1. (a) The combustion of methyl stearate follows the equation:

\[
\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3 + \frac{55}{2}\text{O}_2 \rightarrow 19\text{CO}_2 + 19\text{H}_2\text{O}
\]

As \(\Delta_{\text{rxn}}H^\circ = \Sigma m\Delta_fH^\circ(\text{products}) - \Sigma n\Delta_fH^\circ(\text{reactants})\) and \(\Delta_fH^\circ(\text{O}_2) = 0\), the heat of combustion is

\[
\Delta_{\text{rxn}}H^\circ = [19\Delta_fH^\circ(\text{CO}_2) + 19\Delta_fH^\circ(\text{H}_2\text{O})] - [\Delta_fH^\circ(\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3)]
\]

Using \(\Delta_fH^\circ(\text{CO}_2) = -393 \text{ kJ mol}^{-1}\), \(\Delta_fH^\circ(\text{H}_2\text{O}) = -242 \text{ kJ mol}^{-1}\) and \(\Delta_fH^\circ(\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3) = -945.6 \text{ kJ mol}^{-1}\):

\[
\Delta_{\text{rxn}}H^\circ = ([19 \times -393 + 19 \times -242] - [-945.6]) \text{ kJ mol}^{-1} = -11100 \text{ kJ mol}^{-1}
\]

(b) The molecular structures and the number of each type of bond present are shown below.

![Molecular structures](image)

- \(38 \times \text{C-H}\), \(17 \times \text{C-C}\), \(1 \times \text{C=O}\) and \(2 \times \text{C-O}\)
- \(2 \times \text{C=O}\), \(2 \times \text{O-H}\), \(1 \times \text{O=O}\)

The enthalpy change for the reaction is

\[
\Delta_{\text{rxn}}H^\circ = [\Delta_{\text{atom}}H^\circ(\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3)] + \frac{55}{2}\Delta_{\text{atom}}H^\circ(\text{O}_2) - [19\Delta_{\text{atom}}H^\circ(\text{CO}_2) + 19\Delta_{\text{atom}}H^\circ(\text{H}_2\text{O})]
\]

Using the bond enthalpies, the enthalpy change is:

\[
\Delta_{\text{rxn}}H^\circ = [(38 \times 413 + 17 \times 348 + 745 + 2 \times 358) + (\frac{55}{2} \times 498)] - [19 \times (2 \times 745) + 19 \times (2 \times 463))]) \text{ kJ mol}^{-1} = -9140 \text{ kJ mol}^{-1}
\]

(c) The molecular weight of \(\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3\) is:

\[
(19 \times 12.01 (\text{C}) + 38 \times 1.008 (\text{H}) + 2 \times 16.00 (\text{O})) \text{ g mol}^{-1} = 298.5 \text{ g mol}^{-1}
\]

Using the \(\Delta_{\text{rxn}}H^\circ = -11100 \text{ kJ mol}^{-1}\) from (a), the nett calorific value is:
nett calorific value = \frac{\text{molar enthalpy change}}{\text{molar mass}}

= \frac{11100 \text{ kJ mol}^{-1}}{298.5 \text{ g mol}^{-1}} = 37.3 \text{ kJ g}^{-1}

This value is \textit{slightly} less than for conventional diesel.

2. The reaction is:

\[ \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{NO}(g) \]

(a) The reaction as written is the formation of NO from its elements in their standard states.

\[ \Delta_s^\circ (\text{NO}(g)) = S^\circ (\text{NO}(g)) - \left( \frac{1}{2} S^\circ (\text{N}_2(g)) + \frac{1}{2} S^\circ (\text{O}_2(g)) \right) \]

\[ = \left( 211 - \left( \frac{1}{2} \times 192 + \frac{1}{2} \times 205 \right) \right) \text{ J K}^{-1} \text{ mol}^{-1} = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}. \]

(The reaction involves no change in the number of gaseous molecules so the entropy change is quite small and probably arises from the freedom associated with the unpaired electron in NO, which can be spin-up or down).

(b) The reaction enthalpy corresponds to \( \Delta_f H^\circ (\text{NO}(g)) \) endothermic so this heat is \textit{lost} by the surroundings is

\[ q_{\text{surr}} = -\Delta_f H^\circ = -90 \text{ kJ mol}^{-1} \]

Hence, the entropy change of the surroundings is:

\[ \Delta_{\text{surr}} S = \frac{q_{\text{surr}}}{T} = \frac{-90 \times 10^3 \text{ J K}^{-1} \text{ mol}^{-1}}{T} \]

The entropy change of the universe, assuming that the enthalpy and entropy of formation do not change with temperature is therefore:

\[ \Delta_{\text{universe}} S = \Delta_{\text{system}} S + \Delta_{\text{surr}} S = (+12.5 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{-90 \times 10^3 \text{ J K}^{-1} \text{ mol}^{-1}}{T} \]

The reaction is spontaneous if \( \Delta_{\text{universe}} S > 0 \):

\[ T > \frac{90 \times 10^3}{12.5} \text{ K} \quad \text{or} \quad T > 7200 \text{ K.} \]

3. (a) \[ 2\text{C}_3\text{H}_6\text{N}_6\text{O}_6(s) + 3\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(g) + 6\text{N}_2(g) \]

(b) In the explosive decomposition, it is unlikely that sufficient \( \text{O}_2(g) \) will be available in the timescale of the reaction so that all of the oxygen available is that which is present in RDX. With less oxygen available, it is likely that \( \text{CO} \) rather than \( \text{CO}_2 \) will be produced:

\[ \text{C}_3\text{H}_6\text{N}_6\text{O}_6(s) \rightarrow 3\text{CO}(g) + 3\text{H}_2\text{O}(g) + 3\text{N}_2(g) \]
(c) A solid reacts to form lots of gaseous molecules resulting in a large volume change and hence $P\Delta V$ work. The reaction is highly exothermic as the products are very stable so considerable heat is generated. This heat also ensures that the volume of the gas is large (Charles’ Law).

(d) For the complete combustion reaction as written:

$$\Delta_{rxn}H^\circ = \Sigma m \Delta_f H^\circ_{\text{products}} - \Sigma n \Delta_f H^\circ_{\text{reactants}}$$

$$= (6 \times \Delta_f H^\circ(CO_2(g)) + 6 \times \Delta_f H^\circ(H_2O(g)) - [2 \times \Delta_f H^\circ(\text{RDX})])$$

$$= ((6 \times -394 + 6 \times -242) - [2 \times -65]) \text{kJ mol}^{-1} = -3946 \text{kJ mol}^{-1}$$

As this is for the combustion of two moles of RDX,

$$\Delta_{comb}H^\circ = -1970 \text{kJ mol}^{-1}$$

Molar mass = (3\times12.01 (C) + 6\times1.008 (H) + 6\times14.01 (N) + 6\times16.00 (O)) g mol\(^{-1}\) = 222.138 g mol\(^{-1}\).

So,

$$\Delta_{comb}H^\circ = -1970 \text{kJ mol}^{-1} \text{ or } \frac{-1970 \text{kJ mol}^{-1}}{222.138 \text{g mol}^{-1}} = -8.88 \text{kJ g}^{-1}$$

Hence 100 g will generate 888 kJ.

The enthalpies for the explosive decomposition and complete combustion reactions differ by the enthalpy of the combustion of three moles of CO:

$$3\text{CO}(g) + \frac{3}{2}\text{O}_2(g) \rightarrow 3\text{CO}_2(g)$$

$$\Delta H = 3\Delta_f H^\circ(\text{CO}_2(g)) - 3\Delta_f H^\circ(\text{CO}(g))$$

$$= ([3 \times -394] - [3 \times -111]) \text{kJ mol}^{-1} = -849 \text{kJ mol}^{-1}$$

Hence,

$$\Delta_{\text{explosive}}H = (-1970 - (-849)) \text{kJ mol}^{-1}$$

$$= -1124 \text{kJ mol}^{-1} \text{ or } \frac{-1124 \text{kJ mol}^{-1}}{222.138 \text{g mol}^{-1}} = -5.06 \text{kJ g}^{-1}$$

Hence 100 g will generate 506 kJ – much less than for the full combustion.

4. $\text{CO}_2(g) \rightarrow \text{CO}(g) + \text{O}(g)$ has $\Delta_r H^\circ$:

$$\Delta_r H^\circ = [\Delta_f H^\circ(\text{CO}(g)) + \Delta_f H^\circ(\text{O}(g))] - \Delta_f H^\circ(\text{CO}_2(g))$$

$$= [\times -111 + 249] - [-394]] \text{kJ mol}^{-1} = 532 \text{kJ mol}^{-1}$$

If this energy is provided by radiation, its wavelength is be given by:

$$\frac{hc}{\lambda} = 532 \times 10^2 \text{kJ mol}^{-1} \text{ or } \lambda = 2.25 \times 10^{-7} \text{m} = 225 \text{nm}$$
As the shortest wavelength in the solar spectrum is ~200 nm, there is insufficient energy to photocatalyse CO$_2$.

5. The decomposition reaction is:

\[ \text{NH}_4\text{NO}_2(s) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g) \]

(a) \[ \Delta_{\text{decomp}} H = 2\Delta_l H(\text{H}_2\text{O}(g)) - \Delta_l H(\text{NH}_4\text{NO}_2(s)) = (2 \times (-242) - (-257)) \text{ kJ mol}^{-1} = -227 \text{ kJ mol}^{-1} \]

The molar mass of \( \text{NH}_4\text{NO}_2 \) is \( (2 \times 14.01 \text{ (N)} + 4 \times 1.008 \text{ (H)} + 2 \times 16.00) \text{ kJ mol}^{-1} = 64.052 \text{ g mol}^{-1} \).

Hence, the heat released by 1.00 g is:

\[ q = -227 \times \frac{1.00}{64.052} \text{ kJ} = -3.54 \text{ kJ} \]

(b) 3 mol of gas are produced from each mole of ammonium nitrate. Hence, 1.00 g generates:

\[ n = 3 \times \frac{1.00}{64.052} \text{ mol} = 0.0468 \text{ mol} \]

Assuming perfect gas behaviour, the volume change is therefore:

\[ \Delta V = \frac{\Delta nRT}{P} \]

\[ = \frac{(0.0468 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(250+273) \text{ K}}{(1.00 \text{ atm})} \]

\[ = 2.01 \text{ atm} \]

(c) The heat released by the reaction heats up the products (one mole of \( \text{N}_2(g) \) and two moles of \( \text{H}_2\text{O}(g) \) for every mole of reactant). As \( q = nC\Delta T \):

\[ q = \{(21 \times \frac{1.00}{64.052} \times \Delta T) + (26 \times 2 \times \frac{1.00}{64.052} \times \Delta T)\} \text{ J} = 3.54 \times 10^3 \text{ J} \]

so \( \Delta T = 3110 \text{ K} \)

This is a very large temperature change so neglect of the heat capacity of the container is likely to be a poor approximation.

6. \[ Q = \frac{[\text{SO}_3(g)]^2}{[\text{SO}_3(g)]^2[\text{O}_2(g)]} = \frac{(3.00)^2}{(2.00)^2(1.50)} = 1.5. \]

As \( Q < 4.35 \), the reaction proceeds to the right, producing more \( \text{SO}_3(g) \).