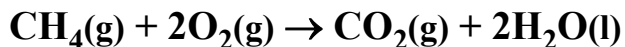


## 6.4 Reaction Enthalpy and Stoichiometry

- **Thermochemical equation** – the chemical equation with physical states and the reaction enthalpy (heat of reaction)  $\rightarrow \Delta H_r$

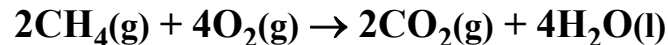


$$\Delta H_r = -890 \text{ kJ}$$

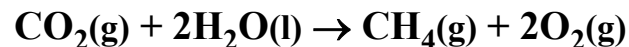
$\Delta H_r$  is for 1 mol  $\text{CH}_4$  and 2 mol of  $\text{O}_2$

- The value of  $\Delta H_r$  depends on the way the chemical equation is written (stoichiometric coefficients)

- Properties of thermochemical equations
  - multiplying an equation by a number multiplies the  $\Delta H_r$  value by the same number
  - reversing the direction of a reaction changes the sign of the  $\Delta H_r$  value



$$\Delta H = -2 \times 890 \text{ kJ}$$

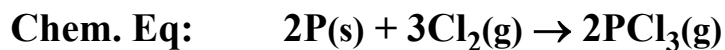


$$\Delta H = +890 \text{ kJ}$$

**Example:** When 2.31 g of solid P reacts with gaseous  $\text{Cl}_2$  to form liquid  $\text{PCl}_3$  in a constant pressure calorimeter 23.9 kJ of heat are released to the surroundings. Write the thermochemical equation.

$P = \text{constant}$

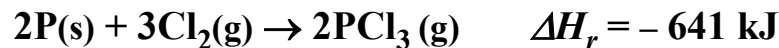
$$\Rightarrow \Delta H = q_p = -23.9 \text{ kJ} \quad (\text{for } 2.31 \text{ g P})$$



$\Rightarrow$  need  $\Delta H_r$  for 2 mol P

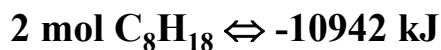
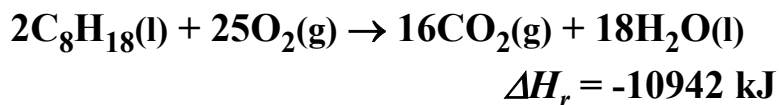
$$2.31 \text{ g P} \times \left( \frac{1 \text{ mol P}}{30.97 \text{ g P}} \right) = 7.46 \times 10^{-2} \text{ mol P}$$

$$\Delta H_r = \frac{-23.9 \text{ kJ}}{7.46 \times 10^{-2} \text{ mol P}} \times 2 \text{ mol P} = -641 \text{ kJ}$$



- The reaction enthalpy ( $\Delta H_r$ ) is treated stoichiometrically as a product of the reaction

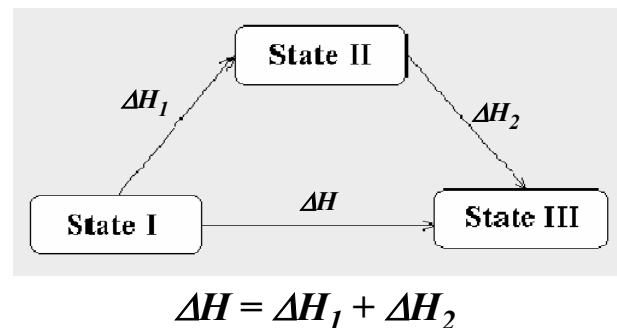
**Example:** Calculate the enthalpy change for the combustion of 15 g of octane by the reaction:



$$15.0 \text{ g C}_8\text{H}_{18} \left( \frac{1 \text{ mol C}_8\text{H}_{18}}{114 \text{ g C}_8\text{H}_{18}} \right) \left( \frac{-10942 \text{ kJ}}{2 \text{ mol C}_8\text{H}_{18}} \right) = -718 \text{ kJ}$$

## 6.5 Hess's Law

- The enthalpy is a state function –  $\Delta H$  is independent of the path of the process



- Hess's law** – the reaction enthalpy of an overall process is the sum of the reaction enthalpies of the individual steps into which the process can be divided

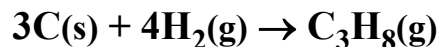
⇒ The addition of two or more thermochemical equations results in an equation with a  $\Delta H$  value equal to the sum of the  $\Delta H$  values of the added equations

⇒ Multiplying an equation by a factor multiplies the  $\Delta H$  value by the same factor

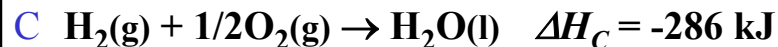
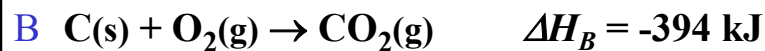
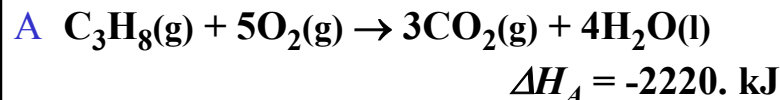
⇒ Reversing the direction of a reaction changes the sign of the  $\Delta H$  value

### Example:

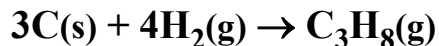
Calculate  $\Delta H$  for the reaction



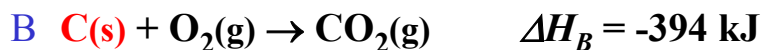
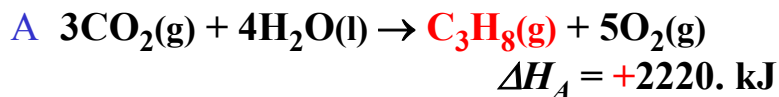
given the following:



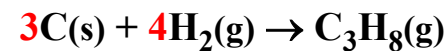
**Procedure:** 1) Rewrite the given equations by placing the reactants and products from the overall equation on the left and right side of the given equations, respectively (if necessary, reverse the direction of the reactions)



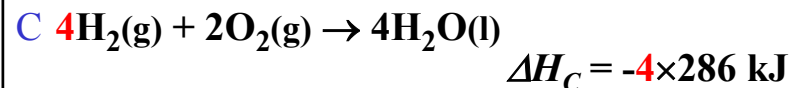
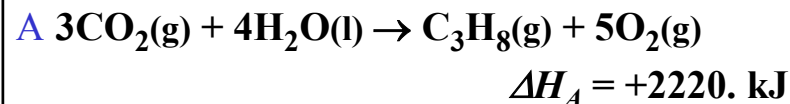
⇒ reverse direction of eq. **A** (change sign of  $\Delta H_f$ )



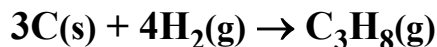
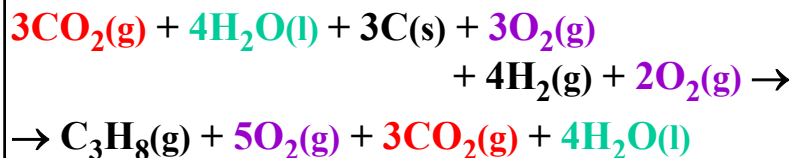
2) Multiply the given equations by factors in order to match the stoichiometric coefficients of the reactants and products in the overall equation



⇒ multiply eq. **B** by 3 and eq. **C** by 4 (multiply  $\Delta H$  by 3 and 4, respectively)



3) Add the sequence of equations and cancel the the species appearing on both sides of the resulting equation



4) Add the resulting reaction enthalpies to obtain the overall reaction enthalpy

$$\Delta H_r = +2220. + (-3 \times 394) + (-4 \times 286) = -106 \text{ kJ}$$

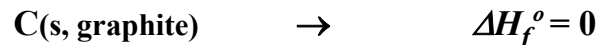


## 6.6 Standard Reaction Enthalpies

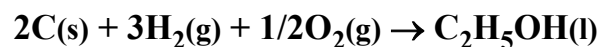
- $\Delta H_r$  depends on the physical states of reactants and products, **P** and **T**
- **Standard state** – the state of a pure substance in its most stable form at **1 atm** and a given temperature (usually **298 K**). For substances in solutions, the standard state is at concentrations **1 mol/L**
- **Standard reaction enthalpy** ( $\Delta H_r^\circ$ ) –  $\Delta H_r$  for a reaction in which all reactants and products are in their standard states

- **Standard enthalpy of formation ( $\Delta H_f^\circ$ )** – the standard enthalpy change for the formation of **1 mol** of a substance from its elements in their most stable form (Appendix B)

– For elements in their standard states,  $\Delta H_f^\circ = 0$



– For compounds,  $\Delta H_f^\circ$  can be positive or negative



$$\Delta H_f^\circ(\text{C}_2\text{H}_5\text{OH, l}) = -277.7 \text{ kJ/mol C}_2\text{H}_5\text{OH}$$

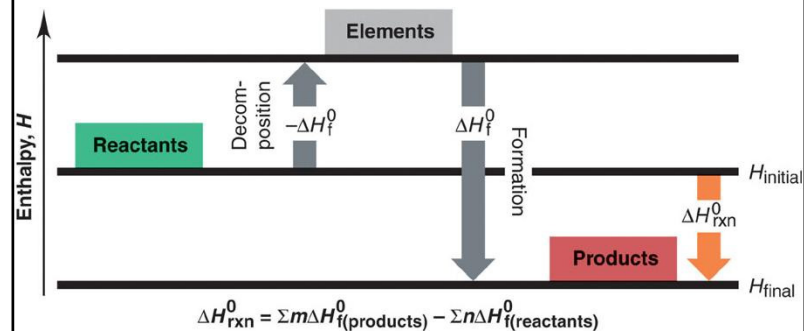
– Most compounds have  $\Delta H_f^\circ < 0$  – such compounds are more stable than their elements

$$\Delta H_r^\circ = H^\circ_{\text{final}} - H^\circ_{\text{initial}}$$

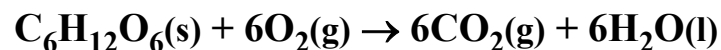
$$\Delta H_r^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$$

( $n, m$  - stoichiometric coefficients of reactants or products)

→ Follows from Hess's law



**Example:** Calculate the standard enthalpy of combustion of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , using  $\Delta H_f^\circ$  data from Appendix B.



$$\Delta H_r^\circ = \sum n \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$$

$$\begin{aligned} \Delta H_r^\circ &= [6 \times \Delta H_f^\circ(\text{CO}_2(\text{g})) + 6 \times \Delta H_f^\circ(\text{H}_2\text{O(l)})] - \\ &\quad - [1 \times \Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6 \times \Delta H_f^\circ(\text{O}_2(\text{g}))] \\ &= [6 \times (-393.5) + 6 \times (-285.8)] - [1 \times (-1273) + 6 \times 0] \\ &= -2803 \text{ kJ} \end{aligned}$$

$$\Delta H_c^\circ = -2803 \text{ kJ/1 mol C}_6\text{H}_{12}\text{O}_6 = -2803 \text{ kJ/mol}$$