

## AS 91164

### Thermochemical principles

#### Classification of reactions as exothermic and endothermic

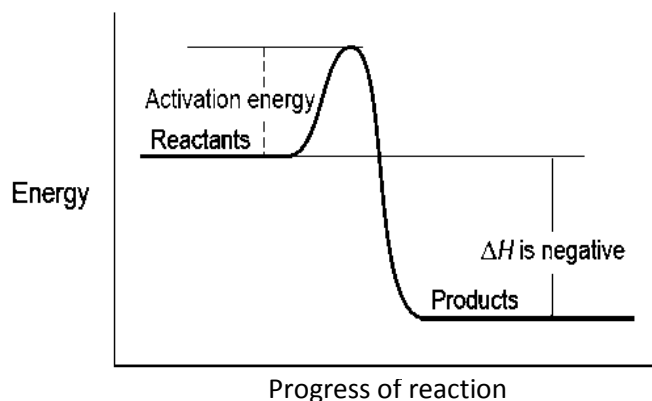
Chemical reactions are accompanied by energy changes. Enthalpy is the “heat content” of a system, or the amount of energy within a substance, both kinetic and potential. It has the symbol  $H$ . It is not possible to actually measure the heat content of a substance just “sitting there” – but it is possible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

*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:

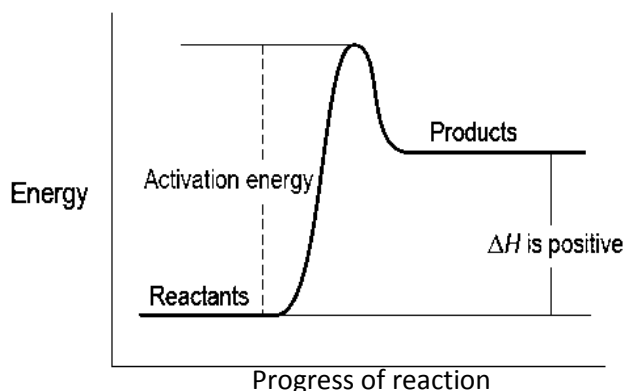
#### Exothermic

- reactants lose chemical potential energy which is converted to heat energy
- reaction mixture warms up (as energy is released to the surroundings)
- $\Delta H$  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.



#### Endothermic

- reactants absorb heat energy which is converted to chemical potential energy
- reaction mixture cools down (as energy is absorbed from surroundings)
- $\Delta H$  is positive
- Enthalpy of reactants < enthalpy of products
- Examples:  $\text{NH}_4\text{Cl}$  dissolving in water, photosynthesis, ice melting, water boiling, making an anhydrous salt from a hydrate e.g.  $\text{CuSO}_4$  from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



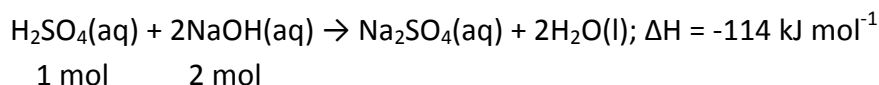
*We also draw energy level diagrams for phase changes such as ice melting to water at  $0^\circ\text{C}$ . These diagrams do not have any activation energy because in phase changes only bond breaking or bond making occurs, not both.*

### Thermochemical equations

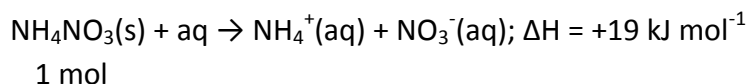
This is a balanced chemical equation that includes an enthalpy term.

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

E.g.



This means that when one mol of dilute sulfuric acid reacts with two mol of aqueous sodium hydroxide, then 114 kJ of heat energy are released (since the sign of  $\Delta\text{H}$  is negative).

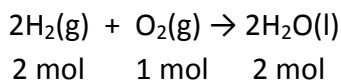


This means that when one mol of ammonium nitrate dissolves in water 19 kJ of heat energy are absorbed (since the sign of  $\Delta\text{H}$  is positive).

### 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.



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

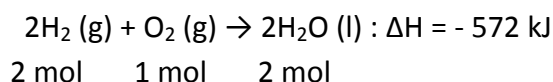
If two moles of oxygen reacts with excess\* hydrogen, 4 moles of water forms. \*excess = more than enough

### What relationship exists between amount of reactant or product substance and change in enthalpy ( $\Delta\text{H}$ )?

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 ( $\Delta\text{H}$ ).

If you double the amount of substance reacted then you will double the heat change.

Examine the following reaction between hydrogen and oxygen to form water



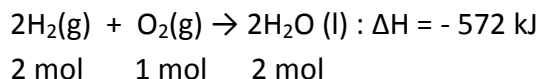
Remind yourself what this means! When 2 moles of hydrogen gas reacts with 1 mole of oxygen gas (to form 2 moles of liquid water), 572 kJ of energy are released

OR

The enthalpy change when 2 mol of hydrogen reacts with 1 mol of oxygen is - 572 kJ,  $\Delta\text{H} = -572 \text{ kJ}$

(NEVER SAY “- 572 kJ of energy are released” since the “-” bit already says “released” AND it’ll be marked wrong.)

But back to this...

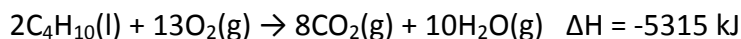


When 2 mol of hydrogen reacts with 1 mol of oxygen, 572 kJ of energy are released

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



The equation tells us that when 2 moles of  $\text{C}_4\text{H}_{10}(\text{g})$  burn in oxygen,  $\Delta\text{H} = -5317 \text{ kJ}$

Since the relationship is a direct one then when 1 mole of  $\text{C}_4\text{H}_{10}(\text{g})$  is burnt, it would release half as much energy:  $\Delta\text{H} = -2657.5 \text{ kJ}$

Extra! Here we could also write  $\Delta\text{H} = -2657.5 \text{ kJ mol}^{-1}$  because ONE mole of  $\text{C}_4\text{H}_{10}(\text{l})$  is being completely burned in oxygen.

If 4 moles of  $\text{C}_4\text{H}_{10}$  were burnt excess oxygen they would release 10630 kJ OR  $\Delta\text{H} = -10630 \text{ kJ}$ . (Note: BUT NOT “release  $-10630 \text{ kJ}$ ”, remember the  $-$  sign tells us it is released/exothermic).

### Calculations involving masses of stuff?

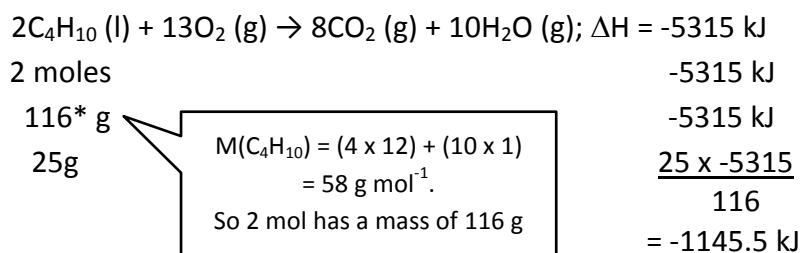
Since the heat released or absorbed in change is directly proportional to the  $\Delta\text{H}$  in the equation, ratios can be used to solve problems involving heat and the amount of substance.

Procedure - perform the following steps

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

E.g.

Calculate the amount of heat released when 25 grams of  $\text{C}_4\text{H}_{10}(\text{l})$  is burned in oxygen using the equation provided.



1145.5 kJ of heat would be released when 25 g is burned OR  $\Delta\text{H} = -1145.5 \text{ kJ}^*$

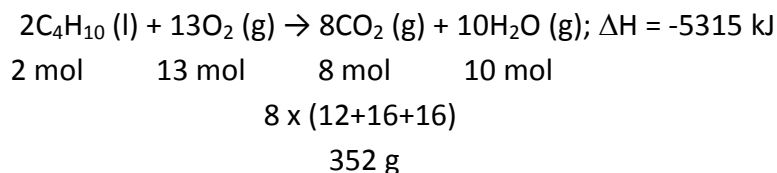
\*kJ and not  $\text{kJ mol}^{-1}$  since we weren't burning a mole of butane, just 25 g.

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

- Write equation & write number of moles underneath.
- Work out the masses this would represent eg  $\text{H}_2\text{O} = 1 + 1 + 16 = 18 \text{ g}$  BUT if the equation says  $3\text{H}_2\text{O}$  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<sub>2</sub> is produced when ΔH = - 5000 kJ, then don’t work out the mass of butane, oxygen and water!

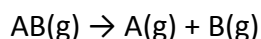
E.g. What mass of CO<sub>2</sub> is produced when H = - 5000 kJ



- 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

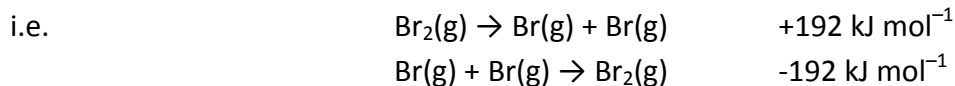
Bond energy is a measure of the intramolecular bond strength in a covalent bond:



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

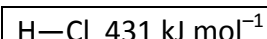
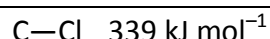
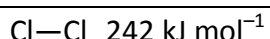
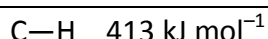
Bond energies are given in data tables and show the average energy required to break one mole of that bond, the value being calculated from many different molecules.

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

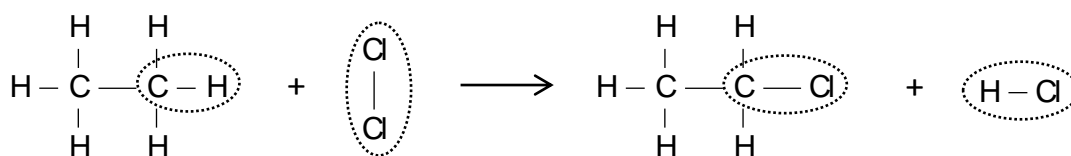


### Bond energy calculations

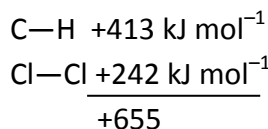
Calculate the heat of reaction for the following:  $\text{C}_2\text{H}_6(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{Cl}(\text{g}) + \text{HCl}(\text{g})$ , given the following bond energies:



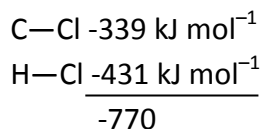
Write out the equation using structural formulae, with every bond shown. Work out which bonds are broken and which will be made.



Bond breaking (+ΔH)



Bond making (-ΔH)

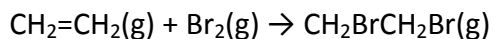


ΔH = bond breaking + bond making

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

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

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

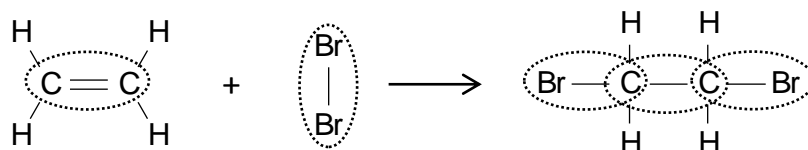


Br—Br $192 \text{ kJ mol}^{-1}$
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C—Br $276 \text{ kJ mol}^{-1}$
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C = C $598 \text{ kJ mol}^{-1}$
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C—C $346 \text{ kJ mol}^{-1}$
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Bond breaking (+ $\Delta H$ )

C = C	+598 $\text{kJ mol}^{-1}$
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Br—Br	+192 $\text{kJ mol}^{-1}$
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	<u>+790 <math>\text{kJ mol}^{-1}</math></u>
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Bond making ( $-\Delta H$ )

C—C	-346 $\text{kJ mol}^{-1}$
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2 x C—Br	2 x -276 $\text{kJ mol}^{-1}$
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	<u>-898 <math>\text{kJ mol}^{-1}</math></u>
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$\Delta H = \text{bond breaking} + \text{bond making}$

$$\Delta H = +790 + (-898) = -108 \text{ kJ mol}^{-1}$$

Notes.