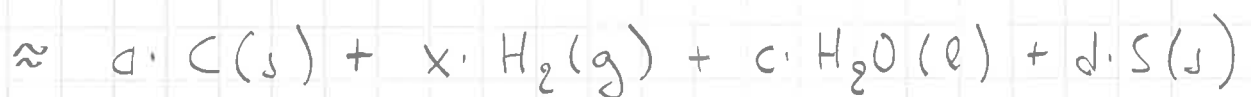


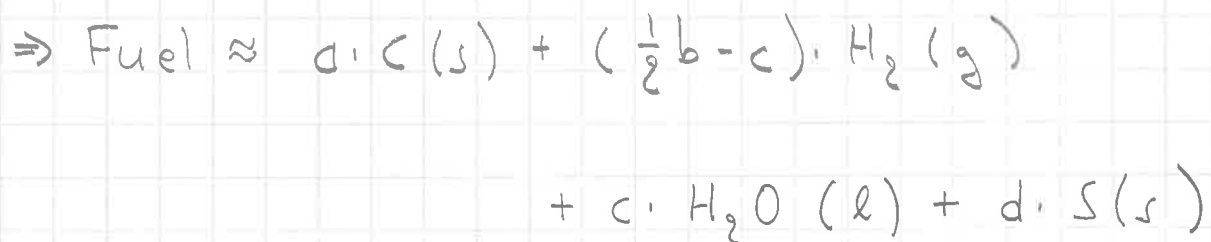
28.9.2014  
TP

## Fuel heating value (HHV) and Dulong formula

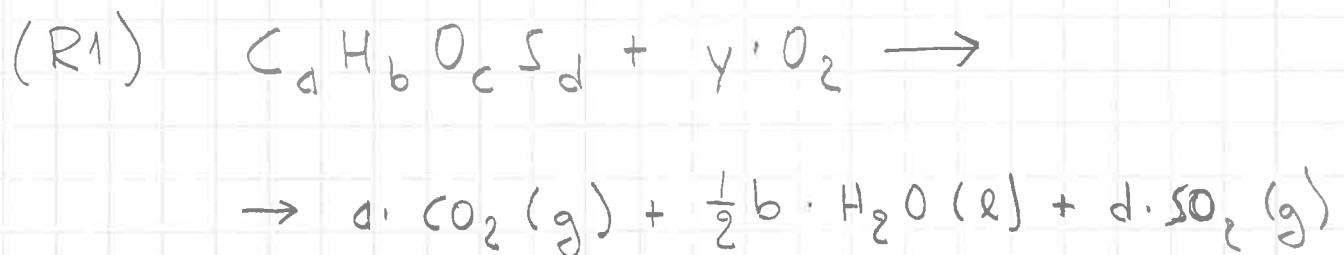


element balance for H:

$$b = 2x + 2c \Rightarrow x = \frac{1}{2}b - c$$



Combustion reaction of the fuel:

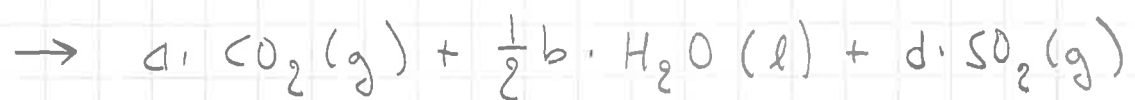
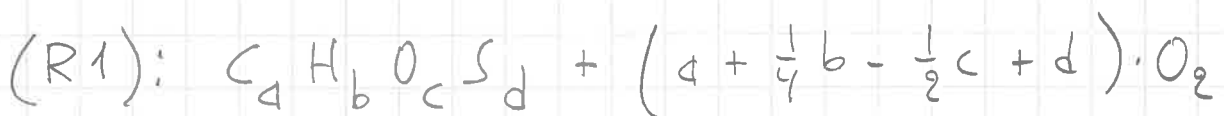


Solve  $y$  from element balance  
for oxygen:

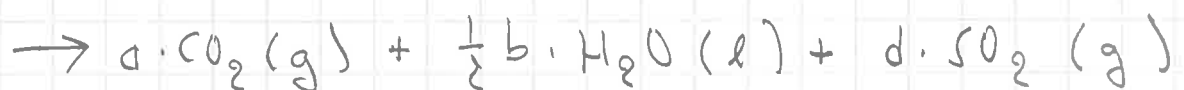
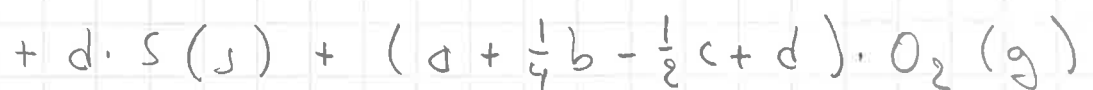
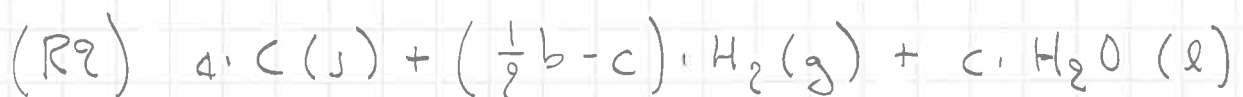
$$\underbrace{c + 2y}_{\text{LHS}} = \underbrace{2a + \frac{1}{2}b + 2d}_{\text{RHS}}$$

$$\Rightarrow y = a + \frac{1}{4}b - \frac{1}{2}c + d$$

$\Rightarrow$  (R1) becomes



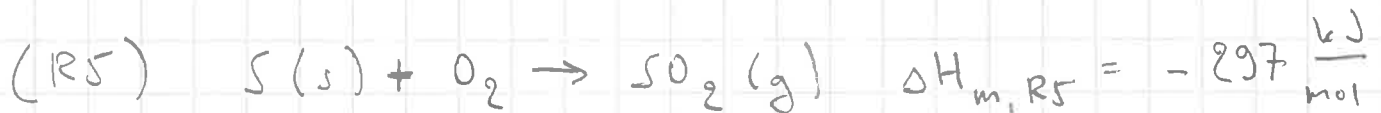
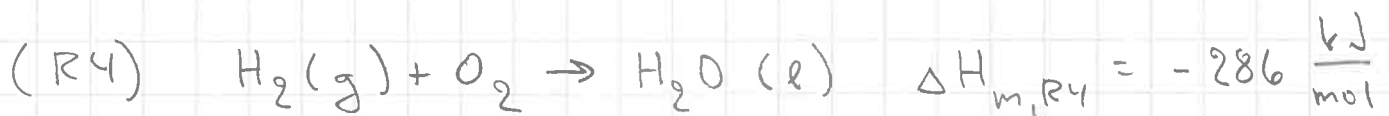
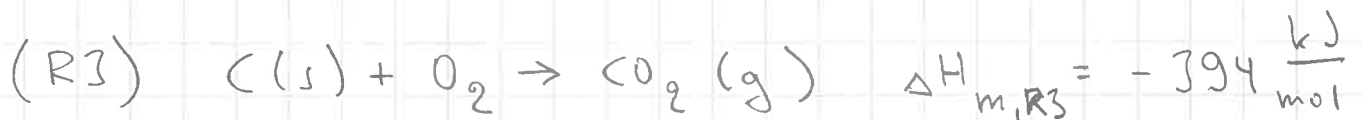
which can be approximated with



but

$$(R2) = a \cdot (R3) + \left(\frac{1}{2}b - c\right) \cdot (R4) + d \cdot (R5)$$

where



(Reaction enthalpies from H.C. pp. 1109, 1116, 1120)

⇒ Reaction enthalpy for (R2) is

$$\Delta H_{m,R2} = a \cdot \Delta H_{m,R3} + \left(\frac{1}{2}b - c\right) \cdot \Delta H_{m,R4} + d \cdot \Delta H_{m,R5}$$

and the molar higher heating value (HHV) of the fuel is

$$Q_{m,H} = -\Delta H_{m,R2} = -a \cdot \Delta H_{m,R3} - \dots$$

Now what remains to be done is:

1<sup>o</sup> Convert from molar HHV (kJ/mol) into heating value (kJ/kg)

2<sup>o</sup> Convert from "stoichiometric coefficients"  $a, b, c, d$  into mass fractions  $w_C, w_H, w_O, w_S$ .

To begin with, compute the "molar mass" of the fuel:

$$M_F = a \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S$$

Now obtain HHV by

$$q_{TH} = \frac{Q_{m,H}}{M_{Fuel}} = \frac{-a \cdot \Delta H_{m,R3} - 111}{a \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S}$$

However, note that

$$w_C = \frac{m_C}{m_{\text{Fuel}}} = \frac{n_C \cdot M_C}{n_{\text{Fuel}} \cdot M_{\text{Fuel}}}$$
$$= \frac{d \cdot M_C}{d \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S}$$

(  $\frac{n_C}{n_{\text{Fuel}}} = d$ , since there are  $d$  atoms of C in one mole of the fuel )

$$\Rightarrow \frac{d}{d \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S} = \frac{w_C}{M_C}$$

Similarly:

$$\frac{\frac{1}{2}b - c}{d \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S} = \frac{1}{2} \frac{w_H}{M_H} - \frac{w_O}{M_O}$$

and

$$\frac{d}{d \cdot M_C + \dots} = \frac{w_S}{M_S}$$

Inserting back into the equation for  $q_H$  in p. (4), we obtain

$$q_H = - \frac{W_C}{M_C} \cdot \Delta H_{m,R3} - \left( \frac{1}{2} \frac{W_H}{M_H} - \frac{W_0}{M_0} \right) \cdot \Delta H_{m,R4} - \frac{W_S}{M_S} \cdot \Delta H_{m,R5}$$

$$\frac{\Delta H_{m,R3}}{M_C} = \frac{-394 \frac{\text{kJ}}{\text{mol}}}{12 \frac{\text{g}}{\text{mol}}} = -32,8 \frac{\text{kJ}}{\text{g}}$$

$$\frac{\Delta H_{m,R4}}{2M_H} = \frac{-286 \frac{\text{kJ}}{\text{mol}}}{2 \cdot 1 \frac{\text{g}}{\text{mol}}} = -143 \frac{\text{kJ}}{\text{g}}$$

$$\frac{\Delta H_{m,R4}}{M_0} = \frac{\Delta H_{m,R4}}{8 \cdot 2M_H} = \frac{1}{8} \cdot \left( -143 \frac{\text{kJ}}{\text{g}} \right)$$

$$\frac{\Delta H_{m,R5}}{M_S} = \frac{-297 \frac{\text{kJ}}{\text{mol}}}{32 \frac{\text{g}}{\text{mol}}} = -9,3 \frac{\text{kJ}}{\text{g}}$$

$$\Rightarrow q_H = -w_C \cdot \left( -32,8 \frac{\text{kJ}}{\text{g}} \right)$$

$$- \left( w_H - \frac{1}{8} w_O \right) \cdot \left( -143 \frac{\text{kJ}}{\text{g}} \right)$$

$$- w_S \cdot \left( -9,3 \frac{\text{kJ}}{\text{g}} \right)$$

$$\Rightarrow q_H = 32,8 \frac{\text{kJ}}{\text{g}} \cdot w_C + 143 \frac{\text{kJ}}{\text{g}} \cdot \left( w_H - \frac{1}{8} w_O \right)$$

$$+ 9,3 \frac{\text{kJ}}{\text{g}} \cdot w_S$$

The original Dulong formula  
as quoted by Channiwala and  
Parikh (2002):

$$\text{HHV} = 0,3383 C^* + 1,443 \left( H^* - \frac{O^*}{8} \right) + 0,0942 S^*$$

where  $C^*$ ,  $H^*$ ,  $O^*$ ,  $S^*$  are  
mass fractions in % on a dry basis.

Example: ethanol  $C_2H_5OH$

$$(a = 2, b = 6, c = 1)$$

$$M_{\text{Fuel}} = aM_C + bM_H + cM_O$$

$$= 2 \cdot 12 \frac{\text{g}}{\text{mol}} + 6 \cdot 1 \frac{\text{g}}{\text{mol}} + 1 \cdot 16 \frac{\text{g}}{\text{mol}}$$

$$= 46 \frac{\text{g}}{\text{mol}}$$

mass fractions of C, H, O:

$$w_C = \frac{a \cdot M_C}{M_{\text{Fuel}}} = \frac{2 \cdot 12 \frac{\text{g}}{\text{mol}}}{46 \frac{\text{g}}{\text{mol}}} = 0.522$$

$$w_H = \frac{b \cdot M_H}{M_{\text{Fuel}}} = \frac{6 \cdot 1 \frac{\text{g}}{\text{mol}}}{46 \frac{\text{g}}{\text{mol}}} = 0.130$$

$$w_O = \frac{c \cdot M_O}{M_{\text{Fuel}}} = \frac{1 \cdot 16 \frac{\text{g}}{\text{mol}}}{46 \frac{\text{g}}{\text{mol}}} = 0.348$$

$$(w_C + w_H + w_O = 0.522 + 0.130 + 0.348 = 1.000 \text{ OK})$$



$$\begin{aligned}
 q_{FH} &= 32.8 \frac{\text{kJ}}{\text{g}} \cdot w_c + 143 \frac{\text{kJ}}{\text{g}} \cdot (w_H - \frac{1}{8} w_o) \\
 &= 32.8 \frac{\text{kJ}}{\text{g}} \cdot 0.522 + 143 \frac{\text{kJ}}{\text{g}} \cdot (0.130 + \frac{0.348}{8}) \\
 &= 29.5 \frac{\text{kJ}}{\text{g}} = 29.5 \frac{\text{MJ}}{\text{kg}}
 \end{aligned}$$

BR App. A Table A.1 p. 567:

For ethanol, HHV =  $29.7 \frac{\text{MJ}}{\text{kg}}$

⇒ Dulong-type calculation resulted  
in an error of  $\approx -0.7\%$

o ————— o