

## CHEMISTRY ONLINE

- TUITION -

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# CHEMISTRY 

## REVISION NOTES

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## ENERGETICS

## Definition

Enthalpy change is the heat energy absorbed or released during a system's change when the pressure is constant.

## Exothermic Reactions

In exothermic reactions, energy is released from the reactants and transferred to the surroundings as the products have lower energy.

## Exothermic Reaction


reaction progress

If an enthalpy change occurs, energy is transferred between the system and its surroundings.
System refers to the chemicals
Surroundings encompass everything outside the chemicals.

Some examples of exothermic reactions are:

- combustion (burning)
- neutralization reactions between acids and alkalis
- the reaction between water and calcium oxide


## Endothermic Reactions

In an endothermic reaction energy is absorbed by the system from its surroundings. For example, the thermal decomposition of copper carbonate requires an input of heat energy.

The products have more energy than the reactants.

## Endothermic Reaction



Some examples of endothermic reactions are:

- electrolysis
- the reaction between ethanoic acid and sodium carbonate
- the thermal decomposition of calcium carbonate in a blast furnace.


## Exam Question

## State the meaning of the term enthalpy change as applied to a chemical

 reaction.
## Standard Enthalpy Change of Formation

The standard enthalpy change of formation of a compound is the enthalpy change that occurs when one mole of the compound is formed from its constituent elements under standard conditions ( 298 K and 100 kPa ), with all reactants and products being in their standard states.

## $\Delta \mathrm{H}$

## Symbol for enthalpy of formation

## Standard Enthalpy Change of Combustion

The enthalpy change when one mole of a substance is completely burned in oxygen under standard conditions is called the standard enthalpy of combustion.
( 298 K and 100 kPa ), all reactants and products being in their standard states.

## $\Delta H^{\ominus}$ <br> C

## Symbol for enthalpy of combustion

## Remember the Standard Conditions

- 100 kPa pressure
- 298 K (room temperature or 250 C )
- Solutions at $1 \mathrm{~mol} \mathrm{dm}-3$
- all substances should have their normal state at 298 K


## Exam Question

## State the meaning of the term standard enthalpy of combustion.

You may be expected to calculate the enthalpy of a reaction based on experimental data.
Learn two important formulas:


Once you have calculated the heat energy after which you can use the formula to calculate the energy per mole by applying the formula,


## Example

A student burns 4 g of propanol, which raises the water temperature from $23^{\circ} \mathrm{C}$ to $40^{\circ} \mathrm{C}$. The mass of water in the copper can is 200 g , and the specific heat capacity of water is $4.18 \mathrm{JK}^{-1} \mathrm{~g}^{-1}$.

Calculate the molar enthalpy change.

- Use the equation $\mathbf{Q}=\mathbf{m c \Delta T}$ to calculate the heat energy released.
- $Q=200 \times 4.18 \times(40-23)=14212 \mathrm{~J}$.
- Calculate the moles of propanol burnt. (Moles = mass / Mr)
- Moles of propanol $=4 / 60=0.067 \mathrm{~mol}$
- Calculate the enthalpy change by dividing $Q$ by the number of moles.

Remember to convert energy in J to kJ .

- Energy change $=14.212 \mathrm{~kJ} / 0.067 \mathrm{~mol}=212.12 \mathrm{~kJ} / \mathrm{mol}$
- Since this is a combustion reaction, we must remember that it is an exothermic reaction and add a negative sign. Our final answer $=-212.12 \mathrm{~kJ} / \mathrm{mol}$

To calculate the enthalpy change of neutralization through an experiment, you can utilize the $Q=m \times c \times \Delta T$ equation.

Firstly, mix the acid and base in a polystyrene cup, and then measure the change in temperature of the solution. In this case, the mass to be considered is the total mass of the solution.

## Example

A student mixed $40.0 \mathrm{~cm}^{3}$ of $4.00 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HCl}$ was neutralized by 35.0 cm 3 of $4.00 \mathrm{~mol} \mathrm{dm}^{-3}$
NaOH .

The temperature increased by 17.5C

Calculate the enthalpy change per mole of HCl .

## Step 1:

Calculate the energy change for the amount of reactants in the calorimeter.
$Q=m x c \times \Delta^{T}$
$Q=75 \times 4.18 \times 17.5$
$Q=5486.25 \mathrm{~J}$

## Step 2:

Calculate the number of moles of the HCl .
Moles of $\mathrm{HCl}=$ conc x vol
$=4 \times 40 / 1000$
$=0.16 \mathrm{~mol}$

## Step 3:

Calculate H the enthalpy change per mole which might be called the enthalpy change of neutralization.
$\mathrm{H}=\mathrm{Q} /$ no of moles
= 34289/0.16
$=34289 \mathrm{~J} \mathrm{~mol}^{-1}$
Convert into KJ
$=-3.429 \mathrm{~kJ} \mathrm{~mol}^{-1}$

## Exam Question

A student does an experiment to determine the enthalpy of combustion of propan-1-ol $\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}, M_{\mathrm{r}}=60.0\right)$.
Combustion of 0.497 g of propan-1-ol increases the temperature of 150 g of water from $21.2{ }^{\circ} \mathrm{C}$ to $35.1^{\circ} \mathrm{C}$

Calculate a value, in $\mathrm{kJ} \mathrm{mol}^{-1}$, for the enthalpy of combustion of propan-1-ol in this experiment.

The specific heat capacity of water is $4.18 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~g}^{-1}$

## Enthalpies may differ from those in a data book due to various factors

- Non-standard conditions used
- Heat lost to the surroundings
- Heat absorbed by the apparatus
- Incomplete combustion
- Evaporation of fuel or water

To improve the accuracy of calorimetry experimental data, minimize heat loss by using a lid or an insulated beaker.

## Exam Question

The enthalpy of combustion determined experimentally is less exothermic than that calculated using enthalpies of formation.

Give one possible reason for this, other than heat loss.

## Practical Work - Calorimetric Method

## General method

- The equipment, including the cup and pipettes, is washed with the solutions that will be used.
- dry the cup after washing
- Place a polystyrene cup inside a beaker to provide insulation and support.
- To accurately measure a specific volume of solutions, use volumetric pipettes. Once you have measured the desired volume, transfer the solution carefully into an insulated cup.
- To properly use the thermometer, securely fasten it and ensure that the bulb of the thermometer is fully submerged in the solution.
- Measure the initial temperatures of the solution(s) every minute for 2-3 minutes.
- At minute 3, add the second reagent to the cup. If using a solid reagent, add the solution to the cup first, then weigh out the solid on balance and add it.
- If using a solid reagent, use the 'before and after' weighing method and stir the mixture to ensure uniform temperature.
- Record temperature every minute after addition for several minutes


If the reaction is slow, obtaining the exact temperature rise can be challenging due to concurrent cooling.

To compensate for this, we take regular temperature readings and extrapolate the temperature curve back to the point when the reactants were mixed together.

Before combining the reactants, we measure their temperature for a few minutes to obtain a more accurate average temperature. In case the reactants are solutions, we must measure the temperature of both solutions before mixing and then use the average temperature.

## Error in methods

- Energy losses from the calorimeter
- Incomplete combustion of fuel
- Incomplete transfer of energy
- Evaporation of fuel after weighing
- Heat capacity of calorimeter not included.
- Measurements not carried out under standard conditions.


## Hess's Law

Hess's law states that the enthalpy change of a reaction is constant regardless of the pathway taken.

The enthalpy change for a reaction can be measured using Hess's law cycles, which involve alternative reactions that can be measured experimentally when the reaction of interest can't be measured directly.

Hess cycle is a diagram showing alternative routes between reactants and products, which allows the indirect determination of an enthalpy change from other known enthalpy changes using Hess' law.


If you know two energy changes for the above reactions, you can calculate the third.

## Enthalpy of Formation

The enthalpy of formation is the energy change that occurs when 1 mole of a compound is formed from its constituent elements in their standard states under standard conditions. The heat of formation of an element in its standard state is zero.

## Calculations using enthalpy of formation



Elements

## Enthalpy of combustion

The enthalpy of combustion is the energy change that occurs when 1 mole of a substance reacts completely with oxygen under standard conditions, all reactants and products being in their standard states.

## Calculations using enthalpy of combustion



Oxidised products

Exam Question

Table 2 gives some values of standard enthalpies of combustion $\left(\Delta_{\mathrm{c}} \mathrm{H}^{\ominus}\right)$.
Table 2

| Substance | $\mathrm{C}(\mathrm{s})$ | $\mathrm{H}_{2}(\mathrm{~g})$ | $\mathrm{C}_{6} \mathrm{H}_{12}(\mathrm{I})$ |
| :--- | :---: | :---: | :---: |
| Standard enthalpy of <br> combustion, $\Delta_{\mathrm{c}} \mathrm{H} \ominus / \mathrm{kJ} \mathrm{mol}^{-1}$ | -394 | -286 | -3920 |

Use the data in Table 2 to calculate the enthalpy change for the reaction represented by this equation

$$
6 \mathrm{C}(\mathrm{~s})+6 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}_{6} \mathrm{H}_{12}(\mathrm{I})
$$

Draw Hess's cycle to answer the question using the values in the table.

Table 1 contains some standard enthalpy of formation data.

## Table 1

|  | $\mathrm{CO}(\mathrm{g})$ | $\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})$ |
| :---: | :---: | :---: |
| $\Delta_{\mathrm{f}} \mathrm{H}^{\circ} / \mathrm{kJ} \mathrm{mol}^{-1}$ | -111 | -822 |

$$
\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+3 \mathrm{CO}(\mathrm{~g}) \rightarrow 2 \mathrm{Fe}(\mathrm{~s})+3 \mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta H=-19 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

Draw Hess's cycle to answer the questions using the values in table 1.

## Mean bond energy

Mean bond energy (also called average bond energy) is the amount of energy needed to break a covalent bond into gaseous atoms averaged over different molecules.

Energy is required to break a bond, making these values positive. This definition applies only to substances in the gaseous state at the start and end.

There are two ways to solve questions related to mean bond energy.

## Simple method - (All being in gases state)

In this method, simply

- add up the energy needed to break all the bonds in the reactants
- add up the energy released, forming bonds in the products
- enthalpy change is:

$$
\Delta H=(S U M \Delta H \text { bonds broken })-(\text { SUM } \Delta H \text { bonds made })
$$

## Another method to be used is by drawing Hess's cycle.

This method applies to any question regarding any bond enthalpies.

- Before breaking bonds, substances must be in the gas state, requiring $\Delta H$ to convert solids and liquids.



## Example

Calculate the enthalpy change for the following reaction given the following bond enthalpies.
$\mathrm{CH}_{3}-\mathrm{CH}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{3}-\mathrm{CH}_{2} \mathrm{Cl}(\mathrm{g})+\mathrm{HCl}(\mathrm{g})$
Bond enthalpies: C-C 348, C-H 412, Cl-Cl 242, C-Cl 338, H-Cl $431 \mathrm{~kJ} / \mathrm{mol}$

Step 1: Calculate the amount of energy absorbed while breaking the bonds.

- $6 \times(\mathrm{C}-\mathrm{H})=412 \times 6=2472$
- $1 \times(\mathrm{C}-\mathrm{C})=348$
- $1 \times(\mathrm{Cl}-\mathrm{Cl})=242$

$$
\text { Total = } 3062
$$

## Step 2:

- $5 \times(\mathrm{C}-\mathrm{H})=2060$
- $1 \times(\mathrm{C}-\mathrm{Cl})=338$
- $1 \times(\mathrm{H}-\mathrm{Cl})=431$

$$
\text { Total = } 2829
$$

## Step 3:

Enthalpy change $=$ Bonds broken - Bonds made

$$
\begin{aligned}
& =3062-2829 \\
& =233
\end{aligned}
$$

It has a positive ion, so the reaction is endothermic.

## Exam Question

Propane undergoes complete combustion.

$$
\mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 3 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \quad \Delta H=-2046 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

The table below shows some bond enthalpy data.

| Bond | $\mathrm{C}-\mathrm{H}$ | $\mathrm{C}=\mathrm{O}$ | $\mathrm{O}-\mathrm{H}$ |
| :--- | :---: | :---: | :---: |
| Mean bond enthalpy / <br> kJ mol |  |  |  |

The bond enthalpy for $\mathrm{O}=\mathrm{O}$ is $496 \mathrm{~kJ} \mathrm{~mol}^{-1}$
For $\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \Delta H=+41 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Use these data to calculate a value for the $\mathrm{C}-\mathrm{C}$ bond enthalpy in propane.

Some enthalpy data are given in Table 2.

Table 2

| Process | $\boldsymbol{\Delta} \boldsymbol{H} /$ kJ $^{2}$ mol $^{-1}$ |
| :--- | :---: |
| $\mathrm{~N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NH}_{3}(\mathrm{~g})$ | -92 |
| $\mathrm{~N}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{~N}(\mathrm{~g})$ | +944 |
| $\mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}(\mathrm{g})$ | +436 |

Use the data from Table 2 to calculate the bond enthalpy for $\mathrm{N}-\mathrm{H}$ in ammonia.


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