



CHAPTER 2

THERMOCHEMISTRY



THERMOCHEMISTRY

SUBTOPIC

CONCEPT OF ENTHALPY

2.1

CALORIMETRY

2.2

HESS' S LAW

2.3

BORN-HABER CYCLE

2.4

A study of heat changes during a chemical reaction.

Almost all chemical reactions is accompanied by absorbing or releasing energy (in the form of heat).



2. 1 CONCEPT OF ENTHALPY

Learning Outcomes :

- a) State standard conditions of reaction. (c1)
- b) Define the following terms: (c1)
 - i. enthalpy
 - ii. standard enthalpy.

STANDARD CONDITIONS OF REACTION

- A standard state for a solid or a liquid is the pure substance in its most stable form at a pressure of 1 atm and temperature at 25 °C.
- Aqueous solution: 1.0 M

ENTHALPY

- The heat content of a system or total energy in the system.

STANDARD ENTHALPY, ΔH°_{rxn}

- Enthalpy change that measured at standard conditions (298 K and 1 atm)

ENTHALPY OF REACTION, ΔH

- Also known as the heat of reaction.
- The difference between the enthalpy of the products and the enthalpy of the reactants of a particular reaction.

$$\Delta H = \sum H_{(products)} - \sum H_{(reactants)}$$

2. 1 CONCEPT OF ENTHALPY

Learning Outcomes :

- c) Define each of the standard enthalpy below: (c1)
 - i. formation
 - ii. combustion
 - iii. neutralisation
 - iv. atomisation
 - v. hydration
 - vi. solution (dissolution)
- d) Write the thermochemical equation for each of the enthalpy in (c) (c3)
- e) Illustrate the energy profile diagram based on the thermochemical equations for (c)(i), (c)(ii) and (c)(iii). (c2, c3, c4)

Thermochemical Equation

A thermochemical equation is a balanced chemical equation that shows the enthalpy changes of a chemical reaction.

The thermochemical equation should be included:

- ☞ the physical state of products and reactants
- ☞ the enthalpy change of a reaction, ΔH_{rxn}

Example: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \quad \Delta H = + 572 \text{ kJ}$

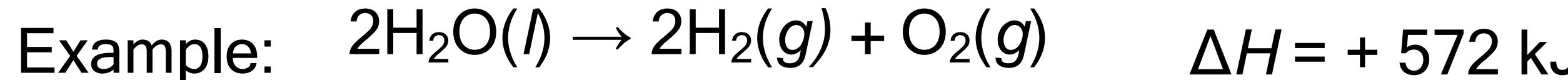
When writing the thermochemical equation, two important aspects of ΔH_{rxn} must be considered :

1 Sign  **positive or negative**



the magnitude of ΔH remains the same but with the opposite sign

2 Magnitude  **stoichiometrical relationship**



Types of Enthalpies

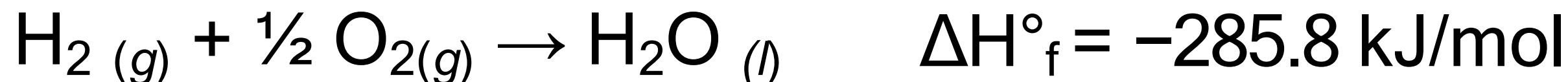
- i. Formation
- ii. Combustion
- iii. Neutralisation
- iv. Atomisation
- v. Hydration
- vi. Solution (dissolution)



Standard Enthalpy of Formation, ΔH°_f

👉 The heat change when 1 mole of a compound is formed from its elements under standard conditions, 1 atm and 298 K.

👉 Example :
the thermochemical equation for the formation of H_2O



 The standard enthalpy of formation of any element in its most stable state form is zero.

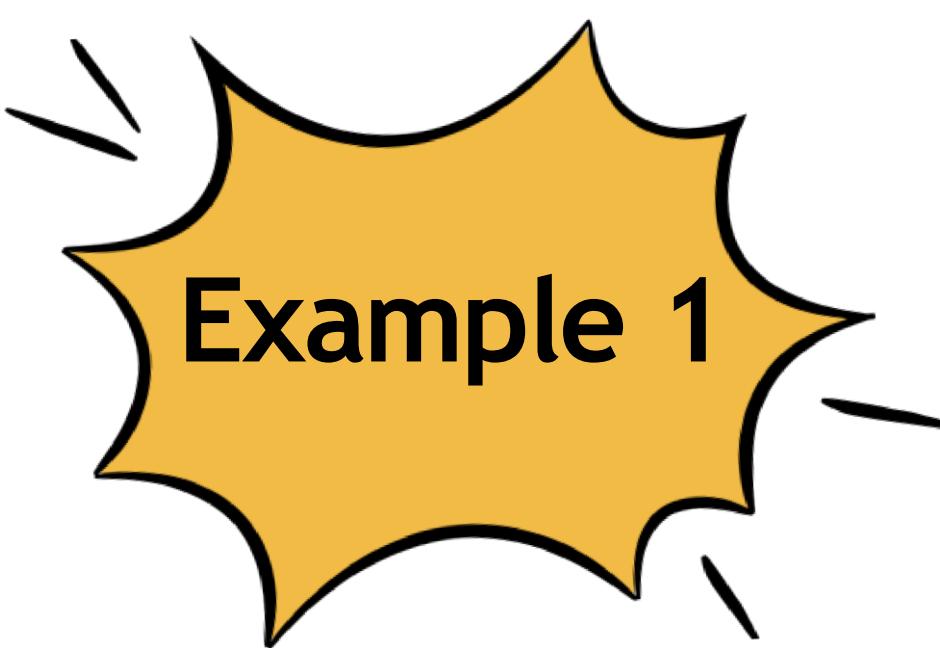
Example : $\Delta H^\circ_f (O_{2(g)}) = 0$

$\Delta H^\circ_f (Br_{2(l)}) = 0$

$\Delta H^\circ_f (Na_{(s)}) = 0$

 Enthalpies of formation can be used to calculate the enthalpy of reaction, ΔH_{rxn} .

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



Example 1

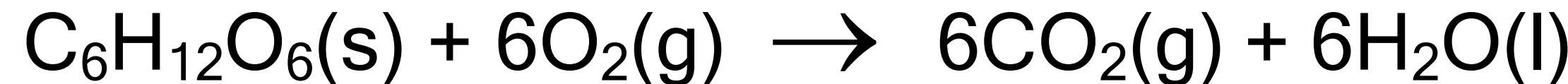
Given:

$$\Delta H_f^0[\text{C}_6\text{H}_{12}\text{O}_6(\text{s})] = -1258 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0[\text{CO}_2(\text{g})] = -392 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0[\text{H}_2\text{O}(\text{l})] = -286 \text{ kJ mol}^{-1}$$

Using the data given above, calculate the enthalpy of the following reaction at standard condition:





Answer

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

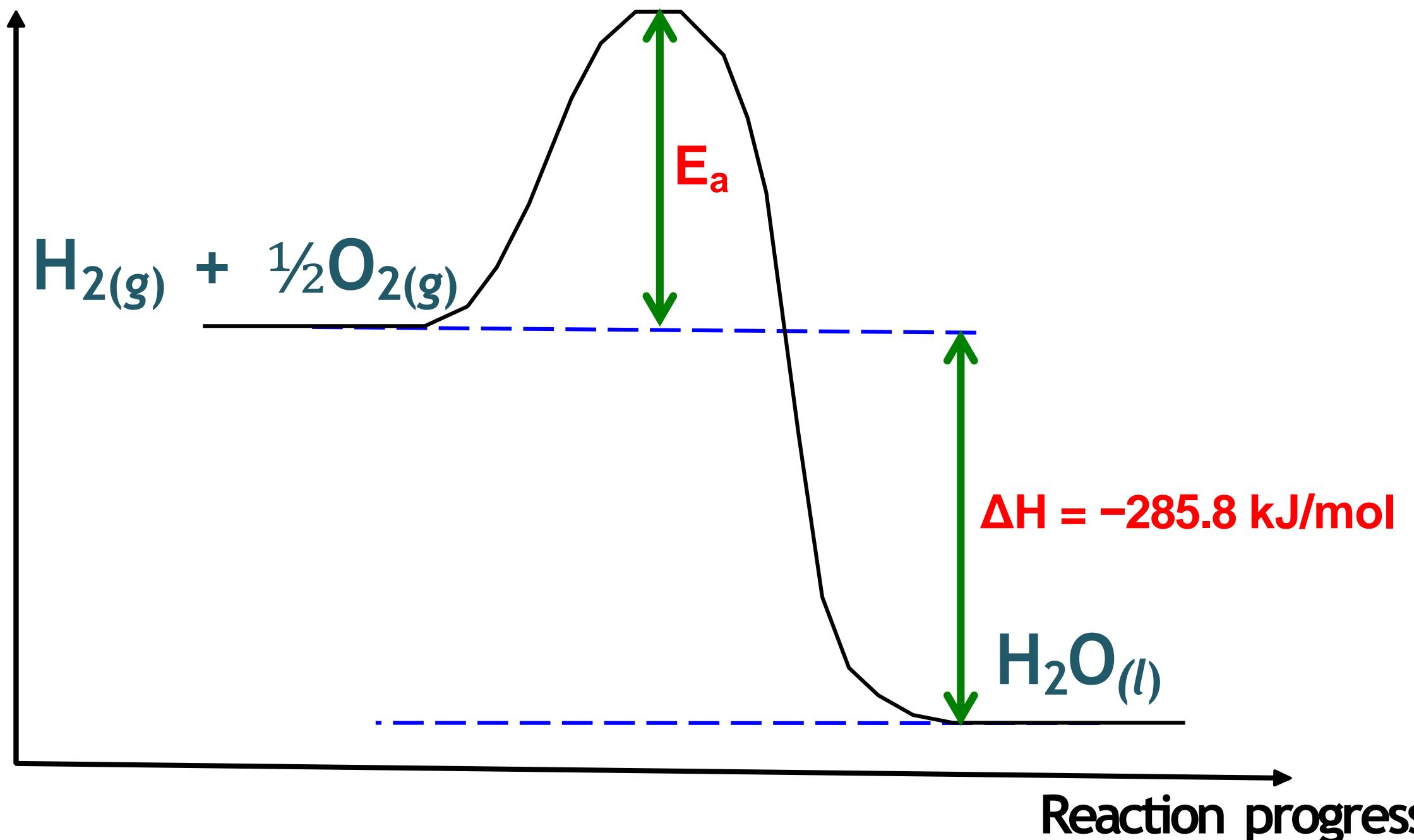
$$\Delta H = [6(-392) + 6(-286)] - (-1258)$$

$$\Delta H = \mathbf{-2810 \text{ kJ}}$$

Energy profile diagram for the enthalpy of formation



Enthalpy



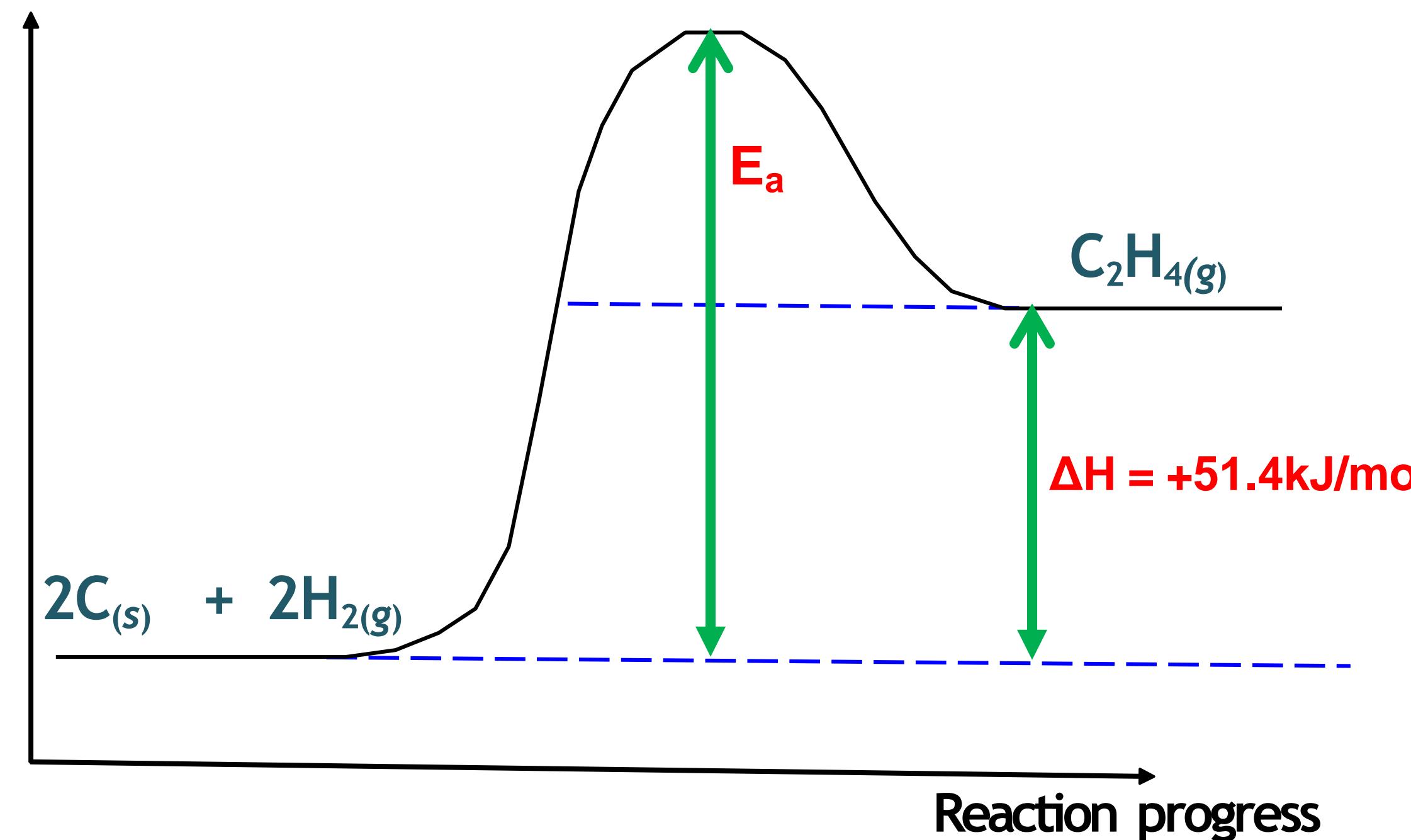
EXOTHERMIC
REACTION

E_a : activation energy
 ΔH : enthalpy change

Energy profile diagram for the enthalpy of formation



Enthalpy



ENDOTHERMIC
REACTION



QUICK TIPS

For endothermic reaction:

- ☞ $\Delta H = \Sigma H_{(products)} - \Sigma H_{(reactants)}$
- ☞ enthalpy of products > enthalpy of reactants
- ☞ $\Delta H = +ve$

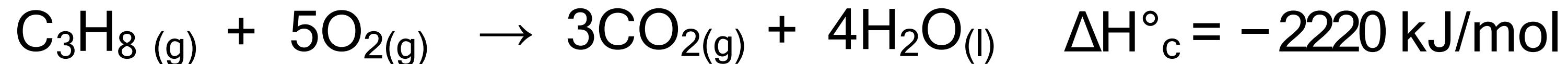
For exothermic reaction:

- ☞ $\Delta H = \Sigma H_{(products)} - \Sigma H_{(reactants)}$
- ☞ enthalpy of products < enthalpy of reactants
- ☞ $\Delta H = -ve$

Standard Enthalpy of Combustion, ΔH°_c

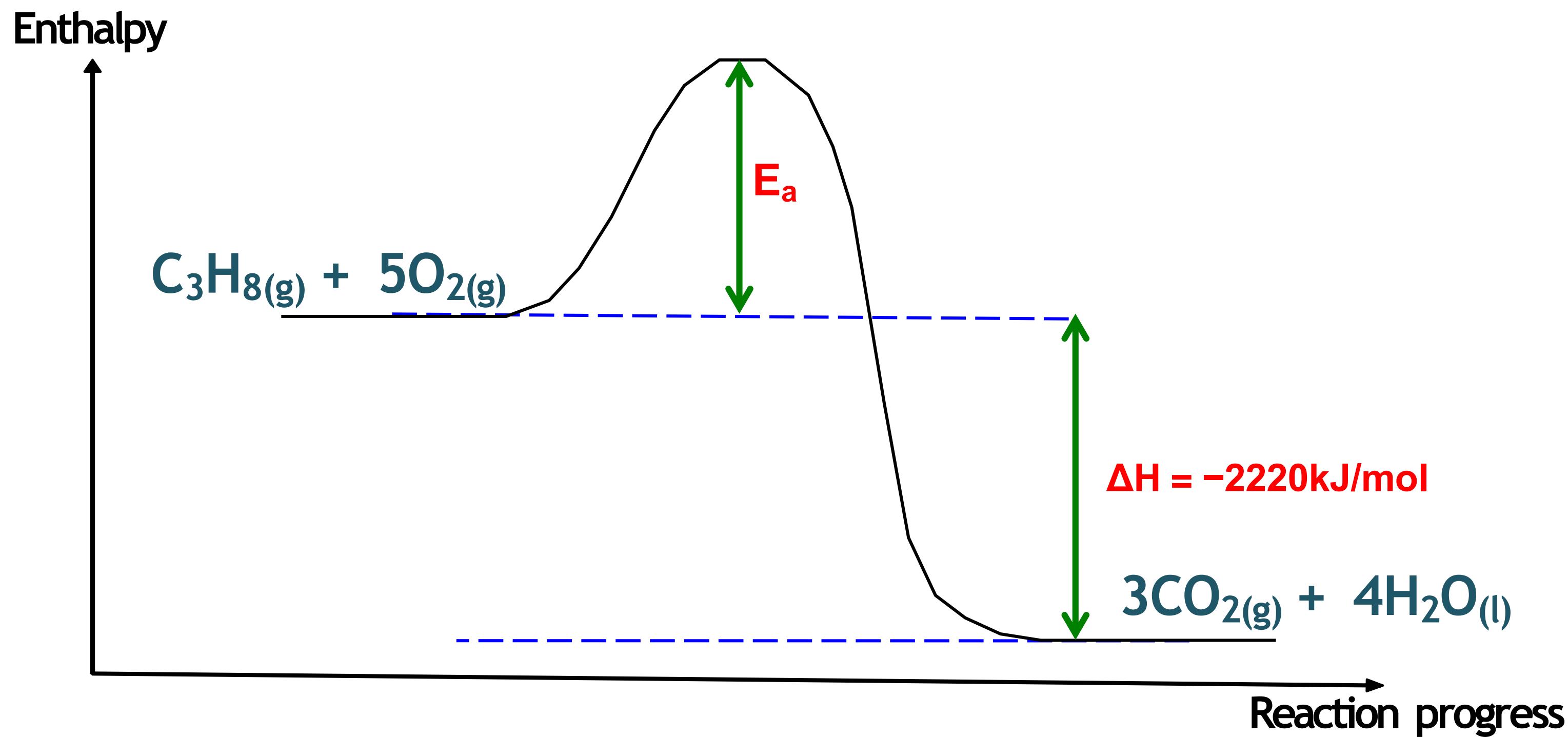
- Heat released when 1 mole of substance is burned completely in excess oxygen under standard conditions, 1 atm and 298 K.
- Example :

the thermochemical equation for the combustion of propane, C₃H₈



Energy profile diagram for the enthalpy of combustion

Example : $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ_c = - 2220 \text{ kJ/mol}$

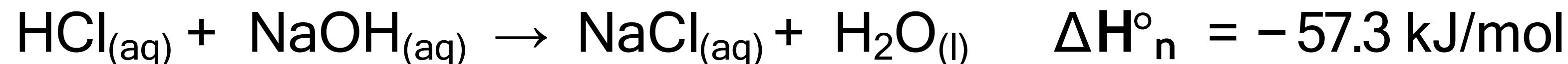


Standard Enthalpy of Neutralisation, ΔH°_n

👉 Heat released when 1 mole of water, H_2O is formed from the neutralization of acid and base under standard conditions, 1 atm and 298 K.

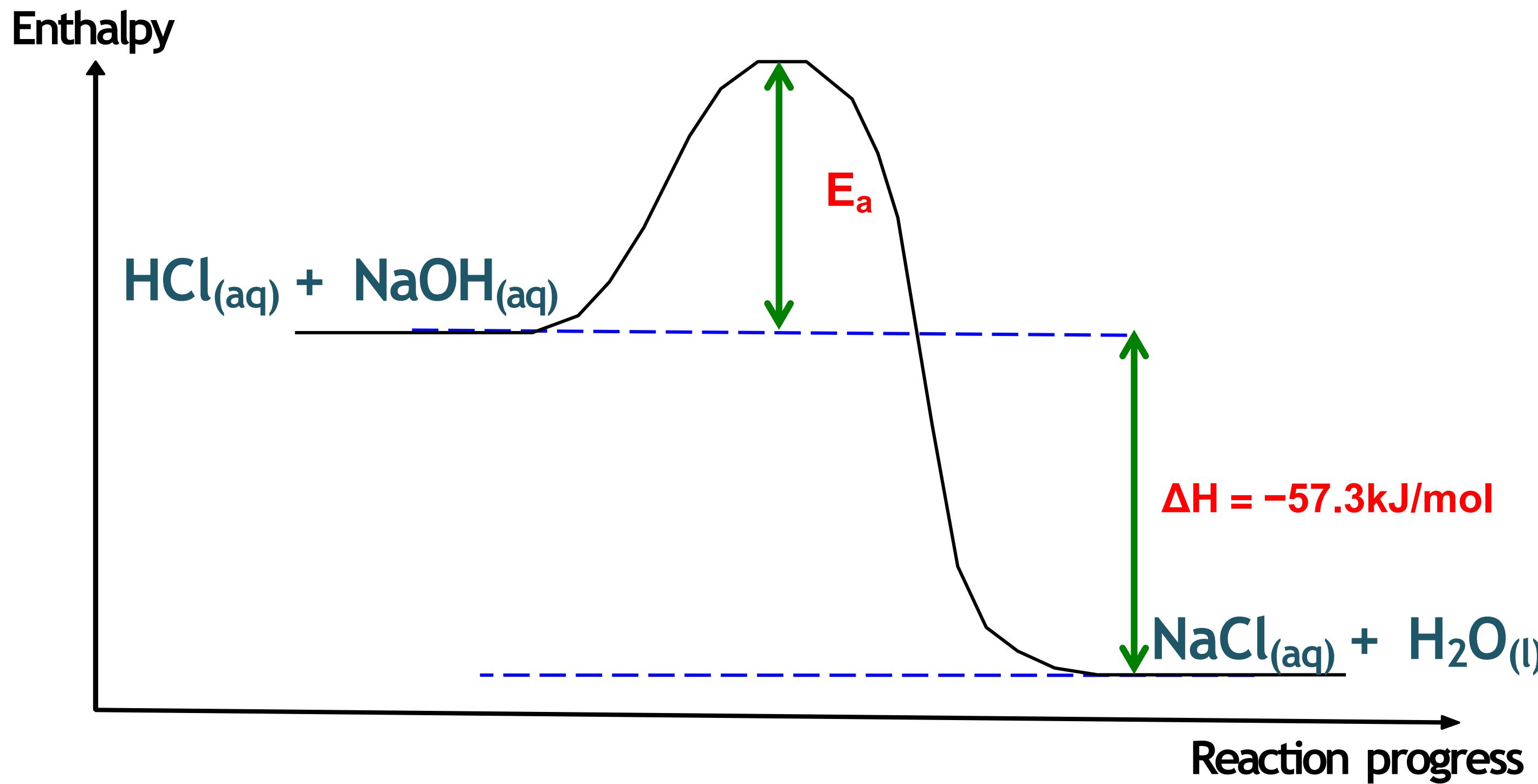
👉 Example :

the thermochemical equation for the neutralization of HCl and $NaOH$



Energy profile diagram for the enthalpy of neutralization

Example : $\text{HCl}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaCl}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$ $\Delta H^\circ_n = - 57.3 \text{ kJ/mol}$



Standard Enthalpy of Atomisation, ΔH_a°

☞ Heat absorbed when 1 mole of gaseous atom is formed from its element under standard conditions, 1 atm and 298 K

☞ Examples :

the thermochemical equation for the atomisation of chlorine



the thermochemical equation for the atomisation of sodium



Standard Enthalpy of Hydration, $\Delta H^\circ_{\text{hyd}}$

- ☞ Heat released when 1 mole of gaseous ion is hydrated in water under standard conditions, 1 atm and 298 K.
- ☞ Examples of thermochemical equation:

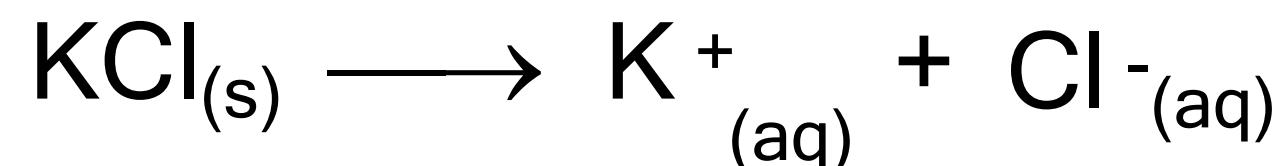


Standard Enthalpy of Solution, $\Delta H^\circ_{\text{soln}}$

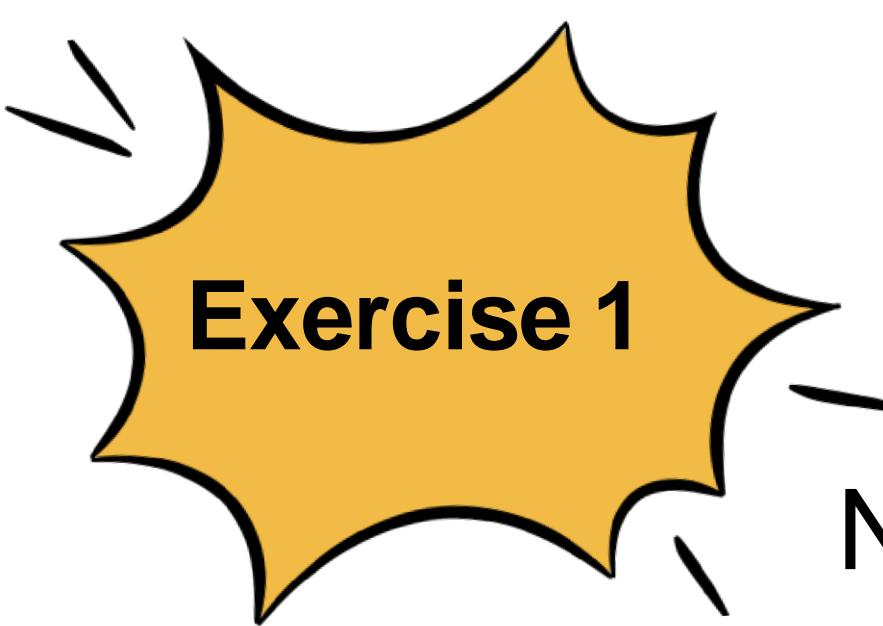
☞ Heat change when 1 mole of a substance is dissolves in excess water to form a very dilute solution under standard conditions, 1 atm and 298 K.

☞ Examples :

the thermochemical equation for the dissolution of KCl

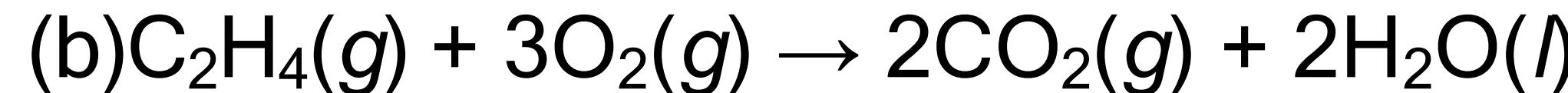
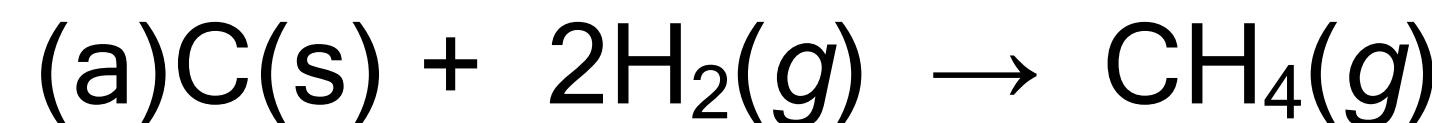


$$\Delta H_{\text{soln}} = + 690 \text{ kJ mol}^{-1}$$

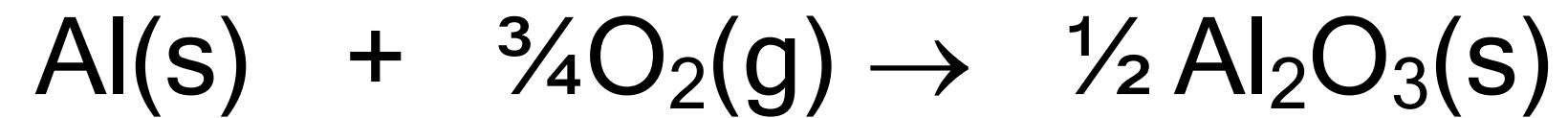
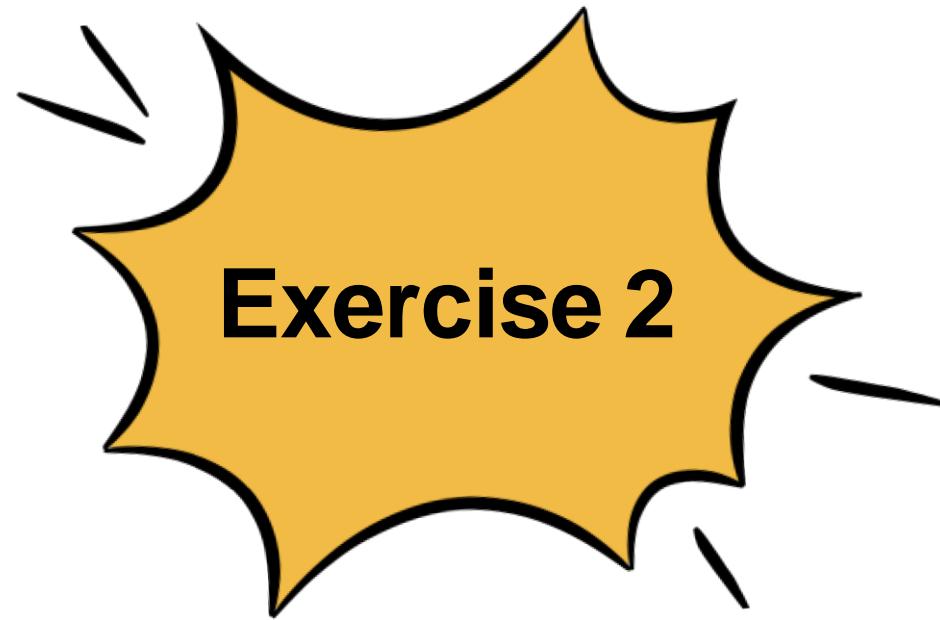


Exercise 1

Name type of enthalpy change for the following reactions.



The combustion of a sample of aluminium produces 0.250 mol of aluminium oxide and releases 419 kJ of heat at standard conditions.



(i) Calculate the standard enthalpy of combustion of aluminium

Ans : - 838 kJ mol⁻¹

(ii) Determine the enthalpy of formation of Al₂O₃ and write its thermochemical equation.

Ans: - 1.68 x10³ kJ mol⁻¹

2. 2 CALORIMETRY

Learning Outcomes

- a) Define (c1)
 - i. heat capacity, C
 - ii. specific heat capacity, c
- b) Calculate the heat change in a constant- volume calorimeter (bomb calorimeter). (c4)
- c) Calculate the heat change in a constant-pressure calorimeter. (c4)

***relate the amount of energy to the stoichiometry of thermochemical equation.*

Important terms in Calorimetry

01

Specific heat capacity, c

☞ the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius.

☞ unit : $\text{Jg}^{-1}\text{C}^{-1}$

$$\text{☞ } c = \frac{q}{m\Delta T} \quad \text{**heat, } q = mc\Delta T$$

02

Heat capacity, C

☞ the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius.

☞ unit : $\text{J}^{\circ}\text{C}^{-1}$

$$\text{☞ } C = \frac{q}{\Delta T} \quad \text{**heat, } q = C\Delta T$$

Example : The specific heat capacity of water is $4.18 \text{ J g}^{-1}\text{K}^{-1}$

☞ We need 4.18 J of heat to increase the temperature of 1 gram of water by 1 K



☞ Heat is a form of energy which flows from a high temperature object to a lower temperature object when they two are placed in thermal contact

☞ The heat released is equal to the heat absorbed

$$-q_{\text{released}} = q_{\text{absorbed}}$$

☞ the quantity of heat absorbed by an object is proportional to its temperature change, ΔT

$$q \propto \Delta T$$

$$q = C \Delta T$$

**C is heat capacity of a substance

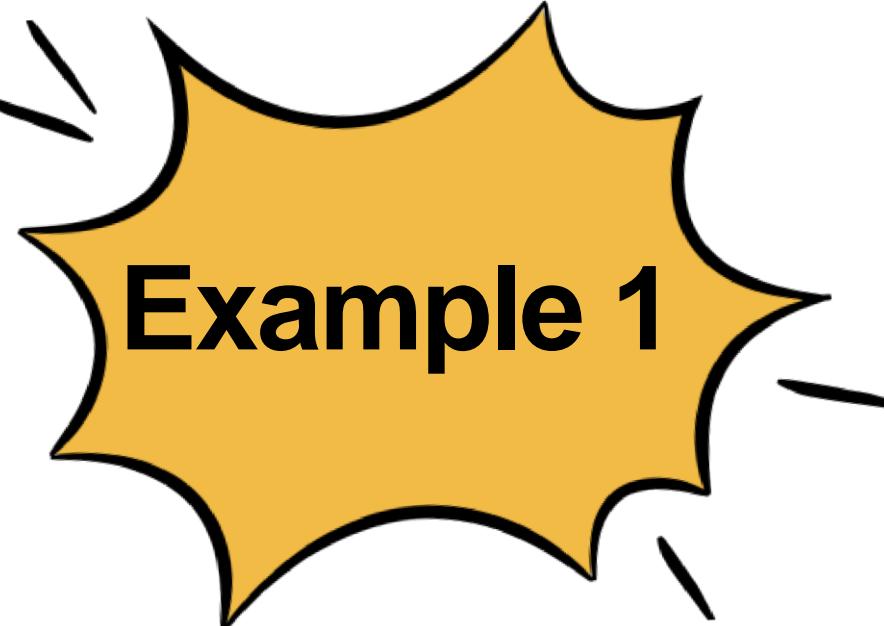
**every object has its own capacity for absorbing heat

 The equation for calculating the heat change, q is given by:

$$q = mc\Delta T \quad @ \quad q = C\Delta T$$

Where;

- q = heat released/absorbed by substance (J)
- m = mass of substance (g)
- c = specific heat capacity ($Jg^{-1}^{\circ}C^{-1}$)
- C = heat capacity ($J^{\circ}C^{-1}$)
- ΔT = temperature change , $T_{final} - T_{initial}$ ($^{\circ}C$)



Example 1

Calculate the amount of heat needed to increase the temperature of 250.0 g of water from 20.0 °C to 56.0 °C.

(specific heat capacity of water = $4.18 \text{ J g}^{-1}\text{K}^{-1}$)

Answer:

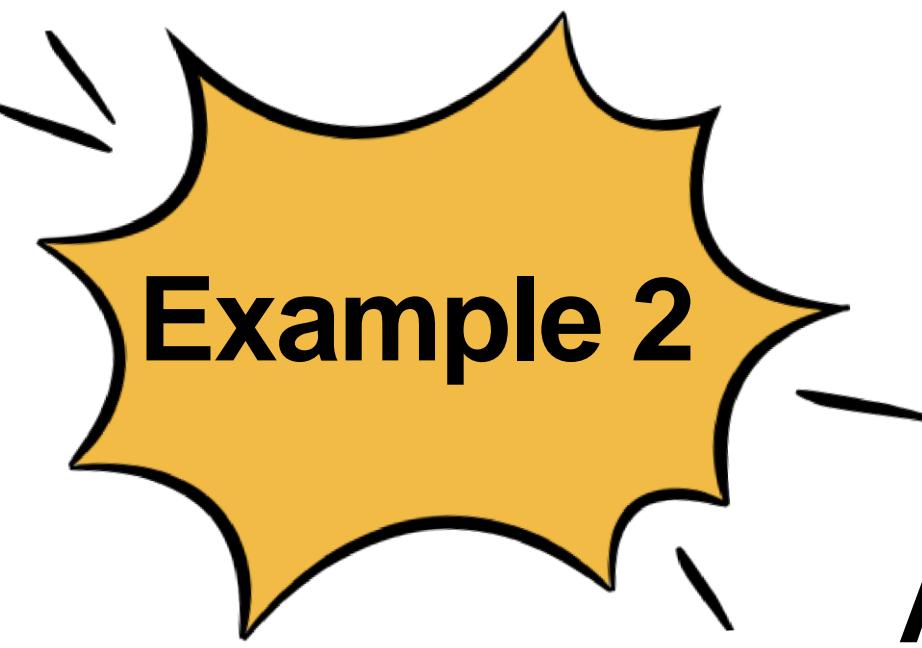
$$q = mc\Delta T$$

$$q = (250 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times (56 - 20) \text{ K})$$

$$= 37\ 620 \text{ J}$$

$$= 37.6 \text{ kJ}$$

∴ Amount of heat needed is **37.6 kJ**



Example 2

A calorimeter contains 400 ml of water at 25.0 °C. If 600 ml of water at 60.0 °C is added to it, determine the final temperature. Assume that the heat absorbed by calorimeter is negligible .

(Ans: 46.0 °C)

$$m_1 = 600 \text{ g}$$

$$m_2 = 400 \text{ g}$$

$$\Delta T_1 = 60^\circ\text{C} - T_f$$

$$\Delta T_2 = T_f - 25^\circ\text{C}$$



Heat released by added H₂O = heat absorbed by H₂O

$$mc\Delta T_1 = mc\Delta T_2$$

$$600 \times 4.18 \times (60 - T_f) = 400 \times 4.18 \times (T_f - 25)$$

$$T_f = 46.0^\circ\text{C}$$



Exercise 1

**Calculate the specific heat capacity of copper given
that 204.75 J of energy raises the temperature of 15.0 g
of copper from 25.0 °C to 60.0 °C.**

(Ans: 0.39 J g⁻¹ °C⁻¹)

CALORIMETER

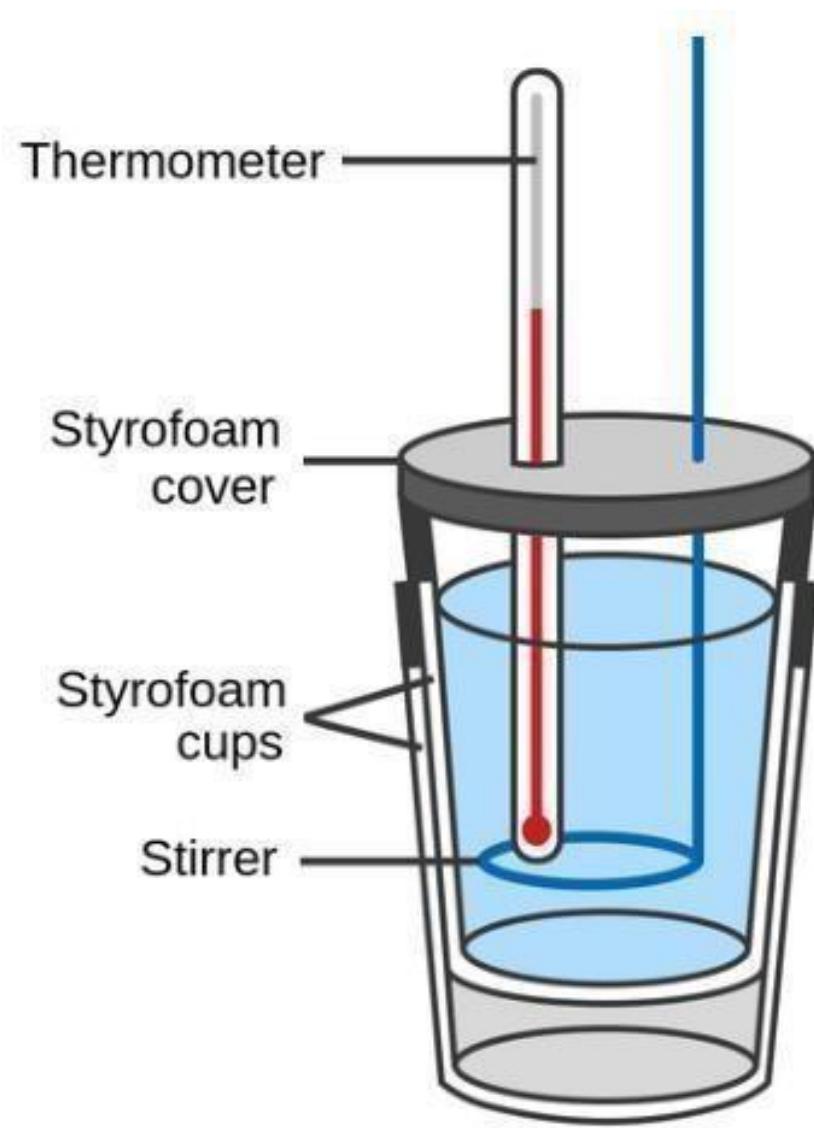
Device used to measure the heat released (or absorbed) by a physical or chemical process

Examples of calorimeter:

- ① Simple calorimeter (coffee cup)
☞ **constant-pressure calorimeter**

- ② Bomb calorimeter
☞ **constant-volume calorimeter**

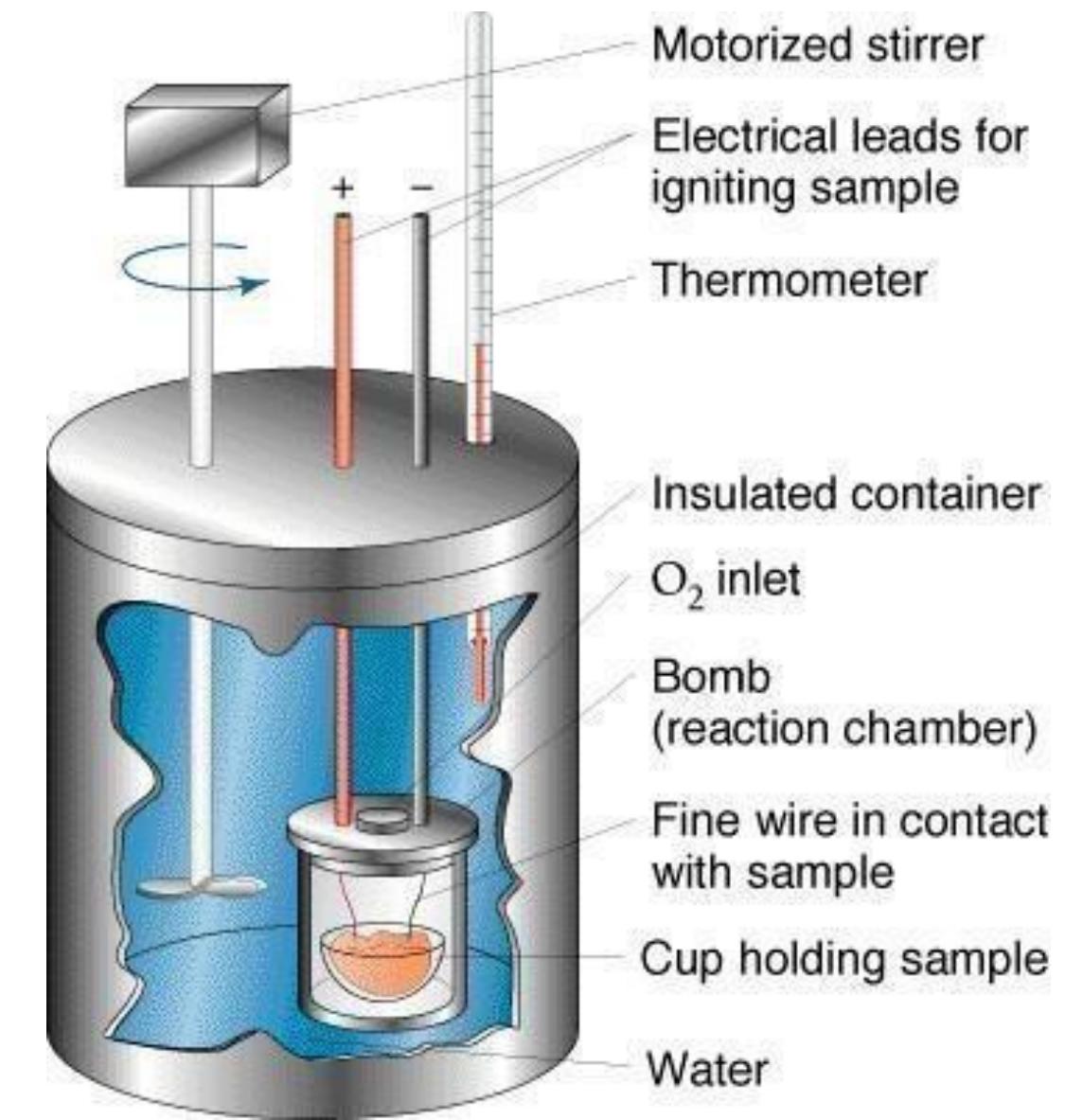
Simple Calorimeter



To measure heat released in non-combustion reaction:

- heat of neutralization
- heat of solution

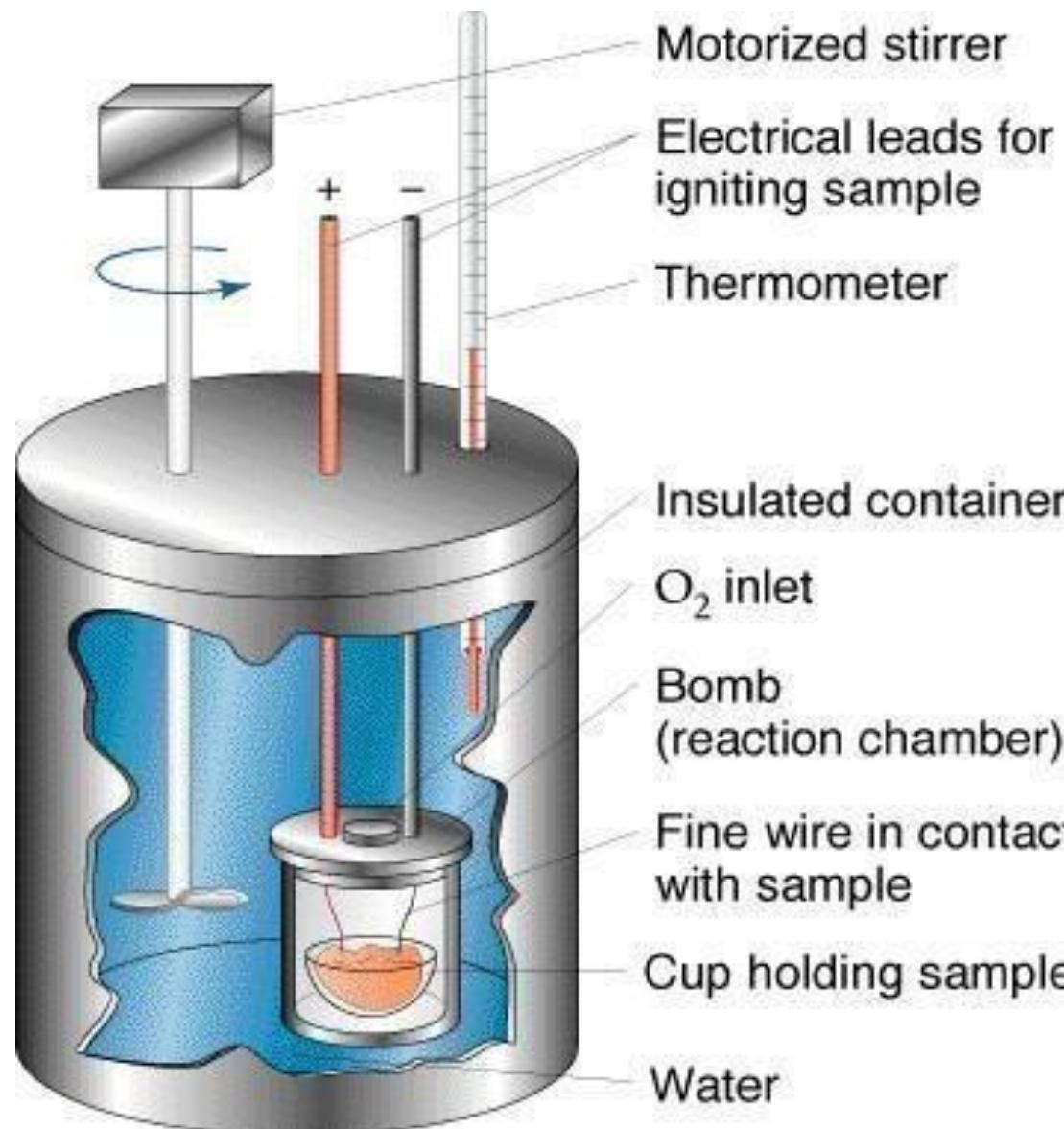
Bomb Calorimeter



To measure

- heat of combustion

BOMB CALORIMETER



- ☞ An instrument used to measure the heat of a combustion reaction
- ☞ A constant-volume calorimeter
- ☞ Reaction occurs at constant volume

BOMB CALORIMETER

$$q_{sys} = q_{water} + q_{cal} + q_{rxn} \Rightarrow q_{sys} = 0$$

***no heat enters or leaves the system*

$$\therefore q_{rxn} = -(q_{water} + q_{cal})$$

heat released by reaction = heat absorbed by water + bomb calorimeter

wheres:

$$q_{water} = m_w c_w \Delta T$$

m_w = mass of water

c_w = specific heat capacity of water

$$q_{cal} = C_{cal} \Delta T$$

C_{cal} = heat capacity of calorimeter

ΔT = temperature change

Example 3

A quantity of 1.435 g of naphthalene ($C_{10}H_8$), a pungent-smelling substance used in mouth repellents, was burned in bomb calorimeter. Consequently, the temperature of water rose from $20.17\text{ }^{\circ}\text{C}$ to $25.84\text{ }^{\circ}\text{C}$.

Calculate heat of combustion of naphthalene (in kJ/mol) if the mass of water surrounding the calorimeter was exactly 2000 g and the heat capacity of the bomb calorimeter was $1.80\text{ kJ}/{}^{\circ}\text{C}$.

[Given, c of $\text{H}_2\text{O} = 4.18\text{ J g}^{-1}{}^{\circ}\text{C}^{-1}$]

1

Heat released from reaction, $q_{rxn} = ?$

$$q_{rxn} = - (q_{water} + q_{cal})$$

$$= - (m_w c_w \Delta T + C_{cal} \Delta T)$$

$$\Delta T = 25.84^\circ\text{C} - 20.17^\circ\text{C} = 5.67^\circ\text{C}$$



$$q_{water} = (2000 \text{ g}) (4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}) (5.67 \text{ }^\circ\text{C}) \\ = 4.74 \times 10^4 \text{ J}$$

$$q_{cal} = (1.80 \times 10^3 \text{ J }^\circ\text{C}^{-1}) (5.67 \text{ }^\circ\text{C}) \\ = 1.02 \times 10^4 \text{ J}$$

$$\begin{aligned} q_{rxn} &= -(q_{\text{water}} + q_{\text{cal}}) \\ &= -(4.74 \times 10^4 \text{ J} + 1.02 \times 10^4 \text{ J}) \\ &= -5.76 \times 10^4 \text{ J} \end{aligned}$$

👉 heat released

2

Mol of substance ?

$$\text{Mol} = \frac{\text{Mass (g)}}{\text{Molar mass (g/mol)}}$$

$$\begin{aligned} \text{Mole of naphthalene (C}_{10}\text{H}_8\text{)} &= \frac{1.435 \text{ g}}{128.0 \text{ g mol}^{-1}} \\ &= 0.01121 \text{ mol C}_{10}\text{H}_8 \end{aligned}$$

Substance ↗

3

Enthalpy of combustion

0.01121 mol naphthalene releases: $- 5.76 \times 10^4 \text{ J}$

So, 1 mol naphthalene releases:

$$\frac{1 \text{ mol} \times (-5.76 \times 10^4 \text{ J})}{0.01121 \text{ mol}}$$
$$= -5.14 \times 10^6 \text{ J}$$

$$\Delta H = -5.14 \times 10^3 \text{ kJ/mol}$$

***Heat of combustion : heat released when 1 mole of substance is burned completely in excess oxygen under stated condition

***-ve sign : heat released

Example 4

Calculate the amount of heat released in a reaction in an aluminium calorimeter with a mass of 3087.0 g and contains 1700.00 mL of water. The initial temperature of the calorimeter is 25.0 °C and it increased to 27.8 °C.

Given:

Specific heat capacity of aluminum= 0.553 J g⁻¹ °C⁻¹

Specific heat capacity of water= 4.18 J g⁻¹ °C⁻¹

Water density = 1.0 g mL⁻¹

$$\Delta T = (27.8 - 25.0)^\circ\text{C} = 2.8^\circ\text{C}$$

$$\Delta T = (27.8 - 25.0)^\circ\text{C} = 2.8^\circ\text{C}$$

heat released by rxn = heat absorbed by the calorimeter + water



$$q_{\text{rxn}} = - (q_{\text{calorimeter}} + q_{\text{water}})$$

$$q_{\text{rxn}} = - (m_c c_c \Delta T + m_w c_w \Delta T)$$

$$= - [(3087.0 \text{ g})(0.553 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(2.8 \text{ }^\circ\text{C}) + (1700.0 \text{ g})(4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(2.8 \text{ }^\circ\text{C})]$$

$$= - 24\ 676.7108 \text{ J}$$

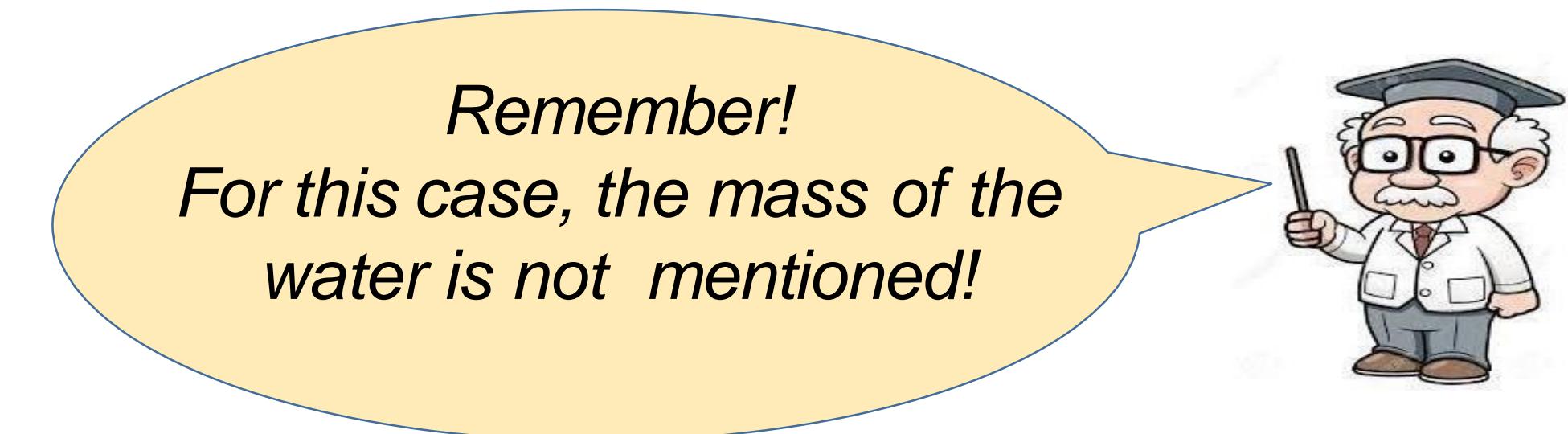
$$q_{\text{rxn}} = \text{ - 24.68 kJ}$$

∴ heat released by the reaction is 24.68 kJ

- Some books include “water” as part of the “calorimeter”
- Value of heat capacity of calorimeter include that of water

$$q_{\text{water}} + q_{\text{calorimeter}} \rightarrow q_{\text{calorimeter}}$$

$$q_{\text{rxn}} = - (q_{\text{water}} + q_{\text{cal}}) \rightarrow q_{\text{rxn}} = - q_{\text{cal}}$$

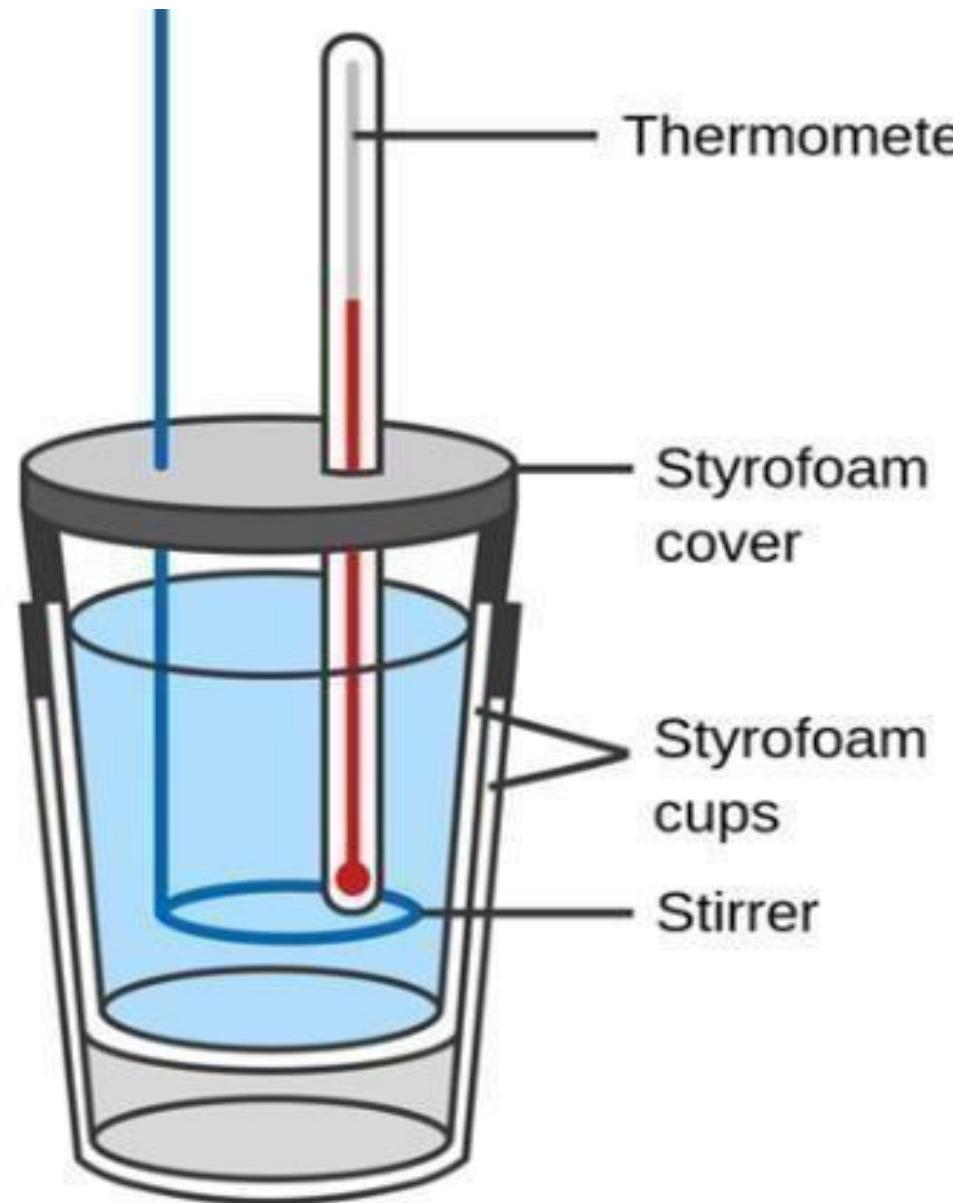


Exercise 2

The combustion of 1.010 g sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in a bomb calorimeter causes the temperature to rise from $24.92\text{ }^\circ\text{C}$ to $28.33\text{ }^\circ\text{C}$. The heat capacity of the calorimeter is 4.90 kJ/ $^\circ\text{C}$. What is the heat of combustion of sucrose expressed in kJ/mol?

(Ans: $-5.66 \times 10^3\text{ kJ/mol}$)

SIMPLE CALORIMETER



- ☞ An instrument used to measure heat released in non-combustion reaction such as heat of neutralization and heat of solution.
- ☞ A constant-pressure calorimeter

SIMPLE CALORIMETER

$$q_{sys} = q_{soln} + q_{cal} + q_{rxn} \Rightarrow q_{sys} = 0$$

***no heat enters or leaves the system*

$$\therefore q_{rxn} = -(q_{soln} + q_{cal})$$

heat released by reaction = heat absorbed by the solution + simple calorimeter

wheres:

$$q_{soln} = m_s c_s \Delta T$$

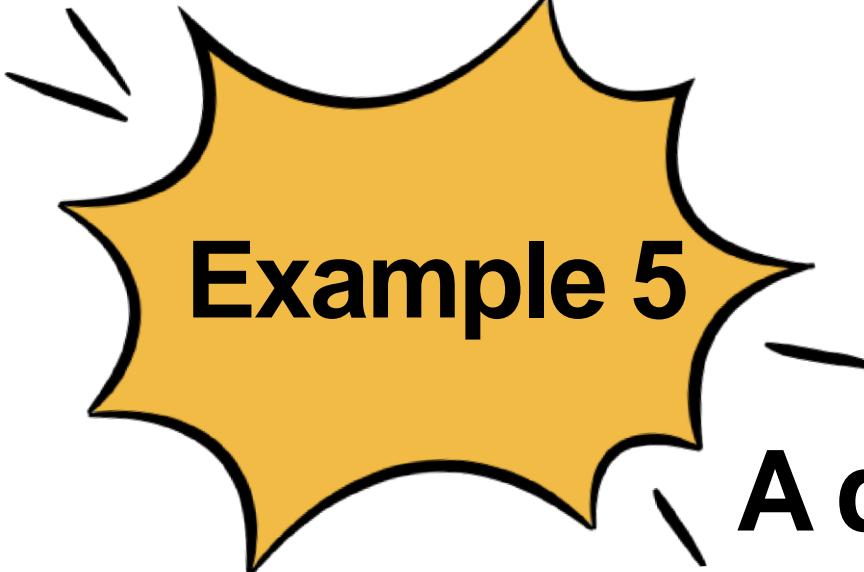
m_s = mass of solution

c_s = specific heat capacity of solution

$$q_{cal} = C_{cal} \Delta T$$

C_{cal} = heat capacity of calorimeter

ΔT = temperature change



Example 5

A quantity of 100 mL of 0.5 M HCl is mixed with 100 mL of 0.5 M NaOH in coffee-cup calorimeter that has a heat capacity of $335 \text{ J } ^\circ\text{C}^{-1}$.

The initial temperature of the HCl and NaOH solution is the same, $22.50 \text{ } ^\circ\text{C}$, and the final temperature of the mixed solution is $24.90 \text{ } ^\circ\text{C}$.

Calculate the heat of neutralization reaction (in kJ/mol).

Assume the densities and specific heat capacities
of the solution as the same as for water
(1.0 g mL⁻¹ and 4.18 J g⁻¹°C⁻¹)

Total Volume solution, $V_T = V_{\text{HCl}} + V_{\text{NaOH}}$
 $V_T = 100 + 100$
= 200 mL



Density, $p = \frac{\text{mass of solution (g)}}{\text{volume of solution (mL)}}$

$$1.0 \text{ g mL}^{-1} = \frac{\text{mass of solution (g)}}{200 \text{ mL}}$$

$$\text{mass of solution} = 200 \text{ g}$$

1

Heat released from reaction, $q_{rxn} = ?$

$$q_{rxn} = - (q_{soln} + q_{cal})$$

$$= - (m_s c_s \Delta T + C_{cal} \Delta T)$$

$$\Delta T = 24.90^\circ\text{C} - 22.50^\circ\text{C} = 2.40^\circ\text{C}$$

$$q_{soln} = (200 \text{ g}) (4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}) (2.40^\circ\text{C}^{-1}) = 2006.4 \text{ J}$$

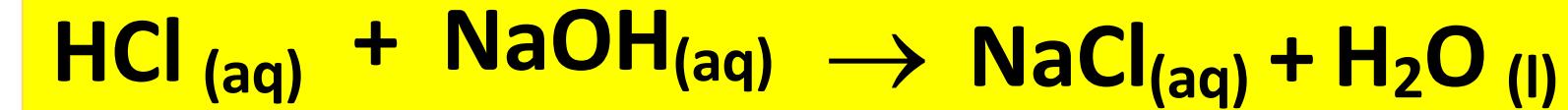
$$q_{cal} = (335 \text{ J }^\circ\text{C}^{-1})(2.40^\circ\text{C}) = 804 \text{ J}$$

$$q_{rxn} = - (2006.4 + 804)$$

$$= - 2810.4 \text{ J}$$

2

Neutralisation reaction:



number of mol = molarity x volume (L)

$$\begin{aligned} n_{\text{HCl}} &= 0.5 \text{ mol/L} \times 0.100 \text{ L} \\ &= 0.05 \text{ mol} \end{aligned}$$

$$\begin{aligned} n_{\text{NaOH}} &= 0.5 \text{ mol/L} \times 0.100 \text{ L} \\ &= 0.05 \text{ mol} \end{aligned}$$

Both HCl and NaOH are in stoichiometric proportions; neither is in excess.



3

Enthalpy of neutralization

The formation of:

0.05 mol H₂O release 2810.4 J of heat

1 mol H₂O releases $\frac{1 \text{ mol} \times (-2810.4 \text{ J})}{0.05 \text{ mol}}$
= 56208 J

$$\Delta H_{neutralization} = -56.2 \text{ kJ/mol}$$

***Heat of neutralisation : heat released when 1 mole of water is formed acid reacts with base under stated condition

***–ve sign : heat released

Some books ignore the heat lost to the “calorimeter” itself (styrofoam, thermometer, etc.)

$$q_{rxn} = - (q_{soln} + q_{cal}) \rightarrow q_{rxn} = - q_{soln}$$



Remember!
For this case, heat capacity of the calorimeter is not mentioned!



Exercise 2

The heat of neutralization for the following reaction is -56.2 kJ mol⁻¹.



100.0 ml of 1.50 M HCl is mixed with 100.0 ml of 1.50 M NaOH in a calorimeter having a heat capacity of 15.2 J °C⁻¹. The initial temperature of HCl and NaOH solution are 23.2 °C.

Calculate the final temperature for this reaction.

(Given $\rho_{\text{solution}} = 1.00 \text{ g ml}^{-1}$; $c_{\text{solution}} = 4.18 \text{ J g}^{-1} \text{ °C}^{-1}$)

(Ans : 33.1°C)

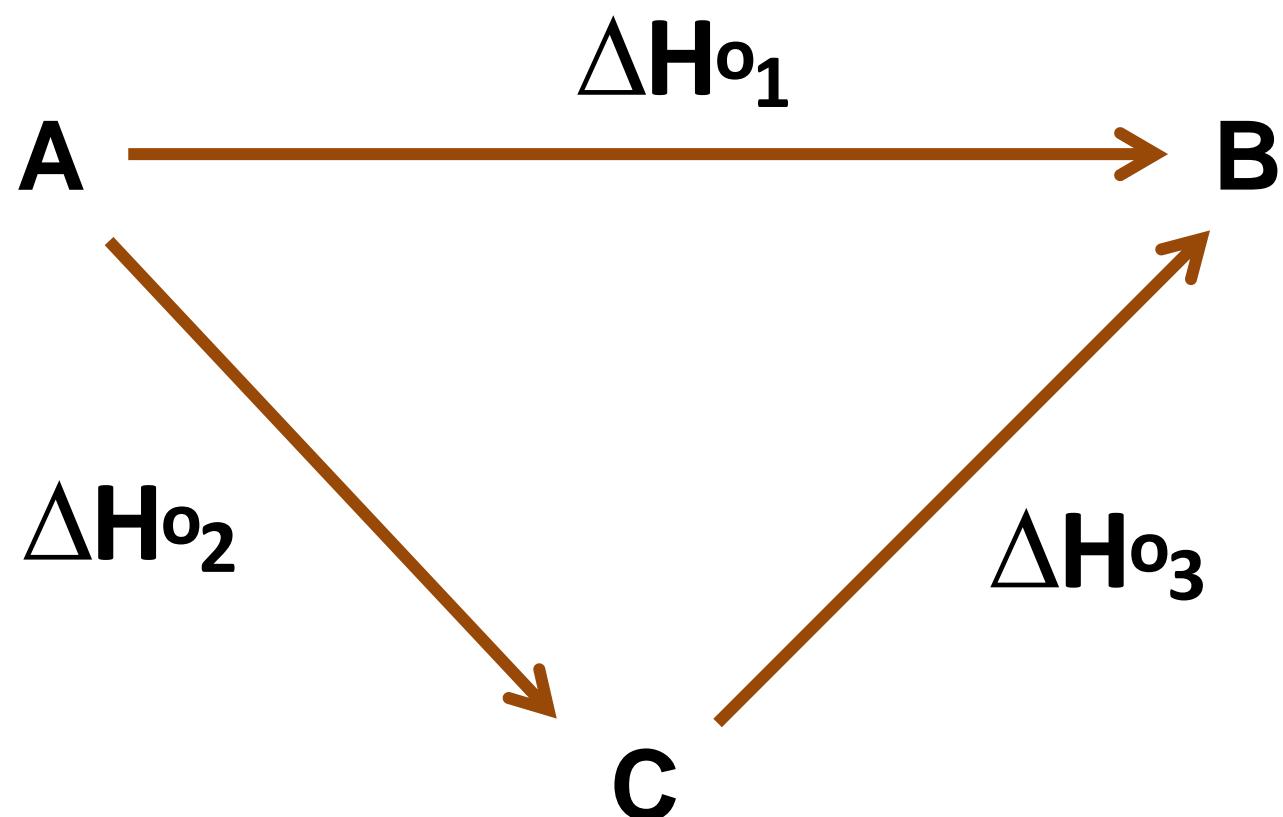
2.3 HESS'S LAW

Learning Outcomes :

- a) State Hess's Law (C1)
- b) Apply Hess's law to calculate enthalpy changes using the algebraic method and energy cycle method. (C3, C4)
- c) Illustrate the dissolution process of ionic solids. (C2, C3, C4)

HESS'S LAW

Hess's Law states that when reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in the series of steps.



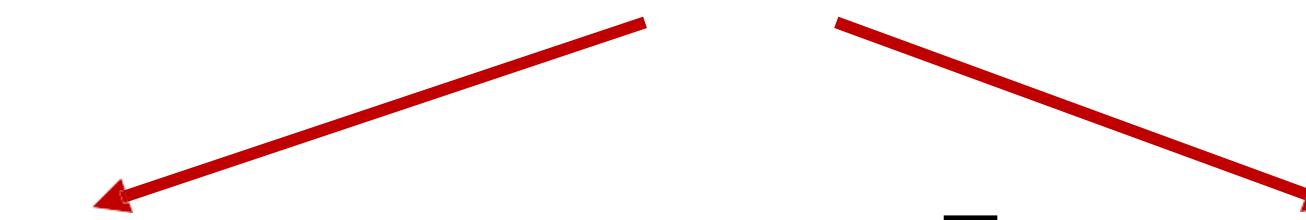
$$\Delta H^\circ_1 = \Delta H^\circ_2 + \Delta H^\circ_3$$

HESS'S LAW

Applying 2 methods

Algebraic method

Energy cycle method



How to Applying Algebraic Method?

01 Write the chemical equation for required enthalpy change.

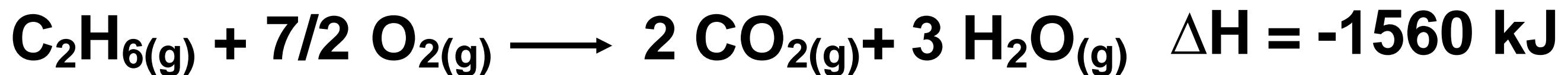
02 List all the thermochemical equations involved.

03 Manipulate the equations to get the required enthalpy change.

Algebraic Method

Example 1

Given the following enthalpies of reaction,



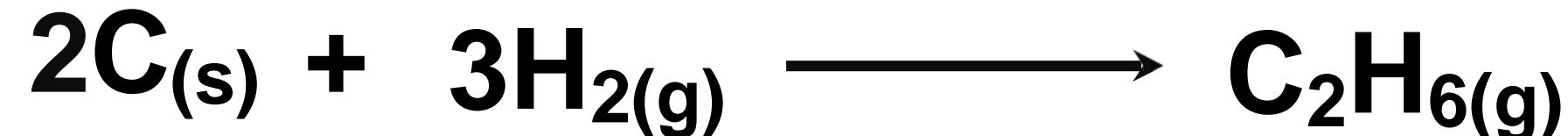
Calculate the enthalpy of formation for ethane, $\text{C}_2\text{H}_{6(\text{g})}$

Algebraic Method

Answer

- 01 Write the chemical equation for required enthalpy change.

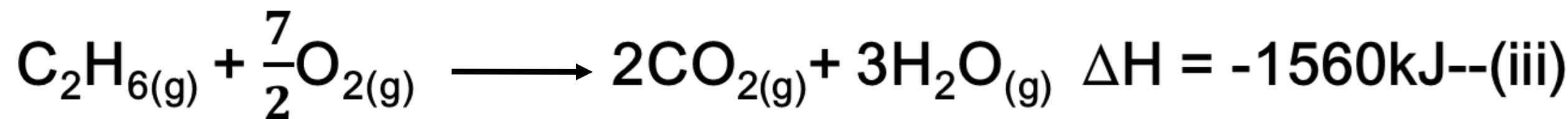
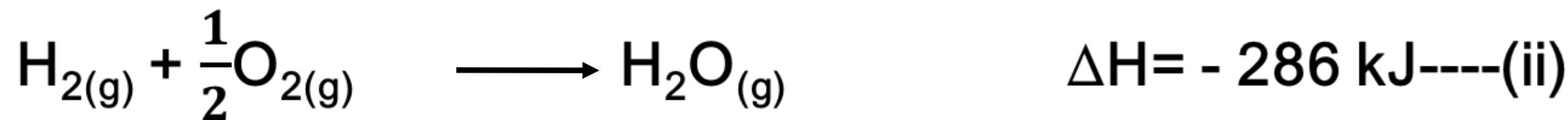
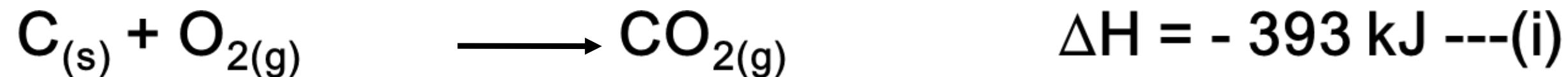
Required enthalpy change: enthalpy of formation for C₂H₆.



Algebraic Method

02

List all the thermochemical equations involved.

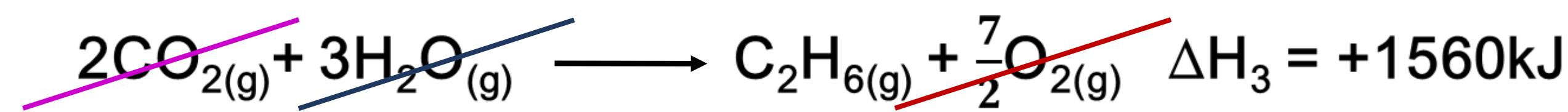


03

Manipulate the equations to get the required enthalpy change.



Reverse (iii)



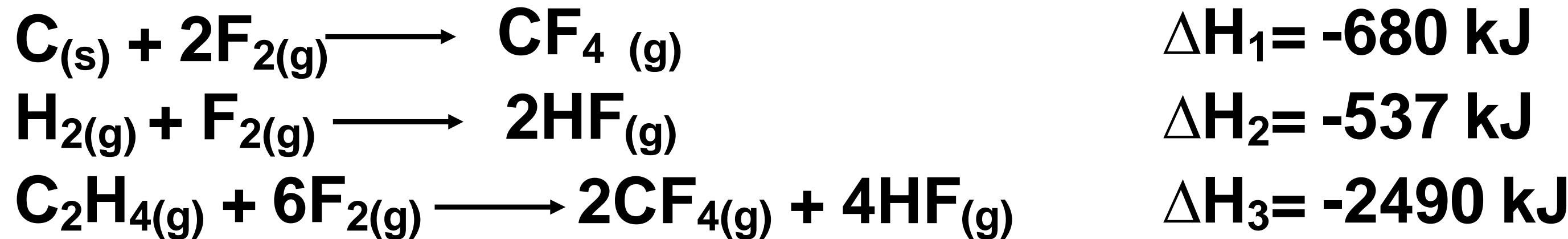
$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$= -84 \text{ kJ/mol}$$

Algebraic Method

Example 2

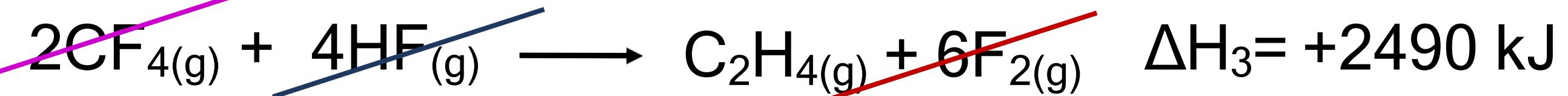
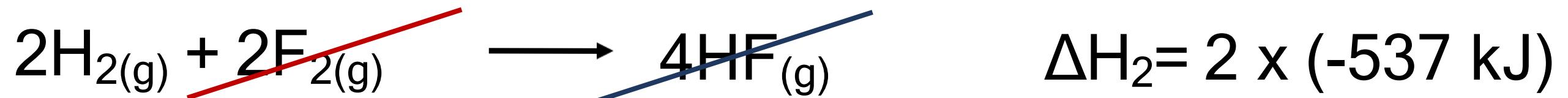
Given the following enthalpies of reaction,



By using the thermochemical equations given;
determine the enthalpy of formation, ΔH_f for
ethene, $\text{C}_2\text{H}_{4(\text{g})}$

Algebraic Method

Answer



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

$$= 2(-680) + 2(-537) + 2490$$

$$= + 56 \text{ kJ/mol}$$

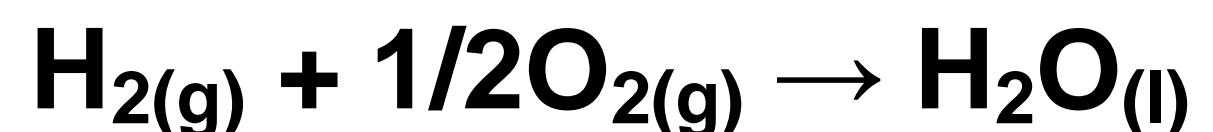
Algebraic Method

Exercise 1

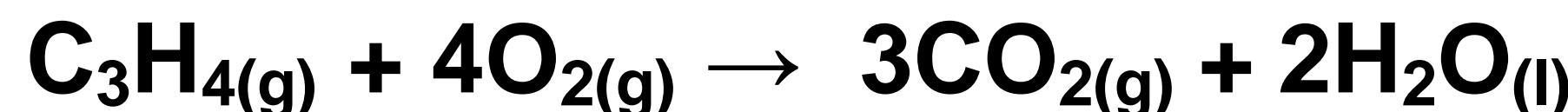
Use Hess's law to determine ΔH for the reaction :



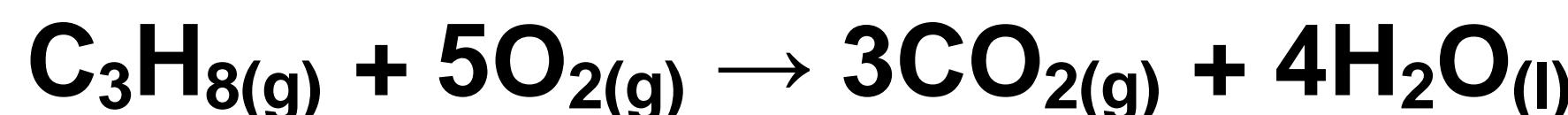
Given that :



$$\Delta H = -285.8 \text{ kJ}$$



$$\Delta H = -1937 \text{ kJ}$$



$$\Delta H = -2219.1 \text{ kJ}$$

$$\text{Ans} = -289.5 \text{ kJ}$$

Algebraic Method

Exercise 2

Given :



Using algebraic method, calculate the enthalpy change, ΔH for the following reaction :



Ans : -2558 kJ

HOW TO APPLYING ENERGY CYCLE METHOD?

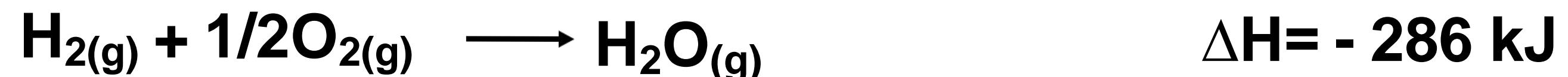
01 Write the chemical equation for required enthalpy change.

02 Draw the cycle and add the values (multiplying by a factor where necessary).

Example 3

Example :

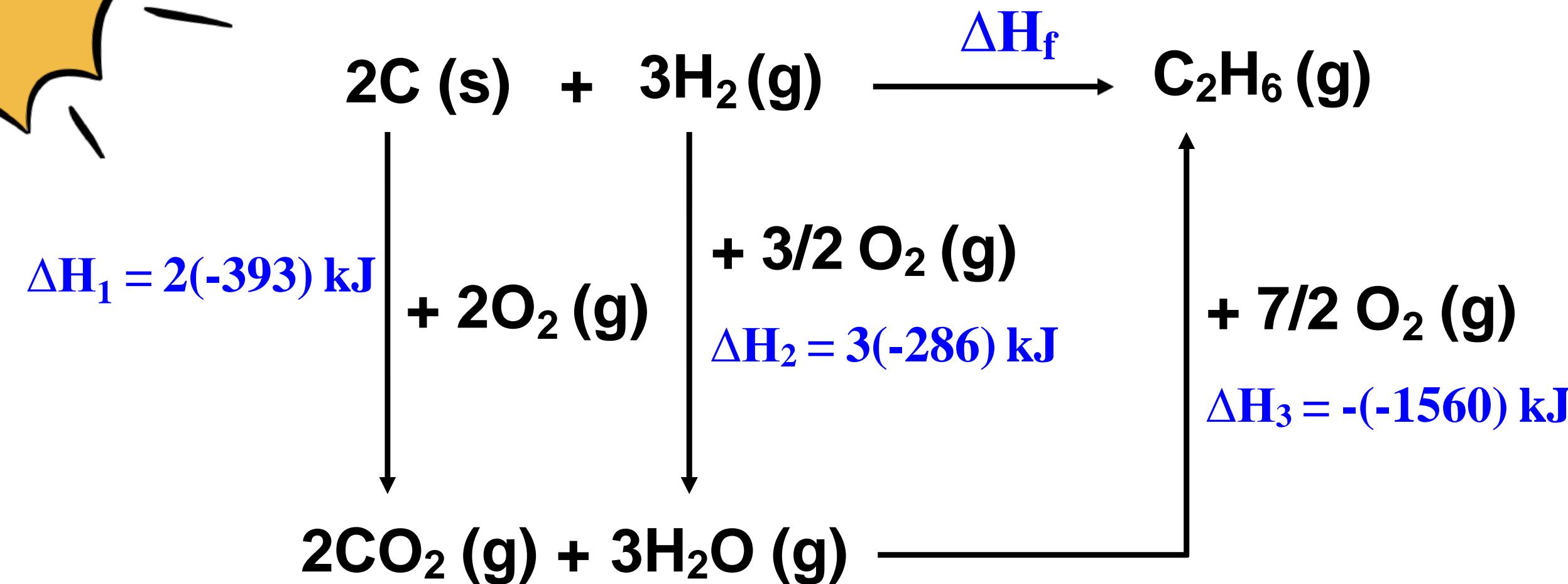
Given the following enthalpies of reaction,



Calculate the enthalpy formation for ethane, $\text{C}_2\text{H}_{6(\text{g})}$ using energy cycle method.

Energy Cycle Method

Answer



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

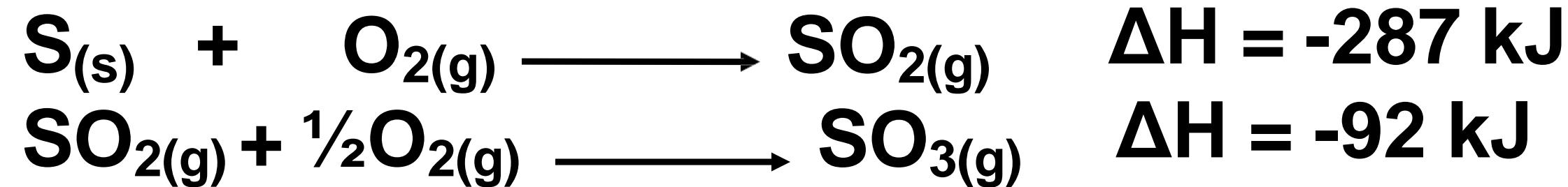
$$= 2(-393) + 3(-286) + 1560$$

$$= -84 \text{ kJ/mol}$$

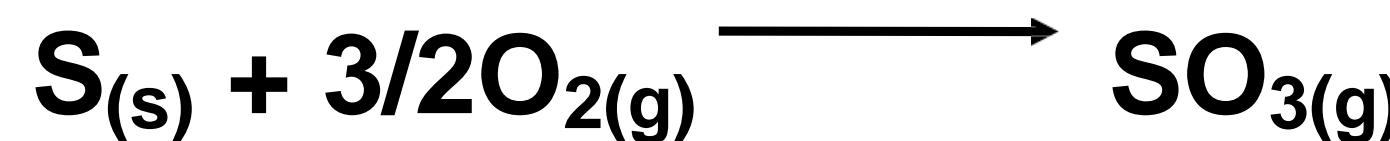
Energy Cycle Method

Example 4

Given:

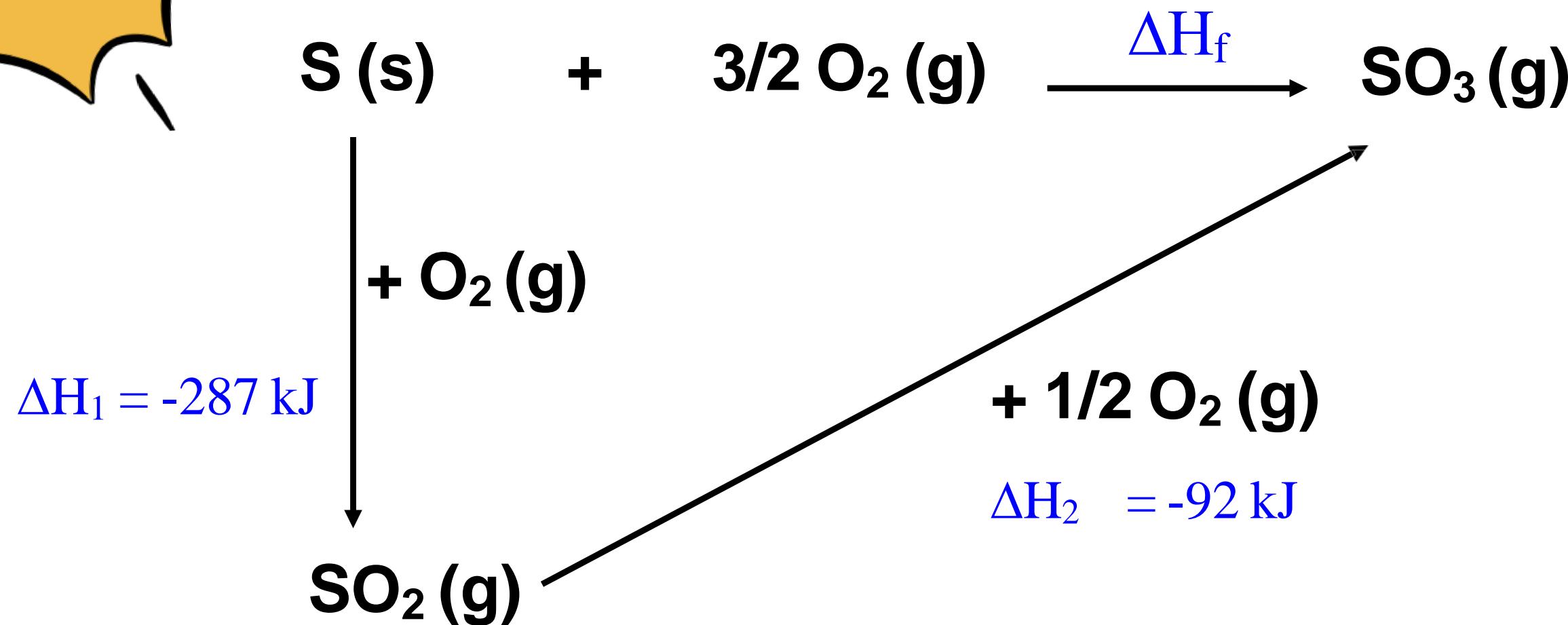


Calculate ΔH_f for the following reaction using energy cycle method:



Energy Cycle Method

Answer



$$\Delta H_f = \Delta H_1 + \Delta H_2$$

$$= (-287) + (-92)$$

$$= -379 \text{ kJ/mol}$$

Exercise 3

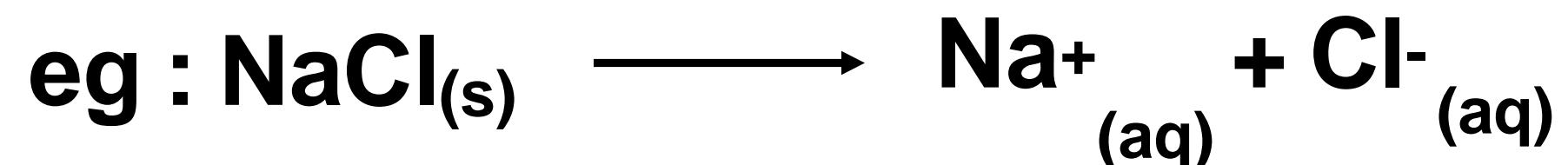
From the information below, determine the enthalpy of combustion of carbon using energy cycle method.



Ans : -393.0 kJ/mol

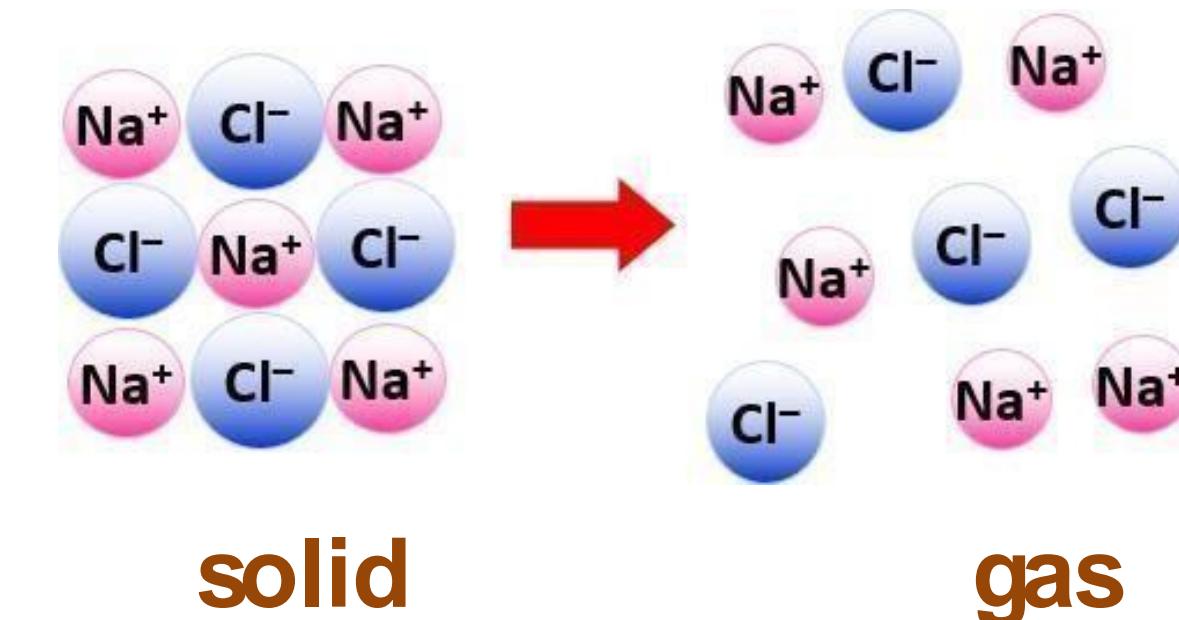
Dissolution Process for NaCl

- ☞ **dissolution is the process by which a solid or liquid forms a solution in a solvent.**
- ☞ **occur when an ionic solid dissolve in water**
- ☞ **water molecules are polar**
- ☞ **most ionic crystals are soluble in water**

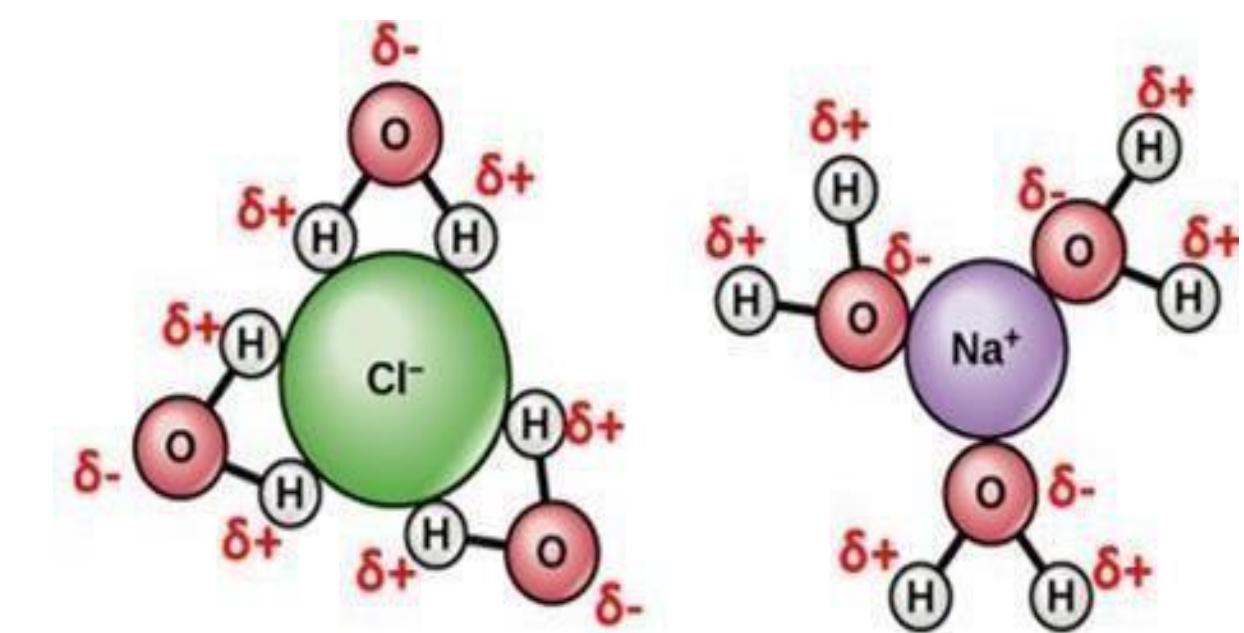


Dissolution Process for NaCl

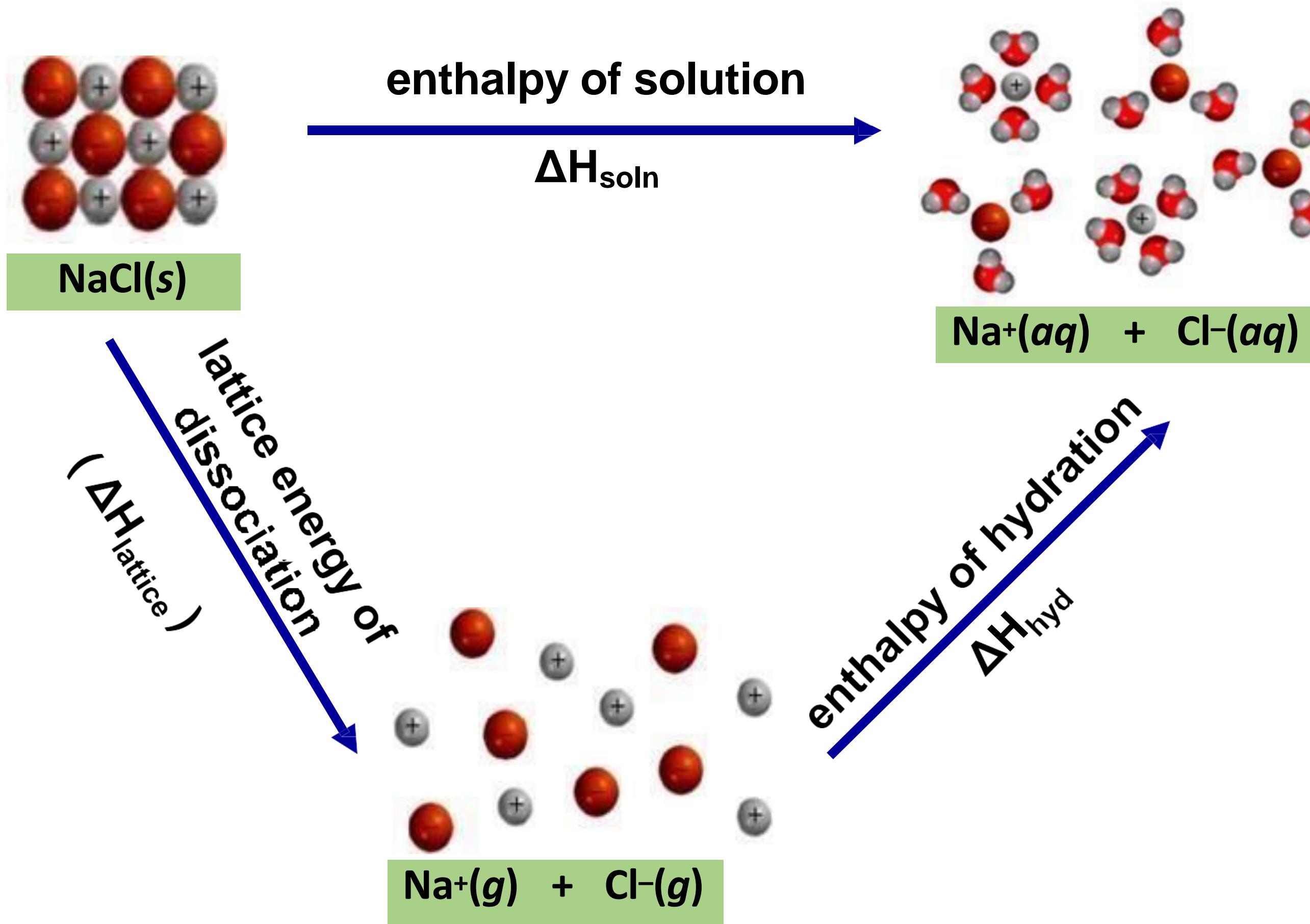
Na⁺ and Cl⁻ ions in the solid crystal are separated from each other and converted to the gaseous state (-ΔH_{lattice})



The electrostatic forces between gaseous ions and polar water molecules cause the ions to be surrounded by water molecules (ΔH_{hydr})



Dissolution Process for NaCl



Enthalpy of Hydration, ΔH_{soln}

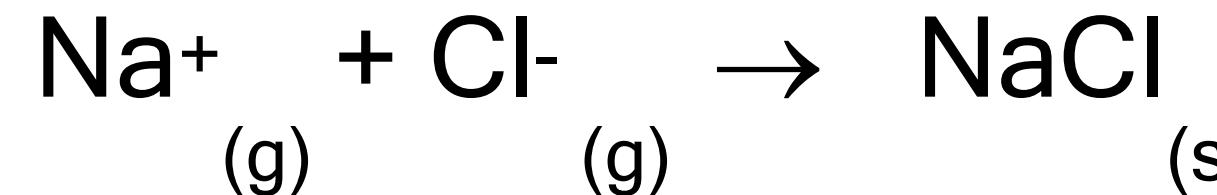
The enthalpy of solution of an ionic crystal in water is the sum of the lattice energy and the total enthalpy of hydration of the ions.

$$\Delta H_{\text{soln}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hyd}}$$

Lattice Energy, $\Delta H_{\text{lattice}}$

1 LATTICE FORMATION

Example given :



$$\Delta H_{\text{lattice}} = -771 \text{ kJ}$$



lattice formation = - ve kJ

2 LATTICE DISSOCIATION

Example given :

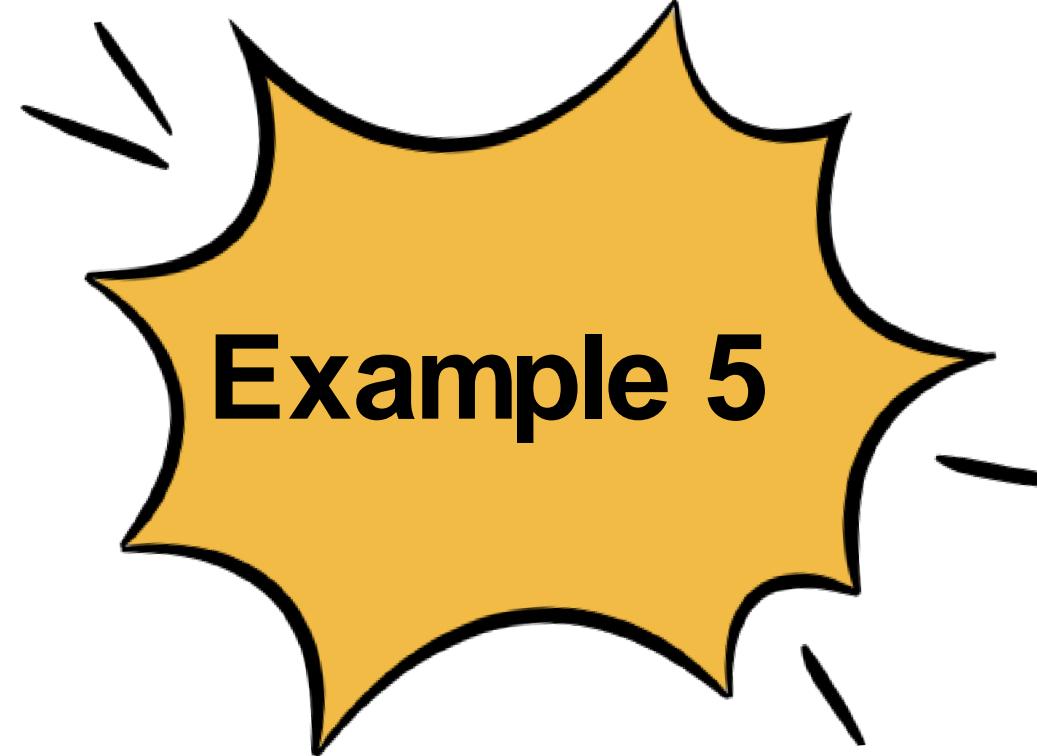
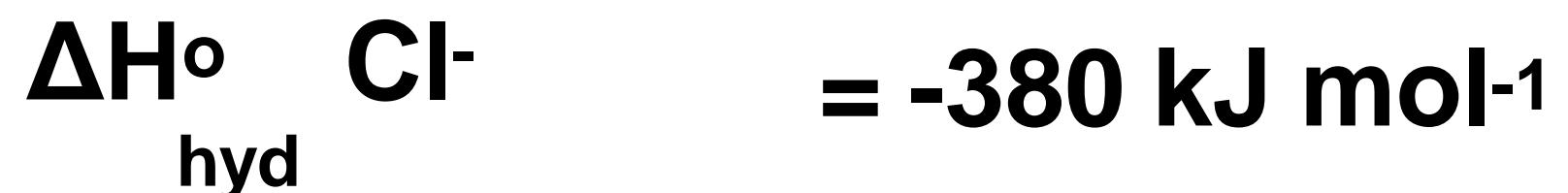
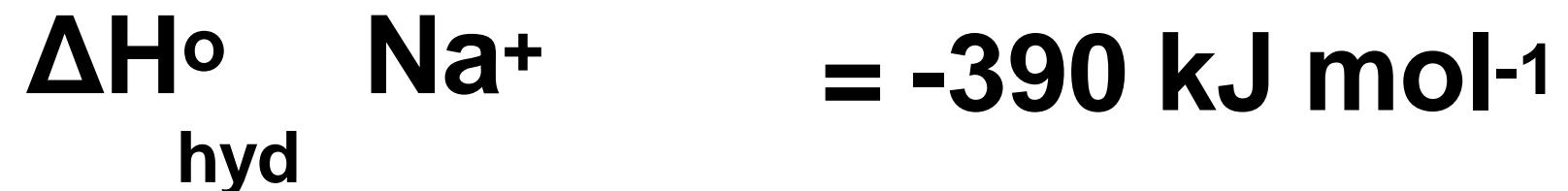


$$\Delta H_{\text{lattice}} = +771 \text{ kJ}$$



lattice dissociation = + ve kJ

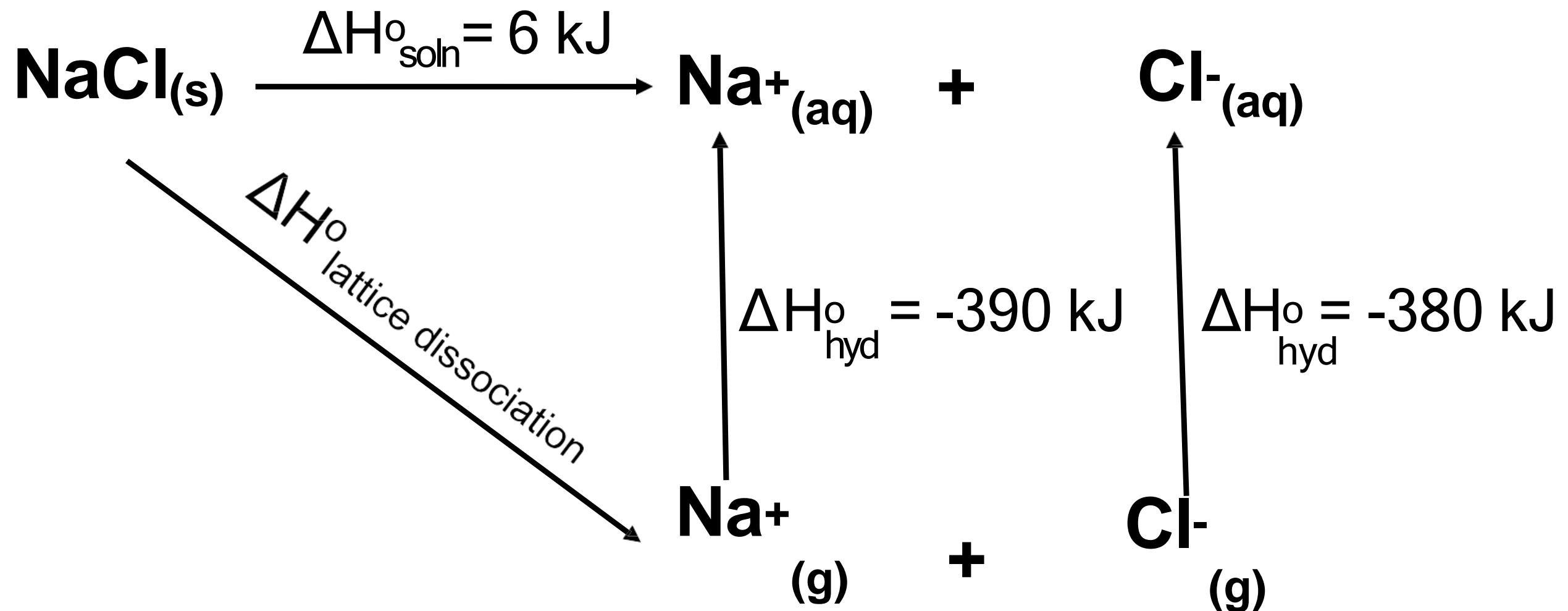
Based on the data given below:



Example 5

Construct energy cycle diagram to represent the dissolution of NaCl.

Calculate the $\Delta H^\circ_{\text{lattice}}$ of NaCl.

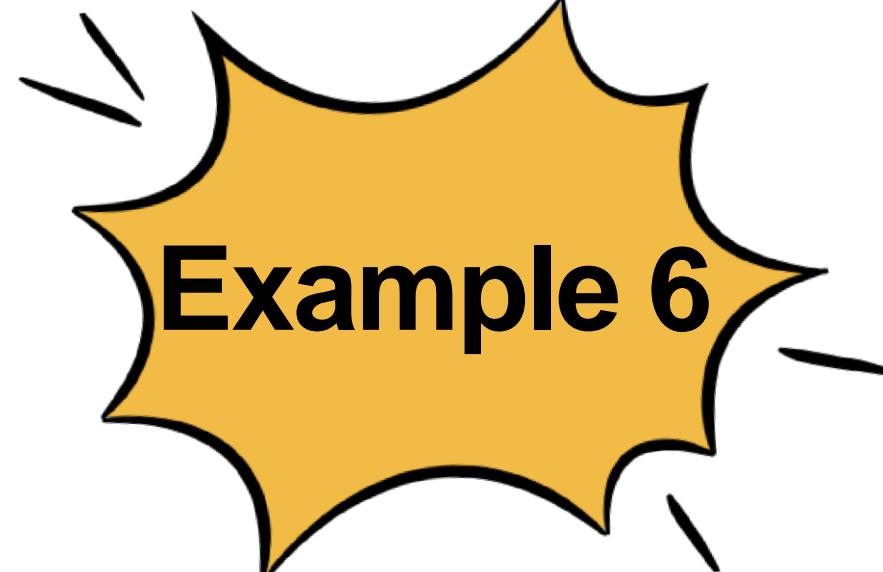


Answer example 5

$$\Delta H_{\text{soln}} = \Delta H_{\text{hyd}} (\text{Na}^{+}) + \Delta H_{\text{hydr}} (\text{Cl}^{-}) + \Delta H_{\text{lattice dissociation}} (\text{NaCl})$$

$$\begin{aligned}
 \Delta H_{\text{lattice NaCl}} &= 390 + 380 + 6 \\
 &= + 776 \text{ kJ mol}^{-1}
 \end{aligned}$$

$$\therefore \Delta H_{\text{lattice dissociation NaCl}} = + 776 \text{ kJ mol}^{-1}$$



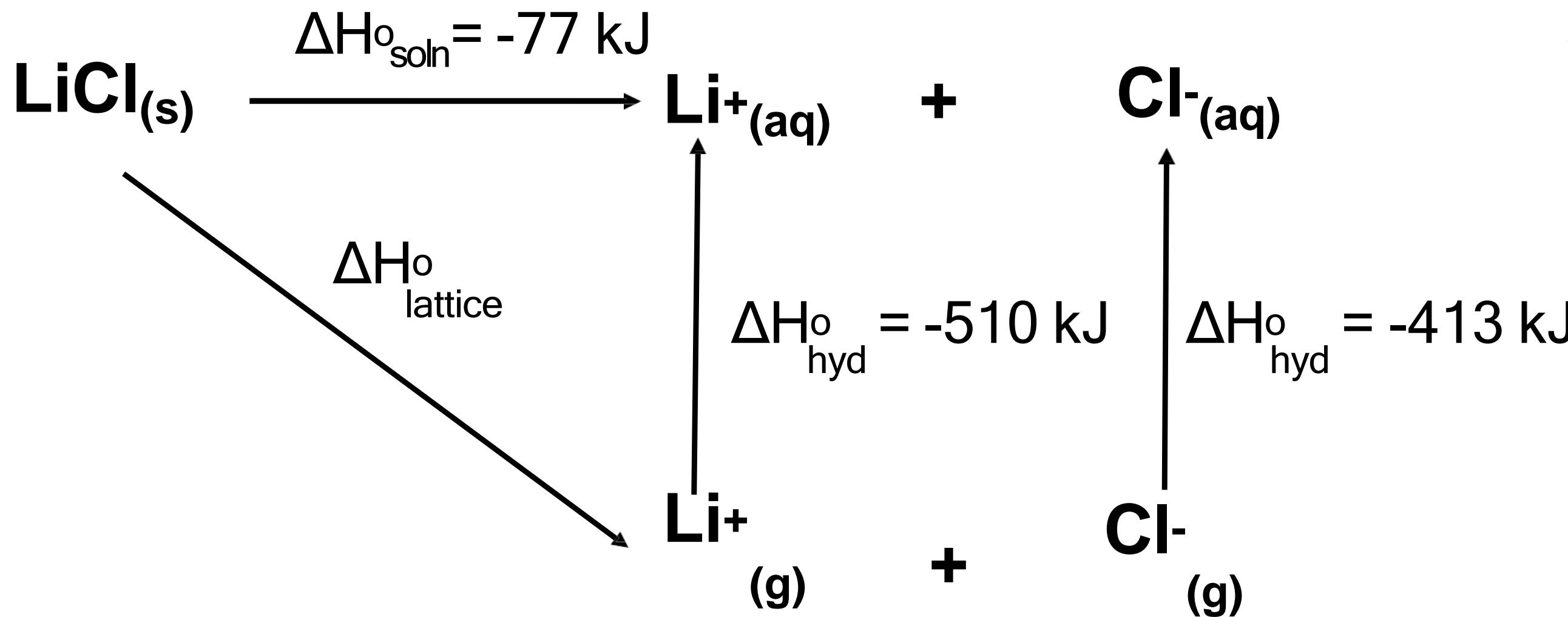
Example 6

Based on the data given below:

Process	Enthalpy of reaction (kJ/mol)
Solution of LiCl	-77
Hydration of Li ⁺	-510
Hydration of Cl ⁻	-413

- i. Construct an energy cycle diagram to represent the dissolution of LiCl.

- ii. Calculate the lattice energy of LiCl.



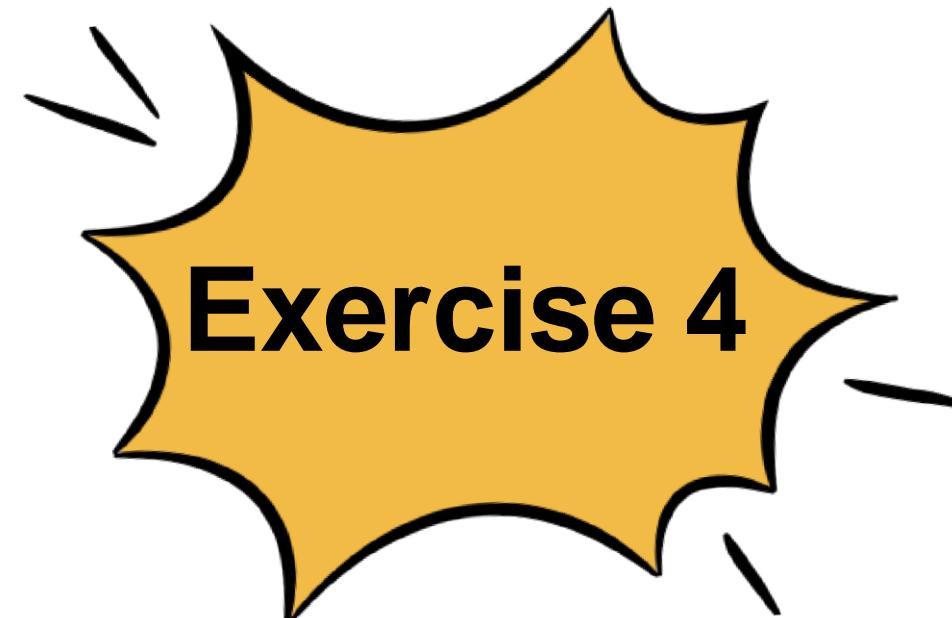
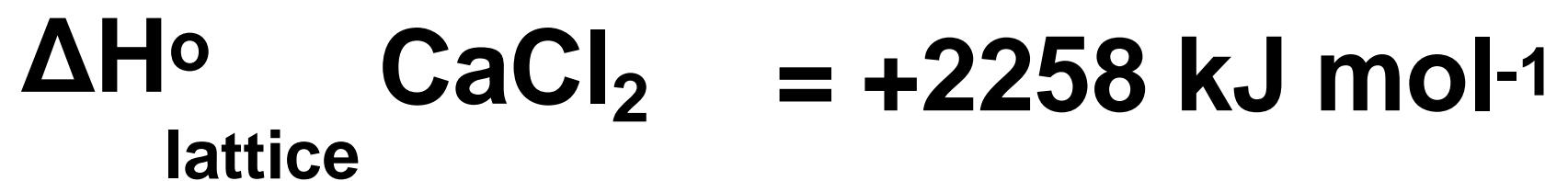
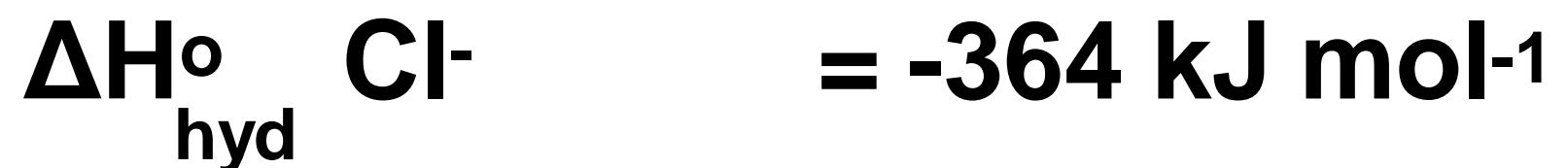
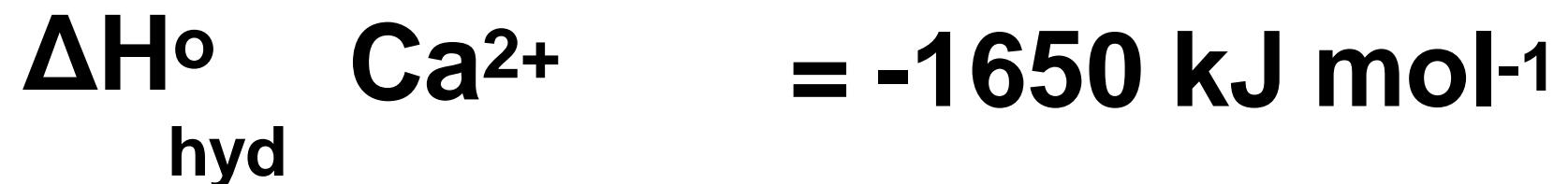
Answer
example 6

$$\Delta H_{\text{soln}} = \Delta H_{\text{hyd}} (\text{Li}^{+}) + \Delta H_{\text{hyd}} (\text{Cl}^{-}) + \Delta H_{\text{lattice}} (\text{LiCl})$$

$$\begin{aligned}\Delta H_{\text{lattice}} \text{ LiCl} &= 510 + 413 - 77 \\ &= 846 \text{ kJ mol}^{-1}\end{aligned}$$

$$\therefore \Delta H_{\text{lattice dissociation}} \text{ LiCl} = + 846 \text{ kJ mol}^{-1}$$

Based on the data given below:



Construct energy cycle diagram to represent the dissolution of CaCl_2 .

Calculate the $\Delta H^\circ_{\text{soln}}$ of CaCl_2 .

Ans : - 120 kJ/mol

2. 4 BORN-HABER CYCLE

Learning Outcomes

- a) Define (C1)
 - i. lattice energy for simple ionic crystals in terms of the change from gaseous ions to solid lattice
 - ii. electron affinity
- b) Explain the following effects on the magnitude of lattice energy (C2, C3, C4)
 - i. ionic charges
 - ii. ionic radii
- c) Construct Born- Haber cycle for simple ionic solids using energy cycle diagram and energy level diagram (C3)
- d) Calculate enthalpy changes using Born-Haber cycle (C4)

BORN-HABER CYCLE

- Is a cycle of reactions used for calculating the lattice energies of ionic crystalline solids that cannot be determined through experiment.
- A Born-Haber cycle summarizes the relationship between the various enthalpy changes involved in the formation of an ionic crystal from the reaction of a metal (often a Group I or Group II element) with a non-metal elements.
- The Born-Haber cycle can be construct using the energy cycle method.
- The cycle connects enthalpy of formation with lattice energy.



Max Born



Fritz Haber

1

LATTICE FORMATION

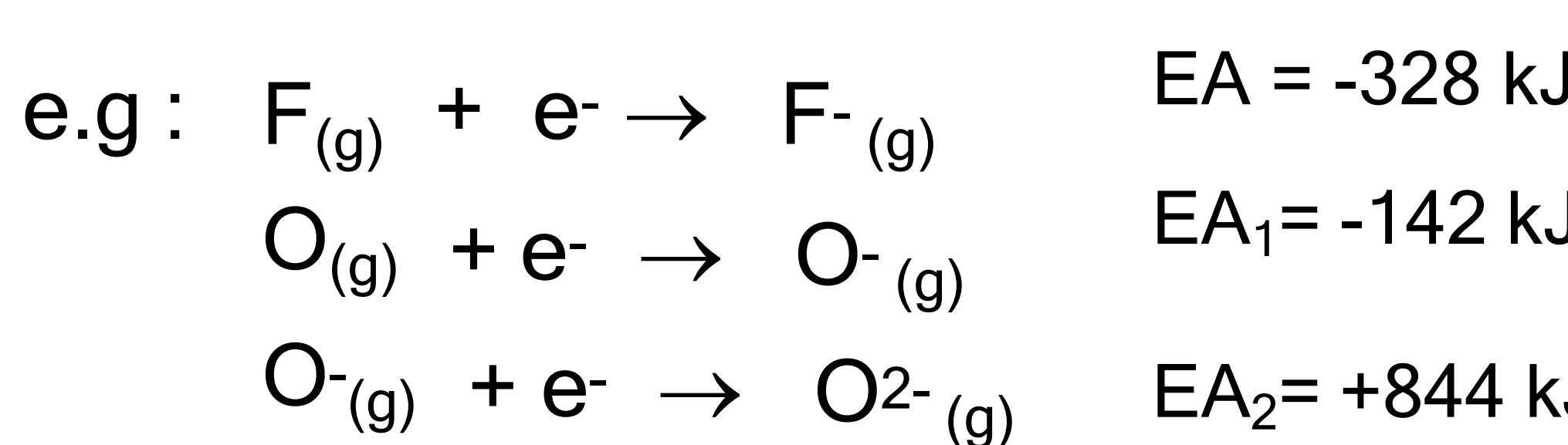
Energy released when 1 mole of solid ionic compound formed from its gaseous ions.



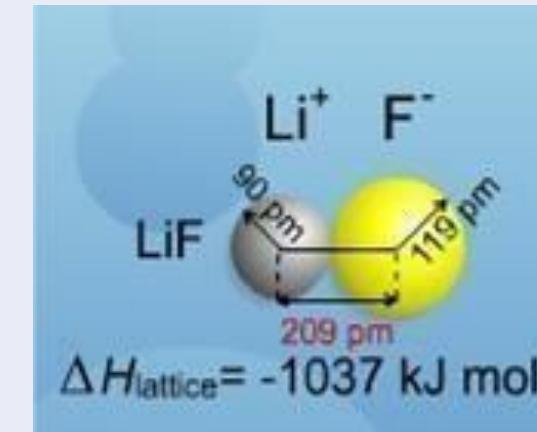
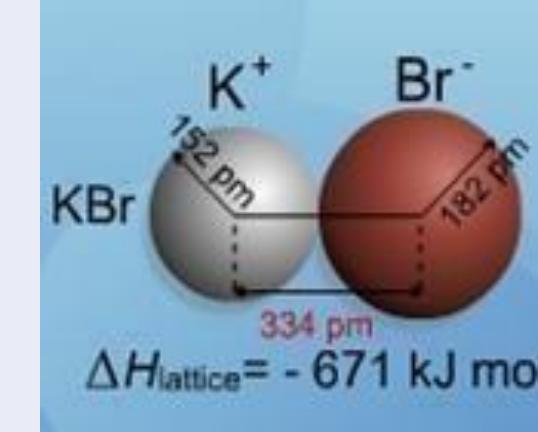
2

ELECTRON AFFINITY

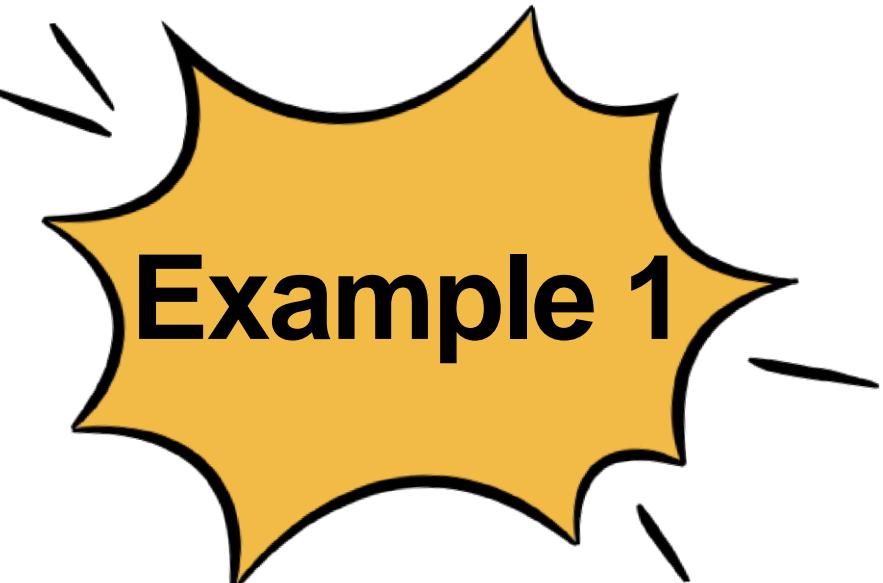
Energy change when 1 mole of gaseous atoms gains one mole of electron to form anion.



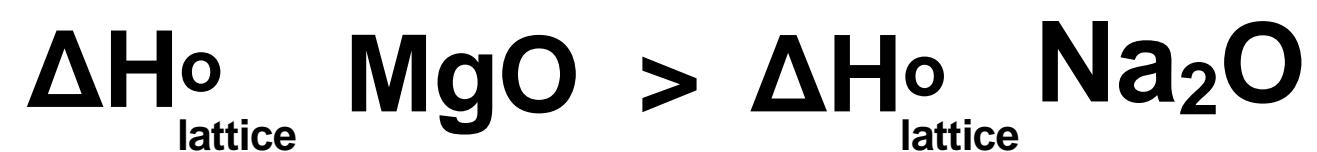
The magnitude of lattice energy increases (more negative/exothermic) as:

The ionic charge increases	The ionic radii decreases
<ul style="list-style-type: none">the stronger the attractive force between the ions	<ul style="list-style-type: none">small ions can be close togetherthe smaller distance of separationthe stronger the attractive force between the ions
<ul style="list-style-type: none">E.g :  	<ul style="list-style-type: none">E.g :   

Which substance, MgO or Na₂O, has a larger lattice energy? Explain.



Answer :



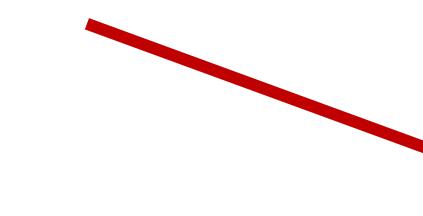
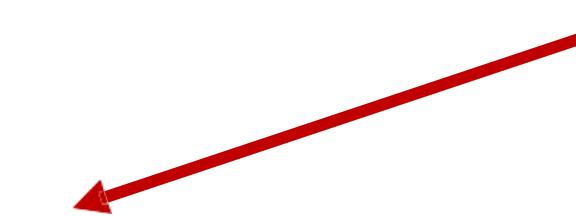
- Mg²⁺ has smaller in size and bigger charge than Na⁺
- attractive forces between Mg²⁺ and O²⁻ are stronger than between Na⁺ and O²⁻

HOW TO CONSTRUCT THE BORN-HABER CYCLE ?

Applying 2 methods

Energy cycle
diagram

Energy level
diagram



Example 2

Calculate the **lattice energy** from the following data:

Enthalpy of atomisation of potassium : +90 kJ mol⁻¹

First ionisation energy of potassium : +418kJ mol⁻¹

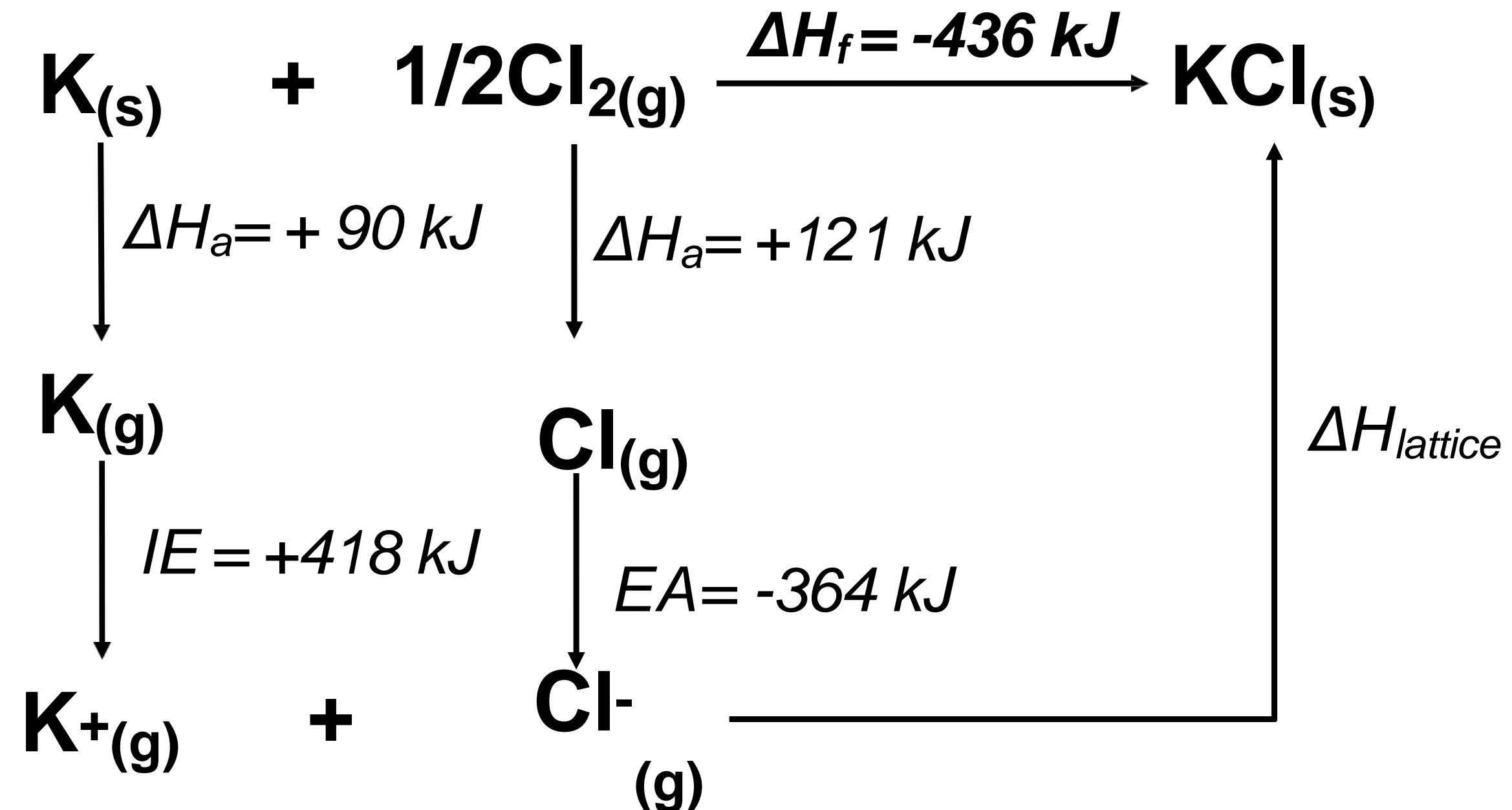
Atomisation energy of chlorine : +121kJ mol⁻¹

Electron affinity of chlorine : -364 kJ mol⁻¹

Enthalpy of formation of potassium chloride : -436 kJ mol⁻¹

Energy cycle diagram

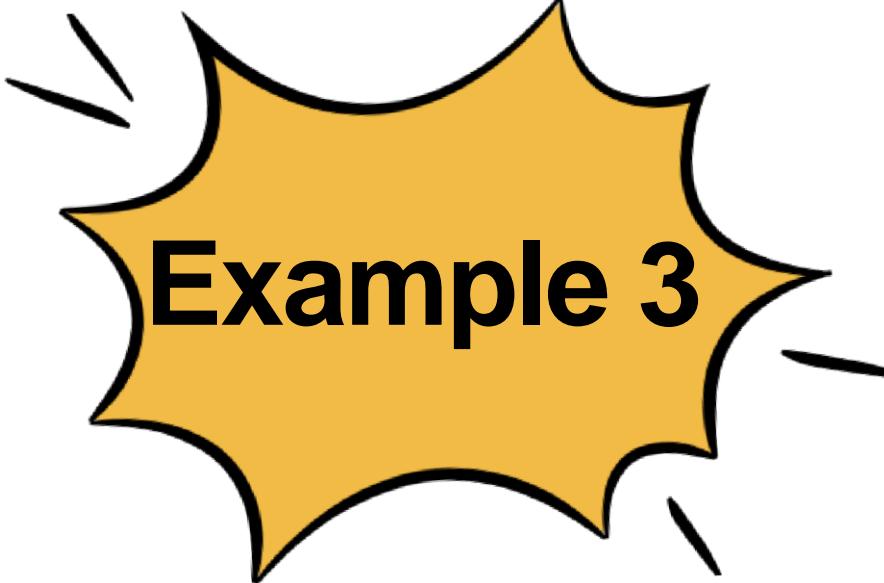
Answer



$$\Delta H_f = \Delta H_{a(K)} + IE + \Delta H_{a(Cl)} + EA + \Delta H_{latt}$$

$$-436 = 90 + 418 + 121 - 364 + \Delta H_{latt}$$

$$\therefore \Delta H_{latt} = -701 \text{ kJ/mol}$$



Example 3

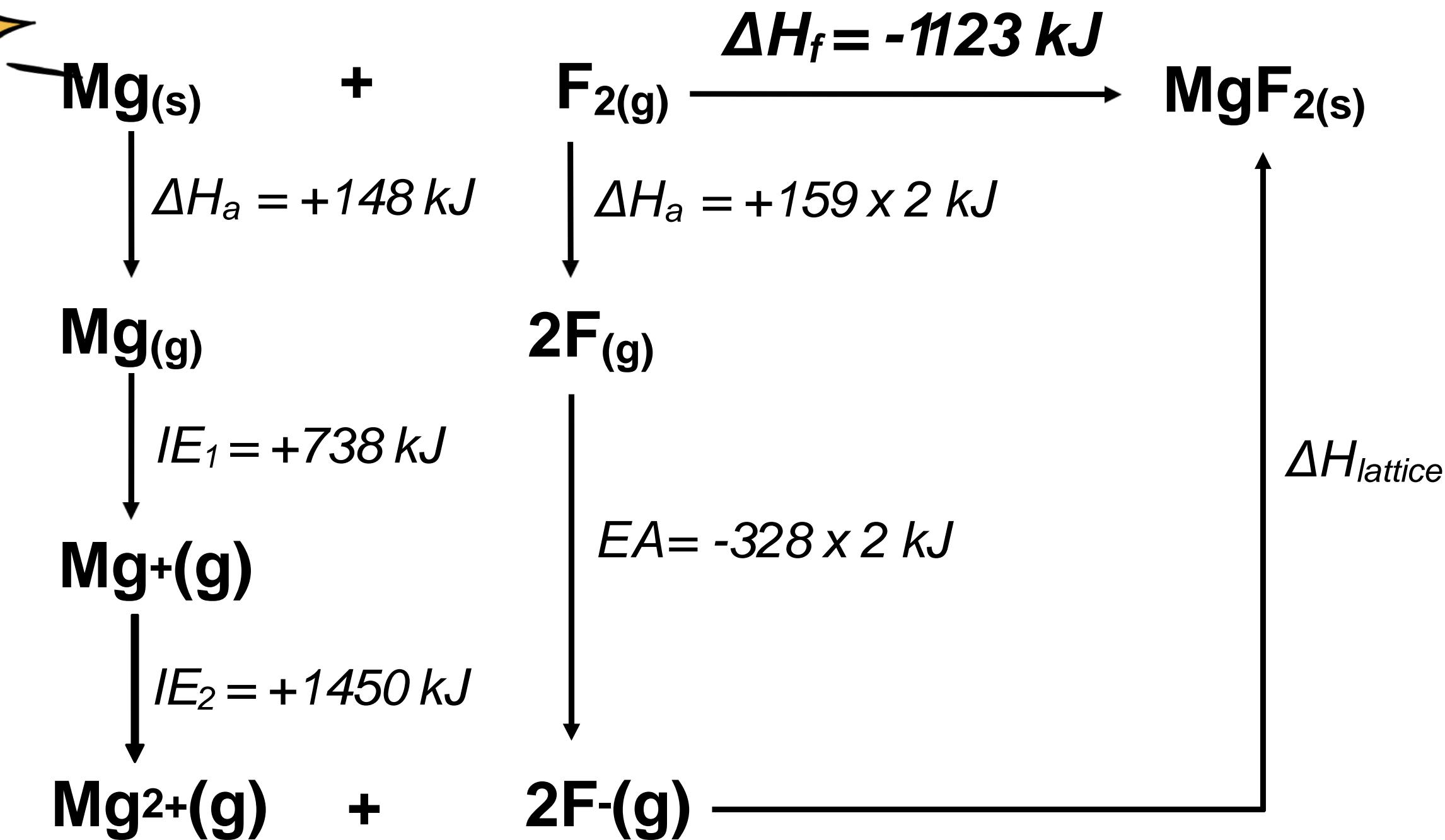
Construct a Born-Haber cycle for the formation of magnesium fluoride, MgF_2 by using the data below :

Enthalpy of atomisation of magnesium	+148 kJ/mol
First ionisation energy of magnesium	+738 kJ/mol
Enthalpy of atomisation of flourine	+159 kJ/mol
Second ionisation energy of magnesium	+1450 kJ/mol
Electron affinity fluorine	-328 kJ/mol
Enthalpy the formation of magnesium fluoride	-1123 kJ/mol

Based on the Born-Haber cycle, determine the lattice energy of magnesium fluoride.

Energy cycle diagram

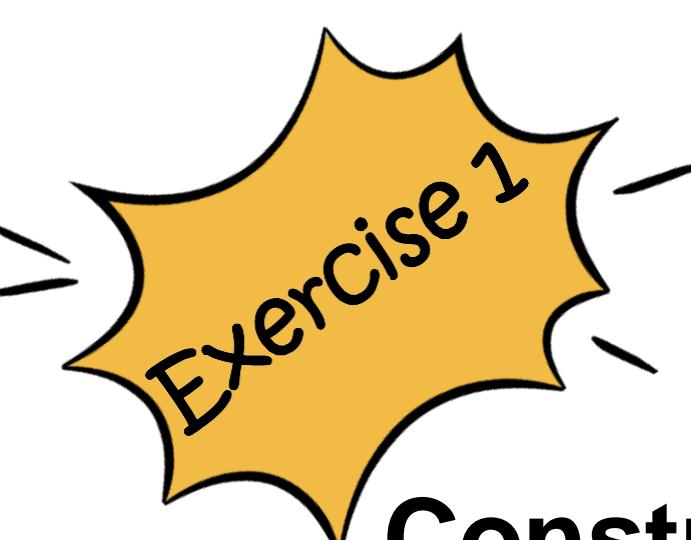
Answer



$$\Delta H_f = \Delta H_{a(Mg)} + I E_1 + I E_2 + \Delta H_{a(F)} + EA + \Delta H_{lattice}$$

$$-1123 = 148 + 738 + 1450 + 318 - 656 + \Delta H_{lattice}$$

$$\Delta H_{lattice} = -3121 \text{ kJ/mol}$$



Exercise 1

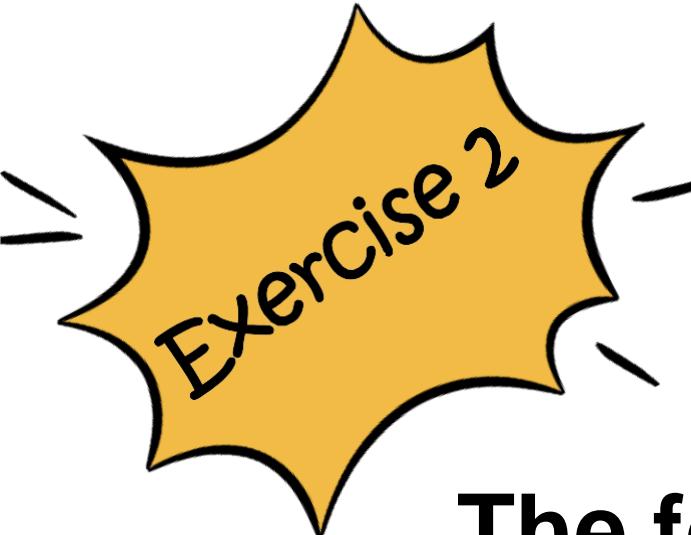
Construct a Born-Haber cycle for the formation of magnesium chloride, MgCl_2 by using the data below :

Enthalpy of atomisation of magnesium	+148 kJ/mol
First ionisation energy of magnesium	+736 kJ/mol
Enthalpy of atomisation of chlorine	+122 kJ/mol
Second ionisation energy of magnesium	+1450 kJ/mol
Lattice energy of magnesium chloride	-2526 kJ/mol
Enthalpy the formation of magnesium chloride	-642 kJ/mol

Based on the Born-Haber cycle, determine the electron affinity of chlorine.

Ans : - 347 kJ/mol

Energy cycle diagram



The following data are given :



Construct the Born-Haber cycle to calculate the lattice energy of CaF_2 .

Ans : - 2800 kJ/mol

Energy Level Diagram

Example 4

Consider the enthalpy changes in the formation of sodium chloride.

Given:

Enthalpy of formation NaCl

= - 411 kJmol⁻¹

Enthalpy of atomisation of Na

= + 108 kJmol⁻¹

First ionization energy of Na

= + 500 kJmol⁻¹

Enthalpy of atomization of Cl

= + 122 kJmol⁻¹

Electron affinity of Cl

= - 364 kJmol⁻¹

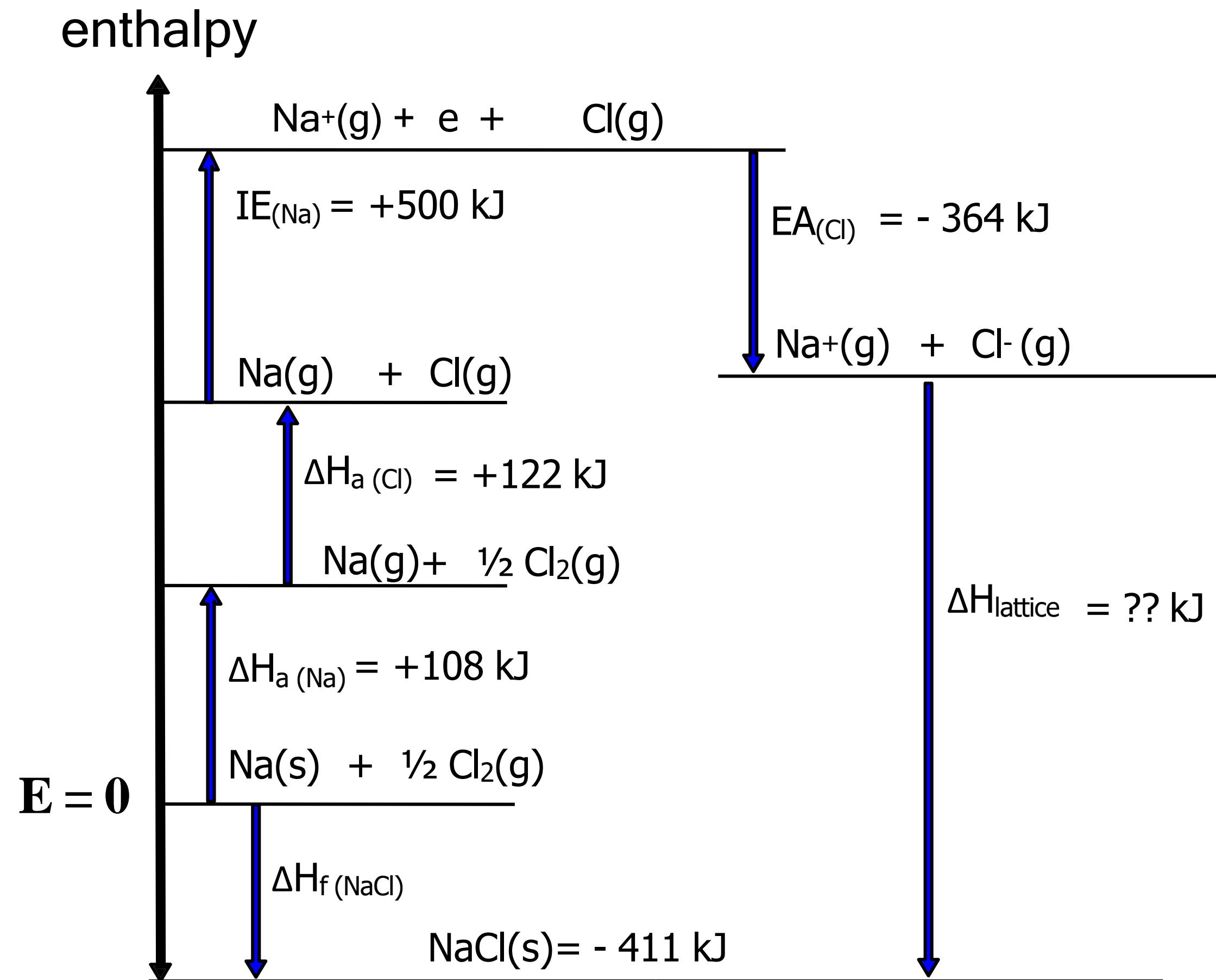
Lattice energy of NaCl

= ?

Construct energy level diagram and calculate its lattice energy.

Energy Level Diagram

Answer



Energy Level Diagram

Answer

From Hess's Law:

$$\Delta H_f \text{ NaCl} = \Delta H_a \text{ Na} + \text{IE Na} + \Delta H_a \text{ Cl} + \text{EA Cl} + \Delta H_{\text{lattice}} \text{ NaCl}$$

$$\Delta H_{\text{lattice}} \text{ NaCl} = \Delta H_f \text{ NaCl} - (\Delta H_f \text{ NaCl} + \text{IE Na} + \Delta H_a \text{ Cl} + \text{EA Cl})$$

$$= -411 - [108 + 122 + 500 + (-364)]$$

$$\Delta H_{\text{lattice}} = \textcolor{red}{-777 \text{ kJ/mol}}$$

Energy Level Diagram

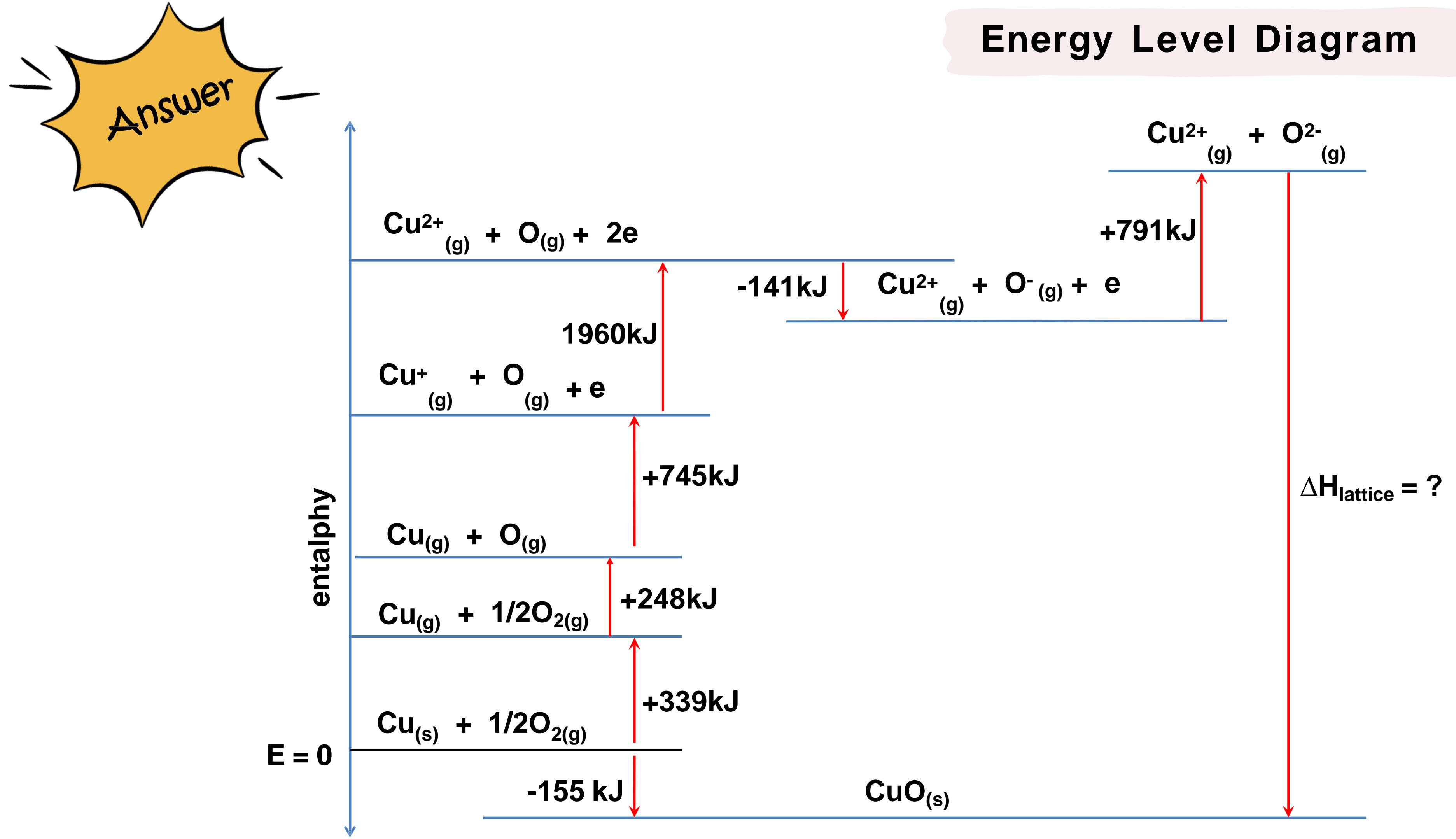
Example 5

Consider the enthalpy changes in the formation of copper(II) oxide.

Enthalpy of atomisation of copper	: +339 kJ mol ⁻¹
First ionisation energy of copper	: +745 kJ mol ⁻¹
Second ionisation energy of copper	: +1960 kJ mol ⁻¹
Enthalpy of atomisation of oxygen	: +248 kJ mol ⁻¹
First electron affinity of oxygen	: -141 kJ mol ⁻¹
Second electron affinity of oxygen	: +791 kJ mol ⁻¹
Enthalpy of formation of copper(II) oxide	: -155 kJ mol ⁻¹

Construct energy level diagram and calculate its lattice energy.

Energy Level Diagram



Energy Level Diagram

From Hess's Law:

$$\Delta H_f \text{ CuO} = \Delta H_a \text{ Cu} + |E_1 \text{ Cu} + |E_2 \text{ Cu} + \Delta H_a \text{ O} + EA_1 \text{ O} + EA_2 \text{ O} + \Delta H_{\text{lattice}} \text{ CuO}$$

$$-155 \text{ kJ} = 339 \text{ kJ} + 248 \text{ kJ} + 745 \text{ kJ} + 1960 \text{ kJ} + (-141 \text{ kJ}) + 791 \text{ kJ} + \Delta H_{\text{lattice}}$$

$$\therefore \Delta H_{\text{lattice}} = -4097 \text{ kJmol}^{-1}$$

Energy Level Diagram

Exercise 3

Consider the enthalpy changes in the formation of magnesium fluoride.

Enthalpy of atomisation of magnesium	: +148 kJ mol ⁻¹
First ionisation energy of magnesium	: +738 kJ mol ⁻¹
Second ionisation energy of magnesium	: +1450 kJ mol ⁻¹
Enthalpy of atomisation of fluorine	: +159 kJ mol ⁻¹
Electron affinity of fluorine	: -328 kJ mol ⁻¹
Enthalpy of formation of magnesium fluoride	: -155 kJ mol ⁻¹

Construct energy level diagram and calculate its lattice energy.

Ans: $\Delta H_{\text{lattice}} = -2153 \text{ kJ/mol}$