Air Pollution
ENV-409
Emissions and Control

Combustion releases energy stored in the form of molecular bonds. Therefore, it is sensible to calculate the net energy released (as heat) from a combustion reaction based on the dissociation/association of the bonds broken/formed during a reaction. The following table† lists bond energies required to dissociate gaseous substance to their constituent elements at 25°C.

Table 4-3
Bond Energies (kcal mole^{-1} at 25°C)[a]

Diatomic Molecules

H—H	104.2	F—F	37.5	H—F	135.9
O=O	118.9	Cl—Cl	58.1	H—Cl	103.1
N≡N	226.8	Br—Br	46.4	H—Br	87.4
C≡O[b]	257.3	I—I	36.5	H—I	71.4

Polyatomic Molecules

C—H	98.7	C—C	82.6	C—F	116
N—H	93.4	C=C	145.8	C—Cl	81
O—H	110.6	C≡C	199.6	C—Br	68
S—H	83	C—N	72.8	C—I	51
P—H	76	C=N	147	C—S	65
N—N	39	C≡N	212.6	C=S[c]	128
N=N	100	C—O	85.5	N—F	65
O—O	35	C=O[d]	192.0	N—Cl	46
S—S	54	C=O[e]	166	O—F	45
N—O	53	C=O[f]	176	O—Cl	52
N=O	145	C=O[g]	179	O—Br	48

[a]The bond energies for diatomic molecules in this table are from the extensive and up-to-date compilation of J. A. Kerr, M. J. Parsonage, and A. F. Trotman-Dickenson in the *Handbook of Chemistry and Physics*, 55th ed., CRC Press, 1975, pp. F-204 to F-208; those for polyatomic molecules are from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

[b]Carbon monoxide. [c]For carbon disulfide. [d]For carbon dioxide. [e]For formaldehyde. [f]Other aldehydes. [g]Ketones.

Bond energies are typically written as positive values, but they are energies released upon formation of the bond so they are equivalent to $-\Delta H^0$. Recall that the enthalpy of reaction is

$$\Delta_c H^0 = \sum_{k \in \text{Products}} \Delta H_k^0 - \sum_{k \in \text{Reactants}} \Delta H_k^0 \ .$$

Example

We will calculate the heat of combustion for methane, a primary constituent of natural gas. Some heating values consider the latent heat recovered from condensation of the water vapor product, but in this case we will assume the water vapor remains in the gas phase.

$$\mathrm{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O}$$

$$\begin{aligned}\Delta_c H^0 &= \left(2\Delta H^0_{\text{C=O}} + 2 \cdot 2\Delta H^0_{\text{O-H}}\right) - \left(4\Delta H^0_{\text{C-H}} + 2\Delta H^0_{\text{O=O}}\right) \\ &= [2 \cdot (-192)\,\text{kcal/mol} + 4 \cdot (-110.6)\,\text{kcal/mol}] - [4 \cdot (-98.7)\,\text{kcal/mol} + 2 \cdot (-118.9)\,\text{kcal/mol}) - \\ &= -193.8\,\text{kcal/mol}\end{aligned}$$

Next we calculate the mass of CO_2 formed ($M_{CO_2} = 44.01\,\text{g/mol}$) per unit of heat generated (the magnitude of negative $\Delta_c H^0$) as kJ (1 kcal = 4.184 kJ):

$$\frac{1\,\text{mol CH}_4}{193.8\,\text{kcal}} \cdot \frac{1\,\text{mole CO}_2}{1\,\text{mole CH}_4} \cdot \frac{44.01\,\text{g CO}_2}{\text{mol CO}_2} \cdot \frac{1\,\text{kcal}}{4.184\text{kJ}} = 0.0543\,\text{g/kJ}$$

Assignment

Calculate the mass of CO_2 per unit of heat generated in units of g/kJ for C_8H_{18} and $C_{14}H_{30}$ (both are saturated alkane compounds) as surrogates for gasoline and diesel fuel, respectively. Among CH_4, C_8H_{18}, and $C_{14}H_{30}$, which compound produces the least CO_2 per unit of energy produced from combustion* (i.e., which is "cleanest" with resepect to CO_2)?

(*technically, heat produced from hypothetical case of complete combustion)

Hint for shortcut

Recall that

$$\mathrm{C}_x\mathrm{H}_y + \left(x + \frac{y}{4}\right)\mathrm{O}_2 \rightarrow x\mathrm{CO}_2 + \frac{y}{2}\mathrm{H}_2\mathrm{O}$$

Saturated alkanes with carbon number of x can be represented as $CH_3(CH_2)_{(x-2)}CH_3$ or $H(CH_2)_xH$. So y can be written as a function of x. Also, you will need to consider the breaking of C−C bonds. The number of these bonds can also be written as a function of x.

†Source: Roberts, John D. and Caserio, Marjorie C. (1977) *Basic Principles of Organic Chemistry*, 2nd edition. W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8.