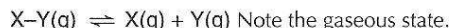


Bond enthalpies and Hess' law

BOND ENTHALPIES

Enthalpy changes can also be calculated directly from bond enthalpies. For a diatomic molecule the bond enthalpy is defined as the enthalpy change for the process



For bond formation the value is negative and for bond breaking the value is positive. If the bond enthalpy values are known for all the bonds in the reactants and products then the overall enthalpy change can be calculated.

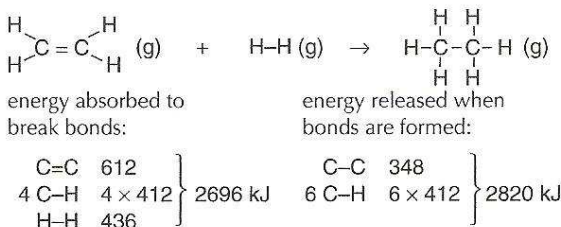
Some average bond enthalpies

All values in kJ mol^{-1}

| | | |
|---------|---------|---------|
| H-H 436 | C=C 612 | C≡C 837 |
| C-C 348 | O=O 496 | N≡N 944 |
| C-H 412 | | |
| O-H 463 | | |
| N-H 388 | | |
| N-N 163 | | |

Worked example 1

Hydrogenation of ethene

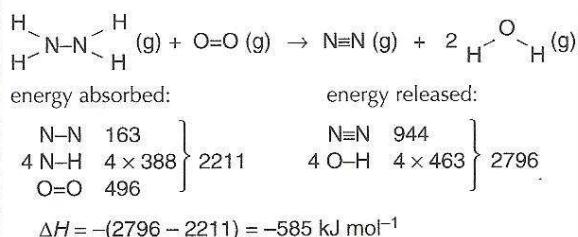


There is more energy released than absorbed so the reaction is exothermic.

$$\Delta H = -(2820 - 2696) = -124 \text{ kJ mol}^{-1}$$

Worked example 2

Combustion of hydrazine in oxygen (this reaction has been used to power spacecraft)



LIMITATIONS OF USING AVERAGE BOND ENTHALPIES

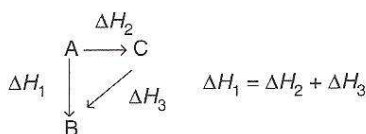
Average bond enthalpies can only be used if all the reactants and products are in the gaseous state. If water were a liquid product in the above example then even more heat would be evolved since the enthalpy change of vaporization of water would also need to be included in the calculation.

In the above calculations **average** bond enthalpies have been used. These have been obtained by considering a number of similar compounds. In practice the energy of a particular bond will vary slightly in different compounds, as it will be affected by neighbouring atoms. So ΔH values obtained from using average bond enthalpies will not necessarily be very accurate.

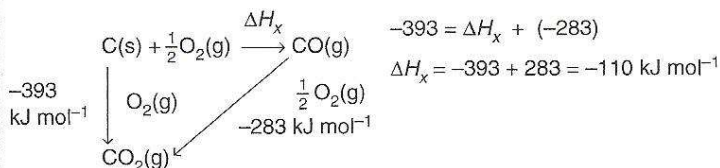
HESS' LAW

Hess' law states that the enthalpy change for a reaction depends only on the difference between the enthalpy of the products and the enthalpy of the reactants. It is independent of the reaction pathway.

The enthalpy change going from A to B is the same whether the reaction proceeds directly to B or whether it goes via an intermediate.



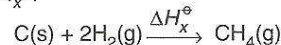
This law is a statement of the law of conservation of energy. It can be used to determine enthalpy changes, which cannot be measured directly. For example, the enthalpy of combustion of both carbon and carbon monoxide to form carbon dioxide can easily be measured directly, but the combustion of carbon to carbon monoxide cannot. This can be represented by an energy cycle.



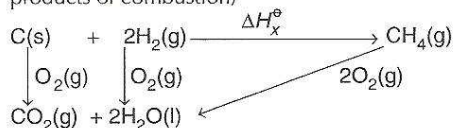
Worked example 3

Calculate the standard enthalpy change when one mole of methane is formed from its elements in their standard states. The standard enthalpies of combustion ΔH_c° of carbon, hydrogen, and methane are -393 , -286 , and -890 kJ mol^{-1} respectively.

Step 1. Write the equation for the enthalpy change with the unknown ΔH_x° value. Call this value ΔH_x° .



Step 2. Construct an energy cycle showing the different routes to the products (in this case the products of combustion)



Step 3. Use Hess' law to equate the energy changes for the two different routes

$$\underbrace{\Delta H_c^\circ(\text{C}) + 2\Delta H_c^\circ(\text{H}_2)}_{\text{direct route}} = \underbrace{\Delta H_x^\circ + \Delta H_c^\circ(\text{CH}_4)}_{\text{route via methane}}$$

Step 4. Rearrange the equation and substitute the values to give the answer

$$\begin{aligned} \Delta H_x^\circ &= \Delta H_c^\circ(\text{C}) + 2\Delta H_c^\circ(\text{H}_2) - \Delta H_c^\circ(\text{CH}_4) \\ &= -393 + (2 \times -286) - (-890) \text{ kJ mol}^{-1} \\ &= -75 \text{ kJ mol}^{-1} \end{aligned}$$