

- For the reaction  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$  at 25 °C

$$\Delta H^\circ = -198.4 \text{ kJ mol}^{-1} \text{ and } \Delta S^\circ = -187.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

Show that this reaction is spontaneous in the forward direction at 25 °C.

$$\text{As } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ,$$

$$\begin{aligned} \Delta G^\circ &= ((-198.4 \times 10^3) \text{ J mol}^{-1}) - ((25 + 273) \text{ K}) \times (-187.9 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -142400 \text{ J mol}^{-1} = -142.4 \text{ kJ mol}^{-1} \end{aligned}$$

As  $\Delta G^\circ < 0$ , the reaction is spontaneous.

If the volume of the reaction system is increased at 25 °C, in which direction will the equilibrium move?

**In the reaction, 3 mol of gas  $\rightarrow$  2 mol of gas. In the volume of the reaction system is increased, the pressure will decrease. The reaction will shift to produce more gas: it will shift to the left (reactants).**

Calculate the value of the equilibrium constant,  $K_p$ , at 25 °C.

Using  $\Delta G^\circ = -RT \ln K_p$ :

$$(-142.4 \times 10^3) \text{ J mol}^{-1} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) \times \ln K_p$$

$$K_p = 9.3 \times 10^{24}$$

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Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature, in which temperature range is the reaction non-spontaneous?

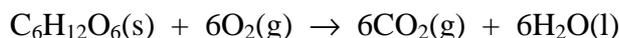
**The reaction is spontaneous as long as  $\Delta H^\circ - T\Delta S^\circ < 0$ .  $\Delta G^\circ = 0$  when**

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-198.4 \times 10^3 \text{ J mol}^{-1})}{(-187.9 \text{ J K}^{-1} \text{ mol}^{-1})} = 1056 \text{ K}$$

**The reaction is spontaneous below this temperature and non-spontaneous above it.**

$$\text{Answer: } T > 1056 \text{ K}$$

- Glucose is a common food source. The net reaction for its metabolism in humans is:



Calculate  $\Delta H^\circ$  for this reaction given the following heats of formation.

$$\Delta H^\circ_f(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) = -1274 \text{ kJ mol}^{-1}, \quad \Delta H^\circ_f(\text{CO}_2(\text{g})) = -393 \text{ kJ mol}^{-1} \text{ and}$$

$$\Delta H^\circ_f(\text{H}_2\text{O}(\text{l})) = -285 \text{ kJ mol}^{-1}$$

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

$$\Delta_{\text{rxn}}H^\circ = [6 \times \Delta_fH^\circ(\text{CO}_2(\text{g})) + 6 \times \Delta_fH^\circ(\text{H}_2\text{O}(\text{l}))] - [\Delta_fH^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s}))]$$

$$= [(6 \times -393) + (6 \times -285)] - [(-1274)] = -2794 \text{ kJ mol}^{-1}$$

(Note that  $\Delta_fH^\circ(\text{O}_2(\text{g})) = 0$  as it is an element in its standard state).

Answer: **-2794 kJ mol<sup>-1</sup>**

If the combustion of glucose is carried out in air, water is produced as a vapour. Calculate the  $\Delta H^\circ$  for the combustion of glucose in air given that



As vaporising liquid water requires energy (+44 kJ mol<sup>-1</sup>), the combustion enthalpy is reduced. Six moles of H<sub>2</sub>O are produced in the combustion so the enthalpy of combustion is reduced to:

$$-2794 + (6 \times +44) = -2530 \text{ kJ mol}^{-1}$$

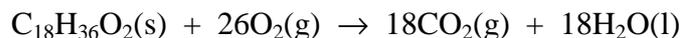
Answer: **-2530 kJ mol<sup>-1</sup>**

Will  $\Delta S$  be different for the two oxidation reactions? If so, how will it differ and why?

As gaseous molecules have higher entropy than liquid phase molecules, oxidation to produce H<sub>2</sub>O(g) will lead to a higher value for  $\Delta S$  than oxidation to produce H<sub>2</sub>O(l).

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- Stearic acid,  $C_{18}H_{36}O_2$ , is a fatty acid common in animal fats and vegetable oils and is a valuable energy source for mammals. The net reaction for its metabolism in humans is:



Calculate  $\Delta H^\circ$  for this reaction given the following heats of formation.

$$\Delta H_f^\circ (C_{18}H_{36}O_2(s)) = -948 \text{ kJ mol}^{-1}, \quad \Delta H_f^\circ (CO_2(g)) = -393 \text{ kJ mol}^{-1} \text{ and}$$

$$\Delta H_f^\circ (H_2O(l)) = -285 \text{ kJ mol}^{-1}$$

Using  $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - \sum n\Delta_fH^\circ(\text{reactants})$ , the heat of the reaction as written is:

$$\begin{aligned} \Delta_{\text{rxn}}H^\circ &= [18\Delta_fH^\circ(CO_2(g)) + 18\Delta_fH^\circ(H_2O(g))] \\ &\quad - [\Delta_fH^\circ(C_{18}H_{36}O_2(s)) + 26\Delta_fH^\circ(O_2(g))] \\ &= [(18 \times -393) + (18 \times -285)] - [(-948) + (26 \times 0)] = -11256 \text{ kJ mol}^{-1} \end{aligned}$$

$\Delta_fH^\circ(O_2(g)) = 0$  for an element already in their standard states.

Answer: **-11256 kJ mol<sup>-1</sup>**

If the combustion of stearic acid is carried out in air, water is produced as a vapour. Calculate the  $\Delta H^\circ$  for the combustion of stearic acid in air given that



**Energy must be provided to vaporize the water so the enthalpy of combustion is reduced:**

$$\Delta_{\text{comb}}H^\circ = -11256 + (18 \times 44) = -10464 \text{ kJ mol}^{-1}$$

Answer: **-10464 kJ mol<sup>-1</sup>**

Will  $\Delta S$  be different for the two oxidation reactions? If so, how will it differ and why?

**The entropy of  $H_2O(g)$  is greater than that of  $H_2O(l)$  so  $\Delta S$  will be greater. In the oxidation reaction which produces  $H_2O(l)$ , 26 mol of gas are converted into 18 mol of gas so that  $\Delta S$  will be negative. In the oxidation reaction which produces  $H_2O(g)$ , 26 mol of gas are converted into  $(18 + 18) = 36$  mol of gas and  $\Delta S$  will be positive.**

**ANSWER CONTINUES ON THE NEXT PAGE**

Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of stearic acid.

**The molar mass of stearic acid,  $C_{18}H_{36}O_2$ , is:**

$$18 \times 12.01 \text{ (C)} + 36 \times 1.008 \text{ (H)} + 2 \times 16.00 \text{ (O)} = 284.468$$

**1.0 g therefore contains:**

$$\text{number of moles of stearic acid} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.00}{284.468} = 0.00352 \text{ mol}$$

**As 18 mol of  $CO_2$  are produced for every mole of stearic acid:**

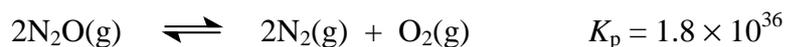
$$\text{number of moles of } CO_2 = 18 \times 0.00352 = 0.0633 \text{ mol}$$

**The molar mass of  $CO_2$  is  $(12.01 \text{ (C)} + 2 \times 16.00 \text{ (O)}) = 44.01$ . The mass of  $CO_2$  is thus:**

$$\text{mass of } CO_2 = \text{number of moles} \times \text{molar mass} = 0.0633 \times 44.01 = 2.78 \text{ g}$$

Answer: **2.78 g**

- Nitrous oxide decomposes at 25 °C according to the following equation.



What is the value for  $K_p$  at 40 °C?

Using  $\Delta_r G^\circ = -RT \ln K_p$ , at 25 °C (= 298 K):

$$\Delta_r G^\circ = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(1.8 \times 10^{36}) = -207 \text{ kJ mol}^{-1}$$

Assuming that  $\Delta_r G^\circ$  does not change over the temperature range, at 40 °C = 313 K:

$$\ln K_p = \frac{\Delta_r G^\circ}{RT} = \frac{(210 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 79$$

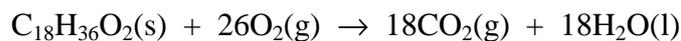
$$K_p = 3.3 \times 10^{34}$$

Answer:  $3.3 \times 10^{34}$

Is the reaction endothermic or exothermic? Give a reason for your answer.

**The equilibrium constant decreases when the temperature increases. This is consistent with an exothermic reaction since these become less favourable as the temperature increases (Le Chatelier's principle).**

- Stearic acid,  $C_{18}H_{36}O_2$ , is a fatty acid common in animal fats and vegetable oils and is a valuable energy source for mammals. The net reaction for its metabolism in humans is:



Calculate  $\Delta H^\circ$  for this reaction given the following heats of formation.

Compound	$C_{18}H_{36}O_2(s)$	$CO_2(g)$	$H_2O(l)$
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-948	-393	-285

Using  $\Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ(\text{products}) - \sum n \Delta_f H^\circ(\text{reactants})$ , the enthalpy of the combustion of the reaction with excess  $O_2$  is:

$$\begin{aligned} \Delta H^\circ &= (18\Delta_f H^\circ(CO_2(g)) + 18\Delta_f H^\circ(H_2O(l))) - (\Delta_f H^\circ(C_{18}H_{36}O_2(s))) \\ &= [(18 \times -393 + 18 \times -285) - (-948)] \text{ kJ mol}^{-1} = -11300 \text{ kJ mol}^{-1} \end{aligned}$$

As  $O_2(g)$  is an element in its standard state, its  $\Delta_f H^\circ$  is zero.

$$\Delta H^\circ = -11300 \text{ kJ mol}^{-1}$$

If the combustion of stearic acid is carried out in air, water is produced as a vapour. Calculate the  $\Delta H^\circ$  for the combustion of stearic acid in air given that:



The reaction now needs vapourisation of  $18H_2O(l)$  which requires *input* of  $(18 \times 44) \text{ kJ mol}^{-1}$ . The combustion enthalpy is reduced to:

$$\Delta H^\circ = (-11300 \text{ kJ mol}^{-1}) + (18 \times 44 \text{ kJ mol}^{-1}) = -10500 \text{ kJ mol}^{-1}$$

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Will  $\Delta S$  be different for the two oxidation reactions? If so, how will it differ and why?

$\Delta S$  will be greater for the air-oxidation as the product  $H_2O(g)$  has a much greater entropy than the product  $H_2O(l)$  - gases are much more disordered than liquids.

Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of stearic acid.

The molar mass of stearic acid,  $C_{18}H_{36}O_2$ , is:

$$\begin{aligned} \text{molar mass} &= (18 \times 12.01 \text{ (C)}) + (36 \times 1.008 \text{ (H)}) + (2 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} \\ &= 284.47 \text{ g mol}^{-1} \end{aligned}$$

ANSWER CONTINUES ON THE NEXT PAGE

**The number of moles in 1.00 g is therefore:**

$$\begin{aligned}\text{number of moles} &= \text{mass} / \text{molar mass} \\ &= (1.00 \text{ g}) / (284.47 \text{ g mol}^{-1}) = 0.00353 \text{ mol}\end{aligned}$$

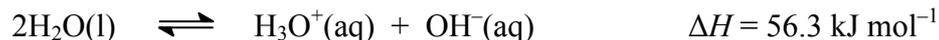
**The chemical equation shows that 18 mol of CO<sub>2</sub>(g) are produced from every 1 mol of C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>(s). The number of moles of CO<sub>2</sub>(g) produced is therefore (18 × 0.00353 mol) = 0.06328 mol.**

**The molar mass of CO<sub>2</sub> is (12.01 (C) + 2 × 16.00 (O)) g mol<sup>-1</sup> = 44.01 g mol<sup>-1</sup>. The mass of CO<sub>2</sub> produced is therefore:**

$$\begin{aligned}\text{mass of CO}_2 &= \text{number of moles} \times \text{molar mass} \\ &= (0.06328 \text{ mol}) \times (44.01 \text{ g mol}^{-1}) = 2.78 \text{ g}\end{aligned}$$

Answer: **2.78 g**

- The autoionisation of water conforms to the following balanced equation:



Is this an exothermic or endothermic reaction?

**Endothermic (as  $\Delta H$  is positive).**

What will happen to the equilibrium if the temperature is raised?

**The reaction will shift to the right. From le Chatelier's principle, the equilibrium will shift to reduce the effect of the change. As the forward reaction is endothermic, it is able to mitigate the increase in temperature by shifting forwards.**

The equilibrium constant,  $K$ , for this reaction is  $1.8 \times 10^{-16}$  at  $25^\circ\text{C}$ . Calculate  $\Delta G$ .

Using  $\Delta G = -RT \ln K$ ,

$$\Delta G = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) \times 1.8 \times 10^{-16} = +89 \text{ kJ mol}^{-1}$$

Answer: **+89 kJ mol<sup>-1</sup>**

Why is  $\Delta G$  not equal to  $\Delta H$  for this reaction?

**By definition,  $\Delta G = \Delta H - T\Delta S$ . As the entropy change for the reaction and the temperature are not zero, so  $\Delta G \neq \Delta H$ .**

The pH of pure water is 6.81 at  $37^\circ\text{C}$ . Is water acidic, basic or neutral at this temperature? Explain.

**Neutral. Pure water is neutral at all temperatures as the chemical equation always gives  $[\text{H}_3\text{O}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$ . A pH value of 7.0 only corresponds to a neutral solution at  $25^\circ\text{C}$ .**