# HESS'S LAW OF HEAT SUMMATION

Enthalpy change of a reaction depends only on the reactants and products.

It is independent of the pathway or the intermediate steps.

**EXAMPLE:**

$C_{(s)} + 1/2\ O_{2(g)} \longrightarrow CO_{(g)}$ $\quad \Delta H^o = -110.5$ kJ

2 steps ←

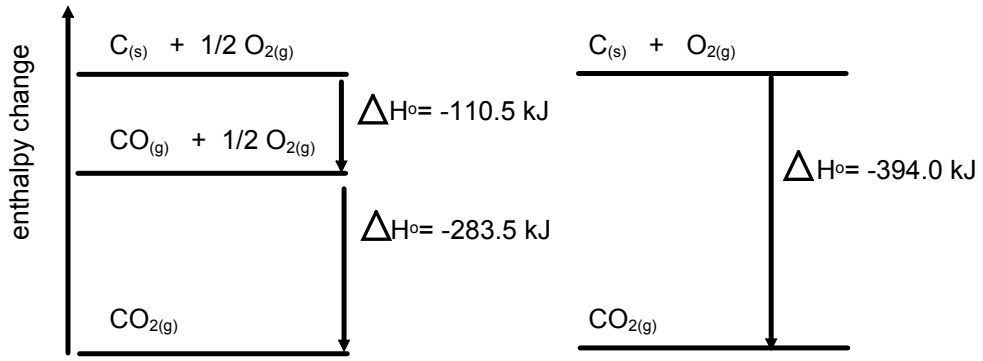
$CO_{(g)} + 1/2\ O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H^o = -283.5$ kJ

$-394.0$ kJ

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H^o = -394.0$ kJ

1 step ←

## Enthalpy Pathway Diagram



## USING HESS' LAW ALGEBRAICALLY GIVEN OTHER REACTIONS

Determine enthalpy change for the reaction: $H_2O_{2(l)} \longrightarrow H_2O_{(l)} + \frac{1}{2}O_{2(g)}$

given the following reactions:

**(1)** $H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{2(l)}$ $\quad \Delta H^o = -188$ kJ

**(2)** $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\quad \Delta H^o = -572$ kJ

- Look at each compound in original equation.
- Notice that the $H_2O_{2(l)}$ is on the wrong side, therefore reverse order of reaction **(1)** and multiply the enthalpy change by -1.
- Also notice that reaction **(2)** is in the correct order, but we need only 1 mole of water, so divide reaction **(2)** by 2.
- Then add the 2 reactions together and determine the overall enthalpy change for the required reaction.

**(1) x -1** $\quad H_2O_{2(l)} \longrightarrow H_{2(g)} + O_{2(g)} \quad \Delta H^o = +188$ kJ

**(2) ÷ 2** $\quad H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H^o = -286$ kJ

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$H_2O_{2(l)} \longrightarrow H_2O_{(l)} + \frac{1}{2}O_{2(g)} \quad \Delta H^o = -98$ kJ

**EXAMPLE:** Calculate the enthalpy change for the reaction...

$$FeO_{(s)} + CO_{(g)} \longrightarrow Fe_{(s)} + CO_{2(g)}$$

Use the following reactions:

**(1)** $Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$ $\quad \Delta H^o = -25$ kJ

**(2)** $3Fe_2O_{3(s)} + CO_{(g)} \longrightarrow 2Fe_3O_{4(s)} + CO_{2(g)}$ $\quad \Delta H^o = -47$ kJ

**(3)** $Fe_3O_{4(s)} + CO_{(g)} \longrightarrow 3FeO_{(s)} + CO_{2(g)}$ $\quad \Delta H^o = +38$ kJ

**EXAMPLE:** Determine the enthalpy change for the reaction:

$$3N_2F_{4(l)} + 4ClF_{3(g)} \longrightarrow 3N_{2(g)} + 12HF_{(g)} + 2Cl_{2(g)}$$

**(1)** $2ClF_{3(g)} + 2NH_{3(g)} \longrightarrow N_{2(g)} + 6HF_{(g)} + Cl_{2(g)}$ $\quad \Delta H^o = -1196$ kJ

**(2)** $N_2F_{4(l)} + O_{2(g)} \longrightarrow N_{2(g)} + 2H_2O_{(l)}$ $\quad \Delta H^o = -622$ kJ

**(3)** $4NH_{3(g)} + 3O_{2(g)} \longrightarrow 2N_{2(g)} + 6H_2O_{(l)}$ $\quad \Delta H^o = -1530$ kJ

# Hess' Law Using Standard Molar Enthalpies of Formation

## A) FORMATION REACTIONS

**EXAMPLE:** $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\quad \Delta H_f^o = -241.8$ kJ/mol

-- a substance formed from its "elements in standard state"

-- the enthalpy of formation of an element in its standard state = **ZERO.**

-- standard conditions are 25°C and 100 kPa

| ELEMENTS | STANDARD STATE | $\Delta H_f^o$ |
|---|---|---|
| nitrogen | $N_{2(g)}$ | 0 |
| mercury | $Hg_{(l)}$ | 0 |
| carbon | $C_{(s)}$ | 0 |

-- use **Table E.8** to determine Standard Enthalpies of Formation for compounds (always expressed as **1 mole of compound**)

$\frac{1}{2}N_{2(g)} + 2H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow NH_4Cl_{(s)}$ $\quad \Delta H_f^o = -314.4$ kJ

**step 1:** always 1 mole

**step 2:** balance (fractions okay)

**step 3:** look up in table

**EXAMPLE:** $\longrightarrow Na_2CO_{3(s)}$ $\quad \Delta H_f^o = ?$

**Table 5.3** Selected Standard Molar Enthalpies of Formation

| Compound | $\Delta H^\circ_f$ | Formation equations |
|---|---|---|
| $CO_{(g)}$ | −110.5 | $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ |
| $CO_{2(g)}$ | −393.5 | $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ |
| $CH_{4(g)}$ | −74.6 | $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ |
| $CH_3OH_{(\ell)}$ | −238.6 | $C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(\ell)}$ |
| $C_2H_5OH_{(\ell)}$ | −277.6 | $2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow C_2H_5OH_{(\ell)}$ |
| $C_6H_{6(\ell)}$ | +49.0 | $6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(\ell)}$ |
| $C_6H_{12}O_{6(s)}$ | −1274.5 | $6C_{(s)} + 6H_{2(g)} + 3O_{2(g)} \rightarrow C_6H_{12}O_{6(s)}$ |
| $H_2O_{(\ell)}$ | −285.8 | $H_{2(s)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$ |
| $H_2O_{(g)}$ | −241.8 | $H_{2(s)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ |
| $CaCl_{2(s)}$ | −795.4 | $Ca_{(s)} + Cl_{2(g)} \rightarrow CaCl_{2(s)}$ |
| $CaCO_{3(s)}$ | −1206.9 | $Ca_{(s)} + C_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow CaCO_{3(s)}$ |
| $NaCl_{(s)}$ | −411.1 | $Na_{(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow NaCl_{(g)}$ |
| $HCl_{(g)}$ | −92.3 | $\frac{1}{2}H_{2(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}$ |
| $HCl_{(aq)}$ | −167.5 | $\frac{1}{2}H_{2(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(ag)}$ |

## B) CALCULATING ENTHALPY CHANGES (FOR CHEMICAL REACTIONS)

$$\Delta H^o = \Sigma ( n \Delta H_f^o \text{ products}) - \Sigma ( n \Delta H_f^o \text{ reactants})$$

- determines enthalpy change of reaction, using table of enthalpies of formation (E.8)

**EXAMPLE 1:** $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$

using table: $1(-74.6\text{ kJ}) + 2(0\text{ kJ})$ $\quad 1(-393.5\text{ kJ}) + 2(-241.8\text{ kJ})$

$= -74.6\text{ kJ}$ $\quad -393.5\text{ kJ} + -483.6\text{ kJ}$

$= -877.1\text{ kJ}$

$\Delta H^o$ = products - reactants

= -877.1 kJ - (-74.6 kJ)

= -802.5 kJ

**EXAMPLE 2:** $Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 3CO_{2(g)} + 2Fe_{(s)}$

**Table E.8** Standard Molar Enthalpies of Formation

| Substance | $\Delta H^\circ_f$ (kJ/mol) | Substance | $\Delta H^\circ_f$ (kJ/mol) | Substance | $\Delta H^\circ_f$ (kJ/mol) |
|---|---|---|---|---|---|
| $Al_2O_{3(s)}$ | −1675.7 | $HBr_{(g)}$ | −36.3 | $NH_{3(g)}$ | −45.9 |
| $CaCO_{3(s)}$ | −1207.6 | $HCl_{(g)}$ | −92.3 | $N_2H_{4(\ell)}$ | +50.6 |
| $CaCl_{2(s)}$ | −795.4 | $HF_{(g)}$ | −273.3 | $NH_4Cl_{(s)}$ | −314.4 |
| $Ca(OH)_{2(s)}$ | −985.2 | $HCN_{(g)}$ | +135.1 | $NH_4NO_{3(s)}$ | −365.6 |
| $CCl_{4(\ell)}$ | −128.2 | $H_2O_{(\ell)}$ | −285.8 | $NO_{(g)}$ | +91.3 |
| $CCl_{4(g)}$ | −95.7 | $H_2O_{(g)}$ | −241.8 | $NO_{2(g)}$ | +33.2 |
| $CHCl_{3(\ell)}$ | −134.1 | $H_2O_{2(\ell)}$ | −187.8 | $N_2O_{(g)}$ | +81.6 |
| $CH_{4(g)}$ | −74.6 | $HNO_{3(\ell)}$ | −174.1 | $N_2O_{4(g)}$ | +11.1 |
| $C_2H_{2(g)}$ | +227.4 | $H_3PO_{4(s)}$ | −1284.4 | $PH_{3(g)}$ | +5.4 |
| $C_2H_{4(g)}$ | +52.4 | $H_2S_{(g)}$ | −20.6 | $PCl_{3(g)}$ | −287.0 |
| $C_2H_{6(g)}$ | −84.0 | $H_2SO_{4(\ell)}$ | −814.0 | $P_4O_{6(s)}$ | −2144.3 |
| $C_3H_{8(g)}$ | −103.8 | $FeO_{(s)}$ | −272.0 | $P_4O_{10(s)}$ | −2984.0 |
| $C_6H_{6(\ell)}$ | +49.1 | $Fe_2O_{3(s)}$ | −824.2 | $KBr_{(s)}$ | −393.8 |
| $CH_3OH_{(\ell)}$ | −239.2 | $Fe_3O_{4(s)}$ | −1118.4 | $KCl_{(s)}$ | −436.5 |
| $C_2H_5OH_{(\ell)}$ | −277.6 | $FeCl_{2(s)}$ | −341.8 | $KClO_{3(s)}$ | −397.7 |
| $CH_3COOH_{(\ell)}$ | −484.3 | $FeCl_{3(s)}$ | −399.5 | $KOH_{(s)}$ | −424.6 |
| $CO_{(g)}$ | −110.5 | $FeS_{2(s)}$ | −178.2 | $Ag_2CO_{3(s)}$ | −505.8 |
| $CO_{2(g)}$ | −393.5 | $PbCl_{2(s)}$ | −359.4 | $AgCl_{(s)}$ | −127.0 |
| $COCl_{2(g)}$ | −219.1 | $MgCl_{2(s)}$ | −641.3 | $AgNO_{3(s)}$ | −124.4 |
| $CS_{2(\ell)}$ | +89.0 | $MgO_{(s)}$ | −601.6 | $Ag_2S_{(s)}$ | −32.6 |
| $CS_{2(g)}$ | +116.7 | $Mg(OH)_{2(s)}$ | −924.5 | $SF_{6(g)}$ | −1220.5 |
| $CrCl_{3(s)}$ | −556.5 | $HgS_{(s)}$ | −58.2 | $SO_{2(g)}$ | −296.8 |
| $Cu(NO_3)_{2(s)}$ | −302.9 | $NaCl_{(s)}$ | −411.2 | $SO_{3(g)}$ | −395.7 |
| $CuO_{(s)}$ | −157.3 | $NaOH_{(s)}$ | −425.6 | $SnCl_{2(s)}$ | −325.1 |
| $CuCl_{(s)}$ | −137.2 | $Na_2CO_{3(s)}$ | −1130.7 | $SnCl_{4(\ell)}$ | −511.3 |
| $CuCl_{2(s)}$ | −220.1 | | | | |

**Note:** The enthalpy of formation of an element in its standard state is defined as zero.

**15.** Mixing household cleansers can result in the production of hydrogen chloride gas, $HCl_{(g)}$. Not only is this gas dangerous in its own right, but it also reacts with oxygen to form chlorine gas and water vapour.

$4HCl_{(g)} + O_{2(g)} \rightarrow 2Cl_{2(g)} + 2H_2O_{(g)}$

Determine the enthalpy change of this reaction, given the following equations.

**(1)** $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)} \quad \Delta H^\circ = -185 \text{ kJ}$

**(2)** $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} \quad \Delta H^\circ = -285.8 \text{ kJ}$

**(3)** $H_2O_{(g)} \rightarrow H_2O_{(\ell)} \quad \Delta H^\circ = -40.7 \text{ kJ}$

**16.** Calculate the enthalpy change of the following reaction between nitrogen gas and oxygen gas, given thermochemical equations (1), (2), and (3).

$2N_{2(g)} + 5O_{2(g)} \rightarrow 2N_2O_{5(g)}$

**(1)** $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)} \quad \Delta H^\circ = -572 \text{ kJ}$

**(2)** $N_2O_{5(g)} + H_2O_{(\ell)} \rightarrow 2HNO_{3(\ell)} \quad \Delta H^\circ = -77 \text{ kJ}$

**(3)** $\frac{1}{2}N_{2(g)} + \frac{3}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} \rightarrow HNO_{3(\ell)} \quad \Delta H^\circ = -174 \text{ kJ}$

## Practice Problems

**17.** Write a thermochemical equation for the formation of each substance. Be sure to include the physical state of all the elements and compounds in the equation. You can find the standard enthalpy of formation of each substance in Appendix E.

**(a)** $CH_4$ **(b)** NaCl **(c)** MgO **(d)** $CaCO_3$

**20.** Solid phosphorus is found in two forms: white phosphorus ($P_4$) and red phosphorus (P). White phosphorus is the standard state.

**(a)** The enthalpy of formation of red phosphorus is –17.6 kJ/mol. Write a thermochemical equation for the formation of red phosphorus.

**(b)** 32.6 g of white phosphorus reacts to form red phosphorus. What is the enthalpy change?

**5** I The standard molar enthalpy of formation of calcium carbonate is –1207.6 kJ/mol. Calculate the enthalpy of formation of calcium oxide, given the following equation.

$CaO_{(g)} + CO_{2(g)} \rightarrow CaCO_{3(s)} \quad \Delta H^\circ = -178.1 \text{ kJ}$