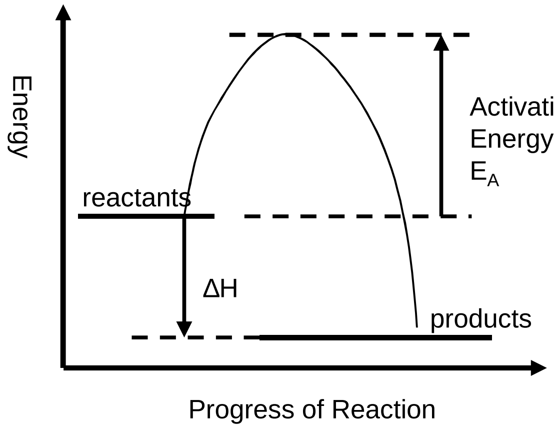
3.2.1. Enthalpy changes

In an exothermic change energy is transferred from the system (chemicals) to the surroundings.

The products have less energy than the reactants



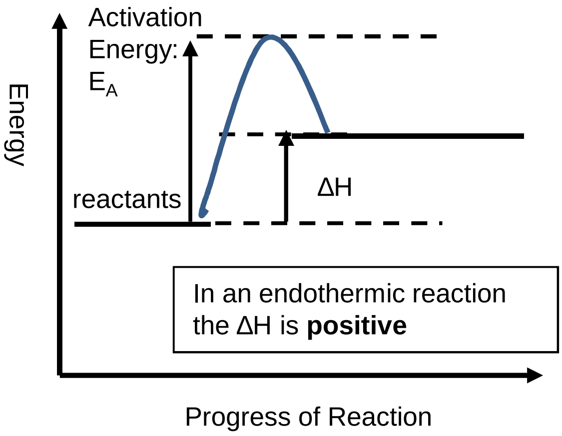
In an exothermic reaction the ΔH is **negative**

Common oxidation exothermic processes are the combustion of fuels and the oxidation of carbohydrates such as glucose in respiration

If an enthalpy change occurs then energy is transferred between **system** and **surroundings .** The system is the chemicals and the surroundings is everything outside the chemicals.

In an endothermic change, energy is transferred from the surroundings to the system (chemicals). They require an input of heat energy e.g. thermal decomposition of calcium carbonate

The products have more energy than the reactants



In an endothermic reaction the ΔH is **positive**

The **activation Energy** is defined as the **minimum** energy which particles need to collide to start a reaction

Enthalpy changes are normally quoted at **standard** conditions.
Standard conditions are :

- 100 kPa pressure
- 298 K (room temperature or 25°C)
- Solutions at 1mol dm^{-3}
- all substances should have their normal state at 298K

When an enthalpy change is measured at standard conditions the symbol $^\ominus$ is used
Eg $\Delta H^\ominus$

Definition: Enthalpy change of reaction $\Delta_r H^\ominus$ is the enthalpy change when the number of moles of reactants as specified in the balanced equation react together

Standard enthalpy change of formation

The standard enthalpy change of formation of a compound is the **enthalpy change** when **1 mole of the compound** is formed from **its elements** under **standard conditions (298K and 100kpa), all reactants and products being in their standard states**
Symbol $\Delta_f H^\ominus$

$Mg (s) + Cl_2 (g) \rightarrow MgCl_2 (s)$
$2Fe (s) + 1.5\ O_2 (g) \rightarrow Fe_2O_3 (s)$

The enthalpy of formation of an element = 0 kJ mol^{-1}

Standard enthalpy change of combustion

The standard enthalpy of combustion of a substance is defined as the **enthalpy change** that occurs when **one mole of** a substance is **combusted completely in oxygen** under **standard conditions. (298K and 100kPa), all reactants and products being in their standard states**
Symbol $\Delta_c H^{\ominus}$

CH_4 (g) + $2O_2$ (g)→ CO_2 (g) + 2 H_2O (l)

Incomplete combustion will lead to soot (carbon), carbon monoxide and water. It will be **less exothermic** than complete combustion.

Enthalpy change of Neutralisation

The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and an alkali react together under standard conditions to produce 1 mole of water.
Symbol $\Delta_{neut} H^{\ominus}$

Measuring the Enthalpy Change for a Reaction Experimentally

Calorimetric method

For a reaction in solution we use the following equation

energy change = mass of solution x heat capacity x temperature change

Q (J) = m (g) x c_p (J $g^{-1}K^{-1}$) x ΔT (K)

This equation will only give the energy for the actual quantities used. Normally this value is converted into the energy change per mole of one of the reactants. (The enthalpy change of reaction, $\Delta_r H$)

Calorimetric method

Practical

One type of experiment is one in which substances are mixed in an insulated container and the temperature rise measured.

This could be a solid dissolving or reacting in a solution or it could be two solutions reacting together

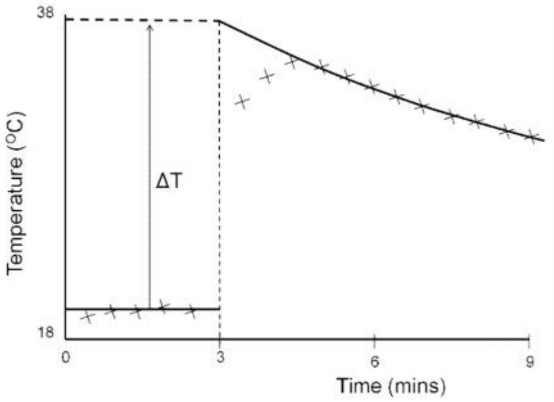
General method

- washes the equipment (cup and pipettes etc) with the solutions to be used
- dry the cup after washing
- put polystyrene cup in a beaker **for insulation and support**
- Measure out desired volumes of solutions with volumetric pipettes and transfer to insulated cup
- clamp thermometer into place making sure the thermometer bulb is immersed in solution
- measure the initial temperatures of the solution or both solutions if 2 are used. Do this every minute for 2-3 minutes
- At minute 3 transfer second reagent to cup. If a solid reagent is used then add the solution to the cup first and then add the solid weighed out on a balance.
- If using a solid reagent then use 'before and after' weighing method
- stirs mixture **(ensures that all of the solution is at the same temperature)**
- Record temperature every minute after addition for several minutes

If the reaction is slow then the exact temperature rise can be difficult to obtain as cooling occurs simultaneously with the reaction

To counteract this we take readings at regular time intervals and extrapolate the temperature curve/line back to the time the reactants were added together.

We also take the temperature of the reactants for a few minutes before they are added together to get a better average temperature. If the two reactants are solutions then the temperature of both solutions need to be measured before addition and an average temperature is used.



Errors in this method

- energy transfer from surroundings (usually loss)
- approximation in specific heat capacity of solution. The method assumes all solutions have the heat capacity of water.
- neglecting the specific heat capacity of the calorimeter- we ignore any energy absorbed by the apparatus.
- reaction or dissolving may be incomplete or slow.
- Density of solution is taken to be the same as water.

Read the question carefully. It may be necessary to describe:

- Method
- Drawing of graph with extrapolation
- Description of the calculation

Calculating the enthalpy change of reaction, a_rH from experimental data

General method

1. Using **$q = m \times c_p \times aT$** calculate energy change for quantities used
2. Work out the moles of the reactants used
3. Divide q by the number of moles of the reactant not in excess to give a**H**
4. Add a sign and unit (divide by a thousand to convert $Jmol^{-1}$ to $kJmol^{-1}$

The heat capacity of water is 4.18 J $g^{-1}K^{-1}$. In any reaction where the reactants are dissolved in water we assume that the heat capacity is the same as pure water.

Also assume that the solutions have the density of water, which is 1g cm^{-3}. Eg $25cm^3$ will weigh 25 g

Example 1. Calculate the enthalpy change of reaction for the reaction where $25.0cm^3$ of 0.200 mol dm^{-3} copper sulfate was reacted with 0.01mol (excess of zinc). The temperature increased 7^oC .

Step 1: Calculate the energy change for the amount of reactants in the calorimeter.

$Q = m \times c_p \times \Delta T$

$Q = 25 \times 4.18 \times 7$

Q = 731.5 J

Note the mass is the mass of the copper sulfate solution only. Do not include the mass of zinc powder.

Step 2 : calculate the number of moles of the reactant not in excess.

moles of $CuSO_4$ = conc x vol
= 0.2 x 25/1000
= 0.005 mol

If you are not told what is in excess, then you need to work out the moles of both reactants and work out using the balanced equation which one is in excess.

Step 3 : calculate the enthalpy change per mole

ΔH = Q/ no of moles
= 731.5/0.005
= 146300 **J mol^{-1}**
= 146 **kJ mol^{-1} to 3 sf**

Finally add in the sign to represent the energy change: if temp increases the reaction is exothermic and is given a minus sign e.g. **–146 kJ mol^{-1}**

Remember in these questions: **sign, unit, 3 sig figs**.

Example 2. $25.0cm^3$ of 2.00 mol dm^{-3} HCl was neutralised by $25.0cm^3$ of 2.00 mol dm^{-3} NaOH. The temperature increased 13.5^oC. Calculate the enthalpy change per mole of HCl?

Step 1: Calculate the energy change for the amount of reactants in the calorimeter.

$Q = m \times c_p \times \Delta T$

$Q = 50 \times 4.18 \times 13.5$

Q = 2821.5 **J**

Note the mass equals the mass of acid + the mass of alkali, as they are both solutions.

Step 2 : calculate the number of moles of the HCl.

moles of HCl = conc x vol
= 2 x 25/1000
= 0. 05 mol

Step 3 : calculate ΔH the enthalpy change per mole which can be called the enthalpy change of neutralisation

ΔH = Q/ no of moles
= 2821.5/0.05
= 56430 **J mol^{-1}**
= -56.4 **kJ mol^{-1} to 3 sf**

Exothermic and so is given a minus sign

Remember in these questions: **sign, unit, 3 sig figs**.

Measuring Enthalpies of Combustion using Calorimetry

Enthalpies of combustion can be calculated by using calorimetry. Generally the fuel is burnt and the flame is used to heat up water in a metal cup.

Example 3. Calculate the enthalpy change of combustion for the reaction where 0.650g of propan-1-ol was completely combusted and used to heat up 150g of water from 20.1 to 45.5°C

Step 1: Calculate the energy change used to heat up the water.

$Q = m \times c_p \times \Delta T$

$Q = 150 \times 4.18 \times 25.4$

$Q = 15925.8$ **J**

Note the mass is the mass of water in the calorimeter and not the alcohol

Step 2 : calculate the number of moles of alcohol combusted.

moles of propan-1-ol = mass/ *M*r
= 0.65 / 60
= 0.01083 mol

Step 3 : calculate the enthalpy change per mole which is called $\Delta_c H$ (the enthalpy change of combustion)

ΔH = Q/ no of moles
= 15925.8/0.01083
= 1470073 **J mol^{-1}**
= 1470 **kJ mol^{-1} to 3 sf**

Finally add in the sign to represent the energy change: if temp increases the reaction is exothermic and is given a minus sign eg **–1470 kJ mol^{-1}**

Remember in these questions: **sign, unit, 3 sig figs**.

Errors in this method

- Energy losses from 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 as H_2O is gas, not liquid, in this experiment

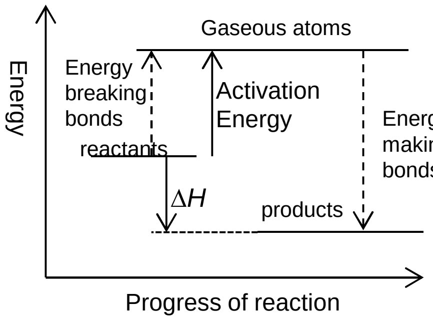
Mean Bond energies

Definition: The mean bond enthalpy is the enthalpy change when one mole of bonds of (gaseous covalent) bonds is broken (averaged over different molecules)

These values are positive because energy is required to break a bond.

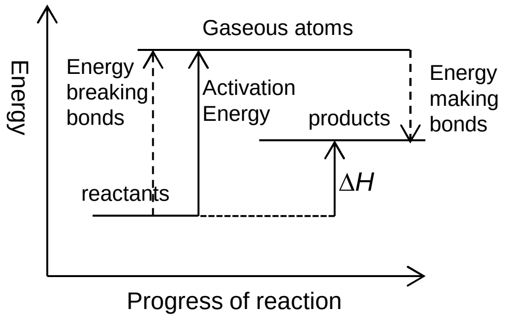
The definition only applies when the **substances start and end in the gaseous state.**

We use values of **mean** bond energies because every single bond in a compound has a slightly different bond energy. E.g. In CH_4 there are 4 C-H bonds. Breaking each one will require a different amount of energy. However, we use an average value for the C-H bond for all hydrocarbons.



Reaction profile for an EXOTHERMIC reaction

Bond breaking absorbs energy and bond making releases energy



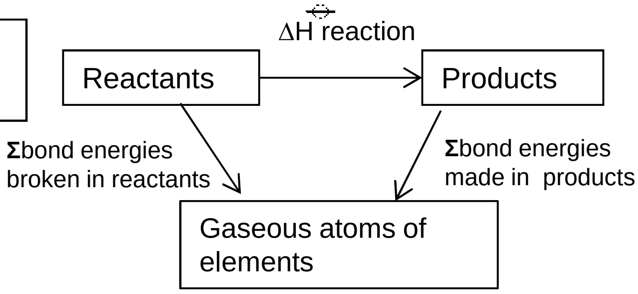
Reaction profile for an ENDOTHERMIC reaction

In an exothermic reaction more energy is released when making bonds than is absorbed when breaking bonds

In an endothermic reaction more energy is absorbed when breaking bonds than is released when making bonds.

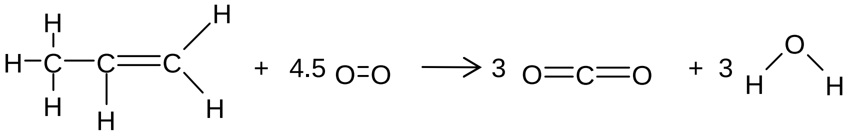
In general (if all substances are gases**)**

ΔH **=** Σ **bond energies broken -** Σ **bond energies made**



ΔH values calculated using this method will be less accuate than using formation or combustion data because the mean bond energies are not exact

Example 4. Use the following mean bond enthalpy data to calculate the enthalpy of combustion of propene



ΔH **=** Σ **bond energies broken -** Σ **bond energies made**

= [E(C=C) + E(C-C) + 6 x E(C-H) + 4.5 x E(O=O)] – [6 xE(C=O) + 6 E(O-H)]

= [612 + 348 + (6 x 412) + (4.5 x 496)] – [(6 x 743) + (6 X 463)]

= - 1572 $kJmol^{-1}$

Bond	Mean enthalpy (kJ mol-1)
C=C	612
C-C	348
O=O	496
O=C	743
O-H	463
C-H	412

Example 5. Use the following mean bond enthalpy data to calculate the enthalpy of formation of NH_3

½ $N_2 + 1.5\ H_2 \rightarrow NH_3$ (note the balancing is to agree with the definition of heat of formation (i.e. one mole of product)

E(N≡N) = 944 kJ mol^{-1} E(H-H) = 436 kJ mol^{-1} E(N-H) = 388 kJ mol^{-1}

a*H* **=** p **bond energies broken -** p **bond energies made**

= [0.5 x E(N≡N) + 1.5 x E(H-H)] – [3 xE(N-H)]

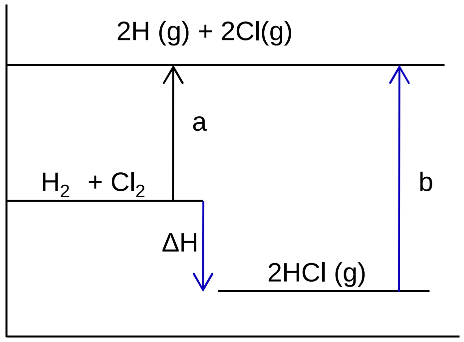
= [(0.5 x 944) + (1.5 x 436)] – [3 x 388)]

= - 38 kJmol^{-1}

Hess's Law

Hess's law states that total **enthalpy change** for a reaction is **independent of the route** by which the chemical change takes place

Hess's law is a version of the first law of thermodynamics, which is that energy is always conserved.



On an energy level diagram the directions of the arrows can show the different routes a reaction can proceed by.

In this example one route is arrow **'a'**
The second route is shown by arrows **ΔH** plus arrow '**b**'

So **a** = **ΔH** + **b**
And rearranged
ΔH = a - b

$$\begin{tikzcd}
H^+ (g) + Br^- (g) \arrow[r, "\Delta H"] & H^+ (aq) + Br^- (aq) \\
H (g) + Br (g) \arrow[u, "a"] \arrow[r, "c"'] & HBr (g) \arrow[u, "d"']
\end{tikzcd}$$

Interconnecting reactions can also be shown diagrammatically.

In this example one route is arrow **'a'** plus **ΔH**
The second route is shown by arrows **'c'** plus arrow '**d**'

So **a**+ **ΔH = c + d**
And rearranged
ΔH = c + d - a

Often Hess's law cycles are used to measure the enthalpy change for a reaction that cannot be measured directly by experiments. Instead alternative reactions are carried out that can be measured experimentally.

$$\begin{tikzcd}
\boxed{CuSO_{4\,(s)} + 5H_2O_{\,(l)}} \arrow[rr, "\Delta H \text{ reaction}"] \arrow[dr, "-66.1 \text{ kJmol}^{-1}"', "+\text{ aq}"] & & \boxed{CuSO_4.5H_2O_{\,(s)}} \arrow[dl, "+\text{ aq}"', "+11\text{kJmol}^{-1}"] \\
& \boxed{CuSO_4 \text{ (aq)}} &
\end{tikzcd}$$

ΔH reaction + 11kJmol^{-1} = -66.1 kJmol^{-1}

ΔH reaction = -66.1 - 11

= -77.1 kJmol^{-1}

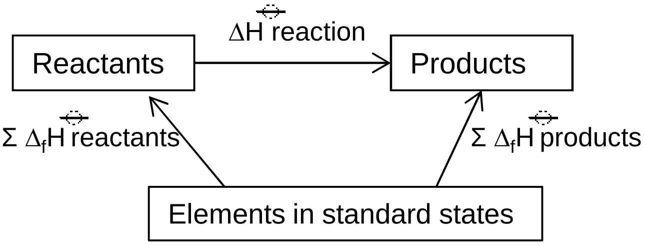
This Hess's law is used to work out the enthalpy change to form a hydrated salt from an anhydrous salt.

This cannot be done experimentally because it is impossible to add the exact amount of water and it is not easy to measure the temperature change of a solid.

Instead both salts are dissolved in excess water to form a solution of copper sulfate. The temperature changes can be measured for these reactions.

Using Hess's law to determine enthalpy changes from enthalpy changes of formation.

a**$H^{\ominus}$ reaction = Σ $\Delta_f H^{\ominus}$ products - Σ $\Delta_f H^{\ominus}$ reactants**



Example 6. Calculate the enthalpy change for this reaction

$Al_2O_3 + 3\ Mg \rightarrow 3\ MgO + 2\ Al$

ΔH **= Σ**$\Delta_f H$ products – **Σ** $\Delta_f H$ reactants

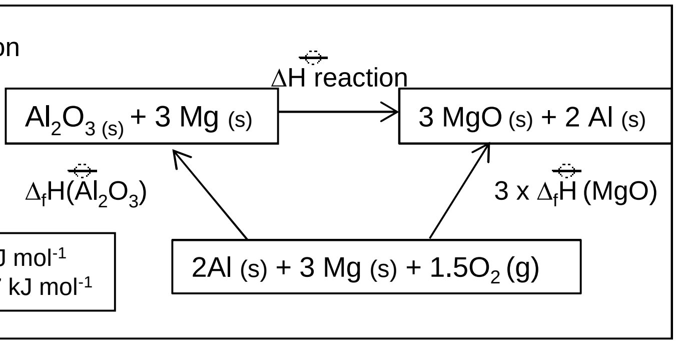
$\Delta H = 3 \times \Delta_f H\ (MgO) - \Delta_f H\ (Al_2O_3)$

$\Delta H = (3 \times -601.7) - -1675.7$

$= -129.4\ kJ\ mol^{-1}$

Remember elements have $\Delta H_f = 0$

$\Delta_f H(MgO) = -601.7\ kJ\ mol^{-1}$
$\Delta_f H(Al_2O_3) = -1675.7\ kJ\ mol^{-1}$



Example 7. Use the following data to calculate the enthalpy of combustion of propene

$\Delta_f H\ C_3H_6(g) = +20\ kJ\ mol^{-1}$ $\Delta_f H\ CO_2(g) = -394\ kJ\ mol^{-1}$ $\Delta_f H\ H_2O(g) = -242\ kJ\ mol^{-1}$

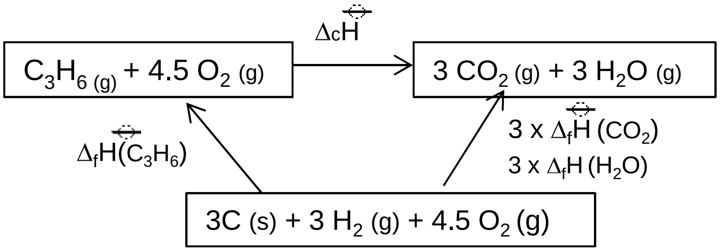
$C_3H_6 + 4.5\ O_2 \rightarrow 3CO_2 + 3H_2O$

$\Delta_c H$ **= Σ** $\Delta_f H$ products – **Σ** $\Delta_f H$ reactants

$\Delta_c H = [3 \times \Delta_f H\ (CO_2) + 3 \times \Delta_f H\ (H_2O)] - \Delta_f H\ (C_3H_6)$

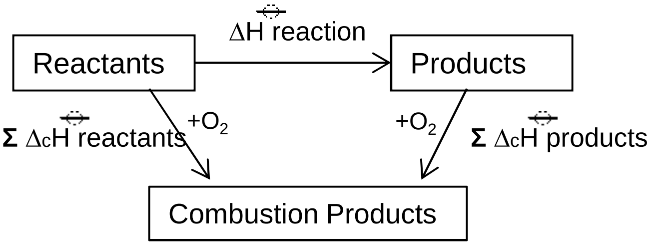
$\Delta_c H = [(3 \times -394) + (3 \times -242)] - 20$

$= -1928\ kJ\ mol^{-1}$



Using Hess's law to determine enthalpy changes from enthalpy changes of combustion.

a**$H^{\ominus}$ reaction = Σ** a$_c$**$H^{\ominus}$ reactants - Σ** a$_c$**$H^{\ominus}$ products**



Example 8. Use the following combustion data to calculate the enthalpy of reaction

$CO\ (g) + 2H_2\ (g) \rightarrow CH_3OH\ (g)$

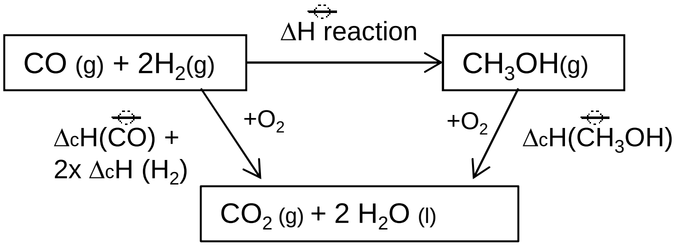
$\Delta_c H\ CO(g) = -283\ kJ\ mol^{-1}$ $\Delta_c H\ H_2\ (g) = -286\ kJ\ mol^{-1}$ $\Delta_c H\ CH_3OH(g) = -671\ kJ\ mol^{-1}$

ΔH reaction = **Σ** $\Delta_c H$ reactants - **Σ** $\Delta_c H$ products

$\Delta H = \Delta_c H\ (CO) + 2 \times \Delta_c H\ (H_2) - \Delta_c H\ (CH_3OH)$

$\Delta H = -283 + 2x -286 - -671$

$= -184\ kJ\ mol^{-1}$



Example 9. Use the following combustion data to calculate the enthalpy of formation of propene

$3C\ (s) + 3H_2\ (g) \rightarrow C_3H_6\ (g)$

$\Delta_c H$ C (s) = -393kJ mol^{-1} $\Delta_c H$ H_2 (g)= –286 kJ mol^{-1} $\Delta_c H$ C_3H_6(g)= –-2058 kJ mol^{-1}

$\Delta H = \mathbf{\Sigma}\ \Delta_c H \text{ reactants} - \mathbf{\Sigma}\ \Delta_c H \text{ products}$

$\Delta_f H = 3 \times \Delta_c H\ (C) + 3 \times \Delta_c H\ (H_2) - \Delta_c H\ (C_3H_6)$

$\Delta_f H = 3x\ {-393} + 3x\ {-286} - {-2058}$

$= +21\ kJ\ mol^{-1}$