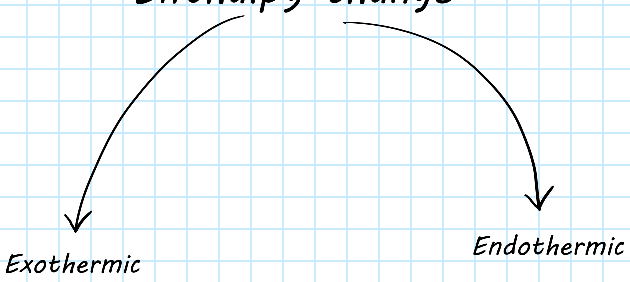
Enthalpy change



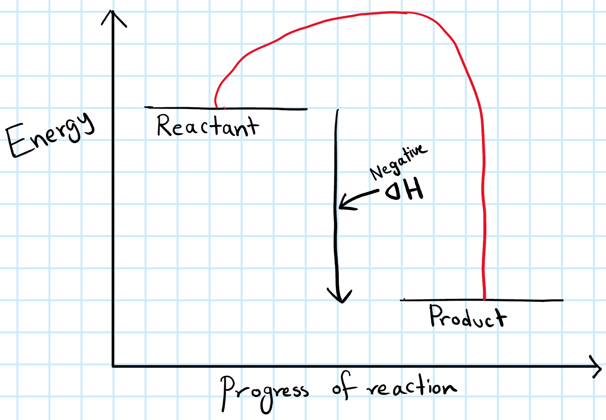
- *Enthalpy change of the a reaction is the energy difference between the reactant and product.*
- *Bond breaking is endothermic, so energy is given out.*
- *Bond forming is exothermic, so energy is taken in.*

Exothermic reaction

- *The type of reaction by which heat energy is given out is called exothermic reaction.*
- *During the reaction, temperature of the reaction mixture increases.*
- *Reactants have more energy than the products.*
- *Heat energy is transferred from the system to the surroundings.*
- *During the chemical reaction, bonds in the reactants are broken and new bonds are formed in the products.*
- *Bond breaking energy is lower than bond formation energy.*
- *Overall, heat energy is given out.*
- *For exothermic reactions the value of enthalpy change is negative.*

$$\Delta H = H_{product} - H_{reactant}$$

Enthalpy profile diagram



Examples of exothermic reaction

1. Combustion

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

2. Respiration

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

3. Neutralization reaction

$NaOH + HCl \longrightarrow NaCl + H_2O$

4. Reaction of a metal with acid

$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$

5. Reaction of a metal oxide with water

$CaO + H_2O \longrightarrow Ca(OH)_2$

6. Fermentation

$C_6H_{12}O_6 \xrightarrow[\text{No } O_2,\ 30°C]{\text{Yeast}} 2C_2H_5OH + 2CO_2$

7. Reaction of Zinc with Copper(II) sulphate

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

8. Rusting of iron

$Fe + O_2 + H_2O \longrightarrow Fe_2O_3.H_2O$

9. Any reaction where bond is forming

$Cl + Cl \longrightarrow Cl_2$

10. Condensation

$H_2O_{(g)} \longrightarrow H_2O_{(l)}$

11. Freezing

$H_2O_{(l)} \longrightarrow H_2O_{(s)}$

12. Hydration

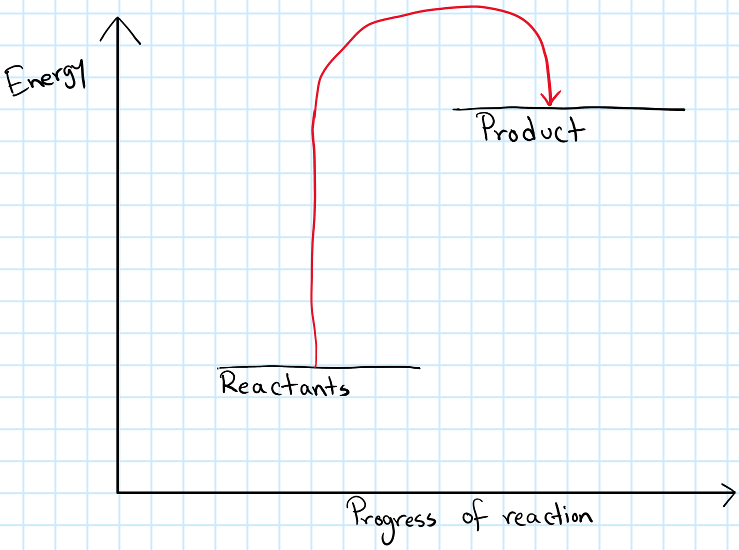
$CoCl_2 + 6H_2O \longrightarrow CoCl_2.6H_2O$

13. Solidification

$I_{2(g)} \longrightarrow I_{2(s)}$

Endothermic reaction

- The type of reaction by which heat energy is taken in is called exothermic reaction.
- During the reaction, temperature of the reaction mixture decreases.
- Products have more energy than the reactants.
- Heat energy is transferred from the surrounding to the system.
- During the chemical reaction, bonds in the reactants are broken and new bonds are formed in the products.
- Bond breaking energy is higher than bond formation energy.
- Overall, heat energy is taken in.
- For endothermic reactions the value of enthalpy change is positive.



Examples of endothermic reaction

- Photosynthesis

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

- Thermal decomposition

$$CaCO_3 \xrightarrow{Heat} CaO + CO_2$$

- Any reaction involving overall bond breaking

$$H_2 \longrightarrow H + H$$

- Dehydration

$$CoCl_2 . 6H_2O \xrightarrow{heat} CoCl_2 + 6H_2O$$

- Melting
- Boiling
- Evaporation

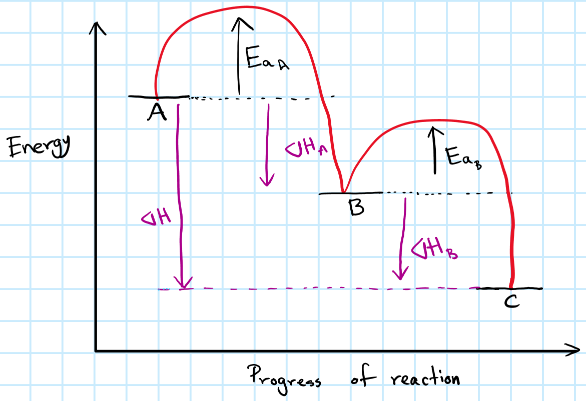
✹ Most of the exothermic reaction are spontaneous and have low activation energy.

✹ Most of the endothermic reaction are non-spontaneous and have high activation energy.

Energy profile diagrams for two step reactions

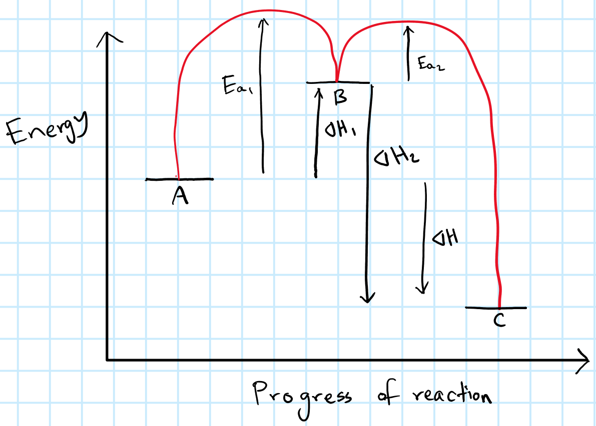
Example 1

A $\xrightarrow[\text{Exothermic}]{\text{Step 1}}$ B $\xrightarrow[\text{Endothermic}]{\text{Step 2}}$ C (Overall exothermic)



Example 2

A $\xrightarrow[\text{Endothermic}]{\text{Step 1}}$ B $\xrightarrow[\text{Exothermic}]{\text{Step 2}}$ Overall exothermic



Standard condition

It is a specific condition where experiments are done to make it standard. In standard condition, temperature is 298K(25°C) and 100KPa (0.98atm).

Standard Enthalpy change of formation

It is the enthalpy change when one mole of a compound is formed from its elements in their standard state and condition.

Examples:

$\Delta H_f^{\ominus}$ of H_2O

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$$

$\Delta H_f^{\ominus}$ of C_2H_5OH

$$2C_{(s)} + 3H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow C_2H_5OH_{(l)}$$

$\Delta H_f^{\ominus}$ of $KMnO_4$

$$K_{(s)} + Mn_{(s)} + 2O_{2(g)} \rightarrow KMnO_{4(s)}$$

$\Delta H_f^{\ominus}$ of CO_2

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

- Value of enthalpy change of formation can be positive or negative depending on the reaction.
- The enthalpy change of formation of any element is zero.
- Must write the state symbols in the equation.
- Make sure ,while writing the equation, to show one mole of compound is forming.

Standard enthalpy change of atomization

It is the enthalpy change when one mole of gaseous atom is formed from its elements in their standard state and condition.

Examples:

$\Delta H_{at}^{\ominus}$ of H

$$\frac{1}{2} H_{2(g)} \rightarrow H_{(g)}$$

$\Delta H_{at}^{\ominus}$ of Cl_2

$$\frac{1}{2} Cl_{2(g)} \rightarrow Cl_{(g)}$$

$\Delta H_{at}^{\ominus}$ of Br_2

$$\frac{1}{2} Br_{2(l)} \rightarrow Br_{(g)}$$

$\Delta H_{at}^{\ominus}$ of Na

$$Na_{(s)} \rightarrow Na_{(g)}$$

- Value of enthalpy change of atomization is always positive.
- It is because during atomization only bonds are breaking.
- Make sure to give state symbols in the equation.
- Make sure to form one mole of compound in the equation.
- Make sure the state symbol of atoms formed is gas.

Standard enthalpy change of combustion

It is the enthalpy change when one mole of a substance is completely combusted in excess of oxygen under standard condition.

Examples:

$\Delta H_c^\ominus$ of C

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

$\Delta H_c^\ominus$ of $H_{2(g)}$

$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$

As in these reactions no other products are forming,

$\Delta H_c^\ominus(C) = \Delta H_f^\ominus(CO_2)$

$\Delta H_c^\ominus(H_2) = \Delta H_f^\ominus(H_2O)$

Further examples,

$\Delta H_c^\ominus$ of C_2H_5OH

$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_2 + 3H_2O_{(l)}$

- *Value of enthalpy change of combustion is always negative.*
- *This is due to the fact that all combustion reactions are exothermic.*
- *While writing the equation for enthalpy change of combustion of compounds, make sure one mole of compound is being combusted.*

Standard enthalpy change of reaction

It is the enthalpy change when a reaction happens in standard condition. The reactants and products must be in standard state.

Examples:

$\Delta H_r^\ominus$

$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$

$2H_{2(g)} + O_2 \longrightarrow 2H_2O_{(l)}$

- *The enthalpy change of reaction can be positive or negative depending on the reaction.*

Enthalpy change of neutralization

It is the enthalpy change of when one mol of water is formed by the reaction of an acid with an alkali under standard condition.

Examples:

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

- *Only one mole of water will be formed while writing the equation.*
- *It is always negative.*

Calculations

- *Enthalpy change calculation by using standard enthalpy change of formation.*

$$\Delta H_r^\ominus = \Delta H_{f\,(product)}^\ominus - \Delta H_{f\,(reactant)}^\ominus$$

Example 1

$2H_2O_{2(l)} \longrightarrow 2H_2O + O_{2(g)}$

Given,

$\Delta H_f^\ominus (H_2O_2) = -187.8\ Kjmol^{-1}$

$\Delta H_f^\ominus (H_2O) = -285.8\ Kjmol^{-1}$

Calculate the $\Delta H_r^\ominus$

Ans: $\Delta H_r^\ominus = \Delta H_{f\,(product)}^\ominus - \Delta H_{f\,(reactant)}^\ominus$

$= 2(-285.8) - 2(-187.8)$

$= -196\ Kjmol^{-1}$

Example 2

$3FeO_{(s)} + 2Al_{(s)} \longrightarrow 3Fe_{(s)} + Al_2O_{3(s)}$

$\Delta H_f^\ominus (FeO) = -266\ Kjmol^{-1}$

$\Delta H_f^\ominus (Al_2O_3) = -1676\ Kjmol^{-1}$

Calculate $\Delta H_r^\ominus$

Ans $\Delta H_r^\ominus = \Delta H_{f\,(product)}^\ominus - \Delta H_{f\,(reactant)}^\ominus$

$-1676 - 3(-266)$

$= -878\ Kjmol^{-1}$

Example 3

$3Mg_{(s)} + KClO_{3(s)} \longrightarrow 3MgO_{(s)} + KCl_{(s)}$

$\Delta H_f^\ominus (MgO) = -602\ Kjmol^{-1}$

$\Delta H_f^\ominus (KCl) = -437\ Kjmol^{-1}$

$\Delta H_f^\ominus (KClO_3) = -391\ Kjmol^{-1}$

Calculate $\Delta H_r^\ominus$

Ans

$\Delta H_r^\ominus = 3(-602) + (-437) - (-391)$

$= -1852\ Kjmol^{-1}$

- *Enthalpy calculation using bond energy*

$\Delta H_r^\ominus$ = *Bond breaking energy - Bond forming energy*

Example 1

$$H_2C=CH_2 + HF \longrightarrow CH_3CH_2F \quad \Delta H_r^\ominus = -73\ Kjmol^{-1}$$

Calculate the bond energy between carbon and fluorine.
Given data is:
C-H = 410
C=C = 610
H-F = 562
C-C = 35
ANS:

Bond breaking,

$(410\times4) + 610 + 562$
$= 282$

Bond forming,

$5(410) + 350 + x$
$= 2400 + x$

Equating,

$-73 = 2812 - (2400 + x)$
$x = 485$

Example 2

The molecular formula for sulfur is S_8.

$\Delta H_c^\ominus S_8 = -2376\ Kjmol^{-1}$

Energy required to break 1 mol of S_8 *into gaseous atoms is +2232Kjmol*$^{-1}$ *and the bond enthalpy of the double bond between Oxygen (O=O) is 496 Kjmol*$^{-1}$.
What is the value of S=O bond enthalpy?

ANS:
The equation is

$$S_8 + 8O_2 \longrightarrow 8SO_2$$

$-2376 = 2232 + 8(496) - 16x$
$x = 536\ Kjmol^{-1}$

Example 5

$\Delta H_f^\ominus$ (Cyclopropane) = +53.3 $Kjmol^{-1}$

$\Delta H_{at}^\ominus$ (Graphite) = +717 $Kjmol^{-1}$

H–H ⟶ 436 $Kjmol^{-1}$
C–H ⟶ 410 $Kjmol^{-1}$

Calculate the value of C-C bond enthalpy.

$$3C_{(s)} + 3H_{2(g)} \longrightarrow C_3H_{6(g)}$$

$$53.3 = 3(717) + 3(436) - \{6(410) + 3x\}$$

$$x = 315.2\ Kjmol^{-1}$$

Example 6

$$2NF_{3(g)} \longrightarrow 2N_{(g)} + 6F_{(g)}$$

$\Delta H_r^\ominus$ = +1668 $Kjmol^{-1}$

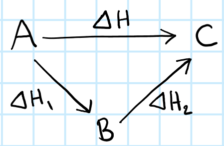
Calculate the bond enthalpy of N-F.

ANS:

$$\frac{1668}{3} = +556\ Kjmol^{-1}$$

Hess's cycle

The overall enthalpy change for a reaction is independent of the route taken or the number of steps involved, provided that the initial and final conditions remain same.



According to Hess's law

$$\Delta H \longrightarrow \Delta H_1 + \Delta H_2$$

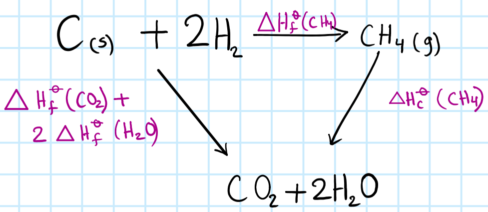
Example 1

$\Delta H_f^\ominus(CO_2) = -394\ \text{kJmol}^{-1}$

$\Delta H_f^\ominus(H_2O) = -286\ \text{kJmol}^{-1}$

$\Delta H_f^\ominus(CH_4) = -74\ \text{kJmol}^{-1}$

By constructing a Hess's Cycle calculate the value of $\Delta H_c^\ominus(CH_4)$.



According to Hess's law,

$$\Delta H_f^\ominus(CO_2) + 2\Delta H_f^\ominus(H_2O) = \Delta H_f^\ominus(CH_4) + \Delta H_c^\ominus(CH_4)$$

$$-394 + 2(-286) = -74 + \Delta H_c^\ominus(CH_4)$$

$$\Delta H_c^\ominus = -892\ \text{kJmol}^{-1}$$

Example 2

$\Delta H_f^\ominus(CO_2) = -393\ \text{kJmol}^{-1}$

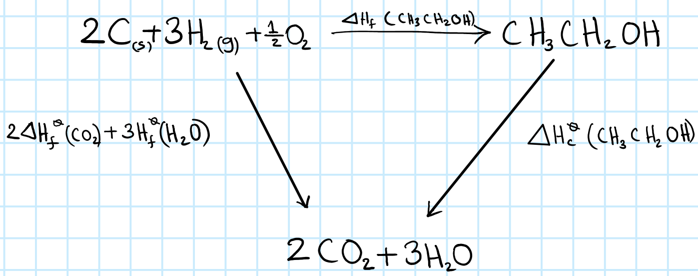
$\Delta H_f^\ominus(H_2O) = -286\ \text{kJmol}^{-1}$

$\Delta H_f^\ominus(CH_3CH_2OH) = -277\ \text{kJmol}^{-1}$

Calculate the value of enthalpy change of combustion of ethanol by drawing a Hess's Cycle.

$$C_2H_5OH + 3O_2 \longrightarrow 3CO_2 + 3H_2O$$

Ans



Ans

$$-277 + \Delta H_c^\ominus = 2(-393) + 3(-286)$$

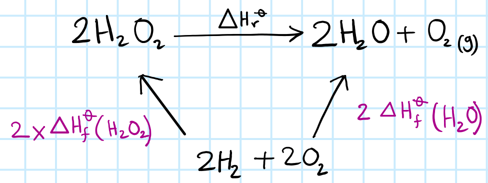
$$\Delta H_c^\ominus = -1367\ \text{kJmol}^{-1}$$

Example 3

$\Delta H_f^{\ominus}(H_2O) = -285.8\ kJmol^{-1}$
$\Delta H_f^{\ominus}(H_2O_2) = -187.8\ kJmol^{-1}$

By drawing a suitable Hess's cycle, calculate the enthalpy change of reaction for the decomposition of hydrogen peroxide.

Ans



$\Delta H_r^{\ominus} + 2\Delta H_f^{\ominus}(H_2O_2) = 2 \times \Delta H_f^{\ominus}(H_2O)$

$\Delta H_r^{\ominus} + 2(-187.8) = 2(-285.8)$

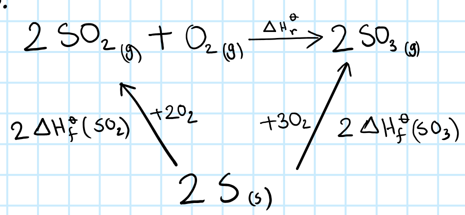
$\Delta H_r^{\ominus} = -196\ Kjmol^{-1}$

Example 4

- $S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \quad \Delta H_f^{\ominus} = -297\ Kjmol^{-1}$
- $S_{(s)} + 3/2\, O_2 \longrightarrow SO_{3(g)} \quad \Delta H_f^{\ominus} = -395\ Kjmol^{-1}$

Calculate the enthalpy change of reaction.

ANS:



$2(-297) + \Delta H_r^{\ominus} = 2(-395)$

$\Delta H_r^{\ominus} = -196\ Kjmol^{-1}$

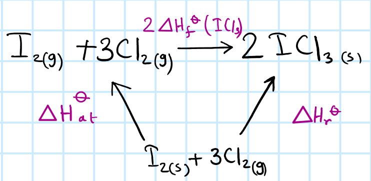
Example 5

$I_{2(g)} + 3Cl_{2(g)} \longrightarrow 2\ ICl_{3(s)} \quad \Delta H_r^{\ominus} = -214\ Kjmol^{-1}$

$I_{2(g)} \longrightarrow I_{2(g)} \quad \Delta H_{at}^{\ominus} = +38\ Kjmol^{-1}$

Calculate enthalpy change of formation of ICl_3

ANS:



$\Delta H_{at}^{\ominus} + 2\Delta H_f^{\ominus}(ICl_3) = \Delta H_r^{\ominus}$

$+33 + 2\Delta H_f^{\ominus}(ICl_3) = -214$

$\Delta H_f^{\ominus}(ICl_3) = -123.5$

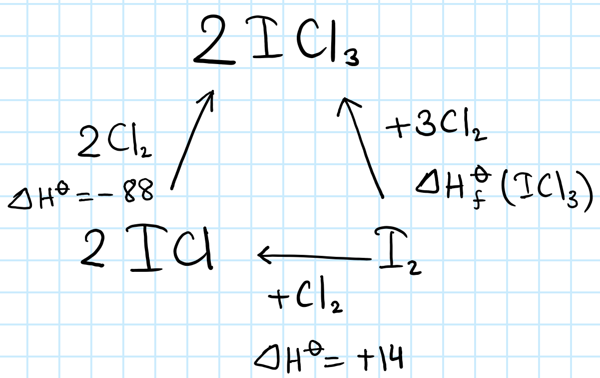
Example 6

$$I_{2(s)} + Cl_{2(g)} \longrightarrow 2\,ICl_{3(s)} \qquad \Delta H^\ominus = +14\ kJmol^{-1}$$

$$ICl_{(s)} + Cl_{2(g)} \longrightarrow ICl_3 \qquad \Delta H^\ominus = -88\ kJmol^{-1}$$

Calculate the value of $\Delta H_f^\ominus\,(ICl_3)$

Solution:



$$+14 + (-88 \times 2) = 2\Delta H_f^\ominus(ICl_3)$$

$$\Delta H_f^\ominus(ICl_3) = -81\ kJmol^{-1}$$

Example 7

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_A^\ominus = -283\ kJmol^{-1}$$

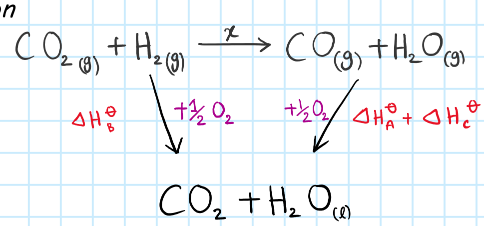
$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow H_2O \qquad \Delta H_B^\ominus = -286\ kJmol^{-1}$$

$$H_2O_{(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H_C^\ominus = -44\ kJmol^{-1}$$

Calculate the value of x of the following equation.

$$CO_{2(g)} + H_{2(g)} \xrightarrow{x} CO_{(g)} + H_2O_{(g)}$$

Solution



$$x + (\Delta H_C^\ominus + \Delta H_A^\ominus) = \Delta H_B^\ominus$$

$$x = +41\ kJmol^{-1}$$