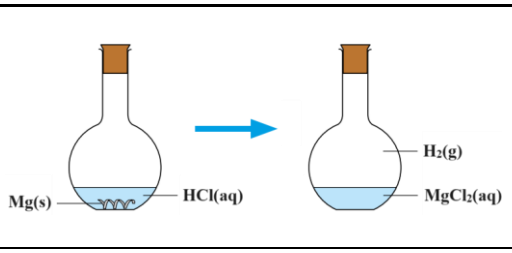
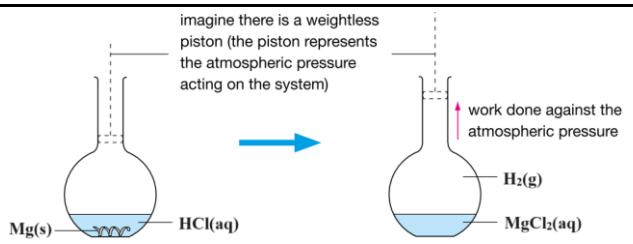
Intensive note (Topic 8: Chemical reactions and energy)

Enthalpy change

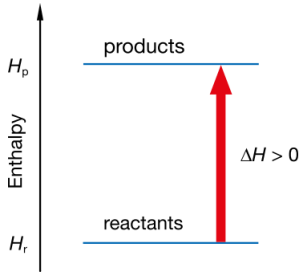
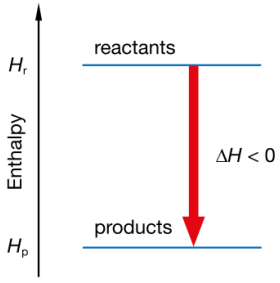
At constant volume		At constant pressure			
					
Heat change (q) = Internal energy change (ΔU)		Enthalpy change (ΔH) = Heat change (q) = Internal energy change (ΔU) + work done on surrounding (w)			
ΔU = –433.8 kJ	q = –433.8 kJ	ΔH = –430.8 kJ	q = –430.8 kJ	ΔU = –433.8 kJ	w = +3 kJ

For reactions that does not involve change in numbers of moles of gas [e.g. $N_2(g) + O_2(g)$ ➔ $2NO(g)$]:

Work done on surrounding (w) = 0 $\Delta H = q = \Delta U + w = \Delta U$ (as w = 0)

Enthalpy change is almost the same as internal energy change.

Endothermic and exothermic reaction

Endothermic reaction	Exothermic reaction
- Heat is absorbed from the surroundings to the system - Temperature of the reaction mixture decreases - $\Delta H = H_p - H_r > 0$ $(H_p > H_r)$ - Reactants are more energetically stable (As reactants have a lower energy content)	- Heat is given out from the system to the surroundings - Temperature of the reaction mixture increases - $\Delta H = H_p - H_r < 0$ $(H_r > H_p)$ - Products are more energetically stable (As products have a lower energy content)
	
*Examples: Thermal decomposition of $CaCO_3$ / Ag_2O etc, cracking, ionization of weak acids / alkalis, evaporation, melting, sublimation	*Examples: Combustion, neutralization, Precipitation, displacement, diluting concentrated acids / alkalis, condensation, freezing, deposition
For endothermic reactions, energy absorbed in breaking bonds in reactants is greater than the energy released in forming bonds in products (if any)	For exothermic reactions, energy absorbed in breaking bonds in reactants (if any) is smaller than the energy released in forming bonds in products

*Enthalpy change of formation and dissolving salts can be either endothermic or exothermic

Standard enthalpy change of combustion

Standard enthalpy change of reaction is the enthalpy change when the numbers of moles of reactants specified in the thermochemical equation react completely under standard conditions.

Standard conditions:
1. Temperature at 298 K
2. Pressure at 1 atm
3. Substances are in their standard states (the most stable form of a substance at 298 K and 1 atm)

Standard enthalpy change of combustion

Standard enthalpy change of combustion is the enthalpy change when 1 mole of substance is burnt in air completely under standard conditions.

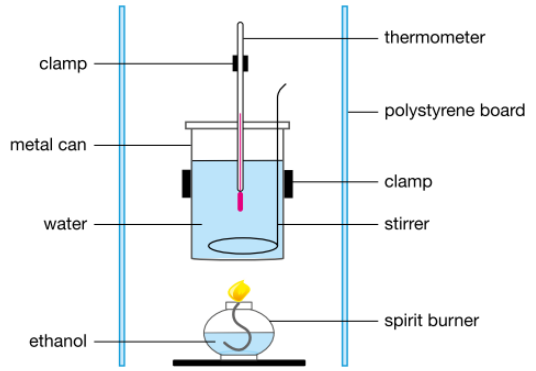
Example: Standard enthalpy change of combustion of hexane.

Thermochemical equation: $C_6H_{14}(l) + 19/2\ O_2(g) \rightarrow 6\ CO_2(g) + 7\ H_2O(l)$ $\Delta H_c^{\ominus} = -4163\ kJ\ mol^{-1}$

Determining enthalpy change of combustion from experiment using simple calorimetric methods

Example 1

In an experiment, the combustion of 0.46 g of ethanol (molecular mass = 46.0) increased the temperature of 200.0 g of water by 8.5 °C in a calorimeter. Calculate the enthalpy change of combustion of ethanol, in kJ mol^{-1}, under these experimental conditions. (Assume the heat capacity of the metal can is negligible and the specific heat capacity of water is 4.20 J g^{-1} K^{-1}.)



$$\Delta H = -\frac{(m)(c)(\Delta T)}{(\text{mol of fuel burnt})}$$

Heat released = (m)(c)(ΔT)

= (200)(4.2)(8.5) = 7140 J

Mole of ethanol used = (Mass of ethanol) / (Molar mass of ethanol)

= 0.46 / 46 = 0.01

Enthalpy change of combustion

= – [(7140) / (0.01)] = –714000 J mol^{-1} = –714 kJ mol^{-1}

Sources of error in the above experiment.

1. Heat loss to surrounding
2. Incomplete combustion of fuel
3. Heat capacities of metal can were neglected
4. Fuel may vaporize without being burnt

Example 2

When 5 g of ethanol (molecular mass = 46.0) are burnt in a calorimeter, the temperature rise of the calorimeter is 10.2 °C. Using the same calorimeter and experimental conditions, burning 4 g of butanone (molecular mass = 72.0) gives a temperature rise of 8.9 °C. Given that the standard enthalpy change of combustion of ethanol is -1367 kJ mol^{-1}. Calculate the standard enthalpy change of combustion of butanone.

$\Delta H = -\frac{(C)(\Delta T)}{(\text{mol of fuel burnt})}$	**From the combustion of ethanol:**	**From the combustion of butanone:**
	$-1367 = -\frac{(C)(10.2)}{\frac{5}{46}}$	$\Delta H = -\frac{(C)(8.9)}{\frac{4}{72}}$
$\Delta H = -2334\ kJ\ mol^{-1}$		

Standard enthalpy change of neutralization

Standard enthalpy change of neutralization is the enthalpy change when one mole of water is produced from the neutralization between an acid and an alkali under standard conditions.

Example: Standard enthalpy change of neutralization between NaOH(aq) and H_2SO_4(aq)

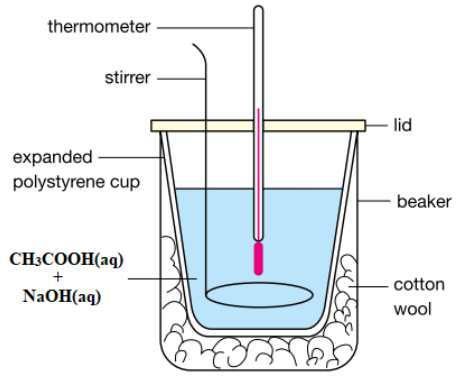
Thermochemical equation: $NaOH(aq) + 1/2\ H_2SO_4(aq) \rightarrow 1/2\ Na_2SO_4(aq) + H_2O(l)$ $\Delta H_n^{\ominus} = -57.3$ kJ mol^{-1}

Determining enthalpy change of neutralization from experiment using simple calorimetric methods

Example 1

In an experiment, 50.0 cm^3 of 2.0 M CH_3COOH(aq) and 50.0 cm^3 of 2.0 M NaOH(aq) are mixed in a simple calorimeter. The maximum temperature rise of the reaction mixture was 11.8 °C. Calculate the enthalpy change of neutralization between CH_3COOH(aq) and NaOH(aq), in kJ mol^{-1}, under these experimental conditions.

(Density of the reaction mixture = 1.0 g cm^{-3}; specific heat capacity of the reaction mixture = 4.20 J g^{-1} K^{-1})



$$\Delta H = -\frac{(m)(c)(\Delta T)}{(\text{mol of water formed})}$$

Heat released = (m)(c)(ΔT)

= [(50 + 50)(1.0)](4.2)(11.8) = 4956 J

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Mole of water formed = mol of CH_3COOH(aq) (or mol of NaOH(aq))

= (50/1000) x (2.0) = 0.1

Enthalpy change of neutralization

= –[(4956) / (0.1)] = –49560 J mol^{-1} = –49.56 kJ mol^{-1}

The enthalpy change of neutralization between CH_3COOH(aq) and NaOH(aq) (–49.56 kJ mol^{-1}) is lower than that between H_2SO_4(aq) and NaOH(aq). It is because CH_3COOH is a weak acid. Heat is absorbed for the ionization of weak acid

Sources of error in the above experiment.

1. Heat loss to surrounding
2. Specific heat capacity of the mixture was not same as that of water
3. Heat capacity of polystyrene was neglected
4. Density of the mixture was not the same as that of water

Example 2

In an experiment, 60.0 cm^3 of 0.5 M H_2SO_4(aq) and 40.0 cm^3 of 2.0 M KOH(aq) are mixed in a simple calorimeter. The maximum temperature rise of the reaction mixture was 8.1 °C. Calculate the enthalpy change of neutralization between H_2SO_4(aq) and KOH(aq), in kJ mol^{-1}, under these experimental conditions.

(Density of the reaction mixture = 1.0 g cm^{-3}; specific heat capacity of the reaction mixture = 4.20 J g^{-1} K^{-1})

Answer: **Heat released** = [(60 + 40)(1)](4.2)(8.1) = 3402 J

$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

Mol of KOH = (40/1000)(2.0) = 0.08. 0.08 mol of KOH requires 0.08 x 1/2 = 0.04 mol H_2SO_4 for complete reaction.

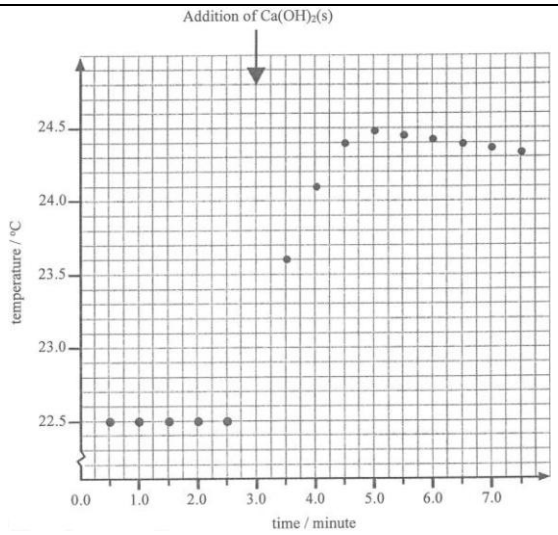
Mole of H_2SO_4 = (60/1000)(0.5) = 0.03 < 0.04. H_2SO_4 is the limiting reagent.

Mole of H_2O formed = mole of H_2SO_4 x 2 = 0.03 x 2 = 0.06

Enthalpy change of neutralization = –[(3402) / (0.06)] = –56700 J mol^{-1} = –56.7 kJ mol^{-1}

Example 3

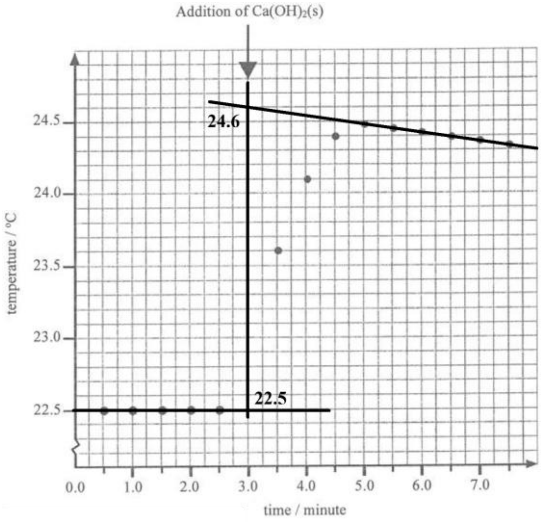
In an experiment, 100 cm^3 of 1.0 M HCl(aq) (in excess) was placed in an expanded polystyrene cup. The temperature of the contents in the cup was measured at half-minute intervals. Right at the third minute, 0.502 g of $Ca(OH)_2(s)$ was added to the cup with thorough stirring. The recordings of temperature are shown in the graph below:



Calculate the enthalpy change of neutralization between $Ca(OH)_2(s)$ and HCl(aq) under the experimental conditions.

(Molar mass of $Ca(OH)_2$ = 74.1 g; specific heat capacity of the mixture = 4.2 J g^{-1} K^{-1}; volume of the mixture = 100.0 cm^3; density of the mixture = 1.00 g cm^{-3})

Answer



Heat released = (100)(1)(4.2)(24.6 – 22.5) = 882 J

$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

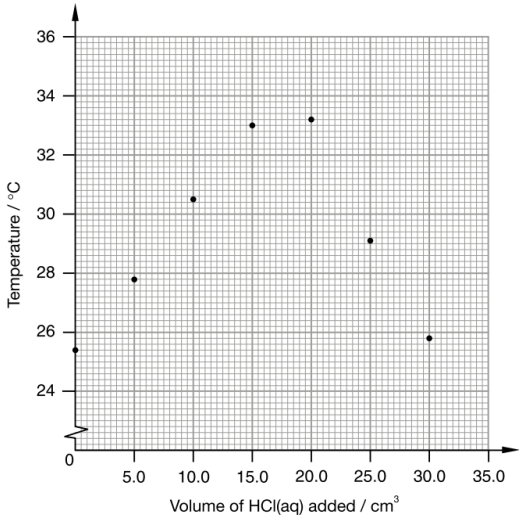
^nH_2O formed = $^nCa(OH)_2$ x 2 = 0.502/74.1 x 2 = 0.01355

Enthalpy change of neutralization

= –(882)/(0.01355) = –65100 J mol^{-1} = –65.1 kJ mol^{-1}

Example 4

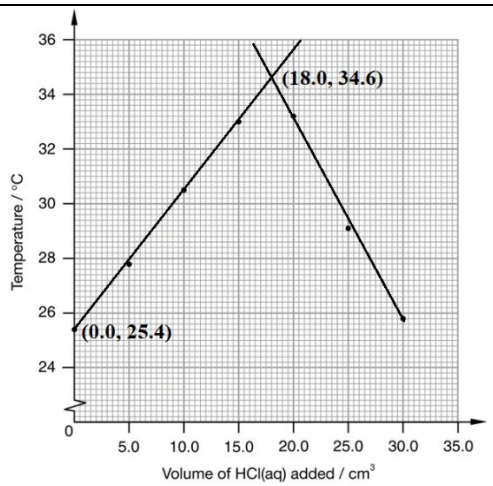
20.0 cm^3 of 1.50 M NaOH(aq) was placed in an expanded polystyrene cup and its temperature was measured. Portions of 5.00 cm^3 of HCl(aq) were then added to the alkali from a burette. The mixture was stirred and the temperature of the mixture was measured after each addition. The results obtained were plotted on a graph as shown below.



Calculate the enthalpy change of neutralization between NaOH(aq) and HCl(aq).

(Density of the mixture = 1.0 g cm^{-3}; specific heat capacity of the mixture = 4.20 J g^{-1} K^{-1})

Answer



Heat released = [(20 + 18)(1)](4.2)(34.6 – 25.4) = 1468 J

$NaOH + HCl \rightarrow NaCl + H_2O$

^nH_2O formed = ^nNaOH = (20/1000)(1.5) = 0.03

Enthalpy change of neutralization

= –(1468)/(0.03) = –48900 J mol^{-1} = –48.9 kJ mol^{-1}

Standard enthalpy change of formation

Standard enthalpy change of formation is the enthalpy change when one mole of the substance forms from its constituent elements in their standard states under standard conditions.

Example: Standard enthalpy change of formation of ammonium hydrogencarbonate, $NH_4HCO_3(s)$

Thermochemical equation: $1/2\ N_2(g) + 5/2\ H_2(g) + C(graphite) + 3/2\ O_2(g) \rightarrow NH_4HCO_3(s)$ $\Delta H_f^{\ominus} = -849.4\ kJ\ mol^{-1}$

- Standard enthalpy changes of formation of elements in their standard states are zero.

Formation of graphite:

$C(graphite) \rightarrow C(graphite)$ $\Delta H_f^{\ominus} = 0\ kJ\ mol^{-1}$

Formation of diamond:

$C(graphite) \rightarrow C(diamond)$ $\Delta H_f^{\ominus} = +1.9\ kJ\ mol^{-1}$

- In most cases, it is difficult or impossible to determine the standard enthalpy changes of formation of the compounds
  1. The constituent elements do not react to give the desired compound under standard conditions
  2. The constituent elements do not react to give the desired compound only (i.e. side products are produced).
  3. Some reactions proceed too slowly under standard conditions.
  4. Some reactions are highly exothermic and so the experiments cannot be carried out safely.
- The enthalpy change of formation of $H_2O(l)$ is equivalent to the enthalpy change of combustion of $H_2(g)$

$$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$$

- The enthalpy change of formation of $CO_2(g)$ is equivalent to the enthalpy change of combustion of C(graphite)

$$C(graphite) + O_2(g) \rightarrow CO_2(g)$$

Hess's Law

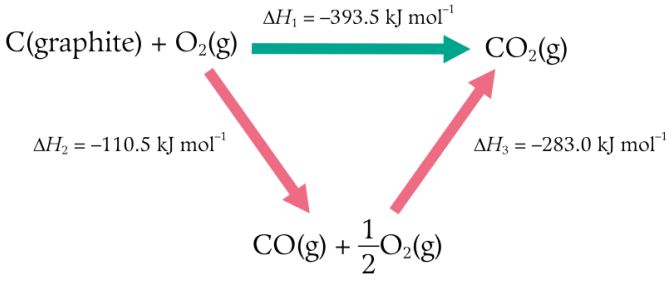
Hess's Law states that the total enthalpy change of a chemical reaction depends on the initial and final states of the reaction, but is independent of the route taken.

Example

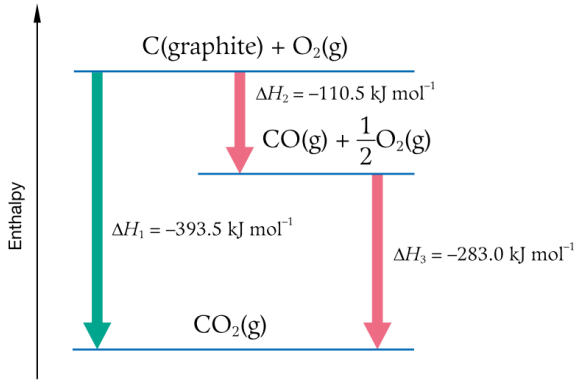
$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_1 = -393.5\ kJ\ mol^{-1}$

$C(graphite) + 1/2\ O_2(g) \rightarrow CO(g)$ $\Delta H_2 = -110.5\ kJ\ mol^{-1}$

$CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$ $\Delta H_3 = -283.5\ kJ\ mol^{-1}$



Enthalpy change cycle



Enthalpy level diagram

By Hess's Law:

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

ΔH = [Sum of enthalpy changes of formation of products] – [Sum of enthalpy changes of formation of reactants]

$\Delta H = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$	For **n** thermochemical equations, if **(n – 1)** of them are enthalpy change of **formation**, this equation can be used.

Example 1

It is given that:

Standard enthalpy change of formation of CO(g)	$\Delta H_f^\ominus[CO(g)] = -110.5$ kJ mol^{-1}
Standard enthalpy change of formation of NO(g)	$\Delta H_f^\ominus[NO(g)] = +91.3$ kJ mol^{-1}
Standard enthalpy change of formation of $CO_2(g)$	$\Delta H_f^\ominus[CO_2(g)] = -393.5$ kJ mol^{-1}
$2\ CO(g) + 2\ NO(g) \rightarrow 2\ CO_2(g) + N_2(g)$	$\Delta H^\ominus$

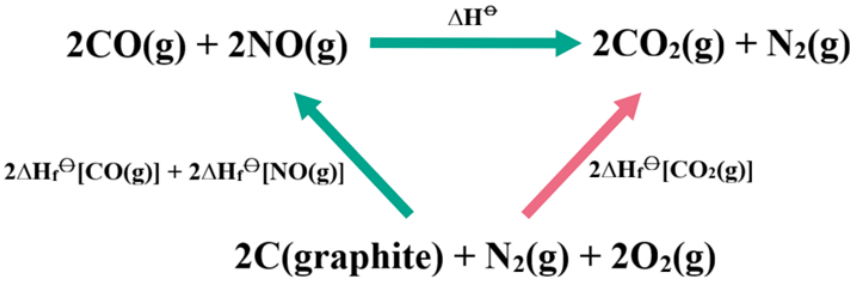
Calculate the value of $\Delta H^\ominus$

Answer: By applying Hess's Law

$$\Delta H^\ominus = [2(\Delta H_f^\ominus[CO_2(g)]) + (\Delta H_f^\ominus[N_2(g)])] - [2(\Delta H_f^\ominus[CO(g)]) + 2(\Delta H_f^\ominus[NO(g)])]$$

$$\Delta H^\ominus = [2(-393.5) + (0)] - [2(-110.5) + 2(+91.3)]$$

$$\Delta H^\ominus = -748.6 \text{ kJ mol}^{-1}$$



Example 2

It is given that:

$4\ NH_3(g) + 7\ O_2(g) \rightarrow 4\ NO_2(g) + 6\ H_2O(l)$	$\Delta H^\ominus = -1394.4$ kJ mol^{-1}
Standard enthalpy change of formation of $NH_3(g)$	$\Delta H_f^\ominus[NH_3(g)] = -45.9$ kJ mol^{-1}
Standard enthalpy change of formation of $H_2O(l)$	$\Delta H_f^\ominus[H_2O(l)] = -285.8$ kJ mol^{-1}
Standard enthalpy change of formation of $NO_2(g)$	$\Delta H_f^\ominus[NO_2(g)]$

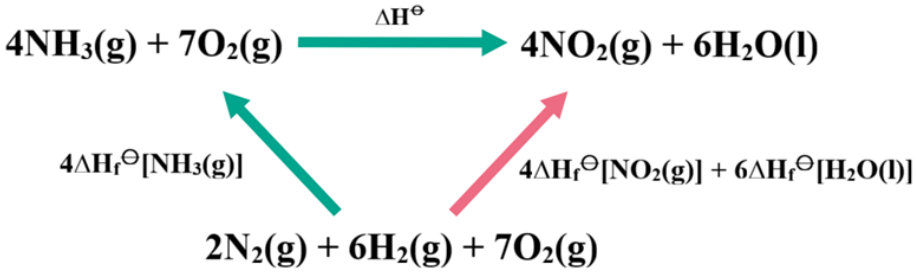
Calculate the value of $\Delta H_f^\ominus[NO_2(g)]$

Answer: By applying Hess's Law

$$\Delta H^\ominus = [4(\Delta H_f^\ominus[NO_2(g)]) + 6(\Delta H_f^\ominus[H_2O(l)])] - [4(\Delta H_f^\ominus[NH_3(g)]) + 7(\Delta H_f^\ominus[O_2(g)])]$$

$$-1394.4 = [4(\Delta H_f^\ominus[NO_2(g)]) + 6(-285.8)] - [4(-45.9) + 7(0)]$$

$$\Delta H_f^\ominus[NO_2(g)] = +34.2 \text{ kJ mol}^{-1}$$



ΔH = [Sum of enthalpy changes of formation of products] – [Sum of enthalpy changes of formation of reactants]

$\Delta H = \sum \Delta H_c(\text{Reactants}) - \sum \Delta H_c(\text{Products})$	For **n** thermochemical equations, if **(n – 1)** of them are enthalpy change of **combustion**, this equation can be used.

Example 1

It is given that:

Standard enthalpy change of combustion of $C_2H_2(g)$	$\Delta H_c^\ominus[C_2H_2(g)] = -1301.1$ kJ mol^{-1}
Standard enthalpy change of combustion of $H_2(g)$	$\Delta H_c^\ominus[H_2(g)] = -285.8$ kJ mol^{-1}
Standard enthalpy change of combustion of $C_2H_6(g)$	$\Delta H_c^\ominus[C_2H_6(g)] = -1560.7$ kJ mol^{-1}
$C_2H_2(g) + 2\ H_2(g) \rightarrow C_2H_6(g)$	$\Delta H^\ominus$

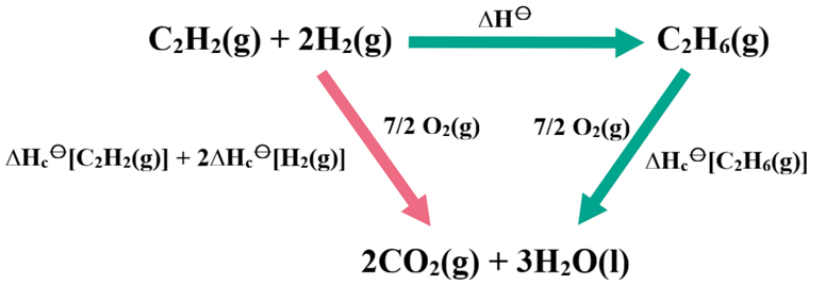
Calculate the value of $\Delta H^\ominus$

Answer: By applying Hess's Law

$$\Delta H^\ominus = [(\Delta H_c^\ominus[C_2H_2(g)]) + 2(\Delta H_c^\ominus[H_2(g)])] - [\Delta H_c^\ominus[C_2H_6(g)]]$$

$$\Delta H^\ominus = [(-1301.1) + 2(-285.8)] - [-1560.7]$$

$$\Delta H^\ominus = -312 \text{ kJ mol}^{-1}$$



Example 2

It is given that:

$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(l)$	$\Delta H^\ominus = -128.5$ kJ mol^{-1}
Standard enthalpy change of combustion of $CO(g)$	$\Delta H_c^\ominus[CO(g)] = -283.0$ kJ mol^{-1}
Standard enthalpy change of combustion of $H_2(g)$	$\Delta H_c^\ominus[H_2(g)] = -285.8$ kJ mol^{-1}
Standard enthalpy change of combustion of $CH_3OH(l)$	$\Delta H_c^\ominus[CH_3OH(l)]$

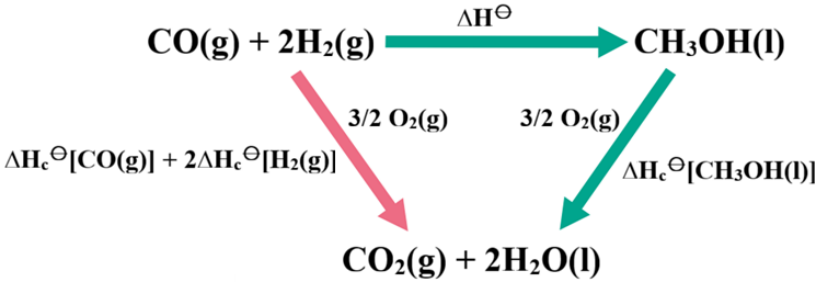
Calculate the value of $\Delta H_c^\ominus[CH_3OH(l)]$

Answer: By applying Hess's Law

$$\Delta H^\ominus = [(\Delta H_c^\ominus[CO(g)]) + 2(\Delta H_c^\ominus[H_2(g)])] - [\Delta H_c^\ominus[CH_3OH(l)]]$$

$$-128.5 = [(-283.0) + 2(-285.8)] - [\Delta H_c^\ominus[CH_3OH(l)]]$$

$$\Delta H_c^\ominus[CH_3OH(l)] = -726.1 \text{ kJ mol}^{-1}$$



Calculation of enthalpy change by algebraic method

Example 1

Based on the thermochemical equations given below, calculate ΔH_4.

$Fe(s) + CO_2(g) \rightarrow FeO(s) + CO(g)$	$\Delta H_1 = +11.0$ kJ mol^{-1}
$3\ Fe_2O_3(s) + CO(g) \rightarrow 2\ Fe_3O_4(s) + CO_2(g)$	$\Delta H_2 = -47.2$ kJ mol^{-1}
$Fe_3O_4(s) + CO(g) \rightarrow 3\ FeO(s) + CO_2(g)$	$\Delta H_3 = +19.4$ kJ mol^{-1}
$Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$	ΔH_4

Step 1: Identify the species that:

1. Occur ONCE in the target reaction (i.e. ONCE in ΔH_4)
2. Occur ONCE in the other thermochemical equations (i.e. ONCE in ΔH_1, ΔH_2 and ΔH_3)

$$Fe(s) + CO_2(g) \rightarrow FeO(s) + CO(g)$$
$$3\ Fe_2O_3(s) + CO(g) \rightarrow 2\ Fe_3O_4(s) + CO_2(g)$$
$$Fe_3O_4(s) + CO(g) \rightarrow 3\ FeO(s) + CO_2(g)$$
Target reaction: $Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

Step 2: Check the species identified in step 1:

1. Position (reactant vs product)
2. Mole ratio

There is **2 Fe(s)** in the **product side** in the target reaction while there is **1 Fe(s)** in the **reactant side** in ΔH_1

➔ ΔH_1 should multiply by (2) and (–1)

There is **1 Fe_2O_3(s)** in the **reactant side** in the target reaction while there is **3 Fe_2O_3(s)** in the **reactant side** in ΔH_2

➔ ΔH_2 should multiply by (1/3)

	Reactant	**Product**
$(2)(-1)(\Delta H_1)$	$2\ FeO(s) + 2\ CO(g)$	$2\ Fe(s) + 2\ CO_2(g)$
$(1/3)(\Delta H_2)$	$Fe_2O_3(s) + 1/3\ CO(g)$	$2/3\ Fe_3O_4(s) + 1/3\ CO_2(g)$
Summation 1	$2\ FeO(s) + 2\ CO(g) + Fe_2O_3(s) + 1/3\ CO(g)$ $= \boxed{2\ FeO(s)} + 7/3\ CO(g) + Fe_2O_3(s)$	$2\ Fe(s) + 2\ CO_2(g) + 2/3\ Fe_3O_4(s) + 1/3\ CO_2(g)$ $= 2\ Fe(s) + 7/3\ CO_2(g) + \boxed{2/3\ Fe_3O_4(s)}$

Step 3 (if necessary): After adding $[(2)(-1)(\Delta H_1)]$ and $[(1/3)(\Delta H_2)]$, there are unwanted species:

There is **2 unwanted FeO(s)** in the **reactant side** and **2/3 unwanted Fe_3O_4(s)** in the **product side**

➔ **2/3 Fe_3O_4(s)** should be added to the **reactant side** and **2 FeO(s)** should be added to the **reactant side**

These unwanted species can be eliminated by the unused ΔH_3

➔ ΔH_3 should multiply by (2/3)

	Reactant	**Product**
Summation 1	$\boxed{2\ FeO(s)} + 7/3\ CO(g) + Fe_2O_3(s)$	$2\ Fe(s) + 7/3\ CO_2(g) + \boxed{2/3\ Fe_3O_4(s)}$
$(2/3)(\Delta H_3)$	$\boxed{2/3\ Fe_3O_4(s)} + 2/3\ CO(g)$	$\boxed{2\ FeO(s)} + 2/3\ CO_2(g)$
Summation 2	$Fe_2O_3(s) + 3\ CO(g)$	$2\ Fe(s) + 3\ CO_2(g)$

Note that summation 2 should be the same as the target reaction

$\Delta H_4 = (2)(-1)(\Delta H_1) + (1/3)(\Delta H_2) + (2/3)(\Delta H_3)$

$\Delta H_4 = (2)(-1)(+11) + (1/3)(-47.2) + (2/3)(+19.4) = -24.8$ kJ mol^{-1}