completing the flush procedure by closing the purger at the bomb should stay under load and the oxygen pressure should be increased to 20 bar (by turning the knob on the reducing valve to the right). Wait at this level for approximately one minute (this step is necessary because the capillary in the ingoing tube strongly reduces the gas flow and delays the resulting pressure increase). Now the filled bomb has to be separated from the oxygen gas bottle: First, close the needle valve and afterwards close the main valve at the gas bottle (right turn) and finally unscrew the entrance capillary at the bomb and seal the access with the small screw plug.

Now we can place both components into the calorimeter: First the foot holder has to be placed in the water-filled tank and after connecting the electrodes on the bomb with the power supply the bomb has to be located inside the tank. The apparatus is equipped with an electric power supply which provides controlled pulses for ignition of the combustion process (the pulse current passing through the iron wire embedded in the sample releases heat and consequently triggers the combustion by fusing the wire). The cover of the calorimeter is divided into two halves and consequently fulfils three aims: (1) act as the holder for a K-type thermocouple recording the temperature of water bath, **T**(t), (2) act as a leading edge for the electric stirrer, and (3) it provides a considerable reduction of the heat losses. Ignition: by pushing the red button on the wall of the apparatus the measuring cycle will be activated. In order to warranty that all parts of the system become equilibrated it is recommended to stir the water bath for 10 minutes prior to activate the ignition. The stirrer becomes activated by pressing the white button on the chassis.

D. Measurements of the combustion enthalpy

The real measurement of the reaction heat proceeds via recording the reaction-conditioned time evolution of the water-bath temperature T(t), within a time period of 10 minutes before and 10 minutes after ignition point. The current bath temperature is measured by a thermocouple (K-type) and transferred via an RS232-interface in the voltmeter to the computer where it is recorded with the Datalogger DMM software. The recommended settings in the recording program: Option → Recording-Continue with the value Time →2000s and the time interval→ 1s; the interface RS232 on the voltmeter must be activated.

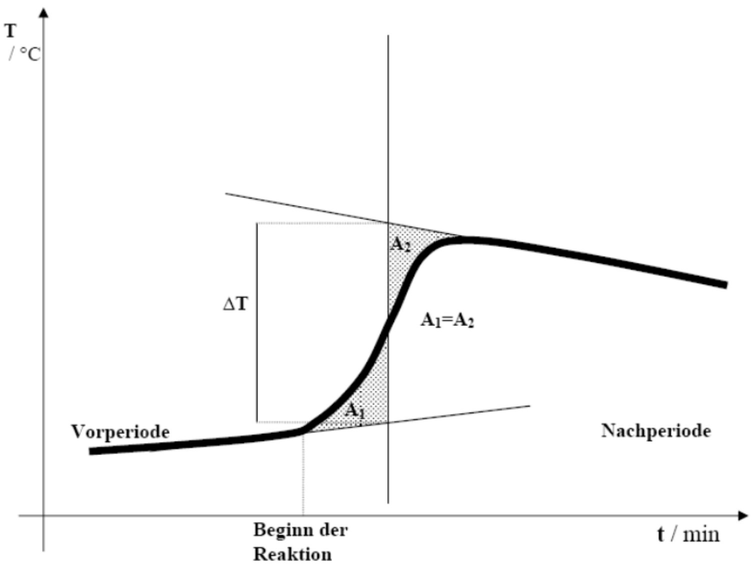
The ignition of the combustion process has to be performed only after a foregoing period of 10 minutes after all parts of the system have been thermodynamically equilibrated. The ignition is triggered by pressing the red button on the apparatus. If there was no igniting fusion, the display on top will show a white cross. In such a case one should increase the pulse voltage by roughly 20% and repeat the ignition even. When the ignition was successful (the iron wire has been fused) the sensor remains black and the combustion process is in progress.

It happens in some rare cases that the combustion does not proceed, despite the iron wire was fused and properly indicated by the sensor. In this case, within a time period of 1-2 minutes after the apparent ignition no temperature increase can be detected.

Similarly, sometimes after a long series of failed ignition trials the failure of the electric fuse is signaled. In this case the whole system can be reactivated simply by pressing the small button at the power plug.

Basing on the **T**(t) curves recorded during the combustion process the for the reaction enthalpy relevant temperature increase **ΔT** can be calculated by the area compensation procedure (see the scheme of the compensation method below). For a known heat capacity C of our calorimeter the related combustion heat q_v is simply $q_v = C\Delta T$.

The recorded T(t) curves should be presented graphically and evaluated according to the area compensation method. The scheme shown below illustrates how to derive the ΔT values.



The vertical line is chosen in such a way that the areas marked A_1 and A_2 for the periods before and after the ignition, are equal. (A: the area between the curve T(t) and the regression straight line R(t)). One has to calculate the differences d(t) =T(t)-R(t) and integrate them. You can find a detailed description of the compensation procedure in the supplement.

Remark: When the T(t) curve recorded exhibits exactly horizontal regression lines then the temperature jump **ΔT** equals simply the normal distance between the two straight lines. In such a case you can skip the compensation procedure.

D. Data Analysis

For all there measurements the data analysis starts with the stoichiometric reaction equation.

The calibration of the calorimeter is based here on the measurements of the combustion of benzoic acid $C_7H_6O_2$ and the subsequent data processing goes along the following route:

m – the mass of the pellet has been determined experimentally, $M(C_7H_6O_2)$= 122,12 g/mol

The molar standard combustion energy for benzoic acid: ΔU(T°)= – 3231,9 kJ/mol

Combustion energy of the iron wire: ΔU(Draht) = - 6.28 J/cm (*l*=12 cm)= -75.36 J

Under standard conditions: $-q = \Delta U(T°)\,(m/M) + \Delta U(\text{wire}) = C\,\Delta T$

$$C(T^0) = -[\,\Delta U(T°)\,(m/M) + \Delta U(\text{wire})] / \mathbf{\Delta T}$$

ΔT has been determined experimentally

When the combustion process starts at the temperature T_A which differs from the standard temperature T° the related combustion heat has to be recalculated according to the Kirchhoff's formula under following approximations:

$$\Delta U(T_A) = \Delta U(T°) + \Delta C_v(T_A - T°)$$

According to the reaction equation: $C_7H_6O_2 + (15/2)\ O_2 \rightarrow 3\ H_2O + 7\ CO_2$

ΔC_v can be calculated as follows:

$$\Delta C_v = 3\ C_v\,(H_2O) + 7\ C_v\,(CO_2) - 7{,}5\ C_v\,(O_2) - C_v\,(C_7H_6O_2)$$

C_v [J/K mol]	75.2	28.3	20.8	146.65

$$\underline{C(T_A) = -[\ (\Delta U(T°) + \Delta C_v(T_A - T°)\ )(\mathbf{m}/M) + \Delta U(\text{wire})]\ /\ \boldsymbol{\Delta T}}$$

According to this route we get the heat capacity of our calorimeter for the initial temperature T_A.

By applying Hess's formula for each reaction the related standard combustion enthalpy should be calculated. Building on the measured temperature jumps DT and the relation $\Delta_v U = q_v = -C\ \Delta T$ one has to calculate the reaction energy $\Delta_v U$ (the parameter C has been determined already in the first experiment) and the temperature jumps for anthracene and salicylic acid were directly measured in experiments 2 and 3. By combining the $\Delta_v U$ values with the equation $\Delta_v H = \Delta_v U + \Delta \nu_{gas}\ RT_A$ one should calculate the related combustion enthalpy $\Delta_v H$ for both anthracene und salicylic acid.

One has also to consider the condensation heat of water as well as the sublimation heat of the substance S under study here. The corrected values of the combustion enthalpy $\Delta_v H^*_S$ can be obtained by using the following equation:

$$\Delta_v H^*_S = \Delta_v U + \Delta \nu_{gas} RT + n_S \Delta_{sub} H_S - n_{H2O} \Delta_{vap} H_{H2O}$$

Index S – anthracene und salicylic acid

Relevant Thermochemical Data:

sublimation enthalpy $\Delta_S H_m$:

anthracene: 99.2 kJ/mol

salicylic acid: 79.2 kJ/mol

formation enthalpy:

$H_2O(g)$= -241.82 kJ/mol,

$H_2O(l)$ = -285.83 kJ/mol,

$CO_2(g)$ = -393.51 kJ/mol

$C_6H_5COOH()$= -385.1 kJ/mol,

$C_{14}H_{10}(g)$=-223 kJ/mol,

$C_7H_6O_3$ (g) = -495.8 kJ/mol

Relevant issues

1. Endothermic und Exothermic Reactions.
2. Reaction enthalpy, standard reaction enthalpy, standard state of a substance.
3. Standard formation enthalpy of a molecule.
4. Examples for an application of Hess's equation.
5. Kirchhoff's law.
6. The relation between the reaction enthalpy and reaction energy.
7. Definition and interpretation of the following concepts:
   - combustion enthalpy;
   - atomization energy;
   - sublimation enthalpy;
   - evaporation enthalpy;
   - dissociation enthalpy.

Literature

Peter W. Atkins „Physikalische Chemie“, VCH Verlagsgesellschaft, Weinheim, 1987

Peter W. Atkins „Physikalische Chemie: Arbeitsbuch“, VCH Verlagsgesellschaft, Weinheim, 1988

G. Wedler „Lehrbuch der Physikalischen Chemie“, WILEY VCH, 1997

Additional questions

1. Please, estimate the possible reduction of the CO_2 release when replacing Iso-Octane (gasoline) by methane (natural gasoline) in all combustion engines. You can use the standard combustion enthalpies (see e.g. related tables in Atkins)

2. One has to calculate the standard formation enthalpy of ethanol by using the related values of for the binding and atomization enthalpies.

Estimation of the error bars in the measurement of $\Delta_v H^*_S$

The source for rough errors in our measurements is the rather limited accuracy for determination of the sample mass **m** and the reaction induced temperature jumps ΔT. The error in the measurement of the calorimeter capacity ΔC can be calculated according to the following equation:

$$\Delta C(T_A) = \left|\frac{\partial C(T_A)}{\partial \Delta T}\right| \Delta(\Delta T) + \left|\frac{\partial C(T_A)}{\partial m}\right| \Delta m$$

Consequently the error in the determination of the standard combustion enthalpy $\Delta_v H^*_S$ can be calculated for both anthracene und salicylic acid in the following manner:

$$\Delta(\Delta_v H_s^*) = \left|\frac{\partial \Delta_v H_s^*}{\partial C(T_A)}\right| \Delta C(T_A) + \left|\frac{\partial \Delta_v H_s^*}{\partial \Delta T_s}\right| \Delta(\Delta T_s) + \left|\frac{\partial \Delta_v H_s^*}{\partial m}\right| \Delta m$$

One has to reasonably estimate the possible rough deviations by measuring the temperature and the sample mass. The easiest way is to take the accuracy limits documented for the instruments used (for thermocouple and for the electronic balance in our laboratory).

Area compensation procedure using Origin 8.5G or newer:

1. Plot *T* vs. Time in a point diagram.

2. Select the data points for the pre- and postexperimental periods using the button ↕ (left symbol strip, fix by double click after selection) and determine regression lines for both periods.

3. Calculate the differences (measured data-preexp. regression line) and (postexp. Regression line-measured data) in the data book. (*Mark empty column/ click right/ set column values/ enter function/OK*).

Example: Let a be the slope and b the intersect of your preexperimental regression; your calculated temperature increase can be found in column B, the times in column A. Then your function will be: col(B)-(a*col(A)+b)

For the postexperimental period the sutraction must be conducted the other way round.

4. Plot both new data sets vs. T and integrate them (*Analysis / Mathematics/ Integration*). Choose the integration areas with ↕ . The result of this integration can be found as an additional column in your data point table.

5. Calculate the difference between the last value of the integral column of the postexperimental period and the values of that same column in a new column.

6. Plot this difference function and the integral for the preexperimental period as shown in Fig.. 2b. Calculate the difference between both regression lines at the intersection time t_{sub}, this is your desired increase ΔT.

Both diagrams have to be included in the protocol!.

Fig. 2a:

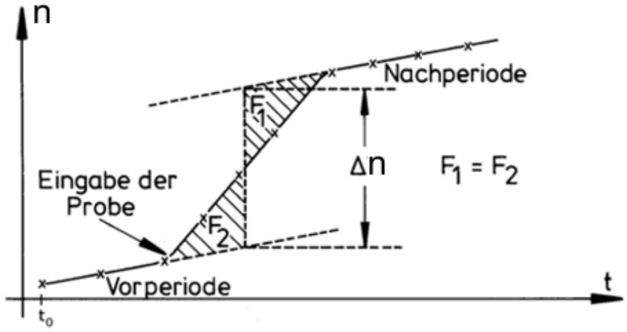


Fig. 2b: