Theoretical Basics

The course of a chemical reaction in a closed system, with V = const, leads to distribution of the heat of reaction q_v between the reactor and its environment. If there isn't any mechanical work, ~~then~~ is the internal energy equal to the generated heat: $U = q_v$

If the pressure is constant is the energy equal the enthalpy: $H = q_p$

- exothermic reaction: $\Delta H < 0$
- endothermic reaction: $\Delta H > 0$

The enthalpy is a path-indepent state function. As a result we can say (Hess): $\Delta_r H^\circ = \sum_i \nu_i \Delta_b H_i^\circ$

for $\nu_a A + \nu_b B \rightarrow \nu_c C + \nu_d D \cdots + \nu_z Z$

$\nu_i > 0$ for products
$\nu_i < 0$ for reactants

In order to be able to compare the obtained data, we need the temperature dependence of the reaction enthalpy. This results from the molar heat capacities $c_{p,i}(T)$ of all substances involved in the reaction:

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r c_p(T)\, dT \quad \text{with } \Delta_r c_p = \sum_i \nu_i c_{p,i}(T)$$

(Kirchhoff)

The temperature dependence of the heat capacities of the substances can be described with: $c_{p,i}(T) = \frac{a+b}{T} + \frac{c}{T^2}$ (a,b,c are empirical parameters)

From the general definition of the enthalpy ~~($H = \Delta_r U + \Delta \nu_{gas} RT$)~~ ($H = U + pV$) follows the relation between the reaction enthalpy $\Delta_r H$ and the reaction energy $\Delta_r U$:

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

$\Delta \nu_{gas}$: changing the number of moles in the gas phase

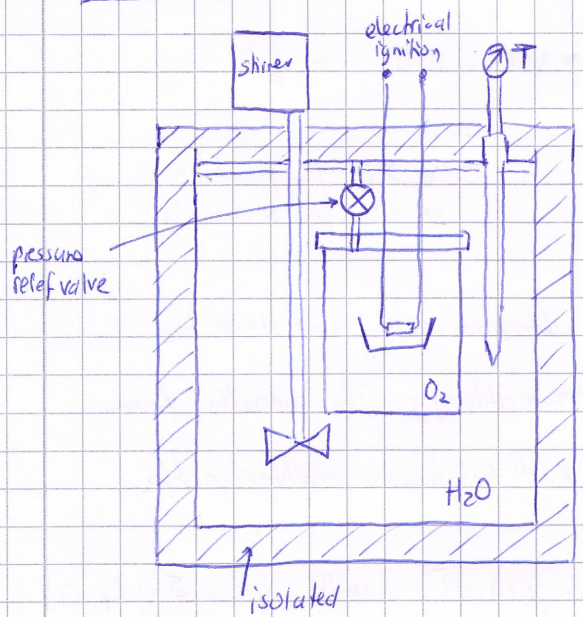
If there are only solids and liquids involved it is considered as $\Delta_r H \cong \Delta_r U$

The most important device for determining the reaction enthalpy is the adiabatic bomb calorimeter. The measurement is based on the relation $\Delta_r U = q_V$ and $\Delta_r H = q_p$.

If the heat of reaction in an isolated system, like a calorimeter, with the heat capacity C leads to the temperature change ΔT, then it is considered as: $q = C \Delta T$.

Depending on the reaction conditions ($\Delta p = 0$ or $\Delta V = 0$) $\Delta_r H$ or $\Delta_r U$ is determined: $\Delta_r H = q_p = C \Delta T$ or $\Delta_r U = q_V = C \Delta T$.

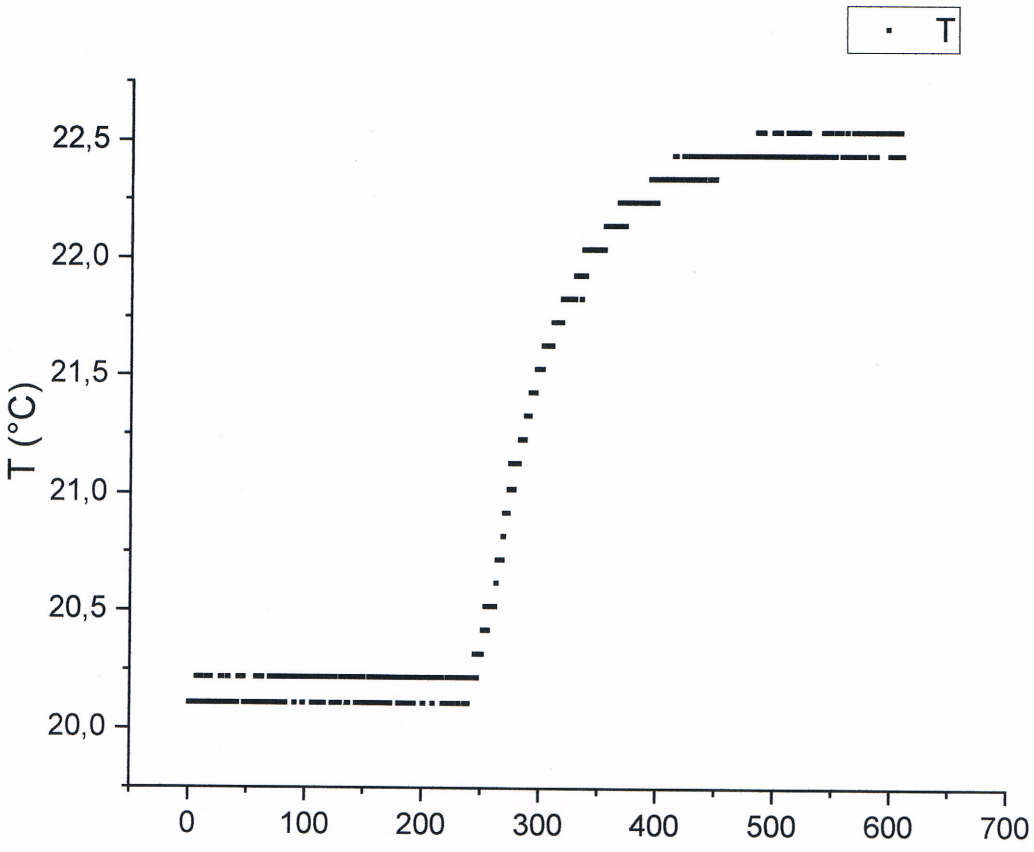
Execution



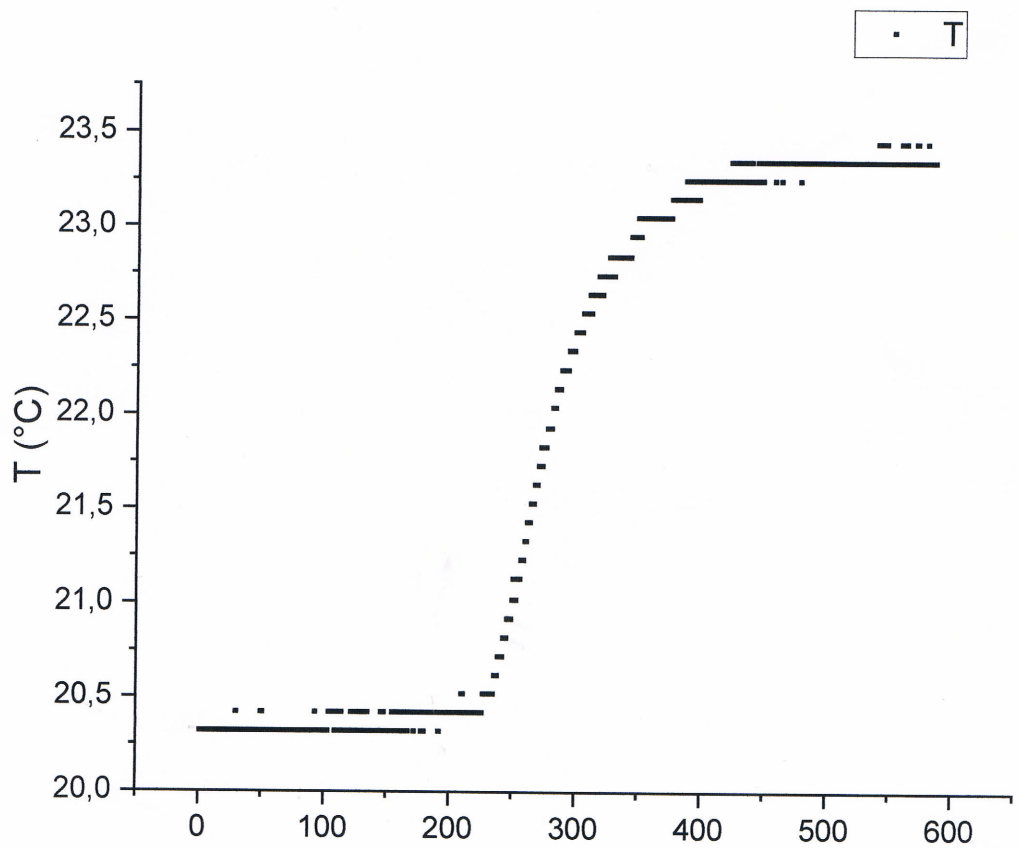
The aim is to measure the difference of the temperature of the water when we burn our substance.

First of all we have to pressure our pulver to a tablet with an iron wire in it. We need the iron wire for a successful ignition.

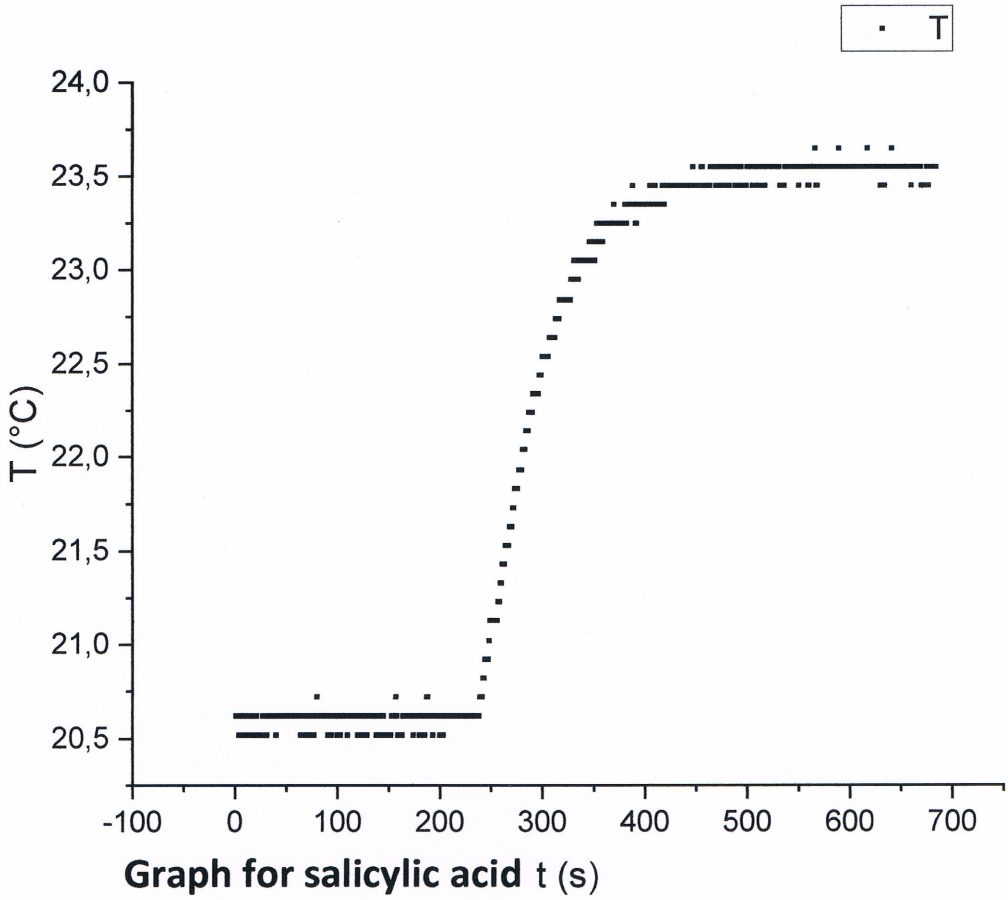
The tablet is then placed in the quarz crucible and then the whole construction is placed in the holder of the bomb. Then the bomb has to be closed and filled with oxygen. Now we can fill the calorimeter with water, start the shiver, put in the bomb and make an ignition while we're measuring the temperatur.



Graph for benzoic acid



Graph for anthracene


T
24,0
23,5
23,0
22,5
22,0
21,5
21,0
20,5
T (°C)
-100
0
100
200
300
400
500
600
700
Graph for salicylic acid t (s)

1. Calculation of $\Delta_R H_m^\circ$ with Hess's law

- for benzoic acid

$$C_6H_5COOH(s) + 7{,}5\ O_2(g) \longrightarrow 7\ CO_2(g) + 3\ H_2O(g)$$

$$\Delta_R H_m^\circ = 7 \cdot \Delta_f H_m^\circ(CO_2) + 3 \cdot \Delta_f H_m^\circ(H_2O(g)) - \Delta_f H_m^\circ(C_6H_5COOH)$$

$$= \underline{-3094{,}93\ kJ/mol}$$

- for anthracene

$$C_{14}H_{10}(s) + 16{,}5\ O_2(g) \longrightarrow 14\ CO_2(g) + 5\ H_2O(g)$$

$$\Delta_R H_m^\circ = 14 \cdot \Delta_f H_m^\circ(CO_2) + 5 \cdot \Delta_f H_m^\circ(H_2O(g)) - \Delta_f H_m^\circ(C_{14}H_{10})$$

$$= \underline{-6480{,}2\ kJ/mol}$$

- for salicylic acid

$$C_7H_6O_3(s) + 7\ O_2 \longrightarrow 7\ CO_2(g) + 3\ H_2O(g)$$

$$\Delta_R H_m^\circ = 7 \cdot \Delta_f H_m^\circ(CO_2) + 3 \cdot \Delta_f H_m^\circ(H_2O(g)) - \Delta_f H_m^\circ(C_7H_6O_3)$$

$$= \underline{-2984{,}23\ kJ/mol}$$

2. Calculation of the ~~spec~~ specific heat capacity

- Note:

The areas, in the graphs, before and after the reaction were seen as lines.

given values: $m(C_7H_6O_2) = 0{,}854\ g \pm 0{,}001\ g$

$M(C_7H_6O_2) = 122{,}12\ g/mol$

$\Delta U(T^\circ) = -3231{,}9\ kJ/mol$ for $T^\circ = 25\,^\circ C$

$\Delta U(wire) = -75{,}36 \pm 12{,}56\ J$

$T_1 = 20{,}11\,^\circ C$ $T_2 = 22{,}54\,^\circ C$ $\Delta T = 0{,}1\,^\circ C$

$$C(T^\circ) = -\frac{\Delta U(T^\circ) \cdot n + \Delta U(wire)}{\Delta T_{2-1}} \quad \text{with } n = \frac{m}{M}$$

$$\downarrow \text{Kirchhoff's law: } \Delta(T_1) = \Delta U(T^\circ) + \Delta C_v (T_1 - T^\circ)$$

$$C(T_1) = -\frac{(\Delta U(T^\circ) + \Delta C_v (T_1 - T^\circ)) \cdot n + \Delta U(wire)}{\Delta T_{2-1}}$$

$$\Delta C_v = \sum_{i=1} \nu_i \cdot C_{v,i} = 8 \cdot C_v(H_2O) + 7 \cdot C_v(CO_2) - C_v(C_7H_6O_2) - 7{,}5\ C_v(O_2)$$

$$= 121{,}05 \ \text{J/mol·K}$$

$$n = \frac{m}{M} = 0{,}00699 \ \text{mol} \pm 8{,}19 \cdot 10^{-6}$$

$$\Delta T_{2-1} = T_2 - T_1 = 2{,}43 \pm 0{,}1 \ \text{K}$$

$$\Rightarrow \quad C(T_1) = 9329{,}42 \ \text{J/K} \ \checkmark$$

$$\Delta C(T_1) = \left|\frac{\partial C(T_1)}{\partial \Delta T}\right| \cdot \Delta(\Delta T) + \left|\frac{\partial C(T_1)}{\partial m}\right| \Delta m + \left|\frac{\partial C(T_1)}{\partial \Delta U(wire)}\right| \Delta(\Delta U(wire))$$

with $$\left|\frac{\partial C(T_1)}{\partial \Delta T}\right| \cdot \Delta(\Delta T) = \Delta(\Delta T) \cdot \frac{(\Delta U(T^\circ) + \Delta C_v(T_1 - T^\circ))n + \Delta U(w)}{\Delta T_{2-1}^2}$$

$$\left|\frac{\partial C(T_1)}{\partial m}\right| \cdot \Delta m = \Delta m \cdot \frac{\Delta U(T^\circ) + \Delta C_v(T_1 - T^\circ)}{M \cdot \Delta T_{2-1}}$$

$$\left|\frac{\partial C(T_1)}{\partial \Delta U(w)}\right| \cdot \Delta(\Delta U(w)) = \Delta(\Delta U(w)) \cdot \frac{1}{\Delta T_{2-1}}$$

$$\Rightarrow \Delta C(T_1) = 399{,}991 \ \text{J/K}$$

$$\Rightarrow \quad C(T_1) = \underline{9329{,}42 \pm 399{,}991 \ \text{J/K}} \ \checkmark$$

3. Calculation of $\Delta_v H$ and $\Delta_v H_A^*$ for anthracene

given values: $m(C_{14}H_{10}) = 0{,}7349 \pm 0{,}001 \ g$

$M(C_{14}H_{10}) = 178{,}24 \ \text{g/mol}$

$T_1 = 20{,}32 \pm 0{,}1 \ ^\circ C \quad T_2 = 23{,}55 \pm 0{,}1 \ ^\circ C$

$$\Delta T_{2-1} = T_2 - T_1 = 3{,}03 \pm 0{,}1 \ \text{K}$$

$$\Delta_v U(C_{14}H_{10}) = -C \cdot \Delta T = \underline{-28{,}267 \pm 2{,}14 \ \text{kJ}} \ \checkmark$$

$$\Delta_v U_m(C_{14}H_{10}) = \frac{1}{n} \cdot \Delta_v U(C_{14}H_{10}) = -6\,855{,}745 \ \text{kJ/mol} \pm 528{,}357$$

$$\Delta_v H(C_{14}H_{10}) = \Delta_v U + \Delta\nu_g RT_1$$

with $\Delta\nu_g = 14 + 5 - 16{,}5 = 2{,}5 \qquad R = 8{,}314 \ \text{J/mol·K}$

$$\Rightarrow \Delta_v H(C_{14}H_{10}) = \underline{-22{,}17 \pm 2{,}14 \ \text{kJ}} \ \checkmark$$

$$\Delta_v H_m(C_{14}H_{10}) = \frac{1}{n} \cdot \Delta_v H(C_{14}H_{10}) = -5\,377 \pm 511{,}71 \ \text{kJ/mol}$$

$$\Delta_v H_A^* = \Delta_v H(C_{14}H_{10}) + n_A \cdot \Delta_{sub} H_A - n_{H_2O} \Delta_{vap} H_{H_2O}$$

with $n_A = \frac{m}{M} = 0{,}00412 \pm 5{,}61 \cdot 10^{-6}$ mol

$n_{H_2O} = 5 \cdot n_A = 0{,}0206 \pm 28{,}05 \cdot 10^{-6}$ mol

$\Delta_{sub} H_A = 98{,}2$ kJ/mol $\quad \Delta_v H_{H_2O} = 40{,}657$ kJ/mol [1]

$\Delta_v H_A^* =$ <u>$-22{,}599 \pm 2{,}139$ kJ</u> .

with $\Delta(\Delta_v H_A^*) = \Delta(\Delta_v H(C_{14}H_{10})) + \Delta n_A \cdot \Delta_{sub} H_A - \Delta n_{H_2O} \cdot \Delta_{vap} H_{H_2O}$

Source:

[1] https://de.wikipedia.org/wiki/Verdampfungswärme#Verdampfungswärme_und_Verdampfungsenthalpie, last visited: 2018/3/17

4. Calculation of $\Delta_v H$ and $\Delta_v H_S^*$ for salicylic acid

given values: $m(C_7H_6O_3) = 1{,}3131$ g $\pm 0{,}001$

$M(C_7H_6O_3) = 138{,}12$ g/mol

$T_1 = 20{,}62 \pm 0{,}1$ °C $\quad T_2 = 23{,}55 \pm 0{,}1$ °C

$\Delta T_{2-1} = T_2 - T_1 = 2{,}93 \pm 0{,}1$ K

$\Delta_v U(C_7H_6O_3) = -C \cdot \Delta T =$ <u>$-27{,}335 \pm 2{,}1$ kJ</u>

$\Delta_v U_m(C_7H_6O_3) = \frac{1}{n} \cdot \Delta_v U(C_7H_6O_3) = -2875{,}26 \pm 221{,}64$ kJ/mol

$\Delta_v H(C_{xx}H_6O_3) = \Delta_v U + \Delta \nu_g RT_1$

with $\Delta \nu_g = 7 + 3 - 7 = 3$ $\quad R = 8{,}314$ J/mol·K

$\Rightarrow \Delta_v H(C_7H_6O_3) =$ <u>$-20{,}012 \pm 2{,}1$ kJ</u> .

$\Delta_v H_m(C_7H_6O_3) = \frac{1}{n} \cdot \Delta_v H(C_7H_6O_3) = -2104{,}986 \pm 222{,}5$ kJ/mol

$\Delta_v H_S^* = \Delta_v H(C_7H_6O_3) + n_S \cdot \Delta_{sub} H_S - n_{H_2O} \Delta_{vap} H_{H_2O}$

with $n_S = \frac{m}{M} = 0{,}00951 \pm 7{,}24 \cdot 10^{-6}$ mol

$n_{H_2O} = 3 \cdot n_S = 0{,}0285 \pm 21{,}72 \cdot 10^{-6}$ mol

$\Delta_{sub} H_S = 79{,}2$ kJ/mol $\quad \Delta_v H_{H_2O} = 40{,}657$ kJ/mol [1]

$\Delta_v H_S^* =$ <u>$-20{,}418 \pm 2{,}1$ kJ</u>

with $\Delta(\Delta_v H_S^*) = \Delta(\Delta_v H(C_7H_6O_3)) + \Delta n_S \cdot \Delta_{sub} H_S - \Delta n_{H_2O} \cdot \Delta_{vap} H_{H_2O}$

5. Comparison with the theoretical values

anthracene	theoretical value	$\Delta_R H^\circ_m$ =	-6490,2 kJ/mol
	experimental value	$\Delta_v H_m$ =	-5377 ± 511,17 kJ/mol
	percentage difference	17,2 %	
salicylic acid	theoretical value	$\Delta_R H^\circ_m$ =	-2984,23 kJ/mol
	experimental value	$\Delta_v H_m$ =	-2104,986 ± 222,5 kJ/mol
	percentage difference	29,5 %	

6. error discussion

- the high differences in the values is mostly caused by the different pressures and temperatures. The theoretical values are for p = 1 bar and T = 25°C, while the experimental values are for p = 20 bar
- small heat exchange with the surrounding, because the calorimeter isn't complety adiabatic
- errors in the measuring of the temperature and weight (included in the error analysis)
- small error in the specific capacity of the calorimeter, because of small weight differences of the water bath (not included in the error analysis)
- the small errors increase when the values are calculated (→ progation of uncertainity)

Additional questions

1) a) $2\,C_8H_{18} + 25\,O_2 \longrightarrow 18\,H_2O_{(g)} + 16\,CO_2$

b) $CH_4 + 2\,O_2 \longrightarrow 2\,H_2O_{(g)} + CO_2$

$\Delta H_{gs}^\circ = \sum \nu_i \Delta H_f^\circ$

zu a): $\Delta H_f^\circ(C_8H_{18}) = -249,9 \frac{kJ}{mol}$

$\Delta H_f^\circ(H_2O) = -241,82 \frac{kJ}{mol}$

$\Delta H_f^\circ(CO_2) = -393,51 \frac{kJ}{mol}$

$\Delta H_f^\circ(O_2) = 0 \frac{kJ}{mol}$

$\Delta H_{gs}^\circ = (18 \cdot \Delta H_f(H_2O) + 16\,\Delta H_f(CO_2)) - (2 \cdot \Delta H_f(C_8H_{18}))$

$= -10.149,12 \frac{kJ}{mol}$

zu b): $\Delta H_{gs}^\circ = (2 \cdot \Delta H_f^\circ(H_2O) + 0 H_f(CO_2)) - (\Delta H_f(CH_4)) = -802,15 \frac{kJ}{mol}$

to compare we need the same energie values:

$$\frac{\Delta H_{gs}^\circ(C_8H_{18})}{\Delta H_{gs}^\circ(CH_4)} = 12,65$$

CO_2(a)) = 16

CO_2(b)) = 12,65 $\quad \Delta CO_2 = 3,35$

We would save 3.35 äq. CO_2 if we would drive with CH_4 instead of C_8H_{18}.

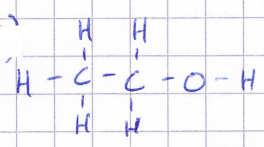
2) The enthalpy of formation can be calculated as follows:

$\Delta_f H^\circ(C_2H_5OH(g)) = -\sum \Delta_B H + \sum \Delta_A H$

$\Delta_f H$ - Enthalpy of formation
$\Delta_B H$ - Enthalpy of bond
$\Delta_A H$ - Enthalpy of atomization

$2\,C(g) + 6\,H(g) + O(g) \longrightarrow C_2H_5OH(g)$

Calculation of the enthalpy of bond ($\Delta_B H$)



$\Delta_B H = 5 \cdot \Delta_B H(\text{C-H-bond}) + 1 \cdot \Delta_B H(\text{C-C-bond}) + 1 \cdot \Delta_B H(\text{C-O-bond}) + 1 \cdot \Delta_B H(\text{O-H-bond})$

with the following values [1]

C-H	412	kJ/mol
C-C	348	kJ/mol
C-O	360	kJ/mol
O-H	463	kJ/mol

$\Rightarrow \Delta_B H = 3231 \text{ kJ/mol}$

Calculation of the enthalpy of atomization ($\Delta_A H$)

reactions of atomization:

$C(s)$	$\rightarrow$	$C(g)$	$\Delta_A H(C) = +716{,}69 \text{ kJ/mol}$ [2]
$\frac{1}{2} O_2$	$\rightarrow$	$O(g)$	$\Delta_A H(O) = +249{,}17 \text{ kJ/mol}$ [3]
$\frac{1}{2} H_2$	$\rightarrow$	$H(g)$	$\Delta_A H(H) = +217{,}86 \text{ kJ/mol}$ [4]

$\Delta_A H = 2 \cdot \Delta_A H(C) + \Delta_A H(O) + 6 \cdot \Delta_A H(H)$

$\Rightarrow \Delta_A H = +2990{,}31 \text{ kJ/mol}$

$\Rightarrow \Delta_f H^\circ(C_2H_5OH(g)) = -3231 \text{ kJ/mol} + 2990{,}31 \text{ kJ/mol} = -240{,}69 \text{ kJ/mol}$

theoretical value [5] $\Delta_f H^\circ(C_2H_5OH(g)) = -235{,}1 \text{ kJ/mol}$

The difference of 2,4% is a result of the incomplete calculation. In molecules with more than two ~~molecules~~ atoms, additional bonds influence the bonding energy. This results in different $\Delta_B H$ which weren't used for the calculation.

Source:

[1] Peter Atkins, Julio de Paula: Physikalische Chemie, WILEY-VCH, 4th edition, 2005, p. 1123 table 11-3

[2] René Rausch, www.periodensystem-online.de/index.php?el=6&id=bonds, last visited: 2018/3/10

[3] René Rausch, www.periodensystem-online.de/index.php?el=8&id=bonds, last visited: 2018/3/10

[4] René Rausch, www.periodensystem-online.de/index.php?el=1&id=bonds, last visited: 2018/10/13

[5] Peter Atkins [...], p. 1105

Benzoesäure	(1)	0,8540 g
Anthracen	(2)	0,7349 g
Salicylsäure	(3)	1,3131 g

m_1 (Wasserbad) = 2444,66 g

m_2 (Wasserbad) = 2445,06 g

m_3 (Wasserbad) = 2444,67 g

+ WS

07.03.08