

1. Using  $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_f H^\circ(\text{products}) - \sum n\Delta_f H^\circ(\text{reactants})$ ,

$$\begin{aligned}\Delta_{\text{rxn}}H^\circ &= [\Delta_f H^\circ(\text{C}_2\text{H}_2(\text{g})) + \Delta_f H^\circ(\text{Ca}(\text{OH})_2(\text{s}))] - [\Delta_f H^\circ(\text{CaC}_2(\text{s})) + 2\Delta_f H^\circ(\text{H}_2\text{O}(\text{l}))] \\ &= [(+227) + (-986)] - [(-60) + (2 \times -285)] \\ &= -129 \text{ kJ mol}^{-1}\end{aligned}$$

The molar mass of  $\text{CaC}_2(\text{s})$  is  $40.08 (\text{Ca}) + 2 \times 12.01 (\text{C}) = 64.1 \text{ g mol}^{-1}$

Hence, 10.0 g corresponds to  $\frac{\text{mass}}{\text{molar mass}} = \frac{10.0 \text{ g}}{64.1 \text{ g mol}^{-1}} = 0.156 \text{ mol}$

As 1 mol releases  $129 \text{ kJ mol}^{-1}$ , this amount will give rise to an enthalpy change of:

$$\Delta_{\text{rxn}}H^\circ = (-129 \text{ kJ mol}^{-1}) \times (0.156 \text{ mol}) = -20.1 \text{ kJ}$$

2. (a)  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH} + 23\text{O}_2 \rightarrow 16\text{CO}_2 + 16\text{H}_2\text{O}$

- (b) Using  $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_f H^\circ(\text{products}) - \sum n\Delta_f H^\circ(\text{reactants})$ :

$$\Delta_{\text{comb}}H^\circ = [16 \times \Delta_f H^\circ(\text{CO}_2) + 16 \times \Delta_f H^\circ(\text{H}_2\text{O})] - [\Delta_f H^\circ(\text{palmitic acid})]$$

as  $\Delta_f H^\circ(\text{O}_2) = 0$  for the formation of an element in its standard state.

As the combustion is an exothermic process,  $\Delta_{\text{comb}}H^\circ = -9980 \text{ kJ mol}^{-1}$ .

Therefore:

$$[16 \times -393.5 + 16 \times -285] - [\Delta_f H^\circ(\text{palmitic acid})] = -9980 \text{ kJ mol}^{-1}$$

or

$$\Delta_f H^\circ(\text{palmitic acid}) = -889 \text{ kJ mol}^{-1}$$

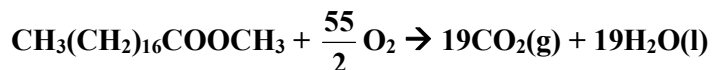
- (c)  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH} \equiv \text{C}_{16}\text{H}_{32}\text{O}_2$ . The molar mass of palmitic acid is:

$$\text{molar mass} = 16 \times 12.01 (\text{C}) + 32 \times 1.008 (\text{H}) + 2 \times 16.00 (\text{O}) = 256.416 \text{ g mol}^{-1}$$

So,

$$\Delta_{\text{comb}}H = -9980 \text{ kJ mol}^{-1} \text{ or } \frac{-9980 \text{ kJ mol}^{-1}}{256.416 \text{ g mol}^{-1}} = -38.9 \text{ kJ g}^{-1}$$

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



As  $\Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants})$  and

$\Delta_f H^\circ (\text{O}_2(\text{g}))$  is zero, the heat of combustion is

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

As  $\Delta_f H^\circ (\text{CO}_2(\text{g})) = -393.5 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ (\text{H}_2\text{O}(\text{l})) = -285 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ (\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3) = -945.6 \text{ kJ mol}^{-1}$ :

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= ([19 \times -393.5 + 19 \times -285] - [-945.6]) \text{ kJ mol}^{-1} \\ &= -11900 \text{ kJ mol}^{-1} \end{aligned}$$

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

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

Using  $\Delta_{\text{rxn}} H^\circ = -11946 \text{ kJ mol}^{-1}$  from (a), the nett calorific value is:

$$\text{nett calorific value} = \frac{11946 \text{ kJ mol}^{-1}}{298.5 \text{ g mol}^{-1}} = 40.0 \text{ kJ g}^{-1}$$

This value is *slightly* less than for conventional diesel.

4. For a reaction to be spontaneous requires  $\Delta G^0 < 0$ , i.e.  $\Delta H^0 - T\Delta S^0 < 0$ .

For the reaction given,  $\Delta H^0$  is positive, which would tend to make  $\Delta G^0$  positive. To counteract this, entropy must increase,  $\Delta S^0$  must be positive (which it is) and  $T\Delta S^0$  must exceed  $\Delta H^0$ .

Thus,  $T\Delta S^0 > \Delta H^0$  and  $T > \Delta H^0 / \Delta S^0 = 5.5 \times 10^3 \text{ J mol}^{-1} / 25 \text{ J K}^{-1} \text{ mol}^{-1} = 220\text{K}$ .

An endothermic reaction is favoured by increasing the temperature (Le Chatelier's principle).

5. Freezing water corresponds to the process:



At  $-10^\circ\text{C}$ , water freezes spontaneously to give ice so  $\Delta G < 0$ .

The liquid  $\rightarrow$  solid process involves the molecules becoming more ordered so  $\Delta S < 0$ .

The liquid  $\rightarrow$  solid process involves the formation of intermolecular H-bonds between the water molecules so  $\Delta H < 0$ .

Water freezes when  $\Delta G^0 < 0$ , i.e.  $\Delta H^0 - T\Delta S^0 < 0$ .

$\Delta S^0$  is negative, which would tend to make  $\Delta G^0$  positive.

To counteract this, the enthalpy change must be negative (which it is) and  $\Delta H^0$  must be more negative than  $T\Delta S^0$ .

Thus,  $|T\Delta S^0| < |\Delta H^0|$  and  $T < |\Delta H^0| / |\Delta S^0|$