5.2 Hess's law

Understandings:
- The enthalpy change for a reaction that is carried out in a series of steps is equal to the sum of the enthalpy changes for the individual steps.
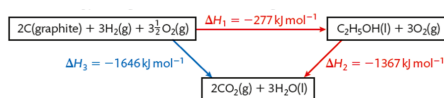
Applications and skills:
- Application of Hess's law to calculate enthalpy changes.
- Calculation of ΔH reactions using $\Delta H_f^\ominus$ data.
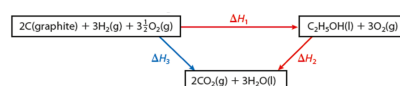 *Guidance*
  - Enthalpy of formation data can be found in the data booklet in section 12.
  - An application of Hess's law is
    $\Delta H_{reactions} = \sum (\Delta H_f^\ominus (products)) - \sum (\Delta H_f^\ominus (reactants))$
- Determination of the enthalpy change of a reaction that is the sum of multiple reactions with known enthalpy changes.

Enthalpy cycles

$$2C(graphite) + 3H_2(g) + 3\tfrac{1}{2}O_2(g) \xrightarrow{\Delta H_1 = -277\,kJ\,mol^{-1}} C_2H_5OH(l) + 3O_2(g)$$

$\Delta H_3 = -1646\,kJ\,mol^{-1}$ $\Delta H_2 = -1367\,kJ\,mol^{-1}$

$$2CO_2(g) + 3H_2O(l)$$

Consider the 2 different routes from the initial reactants to the carbon dioxide and water and the total enthalpy change in each. How similar are they?
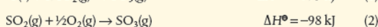
$$2C(graphite) + 3H_2(g) + 3\tfrac{1}{2}O_2(g) \xrightarrow{\Delta H_1} C_2H_5OH(l) + 3O_2(g)$$

ΔH_3 ΔH_2

$$2CO_2(g) + 3H_2O(l)$$

From the law of conservation of energy:

in Figure 5.12, the enthalpy change in a complete cycle $= 0$

$= \Delta H_1 + \Delta H_2 - \Delta H_3$

therefore $\Delta H_1 + \Delta H_2 = \Delta H_3$

This result can be generalized and is known as Hess's law.

Hess's law states that the enthalpy change for any chemical reaction is independent of the route provided the starting conditions and final conditions, and reactants and products, are the same.

Worked example

$S(s) + 1\tfrac{1}{2}O_2(g) \rightarrow SO_3(g)$	$\Delta H^\ominus = -395\,kJ$	(1)
$SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow SO_3(g)$	$\Delta H^\ominus = -98\,kJ$	(2)

Calculate the standard enthalpy change, $\Delta H^\ominus$, for the reaction:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
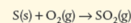
Solution

We can think of the reaction as a journey from $S(s)$ to $SO_2(g)$. As the standard enthalpy change cannot be measured directly, we must go by an alternative route suggested by the equations given.
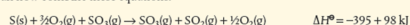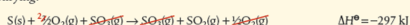
Reaction 1 starts from the required starting point:

$S(s) + 1\tfrac{1}{2}O_2(g) \rightarrow SO_3(g)$ $\Delta H^\ominus = -395\,kJ$ (1)
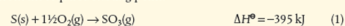
Reaction 2 relates $SO_3(g)$ to $SO_2(g)$. To finish with the required product, we reverse the chemical change and the sign of enthalpy change:
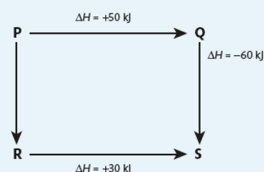
$SO_3(g) \rightarrow SO_2(g) + \tfrac{1}{2}O_2(g)$ $\Delta H^\ominus = +98\,kJ$ (2)

We can now combine these equations:

$S(s) + \tfrac{3}{2}O_2(g) + SO_3(g) \rightarrow SO_3(g) + SO_2(g) + \tfrac{1}{2}O_2(g)$ $\Delta H^\ominus = -395 + 98\,kJ$

Simplifying:

$S(s) + \tfrac{2/2}{}O_2(g) + \cancel{SO_3(g)} \rightarrow \cancel{SO_3(g)} + SO_2(g) + \cancel{\tfrac{1}{2}O_2(g)}$ $\Delta H^\ominus = -297\,kJ$

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H^\ominus = -297\,kJ$

Exercises

16 The diagram illustrates the enthalpy changes of a set of reactions.

$$P \xrightarrow{\Delta H = +50\,kJ} Q$$

$\Delta H = -60\,kJ$

$$R \xrightarrow{\Delta H = +30\,kJ} S$$

Which of the following statements are correct?

I	$P \rightarrow S$	$\Delta H = -10\,kJ$
II	$R \rightarrow Q$	$\Delta H = +90\,kJ$
III	$P \rightarrow R$	$\Delta H = +20\,kJ$

A I and II only   **B** I and III only   **C** II and III only   **D** I, II, and III

17 Calculate the enthalpy change, $\Delta H^\ominus$, for the reaction:
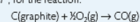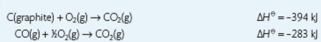
$$C(graphite) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$$

from the information below:

$C(graphite) + O_2(g) \rightarrow CO_2(g)$	$\Delta H^\ominus = -394\,kJ$
$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g)$	$\Delta H^\ominus = -283\,kJ$

18 Calculate the enthalpy change, $\Delta H^\ominus$, for the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

from the information below:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$	$\Delta H^\ominus = +180.5\,kJ$
$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$	$\Delta H^\ominus = +66.4\,kJ$
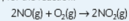
16 A

17 $\Delta H^\ominus = -394\,kJ - (-283)\,kJ = -111\,kJ$

18 $\Delta H^\ominus = -180.5\,kJ + (+66.4\,kJ) = -114.1\,kJ$

Standard enthalpy changes of reaction

Consider the defintion for standard enthalpy change of formation:

The **standard enthalpy change of formation**, $\Delta H_f^{\ominus}$, of a substance is the enthalpy change that occurs when one mole of the substance is formed from its elements in their standard states. These standard measurements are taken at a temperature of 298 K (25 °C) and a pressure of 1.00×10^5 Pa. They are important as they:

- give a measure of the stability of a substance relative to its elements
- can be used to calculate the enthalpy changes of all reactions, either hypothetical or real.
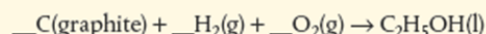
Worked example

The enthalpy of formation of ethanol is given in section 12 of the IB data booklet. Give the thermochemical equation which represents the standard enthalpy of formation of ethanol.

Solution

The value from the IB data booklet = −278 kJ mol⁻¹

Ethanol (C_2H_5OH) is made from the elements (C(graphite)) and hydrogen ($H_2(g)$) and oxygen ($O_2(g)$).

$$\_C(graphite) + \_H_2(g) + \_O_2(g) \rightarrow C_2H_5OH(l)$$

Balance the equation:

$$2C(graphite) + 3H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_5OH(l) \qquad \Delta H = -278 \text{ kJ mol}^{-1}$$

Note that as the enthalpy change of formation refers to one mole of product, there are fractional coefficients in the balanced equation.

Exercises

21 Which of the following does **not** have a standard heat of formation value of **zero** at 25 °C and 1.00×10^5 Pa?

   A $Cl_2(g)$ **B** $I_2(s)$ **C** $Br_2(g)$ **D** $Na(s)$

22 Which of the following **does** have a standard heat of formation value of **zero** at 25 °C and 1.00×10^5 Pa?

   A $H(g)$ **B** $Hg(s)$ **C** C(diamond)   **D** $Si(s)$

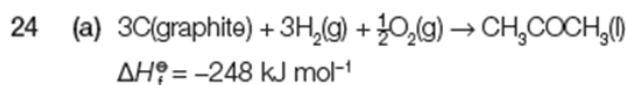**23** For which equation is the enthalpy change described as an enthalpy change of formation?

   A $CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$
   B $Cu(s) + S(s) + 2O_2(g) \rightarrow CuSO_4(aq)$
   C $5H_2O(l) + CuSO_4(s) \rightarrow CuSO_4.5H_2O(s)$
   D $Cu(s) + S(s) + 2O_2(g) \rightarrow CuSO_4(s)$

24 (a) Write the thermochemical equation for the standard enthalpy of formation of propanone (CH_3COCH_3).

   (b) State the conditions under which standard enthalpy changes are measured.

20 B   21 C   22 D   23 D

24   **(a)** $3C(graphite) + 3H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow CH_3COCH_3(l)$

        $\Delta H_f^{\ominus} = -248$ kJ mol⁻¹

    (b) Under standard conditions of 298 K (25 °C) and 1.00×10^5 Pa. If the reaction involves solutions these have a concentration of 1.00 mol dm⁻³.

Using standard enthalpy changes of formation

Standard enthalpy changes of formation can be used to calculate the standard enthalpy change of any reaction. Consider the general energy cycle in Figure 5.15.
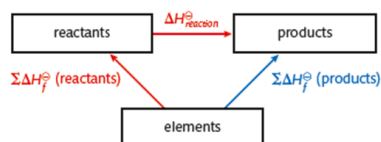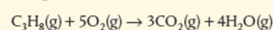

We have from the diagram:

$$\sum \Delta H_f^{\ominus}(\text{reactants}) + \Delta H_{\text{reaction}} = \sum \Delta H_f^{\ominus}(\text{products})$$

This gives the general expression for $\Delta H_{\text{reaction}}$ of any reaction

$$\Delta H_{\text{reaction}} = \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants})$$

Worked example

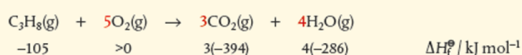Calculate the enthalpy change for the reaction

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

from the following standard enthalpy changes of formation.

Substance	$\Delta H_f^{\ominus}$/ kJ mol^{-1}
$C_3H_8(g)$	−105
$CO_2(g)$	−394
$H_2O(l)$	−286

Solution

First, write down the equation with the corresponding enthalpies of formation underneath:

$$\begin{array}{ccccccc} C_3H_8(g) & + & 5O_2(g) & \rightarrow & 3CO_2(g) & + & 4H_2O(g) \\ -105 & & >0 & & 3(-394) & & 4(-286) \end{array} \quad \Delta H_f^{\ominus}/\text{kJ mol}^{-1}$$

As the standard enthalpies of formation are given per mole they must be multiplied by the number of moles in the balanced equation, shown in red above.

Write down the general expression for the $\Delta H_{\text{reaction}}$

$$\Delta H_{\text{reaction}} = \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants})$$

and express $\Delta H_{\text{reaction}}$ in terms of the data given:

$$\Delta H_{\text{reaction}}^{\ominus} = 3(-394) + 4(-286) - (-105)$$
$$= -2221 \text{ kJ mol}^{-1}$$

Exercises

25 Calculate $\Delta H^{\ominus}$ (in kJ mol^{-1}) for the reaction

$$Fe_3O_4(s) + 2C(\text{graphite}) \rightarrow 3Fe(s) + 2CO_2(g)$$

from the data below:

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$Fe_3O_4(s)$	−1118
$CO_2(g)$	−394

26 Calculate $\Delta H^{\ominus}$ (in kJ mol^{-1}) for the reaction

$$2NO_2(g) \rightarrow N_2O_4(g)$$
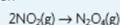
from the data below:

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$NO_2(g)$	+33.2
$N_2O_4(g)$	+9.2

27 Hydrogen peroxide slowly decomposes into water and oxygen:

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$
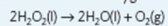
Calculate the enthalpy change of this reaction from the data table.

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$H_2O_2(l)$	−188
$H_2O(l)$	−286

  A +98 kJ mol^{-1} **B** −98 kJ mol^{-1} **C** +196 kJ mol^{-1} **D** −196 kJ mol^{-1}

28 Calculate the enthalpy change for the hypothetical reduction of magnesium oxide by carbon, according to the equation below from the data given. Comment on its feasibility.
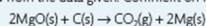
$$2MgO(s) + C(s) \rightarrow CO_2(g) + 2Mg(s)$$

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CO_2(g)$	−394
$MgO(l)$	−602

25   +330 kJ mol^{-1}

26   −57.2 kJ mol^{-1}

27   D

28 $2MgO(s) + C(s) \rightarrow CO_2(g) + 2Mg(s)$

      $\Delta H_{\text{reaction}}^{\ominus} = (-394) - 2(-602) = +810 \text{ kJ mol}^{-1}$

      Such a highly endothermic reaction is unlikely to be feasible.