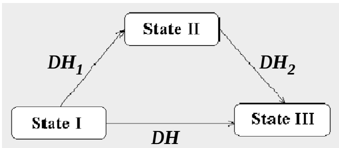
6.14 Hess's Law

- The enthalpy is a state function - ***DH*** is independent of the path of the process



$DH = DH_1 + DH_2$

- **Hess's law** - the overall reaction enthalpy is the sum of the reaction enthalpies of the steps into which the reaction can be divided
  - ⇒**the addition of two or more thermochemical equations results in an equation with a *DH* value equal to the sum of the *DH* values of the added equations**

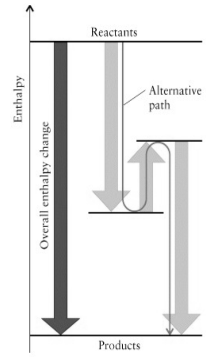


Fig. 6.31

⇒**multiplying an equation by a factor multiplies the *DH* value by the same factor**

⇒**reversing the direction of a reaction changes the sign of the *DH* value**

Example: Calculate DH^o for the reaction
$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$, given the following:

A **$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$** **$DH^o = -2220.$ kJ**

B **$C(s) + O_2(g) \rightarrow CO_2(g)$** **$DH^o = -394$ kJ**

C **$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$** **$DH^o = -286$ kJ**

- Procedure
  - rewrite the given equations by placing the reactants and products from the overall equation on the left and right side of the given equations, respectively (if necessary, reverse the direction of the reactions)

$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$

⇒**reverse direction of eq. A (change sign of DH^o)**

A **$3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g)$** **$DH^o = +2220.$ kJ**

B **$C(s) + O_2(g) \rightarrow CO_2(g)$** **$DH^o = -394$ kJ**

C **$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$** **$DH^o = -286$ kJ**

- multiply the given equations by factors in order to match the stoichiometric coefficients of the reactants and products in the overall equation

$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$

⇒**multiply eq. B by 3 and eq. C by 4 (multiply DH^o by 3 and 4, respectively)**

A **$3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g)$** **$DH^o = +2220.$ kJ**

B **$3C(s) + 3O_2(g) \rightarrow 3CO_2(g)$** **$DH^o = -3\times394$ kJ**

C **$4H_2(g) + 2O_2(g) \rightarrow 4H_2O(l)$** **$DH^o = -4\times286$ kJ**

- add the sequence of equations and cancel the the species appearing on both sides of the resulting equation

$3CO_2(g) + 4H_2O(l) + 3C(s) + 3O_2(g) + 4H_2(g) +$
$+ 2O_2(g) \rightarrow C_3H_8(g) + 5O_2(g) + 3CO_2(g) +$
$+ 4H_2O(l)$

$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$

- add the resulting reaction enthalpies to obtain the overall reaction enthalpy

$DH^o = +2220. + (-3\times394) + (-4\times286) = -106$ kJ

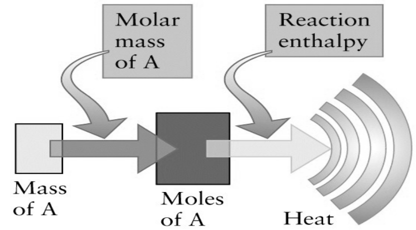
$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ **$DH^o = -106$ kJ**

Stoichiometric Calculations Involving Reaction Enthalpies

- The reaction enthalpy (heat of reaction) is treated stoichiometrically as a product of the reaction
- **Example:** Calculate the standard enthalpy change for the combustion of **15 g** of octane by the reaction:

$$\mathbf{2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)}$$

$$\mathbf{DH^o = -10942\ kJ}$$



2 mol C_8H_{18} ⇔ -10942 J

$$15.0\ \mathrm{g\ C_8H_{18}} \times \left(\frac{1\ \mathrm{mol\ C_8H_{18}}}{114\ \mathrm{g\ C_8H_{18}}}\right) \times \left(\frac{-10942\ \mathrm{kJ}}{2\ \mathrm{mol\ C_8H_{18}}}\right) = -718\ \mathrm{kJ}$$

6.15 Enthalpies of Combustion

- **Standard enthalpy of combustion** (***DH_c^o***) - the standard enthalpy change for the combustion of **1 mol** of a substance in excess oxygen

$$\mathbf{2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)}$$

$$\mathbf{DH^o = -10942\ kJ}$$

$$\Delta H_c^\circ = \frac{-10942\ \mathrm{kJ}}{2\ \mathrm{mol\ C_8H_{18}}} = -5471\ \frac{\mathrm{kJ}}{\mathrm{mol\ C_8H_{18}}}$$

- Heat output of combustion reactions - important measure of the value of fuels
- **Specific enthalpy** of fuels - the enthalpy of combustion per **1 g** of the fuel (measure of the fuel's practical value and efficiency)
- **Enthalpy density** of fuels - the enthalpy of combustion per **1 L** of the fuel (important when the storage space is limited)

Table 6.4 *Thermochemical properties of four fuels*

Fuel	Combustion equation	ΔH_c°, kJ/mol	Specific enthalpy, kJ/g	Enthalpy density,* kJ/L
hydrogen	$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$	−286	142	13
methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−890.	55	40.
octane	$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l)$	−5471	48	3.8×10^4
methanol	$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$	−726	23	1.8×10^4

*At atmospheric pressure and room temperature.

6.16 Standard Enthalpies of Formation

- **Standard enthalpy of formation** (***DH_f^o***) - the standard enthalpy change for the formation of **1 mol** of a substance from its elements in their most stable form (Appendix 2A)
  - for elements in their most stable form, ***DH_f^o* = 0**
    - **C(s, graphite) → DH_f^o = 0**
    - **C(s, graphite) → C(s, diamond) DH_f^o = 1.9 kJ/mol**
  - for compounds, ***DH_f^o*** can be positive or negative

$$\mathbf{2C(s) + 3H_2(g) + 1/2O_2(g) \rightarrow C_2H_5OH(l)}$$

$$\mathbf{DH_f^o(C_2H_5OH, l) = -277.7\ kJ/mol\ C_2H_5OH}$$

$DH^o = H^o_{final} - H^o_{initial}$

$DH^o = \Sigma n DH_f^o$(products) $- \Sigma n DH_f^o$(reactants)

– ***n*** - stoichiometric coefficients of reactants or products
– follows from Hess's law

$\Sigma n DH_f^o$(products) $=$
$\Sigma m DH_f^o$(reactants) $+ DH^o$

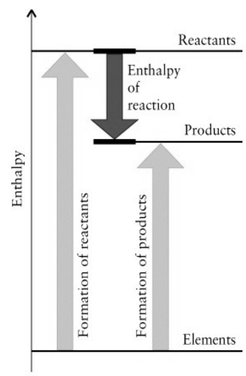


Fig. 6.35

- **Example:** Calculate the standard enthalpy of combustion of glucose, $C_6H_{12}O_6$, using ***DH**$_f^o$* data from Appendix 2A.

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$DH^o = \Sigma n DH_f^o$(products) $- \Sigma n DH_f^o$(reactants)

$DH^o = [6\times DH_f^o(CO_{2(g)}) + 6\times DH_f^o(H_2O_{(l)})] -$
$- [1\times DH_f^o(C_6H_{12}O_{6(s)}) + 6\times DH_f^o(O_{2(g)})] =$
$[6\times(-393.5) + 6\times(-285.8)] - [1\times(-1268) + 6\times 0] =$
$= -2808$ **kJ**

$DH_c^o = -2808$ **kJ/1 mol $C_6H_{12}O_6$ = -2808 kJ/mol**

Assignments:

- **Homework:** Chpt. 6/ 1, 7, 11, 15, 17, 21, 23, 27, 31, 33, **35, 39, 45, 47, 49, 53, 55, 59, 65, 67, 69, 79, 83**

- **Student companion:** 6.1, **6.5, 6.6**