AS 91164
Thermochemical principles

Classification of reactions as exothermic and endothermic

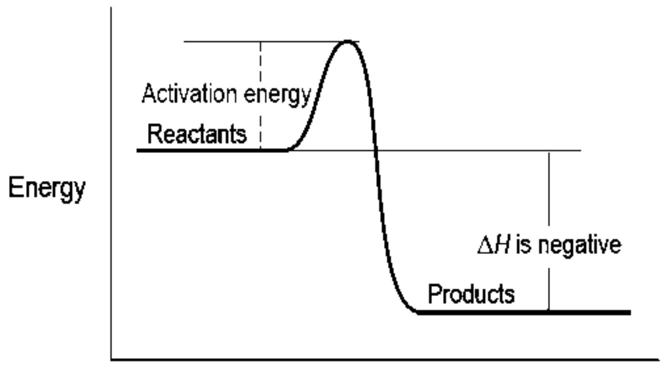
Chemical reactions are accompanied by energy changes. Enthalpy is the "heat content" of a system, or the amount of energy within a substance, both kinetic and potential. It has the symbol H. It is not possible to actually measure the heat content of a substance just "sitting there" – but it is possible to measure how much the enthalpy changes during a reaction. The symbol Δ is used to represent change. Therefore we refer to the change in enthalpy, or ΔH.

Bond breaking is endothermic – energy has to be put IN to break a bond. Imagine the energy you will need to supply to separate your fingers that you have inadvertently and somewhat carelessly "super glued" together! Bond making is exothermic – releases energy. This is a little harder to imagine, but as you glued those fingers together you also noticed they felt a bit warmer!

Enthalpy changes are classified as either:

Exothermic

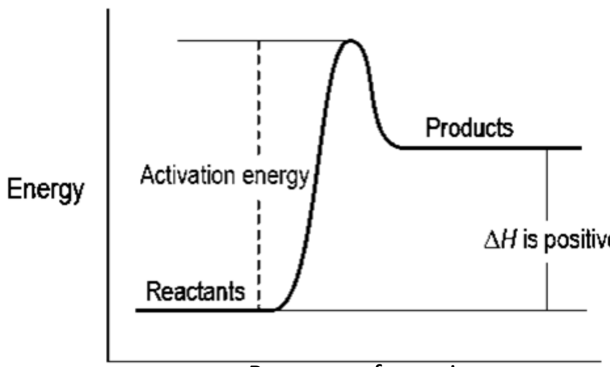
- reactants lose chemical potential energy which is converted to heat energy
- reaction mixture warms up (as energy is released to the surroundings)
- ΔH is negative
- Enthalpy of products < enthalpy of reactants
- Examples: NaOH dissolving in water, Mg reacting with acid, all combustion reactions, rusting iron, mixing water with an anhydrous salt, respiration, steam condensing, water freezing.



Progress of reaction

Endothermic

- reactants absorb heat energy which is converted to chemical potential energy
- reaction mixture cools down (as energy us absorbed from surroundings)
- ΔH is positive
- Enthalpy of reactants < enthalpy of products
- Examples: NH_4Cl dissolving in water, photosynthesis, ice melting, water boiling, making an anhydrous salt from a hydrate e.g. $CuSO_4$ from $CuSO_4.5H_2O$



Progress of reaction

We can also draw energy level diagrams for phase changes such as ice melting to water at 0 °C. These diagrams do not have any activation energy because in phase changes only bond breaking or bond making occurs, not both.

Thermochemical equations

This is a balanced chemical equation that includes an enthalpy term.

State symbols are important in these equations. (s) solid, (l) liquid, (g) gas and (aq) aqueous.

E.g.

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l);\ \Delta_rH = -114\ kJ\ mol^{-1}$$

1 mol 2 mol

This means that when one mol of dilute sulfuric acid solution reacts with two mol of aqueous sodium hydroxide, then 114 kJ of heat energy are released (since the sign of ΔH is negative).

$$NH_4NO_3(s) + aq \rightarrow NH_4^+(aq) + NO_3^-(aq);\ \Delta_rH = +19\ kJ\ mol^{-1}$$

1 mol

This means that when one mol of ammonium nitrate dissolves in water 19 kJ of heat energy are absorbed (since the sign of ΔH is positive).

But what do the equations mean?

There is a direct relationship between the amount of substances that reacts and forms in an equation. The factor that determines the exact relationship is the mole ratio (the numbers in front of the substances in the balanced equation).

E.g.

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

2 mol 1 mol 2 mol

BUT if one mole of hydrogen reacts with 0.5 moles of oxygen, one mole of water forms.

If two moles of oxygen reacts with excess* hydrogen, 4 moles of water forms. *excess means more than enough for complete reaction.

What relationship exists between amount of reactant or product substance and change in enthalpy (ΔH)?

The heat absorbed and produced in a chemical reaction also varies directly as the amount of substance that reacts. The exact amount is determined by the heat change for the reaction (ΔH).

So if you double the amount of substances that are reacting then you will double the enthalpy change.

Examine the following reaction between hydrogen and oxygen to form water:

$$2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (l) :\ \Delta_rH = -\ 572\ kJ$$

2 mol 1 mol 2 mol

Remind yourself what this means! When 2 moles of hydrogen gas reacts with 1 mole of oxygen gas (to form 2 moles of liquid water), 572 kJ of energy are released

OR

The enthalpy change when 2 mol of hydrogen reacts with 1 mol of oxygen is - 572 kJ, Δ_rH = - 572 kJ

(NEVER SAY "– 572 kJ of energy are released" since the " – " bit already says "released" AND it'll be marked wrong.)

But back to this….

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) : \Delta_rH = -572 \text{ kJ}$$
2 mol 1 mol 2 mol

When 2 mol of hydrogen reacts with 1 mol of oxygen, 572 kJ of energy are released
When 1 mol of hydrogen reacts with ½ mol of oxygen, 286 kJ of energy are released
When 4 mol of hydrogen reacts with 2 mol of oxygen, 1046 kJ of energy are released

Another example

$$2C_4H_{10}(l) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g) \quad \Delta_rH = -5315 \text{ kJ}$$

The equation tells us that when 2 moles of $C_4H_{10}(g)$ burn in oxygen, $\Delta H = -5317$ kJ
Since the relationship is a direct one then when 1 mole of $C_4H_{10}(g)$ is burnt, it would release half as much energy: $\Delta H = -2657.5$ kJ
Extra! Here we could also write $\Delta H = -2657.5 \text{ kJ mol}^{-1}$ because ONE mole of C_4H_{10} (l) is being completely burned in oxygen.
If 4 moles of C_4H_{10} were burnt excess oxygen they would release 10630 kJ OR $\Delta H = -10630$ kJ. (Note: BUT NOT "release –10630 kJ", remember the – sign tells us it is released/exothermic).

Calculations involving masses of stuff?

Since the heat released or absorbed in change is directly proportional to the ΔH in the equation, ratios can be used to solve problems involving enthalpy and the amount of substance.
Procedure - perform the following steps

- calculate the number of moles of substance reacted or formed.
- create a proportion using the mole ratio and the enthalpy in the chemical equation.
- solve for missing quantity.

E.g.
Calculate the amount of heat energy released when 25 grams of $C_4H_{10}(l)$ is burned in oxygen using the equation provided.

$$2C_4H_{10}(l) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g);\ \Delta H = -5315 \text{ kJ}$$

2 moles -5315 kJ
116* g -5315 kJ
25g $\frac{25 \times -5315}{116}$ = -1145.5 kJ

$M(C_4H_{10}) = (4 \times 12) + (10 \times 1)$
$= 58 \text{ g mol}^{-1}$.
So 2 mol has a mass of 116 g

1145.5 kJ of heat would be released when 25 g is burned OR $\Delta H = -1145.5$ kJ*
*kJ and not kJ mol^{-1} since we weren't burning a mole of butane, just 25 g.

Okay but the ones in the exams always look more complicated!! Well yes and NO! Same basic principle!!

- Write equation & write number of moles underneath.
- Work out the masses this would represent e.g. $H_2O = 1 + 1 + 16 = 18$ g BUT if the equation says $3H_2O$ then it's 54 g.
- Write the masses you have been given underneath. Work out how much would have reacted with / been made – by ratios.

There is NO NEED to work out the mass of everything in the equation if you have been asked "how much energy is released when x g of butane is burned…. Don't need to work out MASS of oxygen, carbon dioxide and water! If it says what mass of CO_2 is produced when ΔH = - 5000 kJ, then don't work out the mass of butane, oxygen and water!

E.g. What mass of CO_2 is produced when ΔH = - 5000 kJ

$$2C_4H_{10}\ (l) + 13O_2\ (g) \rightarrow 8CO_2\ (g) + 10H_2O\ (g);\ \Delta H = -5315\ \text{kJ}$$

2 mol 13 mol 8 mol 10 mol

8 x (12+16+16)

352 g

- 8 mol ------------ -5315 kJ
- 352 g ----------- -5315 kJ
- x g ----------- -5000 kJ
- so x = (-5000 x 352) / -5315 = 331 g

Calculating ΔH using bond energies

Bond energy is a measure of the intramolecular bond strength in a covalent bond:

$$AB(g) \rightarrow A(g) + B(g)$$

Notice that the reactants and products are all gases. Also notice that the products are atoms.

Bond energies are given in data tables and show the average energy required to break one mole of that bond, the value being calculated from many different molecules.

Bond energies are positive, because bond breaking is an endothermic process. Bond making has the same value but the negative sign.

i.e. $Br_2(g) \rightarrow Br(g) + Br(g)$ $+192\ \text{kJ mol}^{-1}$

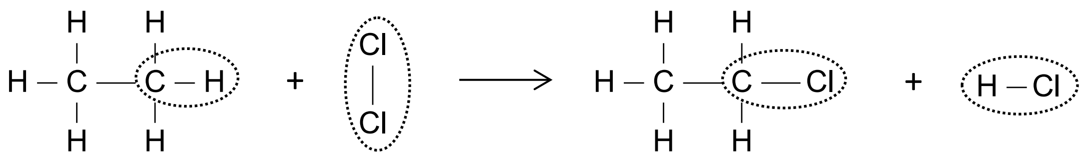
$Br(g) + Br(g) \rightarrow Br_2(g)$ $-192\ \text{kJ mol}^{-1}$

Bond energy calculations

Calculate the heat of reaction for the following: $C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$, given the following bond energies:

C—H 413 kJ mol^{-1} Cl—Cl 242 kJ mol^{-1} C—Cl 339 kJ mol^{-1} H—Cl 431 kJ mol^{-1}

Write out the equation using structural formulae, with every bond shown. Work out which bonds are broken and which will be made.



Bond breaking (+ΔH)	Bond making (–ΔH)
C—H +413 kJ mol^{-1}	C—Cl -339 kJ mol^{-1}
Cl—Cl +242 kJ mol^{-1}	H—Cl -431 kJ mol^{-1}
+655	-770

ΔH = bond breaking + bond making

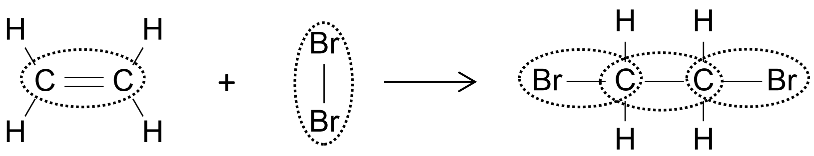
$\Delta H = +655 + (-770) = -115\ \text{kJ mol}^{-1}$

Note: multiple bonds have their own bond energies. For example, it takes 598 kJ mol^{-1} to break the C=C double bond, but 346 kJ mol^{-1} to break the C—C.

Use the bond energy data given to predict the enthalpy of reaction for the equation below.

$$CH_2{=}CH_2(g) + Br_2(g) \rightarrow CH_2BrCH_2Br(g)$$

Br—Br 192 kJ mol^{-1} C—Br 276 kJ mol^{-1} C = C 598 kJ mol^{-1} C—C 346 kJ mol^{-1}



Bond breaking (+ΔH)		Bond making (–ΔH)	
C = C	+598 kJ mol^{-1}	C—C	-346 kJ mol^{-1}
Br—Br	+192 kJ mol^{-1}	2 x C—Br	2 x -276 kJ mol^{-1}
	+790 kJ mol^{-1}		-898 kJ mol^{-1}

ΔH = bond breaking + bond making

ΔH = +790 + (–898) = – 108 kJ mol^{-1}

Notes.