CHEMISTRY LEVEL 4C
(CHM415115)

THERMOCHEMISTRY
&
ENERGY CHANGES

THEORY SUMMARY
&
REVISION QUESTIONS

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INDEX

INTRODUCTION

Most chemical reactions involve energy changes and the energy change is usually observed as the release or absorption of heat.

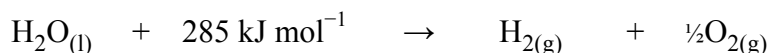> Reactions in which ENERGY IS RELEASED are described as EXOTHERMIC

e.g. in the burning of fuels (such as ethanol below), heat energy is *released* as a *product*.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} + 1364 \text{ kJ mol}^{-1}$$
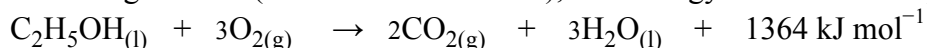
> Reactions in which ENERGY IS ABSORBED are described as ENDOTHERMIC

e.g. in the electrolysis of water, energy is *required* and is shown as a *reactant*.

$$H_2O_{(l)} + 285 \text{ kJ mol}^{-1} \rightarrow H_{2(g)} + \tfrac{1}{2}O_{2(g)}$$

ENTHALPY (H)

Chemical species possess energy best described as either of two types.

    (i) potential energy (E_P) = energy associated with the chemical bonds present and sometimes referred to as 'chemical' energy.

    (ii) kinetic energy (E_K) = energy associated with atomic and molecular movement e.g. translation, vibration and rotation.

The total energy of a chemical species is thus a combination of the two forms of energy and is called the enthalpy and represented by the letter H. The units are normally given as kJ per mole.

      i.e. $H = \{E_P + E_K\}$

CHANGES IN ENTHALPY (ΔH)

Consider the general chemical reaction:

        REACTANTS $\rightarrow$ PRODUCTS
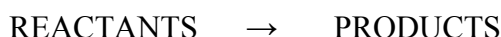
Let the total energy i.e. **enthalpy content** of the reactants = H_R
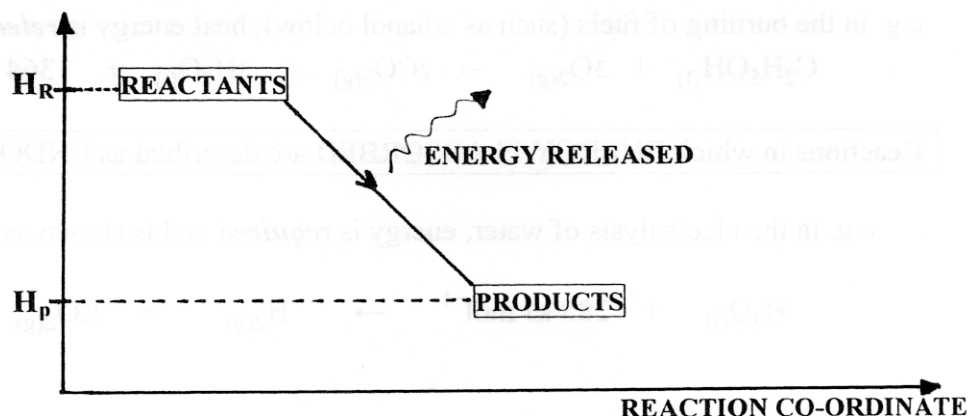Let the total energy i.e. **enthalpy content** of the products = H_P

> The *change* in enthalpy is given by (final – initial) = $(H_P - H_R) = \Delta H$

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EXOTHERMIC REACTIONS

In an exothermic reaction, energy is released, so this means that the products now have a lower total energy (H_P) than the reactants had initially (H_R). The difference is the amount of energy that is released to the surroundings.

The surroundings always become **HOTTER** when an exothermic reaction occurs.

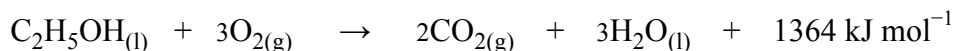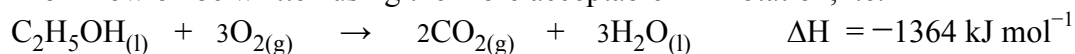i.e. $H_R > H_P ===> (H_P - H_R) = \Delta H = $ NEGATIVE

ALL EXOTHERMIC REACTIONS HAVE $\Delta H = $ NEGATIVE

Thus, all exothermic reactions are easily identified by the fact that they all have a **NEGATIVE** ΔH value.

e.g. Chemical equations that were previously written to show that energy was released such as:

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} + 1364 \text{ kJ mol}^{-1}$$

will from now on be written using the more acceptable ΔH notation; i.e.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H = -1364 \text{ kJ mol}^{-1}$$

NOTE: When ΔH terms are quoted at the end of any chemical equation, they refer to the amounts of reactants and products shown *in moles* according to the balanced chemical equation!

Q1. Rewrite the following chemical equations using the ΔH notation.

(i) $Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)} + 641 \text{ kJ}$

(ii) $4NH_{3(g)} + 3O_{2(g)} \rightarrow 2N_{2(g)} + 6H_2O_{(l)} + 1254 \text{ kJ}$

(iii) $PCl_{3(g)} + Cl_{2(g)} \rightarrow PCl_{5(g)} + 92.9 \text{ kJ}$
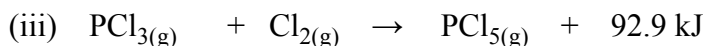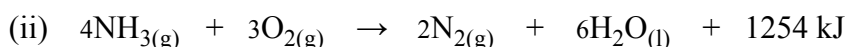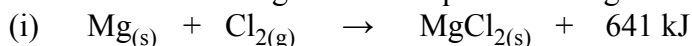
ENDOTHERMIC REACTIONS

In an endothermic reaction, energy is **absorbed**, so this means that the products now have a higher total energy (H_P) than the reactants had initially (H_R). The difference is the amount of energy that is absorbed (taken in) from the surroundings.

The surroundings always become **COLDER** when an endothermic reaction occurs.

ENTHALPY (H)

ENERGY ABSORBED

H_P -- PRODUCTS

H_R ---- REACTANTS

REACTION CO-ORDINATE
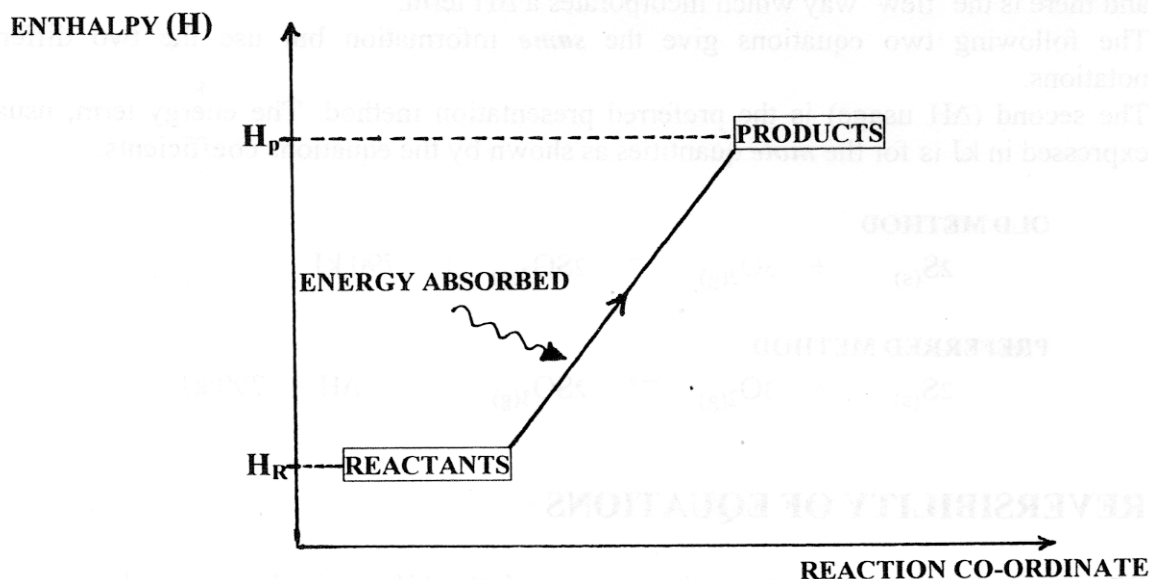
i.e. $H_R < H_P ===> (H_P - H_R) = \Delta H = POSITIVE$

ALL ENDOTHERMIC REACTIONS HAVE ΔH = POSITIVE

Thus, all endothermic reactions are easily identified by the fact that they all have a **POSITIVE** ΔH value.

Under the previous format for writing thermochemical equations, we indicated endothermic reactions by showing energy as being required and had the energy term on the reactant side of the arrow; i.e.

$$H_2O_{(l)} + 285\,kJ\,mol^{-1} \rightarrow H_{2(g)} + \tfrac{1}{2}O_{2(g)}$$
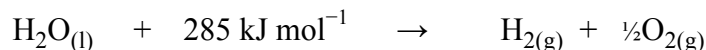
From now on, we will use the more acceptable ΔH notation and indicate that the reaction is endothermic by having a positive ΔH term shown at the end of the equation as shown below:

$$H_2O_{(l)} \rightarrow H_{2(g)} + 1/2O_{2(g)} \qquad \Delta H = +285\,kJ\,mol^{-1}$$
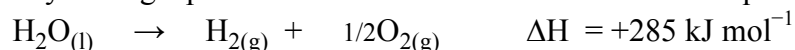
Q2. Rewrite: $NH_4NO_{3(s)} + 92.9\,kJ \rightarrow NH_4NO_{3(aq)}$ using ΔH notation.

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ALTERING ΔH NOTATION

The following examples illustrate variations in ways of expressing thermochemical information.

ΔH & NON-ΔH NOTATION

As previously mentioned, there is the 'old' way of presenting thermochemical information and there is the 'new' way which incorporates a ΔH term.
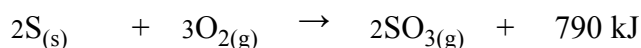The following two equations give the *same* information but use the two different notations.
The second (ΔH usage) is the preferred presentation method. The energy term, usually expressed in kJ is for the *mole* quantities as shown by the equations coefficients.

OLD METHOD
$$2S_{(s)} + 3O_{2(g)} \rightarrow 2SO_{3(g)} + 790 \text{ kJ}$$

PREFERRED METHOD
$$2S_{(s)} + 3O_{2(g)} \rightarrow 2SO_{3(g)} \qquad \Delta H = -790 \text{ kJ}$$

REVERSIBILITY OF EQUATIONS

Whenever a thermochemical equation is reversed, the ΔH sign is also reversed because a previously exothermic reaction, when reversed will now be an endothermic reaction and vice-versa.
e.g.

$$2S_{(s)} + 3O_{2(g)} \rightarrow 2SO_{3(g)} \qquad \Delta H = -790 \text{ kJ}$$

$$2SO_{3(g)} \rightarrow 2S_{(s)} + 3O_{2(g)} \qquad \Delta H = +790 \text{ kJ}$$
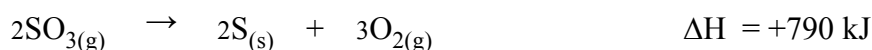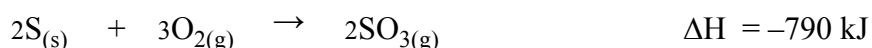
MULTIPLE MOLE QUANTITIES

Whenever a multiple number of moles of reactants is used, the ΔH term is multiplied by that number although, of course, the number of kJ mol^{-1} remains unaltered.
e.g.

$$2B_{(s)} + 3/2O_{2(g)} \rightarrow B_2O_{3(s)} \qquad \Delta H = -1267 \text{ kJ}$$

(x 2)
$$4B_{(s)} + 3O_{2(g)} \rightarrow 2B_2O_{3(s)} \qquad \Delta H = -2534 \text{ kJ}$$
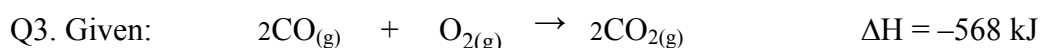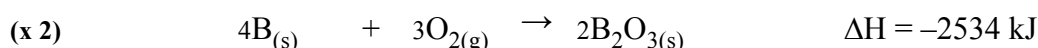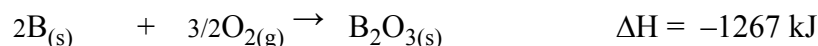
Q3. Given:
$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \qquad \Delta H = -568 \text{ kJ}$$
Find the ΔH value for:
$$CO_{2(g)} \rightarrow CO_{(g)} + \tfrac{1}{2}O_{2(g)} \qquad \Delta H = \text{ ? kJ}$$
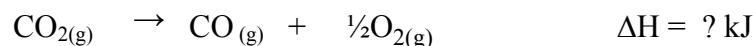
(ΔH = +284 kJ)

PHYSICAL STATE OF REACTANTS & PRODUCTS

Because melting, boiling and sublimation involve energy changes, the ΔH values for thermochemical equations will vary depending on whether reactants or products are in the solid, liquid or gaseous state;

e.g. 1. $\qquad H_{2(g)} \quad + \quad \frac{1}{2}O_{2(g)} \quad \rightarrow \quad H_2O_{(g)} \qquad \Delta H = -242 \text{ kJ}$

$\qquad\qquad H_{2(g)} \quad + \quad \frac{1}{2}O_{2(g)} \quad \rightarrow \quad H_2O_{(l)} \qquad \Delta H = -286 \text{ kJ}$
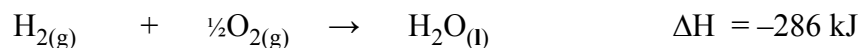
The variation between these two equations is due to the fact that the heat required to vaporise one mole of water is +44 kJ.

i.e. $\qquad\qquad\qquad\qquad H_2O_{(l)} \quad \rightarrow \quad H_2O_{(g)} \qquad \Delta H = +44 \text{ kJ}$

Q4. Consider the two similar thermochemical equations written below.

$\qquad\qquad H_{2(g)} \quad + \quad I_{2(s)} \quad \rightarrow \quad 2HI_{(g)} \qquad \Delta H = +52 \text{ kJ}$
and $\qquad H_{2(g)} \quad + \quad I_{2(g)} \quad \rightarrow \quad 2HI_{(g)} \qquad \Delta H = -10 \text{ kJ}$
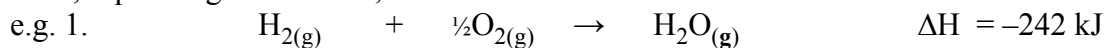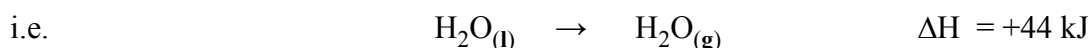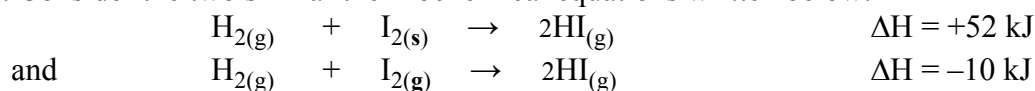
(i) Why do these similar reactions have different ΔH values?
(ii) Use them to deduce the energy required or released for the process:
$\qquad\qquad I_{2(s)} \quad \rightarrow \quad I_{2(g)} \qquad \Delta H = ? \text{ kJ} \qquad \textbf{(}\Delta\textbf{H = +62 kJ)}$
(iii) What is the name used to describe the direct change from 'solid' to 'liquid"
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (sublimation)
(iv) How much energy is required to vaporise 50.0 g of solid iodine I_2?
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(12.2 kJ)**

Q5. Given:

$\qquad\qquad 2B_{(s)} \quad + \quad 3Cl_{2(g)} \quad \rightarrow \quad 2BCl_{3(g)} \qquad \Delta H = -791 \text{ kJ}$
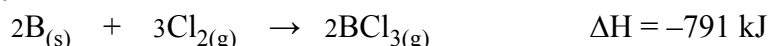
(i) Find: $\quad B_{(s)} \quad + \quad 3/2Cl_{2(g)} \quad \rightarrow \quad BCl_{3(g)} \qquad \Delta H = ? \text{ kJ}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(**Δ**H = –396 kJ)**

(ii) Find: $\quad BCl_{3(g)} \rightarrow \quad B_{(s)} \quad + \quad 3/2Cl_{2(g)} \qquad \Delta H = ? \text{ kJ}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(**Δ**H = +396 kJ)**

(iii) How much heat is released or absorbed when 25.0 g of boron is oxidised by excess chlorine to give BCl_3?
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(915 kJ released)**

Q6. The combustion of ethanol is given by the thermochemical equation:

$\quad C_2H_5OH_{(l)} \quad + \quad 3O_{2(g)} \quad \rightarrow \quad 2CO_{2(g)} \quad + \quad 3H_2O_{(l)} \qquad \Delta H = -1364 \text{ kJ mol}^{-1}$
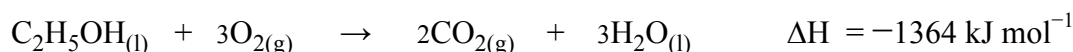
How many grams of ethanol (C_2H_5OH) must be burnt in order to release 1.00 MJ of energy?
(1 MJ = 1000 kJ) $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(33.7 g)**

CALORIMETRY

THEORY:

(i) In order to calculate the energy changes occurring in chemical reactions, a method that chemists frequently employ involves using the released (or absorbed) heat energy to bring about a change in the temperature of a known mass of water.

(ii) The laboratory procedure involves a piece of equipment called a calorimeter which normally holds a known amount of water at a given initial temperature (T_1 ^{o}C).

(iii) The chemical reaction is allowed to occur and the energy released (or absorbed) causes the water to heat up (or cool down) to a final temperature of T_2 ^{o}C.

(iv) The change in temperature is thus $\Delta T = (T_2 - T_1)^o$C

(v) A key property of pure water is that to raise (or lower) the temperature of 1.00 g of water by 1.00^{o}C, requires the addition (or removal) of 4.18 joules of energy.

i.e.

The calorimetry equation is: **E = {(grams of water) x ΔT x 4.18} J**

NOTE: E = energy in joules (J)
                   ΔT = change in temperature
                   4.18 J ^{o}C^{-1} g^{-1} = specific heat of water
                   1.00 g water = 1.00 mL of water

Because a joule (J) is a very small amount of energy, the energy changes encountered in chemical reactions are often expressed in units of kilojoules (kJ) or even megajoules (MJ) or gigajoules (GJ)

TYPICAL LABORATORY SET-UP:

The diagram to the right shows a simple arrangement of equipment that could be used to carry out a *calorimetric* experiment.
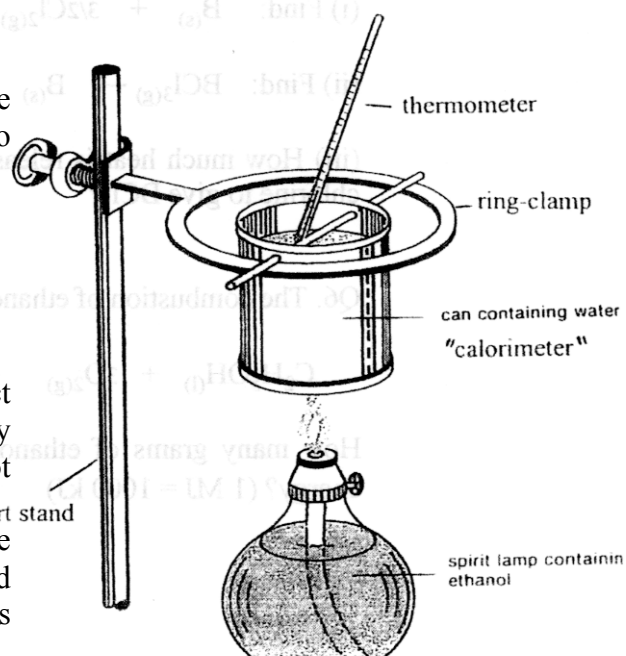
In the experiment we need to know:
- The grams of water heated.
- The water temperature initially.
- The water temperature finally.
- The mass of fuel burnt.

So called "heat losses" are associated with the fact that a significant amount of thermal energy released by the combustion of the fuel, does not end up in the water.

For more accurate calorimetric calculations we need to know the mass of the calorimeter can and the specific heat of the metal from the can is made.

The 'bomb calorimeter' method is sometimes used for more accurate measurements; see page 22.

thermometer

ring-clamp

can containing water
"calorimeter"

spirit lamp containin ethanol

retort stand

SAMPLE EXPERIMENTAL DATA:

Mass of water heated   = 455 g
Initial water temperature   = 21.0^{o}C
Final water temperature   = 57.4^{o}C
Mass of fuel burnt   = 1.76 g

Use these data to calculate the heat of combustion of the fuel in units of kJ g^{-1}.

ANSWER:

$$\text{Energy absorbed by water} = \{(\text{grams of water}) \times \Delta T \times 4.18\} \text{ J}$$
$$= (455 \times 36.4 \times 4.18) \text{ J} \qquad \Delta T = 36.4^o\text{C}$$
$$= 69.2 \text{ kJ released per 1.76 g of fuel}$$

$$\text{Heat of combustion} = (\text{heat released})/\text{grams of fuel}$$
$$= (69.2/1.76) \text{ kJ g}^{-1}$$
$$= 39.3 \text{ kJ g}^{-1} \quad \text{...(*)}$$

Note: the calculation above assumes that the heat released by the burning fuel is the same as the heat absorbed by the water. This of course neglects the heat losses and thus gives us only an *approximate* answer only. The true value would be greater than this.

THERMAL EFFICIENCY:

Suppose that in the example above, the actual (true) heat of combustion for the given fuel is known to be 72.8 kJ g^{-1}.

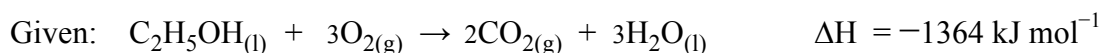The figure we obtained for the heat of combustion above (*) using our rather crude calorimetry equipment was only 39.3 kJ g^{-1}. This suggests that only approximately half the thermal energy released ended up being transferred to the water. Approximately half of the released thermal energy was *lost* to the surroundings.

i.e. Experimentally obtained value for the heat of combustion = 39.3 kJ g^{-1}.
Theoretical value for the heat of combustion = 72.8 kJ g^{-1}.

$$\text{Thus, thermal efficiency} = \{(39.3/72.8) \times 100\}\%$$
$$= 54.0\%$$

~~~~~~~~~~~~~~~~~~~

e.g. What mass of ethanol (C_2H_5OH) is theoretically needed to heat 365 g of water from 26.0^{o}C to 100.0^{o}C?

Given: $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H = -1364 \text{ kJ mol}^{-1}$

ANS: $E = (365 \times 74.0 \times 4.18) \text{ J}$ $\Delta T = 74.0^o\text{C}$
   i.e. energy required = 113 kJ
   $n(C_2H_5OH)$ needed = (energy required in kJ)/1364 kJ mol^{-1}
                = (113/1364) mol = 0.0828 mol
   Thus, mass of ethanol needed = (0.0828 × 46.0)g $M_r(C_2H_5OH) = 46.0$
                  = 3.81 g

CALORIMETRY CALCULATIONS

Q7. How much energy is needed to heat 125 g of water from $16.5^{\circ}C$ to $81.1^{\circ}C$?
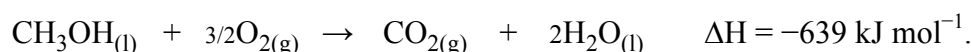
(33.8 kJ)

Q8. If 24.0 kJ of energy is added to 355 g of water, initially at $37.0^{\circ}C$, what will be the final water temperature?

($53.2^{\circ}C$)

Q9. How much energy is needed to heat 1.00 litre (1000 g) of cold tap water initially at a temperature of $19.0^{\circ}C$ to a final temperature of $100.0^{\circ}C$?

(339 kJ)

Q10. When methanol (CH_3OH) burns, the reaction is exothermic, the equation being:

$$CH_3OH_{(l)} \; + \; 3/2O_{2(g)} \; \rightarrow \; CO_{2(g)} \; + \; 2H_2O_{(l)} \qquad \Delta H = -639 \text{ kJ mol}^{-1}.$$

(i) Express the energy release as kJ g^{-1}. **(-20.0 kJ g^{-1})**

(ii) What temperature rise would occur if 1.00 L of water is heated by the burning of 8.00 g of methanol? (assume 100% thermal efficiency)

($\Delta T = 38.2^{\circ}C$)

(iii) What temperature rise would occur if 1.00 L of water (1000 g of water) is heated by the burning of 8.00 g of methanol? (assume only 75.0% thermal efficiency)

($\Delta T = 28.7^{\circ}C$)

Q11. The combustion of the carbohydrate glucose($C_6H_{12}O_6$) is exothermic with the heat of combustion being $\Delta H = -2803$ kJ mol^{-1}.

What mass of glucose must be burnt in order to heat 2.50 L of water from $12.0^{\circ}C$ to boiling point at $100.0^{\circ}C$, assuming:

(i) 100% thermal efficiency? **(59.1 g)**

(ii) 34.0% thermal efficiency? **(174 g)**

Q12. When 5.00 g of butane gas (C_4H_{10}) is burnt, the heat released raises the temperature of 860 g of water from $10.0^{\circ}C$ to $79.2^{\circ}C$.

Find: (i) the energy released. **(249 kJ)**

(ii) the heat of combustion of butane in kJ g^{-1}. **(-49.8 kJ g^{-1})**

(ii) the heat of combustion of butane in kJ mol^{-1}. **(-2886 kJ mol^{-1})**

Q13. Given: $NH_4NO_{3(s)} \rightarrow NH_4NO_{3(aq)}$ $\Delta H = +92.9$ kJ mol^{-1}, what will be the final temperature if 41.8 g of ammonium nitrate is dissolved in 1250 mL of water initially at $40.0^{\circ}C$?

(i) assuming 100% thermal efficiency? **($30.7^{\circ}C$)**

(ii) assuming only 46.0% thermal efficiency? **($35.7^{\circ}C$)**

Q14. Given: $B_{(s)} \; + \; 3/2Cl_{2(g)} \; \rightarrow \; BCl_{3(g)}$ $\Delta H = -396$ kJ:

(a) What mass of boron must be reacted with chlorine gas to release:

(i) 1.00 kJ of energy? **(0.0273 g)**

(ii) 1.00 MJ of energy? **(27.3 g)**

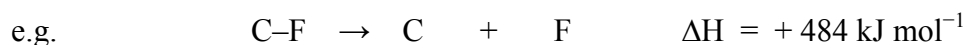(iii) 1.00 GJ of energy? **(27.3 kg)**

(b) What mass of boron must be reacted with chlorine to heat 1.00 m^3 of water from $10^{\circ}C$ to $50^{\circ}C$?   (1.00 m^3 = 1000 L) **(4560 g)**

BOND ENERGY

THEORY:

(i)

THE BREAKING OF A CHEMICAL BOND ***ALWAYS* REQUIRES** ENERGY!
BOND BREAKING IS ENDOTHERMIC.

---

e.g. $\quad C–F \rightarrow C + F \qquad \Delta H = +484$ kJ mol^{-1}

This means that the energy ***required*** to break the covalent bond between a carbon atom and a fluorine atom is +484 kJ per mole of bonds.
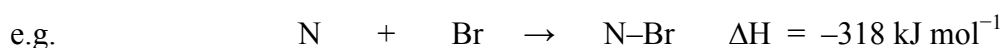
(ii)

THE FORMATION OF A CHEMICAL BOND ***ALWAYS* RELEASES** ENERGY!
BOND FORMING IS EXOTHERMIC.

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e.g. $\quad N + Br \rightarrow N–Br \quad \Delta H = -318$ kJ mol^{-1}
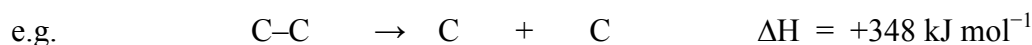
This means that the energy ***released*** in forming the covalent bond between a nitrogen atom and a bromine atom is −318 kJ per mole of bonds.

(iii) If the energy required to break a given chemical bond is +X kJ mol^{-1}, then the energy released when the same bonds form will be −X kJ mol^{-1};
This is a direct consequence of the 'Law of Conservation of Energy'.

e.g. $\quad N + Br \rightarrow N–Br \quad \Delta H = -318$ kJ mol^{-1}

$\quad N–Br \rightarrow N + Br \quad \Delta H = +318$ kJ mol^{-1}

(iv) A table of (average) bond energy values is given on the next page (12) and care should be taken to realize that double and triple bond energies are not multiples of single bond energy values.

e.g. $\quad C–C \rightarrow C + C \qquad \Delta H = +348$ kJ mol^{-1}

$\quad C=C \rightarrow C + C \qquad \Delta H = +612$ kJ mol^{-1}

$\quad C\equiv C \rightarrow C + C \qquad \Delta H = +837$ kJ mol^{-1}

(v) The overall heat of a chemical reaction (ΔH) may be found by calculating the difference between the energy required to break the bonds between atoms in the reactants and the energy released when the new bonds are formed in the products.
(See example question on page 13)

AVERAGE BOND ENERGIES

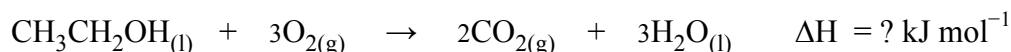| BOND	ΔH (kJ mol^{-1})	BOND	ΔH (kJ mol^{-1})
C–C	348	O=O	496
C=C	612	O–H	463
C≡C	837	Cl–Cl	242
C–H	412	Br–Br	193
C–O	360	F–F	158
C=O	743	H–I	299
C–Cl	338	N–H	388
C–F	484	O–O	146
C–Br	276	H–H	436
C–C(benzene)	436	N–N	163
C–N	305	N=N	409
C=N	613	N≡N	944
C≡N	890	S–S	264
C–I	238	S–H	338
N–Br	318		

THIS LIST IS BY NO MEANS COMPLETE BUT INCLUDES THE BONDS THAT YOU ARE MOST LIKELY TO ENCOUNTER IN CHEMISTRY S.S. LEVEL 5C.

IN ANY TESTS OR EXAMS, THE REQUIRED BOND ENERGY VALUES WILL BE GIVEN TO YOU.

i.e. THE LISTING ABOVE WILL BE PROVIDED FOR YOU TO USE.

ΔH CALCULATED FROM BOND ENERGIES

Use the table of average bond energies to calculate the value of ΔH for:

$$CH_3CH_2OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H = ? \text{ kJ mol}^{-1}$$

At this stage it is important to show the **structures** so as to identify the types of bonds involved.

```
          H   H
i.e.   H–C – C – O –H   +   3(O=O)        →        2(O=C=O)  +  3(H–O–H)
          H   H
```

BONDS BROKEN: (kJ REQUIRED)

1 x (C–C):   1 x 348 = +348 kJ

5 x (C–H):   5 x 412 = +2060 kJ

1 x (C–O):   1 x 360 = +360 kJ

1 x (O–H):   1 x 463 = +463 kJ

3 x (O=O):   3 x 496 = +1488 kJ

TOTAL REQUIRED   = +4719 kJ   *

BONDS FORMED: (kJ RELEASED)

4 x (C=O):   4 x 743 = –2972 kJ

6 x (H–O):   6 x 463 = –2778 kJ

TOTAL RELEASED = –5750 kJ   **

SUMMARY:

> Total energy required to break all the bonds in the reactants = +4719 kJ

> Total energy released when the new bonds in the products are formed = –5750 kJ

Thus, by comparing the total energy required to break the bonds in the reactants (*) with the total energy released in the formation of products (**) we see there is a net **release** of 1031 kJ mol^{-1}

i.e. $CH_3CH_2OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H = -1031 \text{ kJ mol}^{-1}$

The overall reaction above is exothermic because **more energy was released** in the formation of new bonds than **energy was required** for the breaking of the original bonds in the reactants.

BOND ENERGY QUESTIONS

In all questions where you are asked to find ΔH using average bond energies, it is vital to know the bonding structures of the reactants and products in order to see the bonds being broken and the new bonds that are subsequently formed.

Some common structures you need to know are:

(O=O) is oxygen O_2

(O=C=O) is carbon dioxide CO_2

(H–O–H) is water H_2O

Q15. Using the given values of average bond energies (page 12), calculate the heat of reaction (ΔH) for each of the following chemical equations:

(a) CH_4 + $2O_2$ → CO_2 + $2H_2O$ **(ANS. ΔH = −698 kJ)**

(b) C_3H_8 + $5O_2$ → $3CO_2$ + $4H_2O$ **(ANS. ΔH = −1690 kJ)**

(c) C_5H_{12} + $8O_2$ → $5CO_2$ + $6H_2O$ **(ANS. ΔH = −2682 kJ)**

(d) CH_4 + $2Cl_2$ → CCl_4 + $2H_2$ **(ANS. ΔH = −92 kJ)**

(e) $3H_2$ + N_2 → $2NH_3$ **(ANS. ΔH = −76 kJ)**

(f) N_2H_4 + O_2 → N_2 + $2H_2O$ **(ANS. ΔH = −585 kJ)**

(g) C_2H_4 + F_2 → $C_2H_4F_2$ **(ANS. ΔH = −546 kJ)**

(h) cyclohexene + Cl_2 → 1,2-dichlorocyclohexane   **(ANS. ΔH = −170 kJ)**

(i) C_2H_2 + $2Br_2$ → $C_2H_2Br_4$ **(ANS. ΔH = −229 kJ)**

14

SOME SPECIALISED ΔH TERMS

When there is a general chemical reaction and the enthalpy change is shown, we normally refer to this ΔH as 'the heat of reaction'.
However in certain specialised chemical reactions, the ΔH is referred to by the type of reaction it describes.
Some common examples are shown below;

1. **HEAT OF COMBUSTION**:

This is the ΔH term that relates to the enthalpy change occurring when a fuel is being burnt (oxidised) e.g.
The heat of combustion of methanol is $\Delta H = -754$ kJ mol^{-1}.
i.e.

$$CH_3OH_{(g)} \quad + \quad 3/2 O_{2(g)} \quad \rightarrow \quad CO_{2(g)} \quad + \quad 2H_2O_{(l)} \qquad\qquad \Delta H = -754 \text{ kJ}$$

2. **HEAT OF SOLUTION**:

This is the ΔH term that relates to the enthalpy change occurring when a compound is dissolved in a solvent; usually in water e.g.
The heat of aqueous solution of sodium hydroxide is $\Delta H = -41.8$ kJ mol^{-1}.
i.e.

$$NaOH_{(s)} \quad \rightarrow \quad NaOH_{(aq)} \qquad\qquad \Delta H = -41.8 \text{ kJ}$$

3. **HEAT OF NEUTRALIZATION**:

This is the ΔH term that relates to the enthalpy change occurring when an acid is neutralized by a base; e.g.

$$H^+_{(aq)} \quad + \quad OH^-_{(aq)} \quad \rightarrow \quad H_2O_{(l)} \qquad\qquad \Delta H = -57 \text{ kJ}$$

4. **HEAT OF DISSOCIATION**:

This is the ΔH term that relates to the enthalpy change occurring when a compound is broken up into simpler compounds or elements;
e.g. The heat of dissociation of PCl_5 into PCl_3 is $\Delta H = +137$ kJ

$$PCl_{5\,(s)} \quad \rightarrow \quad PCl_{3(g)} \quad + \quad Cl_{2(g)} \qquad\qquad \Delta H = +137 \text{ kJ}$$

*5. **HEAT OF FORMATION**:

This is the ΔH term that relates to the enthalpy change occurring when one mole of a compound is formed from its *elements* in their normal SLC state;
e.g. The heat of formation of sucrose ($C_{12}H_{22}O_{11(s)}$) is $\Delta H = -2226$ kJ
i.e.

$$12C_{(s)} \quad + \quad 11H_{2(g)} \quad + \quad 11/2 O_{2(g)} \quad \rightarrow \quad C_{12}H_{22}O_{11(s)} \qquad\qquad \Delta H = -2226 \text{ kJ}$$

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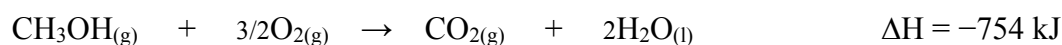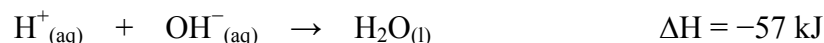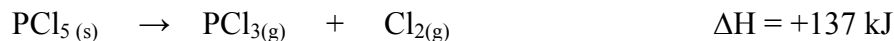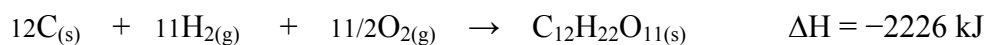
HESS'S LAW ~ THERMOCHEMICAL CYCLES

INTRODUCTION:

Hess's Law is an application of the Law of Conservation of Energy to thermochemical systems.

> **Hess's Law states: "The overall energy change that occurs in a chemical reaction is dependent only upon the reactants and products and is independent of the pathway followed."**

Consider the following chemical reaction:

$$\text{REACTANTS} \quad \rightarrow \quad \text{PRODUCTS}$$
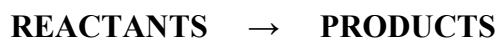
As shown in the diagram below, there are a number of different pathways that can be followed to get from the reactants to the products. Each step in the pathways shown has its own enthalpy change.
The direct pathway has an enthalpy change ΔH_1.
The indirect pathways involve the formation of intermediates which are like 'stepping-stones' in the pathway.
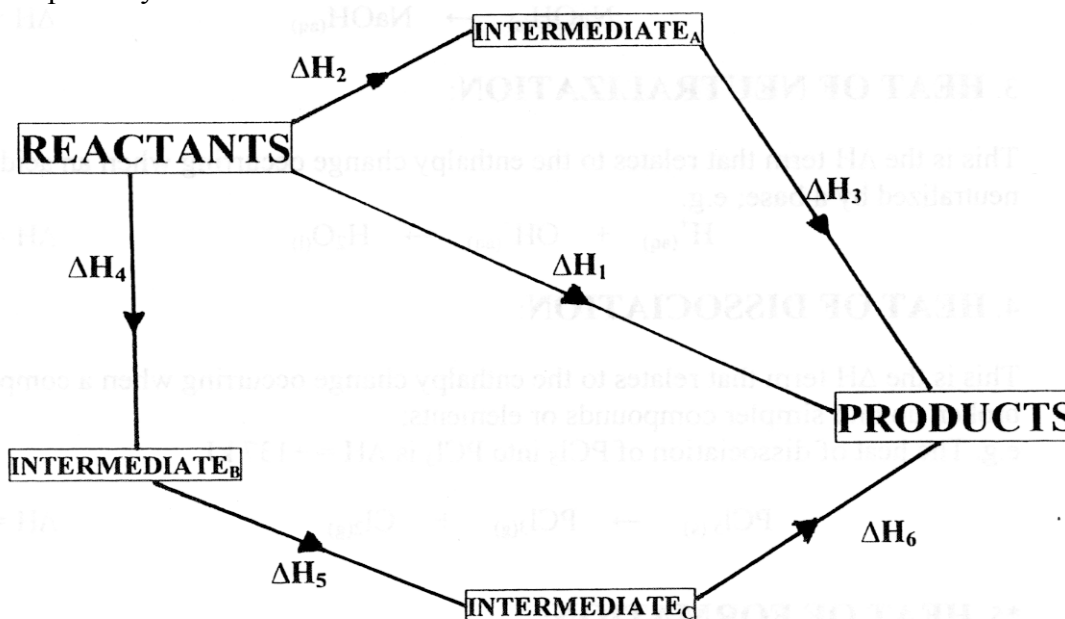
The diagram shows 3 different pathways (one is direct and two are indirect) to get from the reactants to the products.
Hess's Law tells us that the total energy changes in each pathway are identical; i.e.

$$\Delta H_1 \;=\; (\Delta H_2 + \Delta H_3) \;=\; (\Delta H_4 + \Delta H_5 + \Delta H_6)$$

Any two of the pathways may be combined to form a **THERMOCHEMICAL CYCLE**.

APPLICATIONS OF HESS'S LAW:

Hess's Law has many important applications and can be used to calculate the values of ΔH for reactions that might otherwise be difficult to carry out.

In most of the problems you are likely to encounter involving Hess's Law, you will be given the ΔH values for several reactions and then be asked to calculate ΔH for another related chemical reaction

TYPICAL EXAMPLE:
GIVEN:

(1) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\quad\quad\quad\quad\quad\quad\quad$ $\Delta H = -393$ kJ

(2) $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(l)}$ $\quad\quad\quad\quad$ $\Delta H = -285$ kJ

(3) $2C_{(s)} + 3H_{2(g)} + 1/2O_{2(g)} \rightarrow C_2H_5OH_{(l)}$ $\quad$ $\Delta H = -277$ kJ

TO FIND   heat of combustion for ethanol ($C_2H_5OH_{(l)}$).

i.e.

$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\quad\quad$ * $\quad\quad\quad$ $\Delta H = ?$
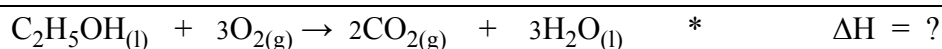
ANSWER:

We now construct the desired equation (*) by rearranging the given equations (1) to (3).

(a) We require one mole of ethanol as a reactant so we take equation (3) and reverse it. Note that reversing (3) changes the sign of ΔH.

(b) We require two moles of carbon dioxide as a product so we take equation (1) and double it. This releases twice as much energy so ΔH for equation (2) is doubled.
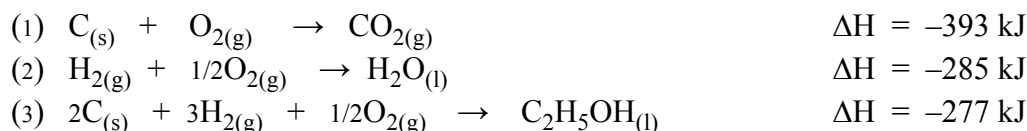
(c) We require three moles of liquid water as a product so we take equation (2) and multiply through by three.

As oxygen appears in all given equations, leave this to the end and it should be balanced if our previous steps were performed correctly.

i.e.

Eqn.(3) reverse.

$\quad\quad\quad C_2H_5OH_{(l)} \rightarrow 2C_{(s)} + 3H_{2(g)} + 1/2O_{2(g)}$ $\quad\quad\quad$ $\Delta H = +277$ kJ

Eqn.(1) x 2

$\quad\quad\quad\quad 2C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)}$ $\quad\quad\quad\quad\quad$ $\Delta H = -786$ kJ

Eqn.(2) x 3

$\quad\quad\quad\quad 3H_{2(g)} + 3/2O_{2(g)} \rightarrow 3H_2O_{(l)}$ $\quad\quad\quad\quad$ $\underline{\Delta H = -855 \text{ kJ}}$
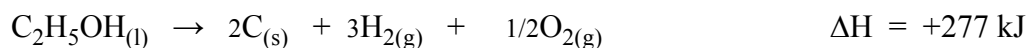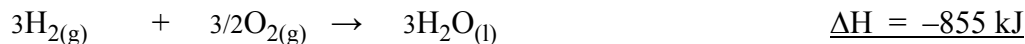
Now apply Hess's Law and add these three equations together. It results in:

$\quad C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\quad\quad\quad\quad$ $\Delta H = -1364$ kJ.

Thus, by following an indirect path in which ethanol was initially decomposed into carbon and hydrogen after which these products were burnt in oxygen, we have found the ΔH corresponding to the direct pathway;

i.e. heat of combustion of ethanol $\Delta H = -1364$ kJ mol^{-1}
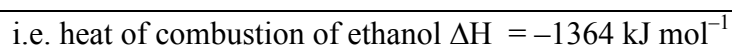
HESS'S LAW ~ PROBLEMS

Q16. Given the following heats of reaction:

$\quad$ (1) $\ C_{(s)} \ + \ O_{2(g)} \ \rightarrow \ CO_{2(g)}$ $\qquad\qquad\qquad\qquad\qquad$ $\Delta H \ = \ -393$ kJ
$\quad$ (2) $\ H_{2(g)} \ + \ 1/2O_{2(g)} \ \rightarrow \ H_2O_{(l)}$ $\qquad\qquad\qquad\qquad$ $\Delta H \ = \ -285$ kJ
$\quad$ (3) $\ 2C_{(s)} \ + \ 3H_{2(g)} \ + \ 1/2O_{2(g)} \ \rightarrow \ C_2H_5OH_{(l)}$ $\qquad$ $\Delta H \ = \ -277$ kJ

(i) Find the heat of combustion for ethanol ($C_2H_5OH_{(l)}$).

i.e. $C_2H_5OH_{(l)} \ + \ 3O_{2(g)} \ \rightarrow \ 2CO_{2(g)} \ + \ 3H_2O_{(l)}$ $\qquad$ $\Delta H \ = \ ?$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(−1364 kJ)**

(ii) What is the quantity of heat released when 150.0g of ethanol is burnt according to the equation above?

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(−4448 kJ)**

~~~~~~~~~~~~~~~~~~~~

Q17. Given the following data:
$\quad$ (1) $\ 2C_{(s)} \quad + \quad H_{2(g)} \quad \rightarrow \quad C_2H_{2(g)}$ $\qquad\qquad\qquad$ $\Delta H \ = \ +227$ kJ
$\quad$ (2) $\ 6C_{(s)} \quad + \quad 3H_{2(g)} \quad \rightarrow \quad C_6H_{6(g)}$ $\qquad\qquad\qquad$ $\Delta H \ = \ +83$ kJ

Find the heat of reaction for the conversion of ethyne into benzene.

$\qquad\qquad$ i.e. $\ \ 3C_2H_2 \quad \rightarrow \quad C_6H_{6(g)}$ $\qquad\qquad\qquad$ $\Delta H \ = \ ?$
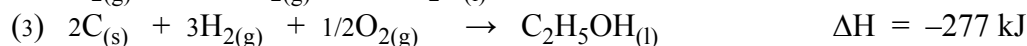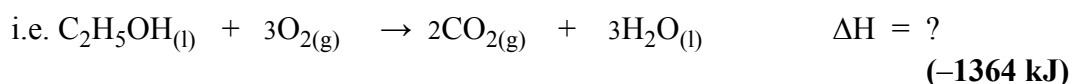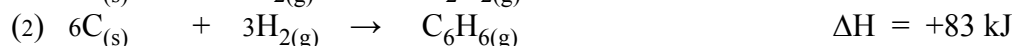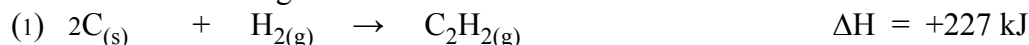
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(−598 kJ)**

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Q18. Given the following data:
$\quad$ (1) $\ H_{2(g)} \qquad + \quad 1/2 \ O_{2(g)} \quad \rightarrow \quad H_2O_{(g)}$ $\qquad\qquad$ $\Delta H \ = \ -242$ kJ mol^{-1}
$\quad$ (2) $\ H_{2(g)} \qquad + \quad 1/2 \ O_{2(g)} \quad \rightarrow \quad H_2O_{(l)}$ $\qquad\qquad$ $\Delta H \ = \ -285$ kJ mol^{-1}
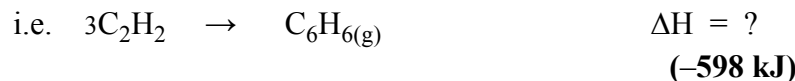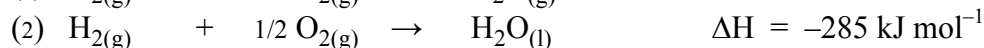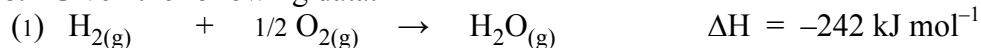
Find the molar heat of vaporization for water.

$\qquad$ i.e. $\qquad\qquad\qquad\qquad H_2O_{(l)} \quad \rightarrow \quad H_2O_{(g)}$ $\qquad\qquad$ $\Delta H \ = \ ?$
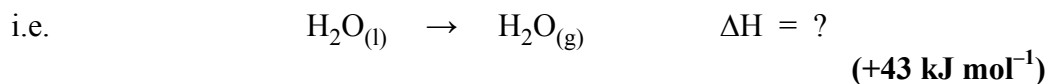
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(+43 kJ mol^{-1})**

~~~~~~~~~~~~~~~~~~~~

Q19. The following data are given for 1.00 atm and 25°C.
$\quad$ (1) $\ 4Al_{(s)} \ + \ 3O_{2(g)} \quad \rightarrow \quad 2Al_2O_{3(s)}$ $\qquad\qquad$ $\Delta H \ = \ -3336$ kJ
$\quad$ (2) $\ 2S_{(s)} \ + \ 3O_{2(g)} \quad \rightarrow \quad 2SO_{3(g)}$ $\qquad\qquad$ $\Delta H \ = \ -790$ kJ
$\quad$ (3) $\ Al_2O_{3(s)} \ + \ 3SO_{3(g)} \quad \rightarrow \quad Al_2(SO_4)_{3(s)}$ $\qquad$ $\Delta H \ = \ -579$ kJ

Find the **heat of formation** of aluminium sulfate in units of kJ mol^{-1}.

$\qquad$ i.e. $\ \ 2Al_{(s)} \ + \ 3S_{(s)} \ + \ 6O_{2(g)} \rightarrow \ Al_2(SO_4)_{3(s)}$ $\qquad$ $\Delta H \ = \ ?$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(−3432 kJ mol^{-1})**

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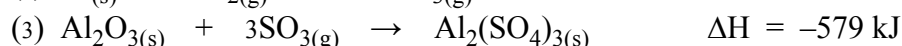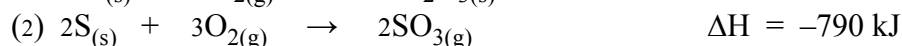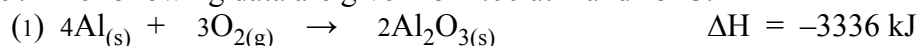
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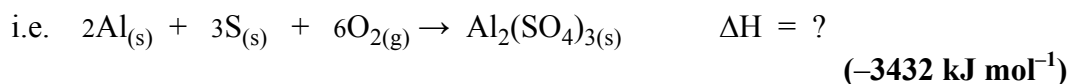
Q20. The following data are given about the rocket fuel diborane (B_2H_6):

(1) $2B_{(s)} + 3H_{2(g)} \rightarrow B_2H_{6(g)}$ $\qquad\qquad\qquad$ $\Delta H = +31$ kJ

(2) $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$ $\qquad\qquad\qquad$ $\Delta H = -242$ kJ

(3) $2B_{(s)} + 3/2O_{2(g)} \rightarrow B_2O_{3(s)}$ $\qquad\qquad\qquad$ $\Delta H = -1267$ kJ
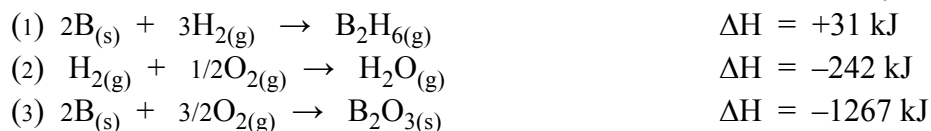
(i) Find the heat of combustion for diborane:

i.e. $\qquad$ $B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O_{(g)}$ $\qquad\qquad$ $\Delta H = ?$

(–2024kJ)
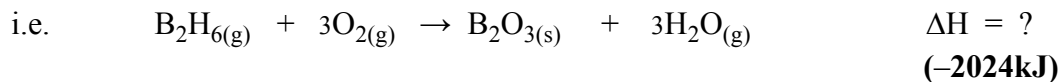
(ii) Find the heat released when 10.00 kg of diborane burns according to the equation given above. **(–733MJ)**

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Q21. Consider the following information relating to the complete combustion of the compound acetone ($(CH_3)_2CO_{(l)}$). Note: ΔH_f refers to the "heat of formation".

(i) $\Delta H_f ((CH_3)_2CO_{(l)})$ $\qquad$ $= -257$ kJ mol^{-1}

(ii) $\Delta H_f (H_2O_{(g)})$ $\qquad\qquad$ $= -242$ kJ mol^{-1}

(iii) $\Delta H_f (CO_{2(g)})$ $\qquad\qquad$ $= -393$ kJ mol^{-1}

(i) From these data find the heat of combustion of acetone.

i.e. $\qquad$ $(CH_3)_2CO_{(l)} + 4O_{2(g)} \rightarrow 3CO_{2(g)} + 3H_2O_{(g)}$ $\qquad$ $\Delta H = ?$

(-1648 kJ)

(ii) Assuming a 65.0 % thermal efficiency in heating, what mass of acetone must be burnt in order to heat 1.60 L of water from 23.0°C to 100.0°C?

(27.9 g)

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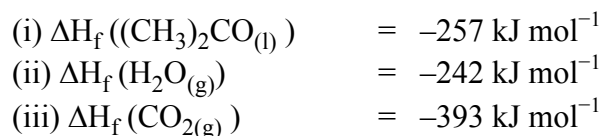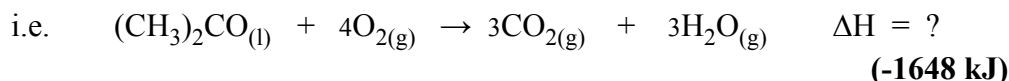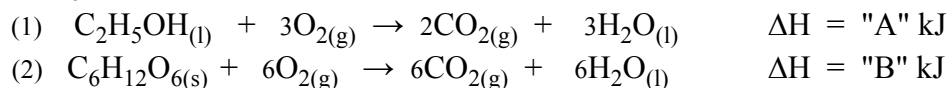
Q22. Given that the ΔH for the complete combustion of the compound naphthalene ($C_{10}H_{8(s)}$) is –5110 kJ mol^{-1} and that the heat of formation of $H_2O_{(l)}$ is –286 kJ mol^{-1} and that the heat of formation of carbon dioxide ($CO_{2(g)}$) is –393 kJ mol^{-1}, calculate the heat of formation of naphthalene. **(+36 kJ)**

~~~~~~~~~~~~~~~~~~~~~

Q23. Given the following data about the compounds ethanol (C_2H_5OH) and glucose ($C_6H_{12}O_6$):

(1) $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\qquad$ $\Delta H =$ "A" kJ

(2) $C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$ $\qquad$ $\Delta H =$ "B" kJ

(i) Find in terms of A and B the enthalpy change for the **fermentation** reaction:

$C_6H_{12}O_{6(s)} \rightarrow 2C_2H_5OH_{(l)} + 2CO_{2(g)}$ $\qquad\qquad$ $\Delta H = ?$ kJ

(B−2A kJ)

(ii) Find in terms of the data above the enthalpy change for the **photosynthesis** reaction:

$6CO_{2(g)} + 6H_2O_{(l)} \rightarrow C_6H_{12}O_{6(s)} + 6O_{2(g)}$ $\qquad$ $\Delta H = ?$ kJ

(−B kJ)

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
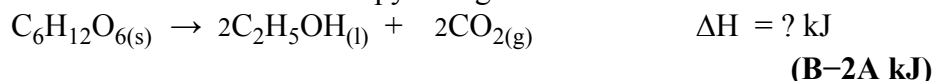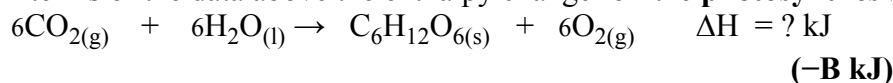
ENERGY CHANGES DURING DISSOLVING

INTRODUCTION:

Some dissolving processes with water as the solvent, are exothermic and others are endothermic.

For example, the dissolving of concentrated sulfuric acid in water is highly exothermic and extreme care must be taken to avoid the solution boiling and possibly ejecting acid into the air. (Always slowly add the concentrated acid to the water and *not* the other way round!)

i.e. $\qquad H_2SO_{4(l)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}_{(aq)} \qquad \Delta H = -75 \text{ kJ mol}^{-1}$

Conversely, some dissolving processes are sufficiently endothermic that the intense cooling effect that results is used medically to provide a 'cold-pack' for muscular injuries.
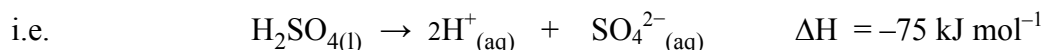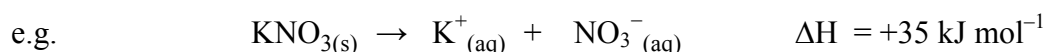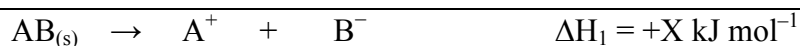
e.g. $\qquad KNO_{3(s)} \rightarrow K^+_{(aq)} + NO_3^-_{(aq)} \qquad \Delta H = +35 \text{ kJ mol}^{-1}$

EXPLANATION:

Consider the dissolving of a general *ionic* solid "AB" in water.

The process needs to be considered as occurring in two distinct steps:

STEP 1 This step involves *breaking* the ionic bonds in the crystal lattice and as such, must always *require* energy; i.e. be ENDOTHERMIC

$$AB_{(s)} \rightarrow A^+ + B^- \qquad \Delta H_1 = +X \text{ kJ mol}^{-1}$$

$+X$ kJ mol^{-1} is called the LATTICE ENERGY and is a measure of the strength of the ionic bonds holding the solid AB together.

STEP 2 This step involves the separated ions from the original crystal lattice attracting water molecules around them and thus *forming* new bonds. As bonds with water are being formed, this process must *release* energy; i.e. be EXOTHERMIC

$$A^+ + B^- \rightarrow A^+_{(aq)} + B^-_{(aq)} \qquad \Delta H_2 = -Y \text{ kJ mol}^{-1}$$
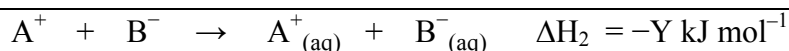
$-Y$ kJ mol^{-1} is called the HYDRATION ENERGY and is a measure of the strength of the new bonds formed between the ions and surrounding water molecules.

COMBINING STEPS 1 & 2
Applying Hess's Law and adding the two steps together, we get:

$$AB_{(s)} \rightarrow A^+_{(aq)} + B^-_{(aq)} \qquad \Delta H_{NET} = (+X - Y) \text{ kJ mol}^{-1}$$
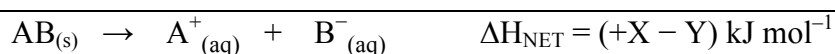
Thus, whether the overall reaction is exothermic or endothermic will depend upon the relative sizes of X and Y.

If the **LATTICE ENERGY > HYDRATION EN**ERGY (i.e. X > Y)

$\Delta H_{NET} = (+X - Y)$ is POSITIVE and thus the reaction will be ENDOTHERMIC

If the **LATTICE ENERGY < HYDRATION ENERGY** (i.e. X < Y)

$\Delta H_{NET} = (+X - Y)$ is NEGATIVE and thus the reaction will be EXOTHERMIC

NOTE: In some cases the lattice energy is so much greater than the hydration energy that the bonds in the crystal can't be broken significantly and in these instances, the solid AB would be described as being ***insoluble*** in water!

Q24. The dissolving of sodium hydroxide crystals in water is strongly exothermic. A student observing this phenomenon states incorrectly "that the energy released in this dissolving process is due to the breaking of the bonds in the NaOH crystal."
Explain why this statement is incorrect and give a proper explanation for the observed release of heat.

Q25. Consider the dissolving of calcium chloride crystals in water:

$$CaCl_{2(s)} \quad \rightarrow \quad Ca^{2+}_{(aq)} \quad + \quad 2Cl^-_{(aq)} \qquad \Delta H = -75.6 \text{ kJ}$$
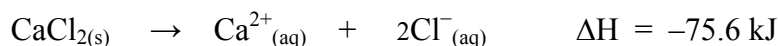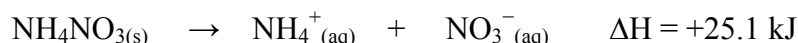
(i) Compare the lattice energy and hydration energy for calcium chloride.
(ii) If 50.0 g of solid calcium chloride is dissolved in 250 mL of water in a well insulated calorimeter, what temperature change would theoretically occur?

(32.6^oC temp. rise)

Q26. Consider the dissolving of ammonium nitrate crystals in water:

$$NH_4NO_{3(s)} \quad \rightarrow \quad NH_4^+_{(aq)} \quad + \quad NO_3^-_{(aq)} \qquad \Delta H = +25.1 \text{ kJ}$$

(i) Compare the lattice energy and hydration energy for calcium chloride.
(ii) Which has the higher enthalpy content, solid ammonium nitrate or the aqueous solution of ammonium nitrate? **(the solution)**
(iii) If 95.0 g of solid ammonium nitrate is dissolved in 550 mL of water in a well insulated calorimeter, what temperature change would theoretically occur?

(13.0^oC temp. fall)

Q27. When 7.25 g of $KOH_{(s)}$ crystals are dissolved in 100.0 mL of water, the temperature of the water increased by 17.2^oC. Find the molar heat of solution for potassium hydroxide.
i.e.

$$KOH_{(s)} \quad \rightarrow \quad K^+_{(aq)} \quad + \quad OH^-_{(aq)} \quad \Delta H = ? \text{ kJ mol}^{-1}$$

($\Delta H = -55.6 \text{ kJ mol}^{-1}$)

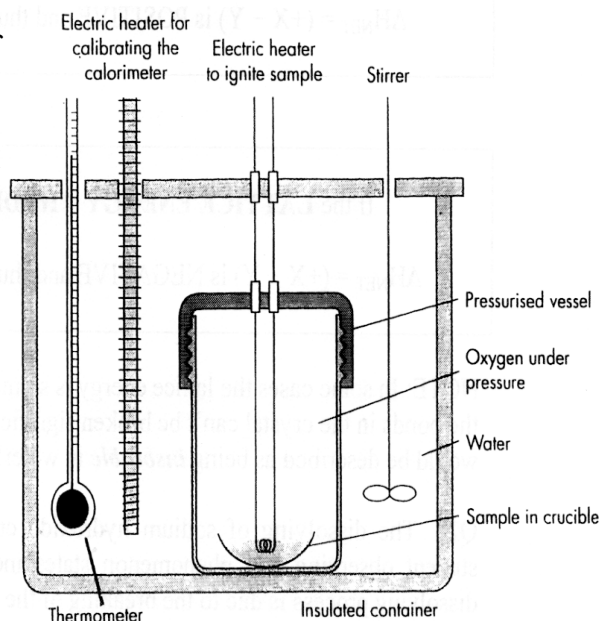~~~~~~

BOMB CALORIMETRY CALCULATIONS

When a more accurate calorimetric result is desired, we usually use a special type of calorimeter called a **BOMB CALORIMETER**.

With this type of calorimeter (see diagram to the right), the unit used has an electric heating unit so that it can be calibrated to see how much energy is needed to cause a given temperature rise.

Once this 'CALIBRATION FACTOR' has been determined, the calorimeter can be used to contain a chemical reaction where the temperature rise or fall is measured.

This change in temperature (ΔT) can then be used to determine the energy change involved.

Electric heater for calibrating the calorimeter
Electric heater to ignite sample
Stirrer
Pressurised vessel
Oxygen under pressure
Water
Sample in crucible
Thermometer
Insulated container

Some basic electrical theory is needed at this stage and the key formula that relates the important measurements is:

$E = (V \times I \times t)$ joules

V = potential difference in volts
t = time in seconds
I = current in amps (A)

STEP 1 "TO FIND THE CALIBRATION COEFFICIENT"

A certain bomb calorimeter is calibrated by passing a current of 0.500 A through the unit for a period of 125 seconds at a P.D. of 12.0 volts. The heat released caused the bomb calorimeter to heat up by $2.17^{o}C$.

$$E = (V \times I \times t) \text{ J}$$
$$E = (12.0 \times 0.500 \times 125) \text{ J}$$
$$E = 750 \text{ J}$$

Thus calibration factor is: $\boxed{\text{C.F.} = (E/\Delta T) \text{ J } ^{o}C^{-1}}$
$$= (750/2.17) \text{ J } ^{o}C^{-1}$$
$$\text{C.F.} = 346 \text{ J } ^{o}C^{-1}$$

STEP 2 "TO FIND ΔH OF REACTION"

This same bomb calorimeter having now been calibrated is then used to contain 0.0124 mole of a fuel which is burnt in oxygen. This combustion reaction caused a $14.1^{o}C$ temperature rise.

Using: $\text{C.F.} = (E/\Delta T) \text{ J } ^{o}C^{-1}$
$E = (\text{C.F.} \times \Delta T) \text{ J}$ substituting C.F. = 346 J $^{o}C^{-1}$
$E = (346 \times 14.1) \text{ J}$
$E = 4.88 \text{ kJ}$

Thus, heat of combustion is $\Delta H = (E/\text{mole}) \text{ kJ mol}^{-1}$
$\Delta H = -(4.88/0.0124) \text{ kJ mol}^{-1}$
$\Delta H = -393 \text{ kJ mol}^{-1}$

THERMOCHEMISTRY REVISION QUESTIONS

Q28. A sample of anthracite coal of mass 5.00 g is burnt in air and the energy released is used to heat 855 mL of water initially at 22.0°C. After complete combustion of the coal, the water temperature has risen to 56.0°C.
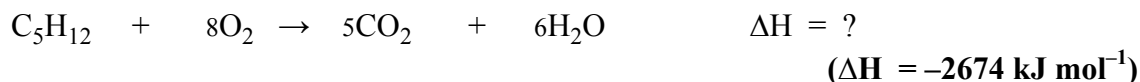(i) How much energy has been absorbed by the water? **(122 kJ)**
(ii) The coal sample used is known to have a heating value of 36.0 kJ per gram. What is the % efficiency of the heat transfer process in this case? Show your workings.
                                                                                                (67.5%)

Q29. Given the following bond energies:

O=O	497 kJ mol^{-1}		C−C	348 kJ mol^{-1}
C−H	412 kJ mol^{-1}		O−H	463 kJ mol^{-1}
C=O	743 kJ mol^{-1}			

Calculate the heat of reaction for the complete combustion of pentane in accordance with the equation:
$$C_5H_{12} \; + \; 8O_2 \; \rightarrow \; 5CO_2 \; + \; 6H_2O \qquad \Delta H \; = \; ?$$
                                                                                                ($\Delta H = -2674$ kJ mol^{-1})

Q30. The energy required to break the covalent bonds between oxygen atoms in hydrogen peroxide (H_2O_2) is 146 kJ mol^{-1} whereas the energy required to break the bonds between oxygen atoms in oxygen gas (O_2) is 497 kJ mol^{-1}. Account for the difference between these values.

Q31. Given that the heat of formation of carbon dioxide gas is -394 kJ mol^{-1} and that the heat of formation of water is -286 kJ mol^{-1} and that the heat of combustion of ethanol (C_2H_6O) is -1386 kJ mol^{-1}, calculate the heat of formation of ethanol. Show all your workings.
                                ($\Delta H = -260$ kJ mol^{-1})

Q32. If 1.00L of water absorbs 1.00 kJ of heat energy, calculate the theoretical temperature rise of the water.   **(0.239°C)**

Q33. Consider the exothermic reaction $X_{(g)} \rightarrow Y_{(g)}$ $\Delta H = -150$ kJ
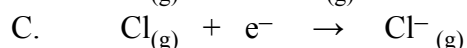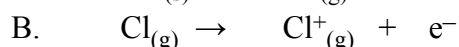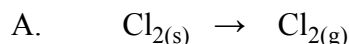(i) Which compound, X or Y has the higher enthalpy?   **(X)**
(ii) Which compound, X or Y has the stronger bonds?   **(Y)**

Q34. Consider the phase change given by: $Al_2O_{3(s)} \rightarrow Al_2O_{3(l)}$:
Would this process be exothermic or endothermic? Explain briefly.   **(endothermic)**

Q35. Which one of the following processes has a ΔH value *different* from the others?
   A. $Cl_{2(s)} \rightarrow Cl_{2(g)}$
   B. $Cl_{(g)} \rightarrow Cl^+_{(g)} + e^-$
   C. $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$
   D. $Cl_{2(g)} \rightarrow 2Cl_{(g)}$ **(C = exo)**

23

Q36. What quantity of energy is needed to heat 500g of water from 20.0°C to 90.0°C?
(146 kJ)

Q37. Consider the thermal equation:
$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \qquad \Delta H = -564 \text{ kJ}$$

How much heat would be released when 28.0 g of $CO_{(g)}$ is burnt?
(282 kJ)

Q38. For the reaction:
$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} \qquad \Delta H = -56 \text{ kJ}$$
Find the heat released when 10.0 mL of 0.25 mol L^{-1} $HCl_{(aq)}$ is reacted with 20.0 mL of 0.15 mol L^{-1} $NaOH_{(aq)}$.
(140 J)

Q39. For the reaction: $2SO_2 + O_2 \rightarrow 2SO_3$ $\qquad \Delta H = y$ kJ
What is the value of ΔH for:
$$SO_3 \rightarrow SO_2 + 1/2 O_2 \qquad \Delta H = ?$$
(-y/2 kJ)

Q40. With a P.D. of 6.00 V, a current of 0.500 A passes through a calorimeter for 100.0 seconds and the temperature rise is 3.00°C.
What is the calibration factor for the calorimeter in J $°C^{-1}$? **(100 J $°C^{-1}$)**

Q41. If the heat of combustion of ethyne (C_2H_2) is $\Delta H = -2599$ kJ mol^{-1} what is this in kJ per gram. **(100 J g^{-1})**
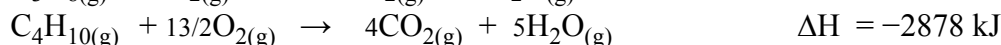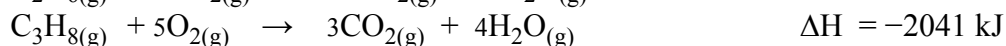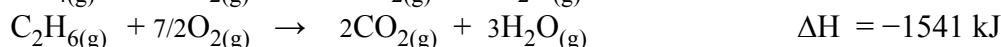
Q42. The bond dissociation energy for H−F is $\Delta H = +563$ kJ mol^{-1}.
Write a thermochemical equation illustrating the meaning of this statement.

Q43. The heat of combustion of glucose ($C_6H_{12}O_6$) is $\Delta H = -2803$ kJ mol^{-1} and the $M_r(C_6H_{12}O_6) = 180$. A person uses energy at a rate of 2.5 kJ per minute. Assuming this energy comes from the oxidation of glucose, find the mass of glucose consumed per minute.
(0.161 g min^{-1})

Q44. Consider the following four combustion reactions:
$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H = -890 \text{ kJ}$$
$$C_2H_{6(g)} + 7/2 O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)} \qquad \Delta H = -1541 \text{ kJ}$$
$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)} \qquad \Delta H = -2041 \text{ kJ}$$
$$C_4H_{10(g)} + 13/2 O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(g)} \qquad \Delta H = -2878 \text{ kJ}$$
Which of the four combustion reactions releases the greatest amount of energy per *gram* of hydrocarbon? **(CH$_4$)**

Q45. Consider the following thermochemical data:

1. $H_{2(g)} + I_{2(solid)} \rightarrow 2HI_{(g)}$ $\qquad \Delta H = +52$ kJ
2. $H_{2(g)} + I_{2(gaseous)} \rightarrow 2HI_{(g)}$ $\qquad \Delta H = ?$ kJ
Will the ΔH value for reaction 2 be greater than +52 kJ or less than +52 kJ ?
(less than 52 kJ)

Q46. The diagram below represents various possible chemical pathways that involve the elements nitrogen, carbon, hydrogen and oxygen and some of their compounds.
The heats of reaction involved in each step are represented by ΔH_1, ΔH_2, ΔH_3, ΔH_4,...............

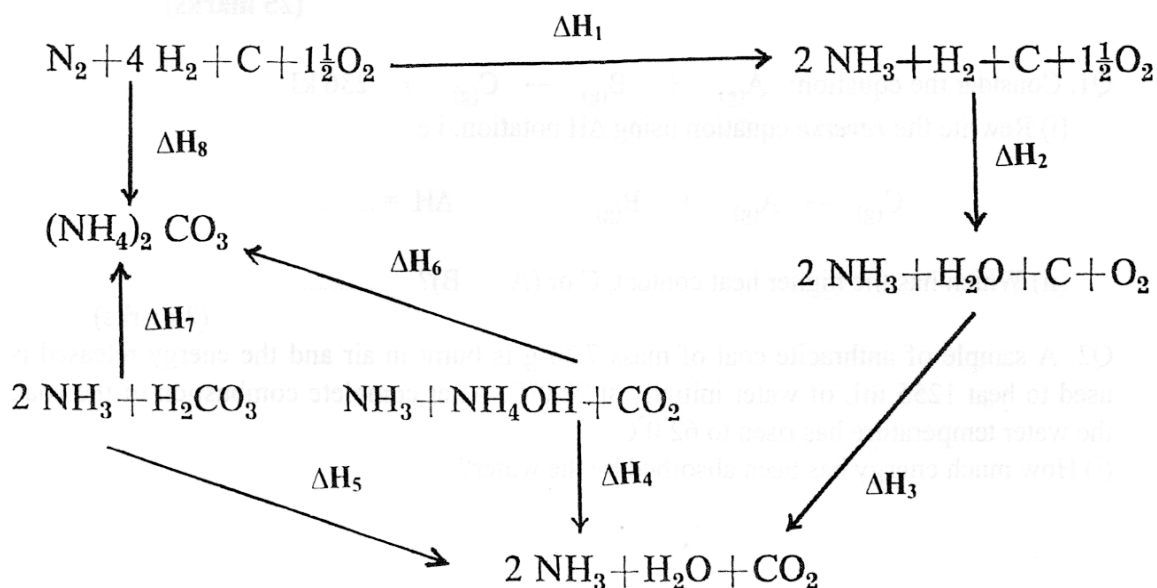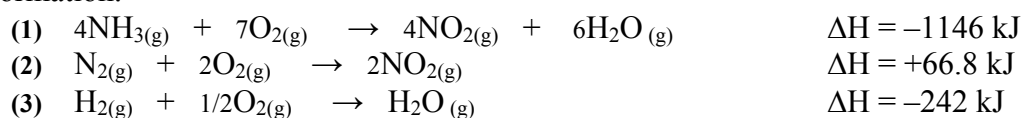$$N_2 + 4\,H_2 + C + 1\tfrac{1}{2}O_2 \xrightarrow{\;\Delta H_1\;} 2\,NH_3 + H_2 + C + 1\tfrac{1}{2}O_2$$

$$\downarrow \Delta H_8 \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \Delta H_2$$

$$(NH_4)_2\,CO_3 \qquad\qquad\qquad 2\,NH_3 + H_2O + C + O_2$$

$$\uparrow \Delta H_7 \qquad \Delta H_6 \nwarrow$$

$$2\,NH_3 + H_2CO_3 \qquad NH_3 + NH_4OH + CO_2$$

$$\Delta H_5 \qquad\qquad \Delta H_4 \downarrow \qquad \Delta H_3$$

$$2\,NH_3 + H_2O + CO_2$$

(i) Using the ΔH terms shown above, give three different expressions for the **heat of formation** of ammonium carbonate $(NH_4)_2CO_3$.

(ΔH₈)
(ΔH₁ + ΔH₂ + ΔH₃ − ΔH₄ + ΔH₆)
(ΔH₁ + ΔH₂ + ΔH₃ − ΔH₅ + ΔH₇)
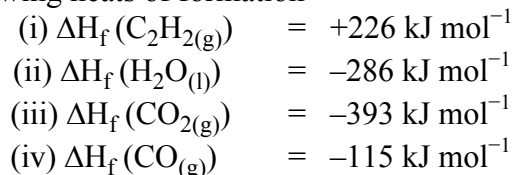
(ii) How do the numerical values of these three expressions compare?

(all identical)

Q47. Find the heat of formation of one mole of ammonia $(NH_{3(g)})$ given the following information.

(1)	$4NH_{3(g)} + 7O_{2(g)} \rightarrow 4NO_{2(g)} + 6H_2O_{(g)}$	$\Delta H = -1146$ kJ
(2)	$N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)}$	$\Delta H = +66.8$ kJ
(3)	$H_{2(g)} + 1/2\,O_{2(g)} \rightarrow H_2O_{(g)}$	$\Delta H = -242$ kJ

(-43.1 kJ mol⁻¹)

Q48. Given the following heats of formation

(i) $\Delta H_f\,(C_2H_{2(g)})$ = +226 kJ mol⁻¹
(ii) $\Delta H_f\,(H_2O_{(l)})$ = −286 kJ mol⁻¹
(iii) $\Delta H_f\,(CO_{2(g)})$ = −393 kJ mol⁻¹
(iv) $\Delta H_f\,(CO_{(g)})$ = −115 kJ mol⁻¹

Calculate the heat evolved when 130.0 g of ethyne $(C_2H_{2(g)})$ is oxidised to:
  (a) carbon dioxide and water. **(6490 kJ)**
  (b) carbon monoxide and water. **(3710 kJ)**
  (c) carbon and water. **(2560 kJ)**
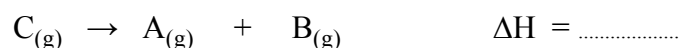 (d) equal amounts of CO gas, CO₂ gas and water. **(5100 kJ)**

25

CHEMISTRY (LEVEL 4C)
THERMOCHEMISTRY TEST 2

(25 marks)

Q1. Consider the equation: $A_{(g)}$ + $B_{(g)}$ → $C_{(g)}$ + 236 kJ

(i) Rewrite the *reverse* equation using ΔH notation. i.e.

$C_{(g)}$ → $A_{(g)}$ + $B_{(g)}$ $\qquad$ ΔH = ...

(ii) Which has the higher heat content, C or (A + B)? ....

(2 marks)

Q2. A sample of anthracite coal of mass 7.36 g is burnt in air and the energy released is used to heat 1255 mL of water initially at 22.0°C. After complete combustion of the coal, the water temperature has risen to 62.0°C.

(i) How much energy has been absorbed by the water?
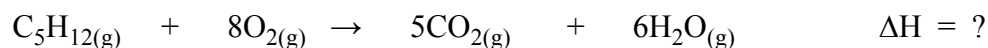
(2 marks)

(ii) The coal sample used is known to have a heating value of 37.4 kJ per gram. What is the % efficiency of the heat transfer process in this case? Show your workings.

(3 marks)

Q3. Consider the following bond energies:

O=O	497 kJ/mole		C−C	348 kJ/mole
C−H	412 kJ/mole		O−H	463 kJ/mole
C=O	743 kJ/mole			

Calculate the heat of reaction for the complete combustion of pentane in accordance with the equation:

$C_5H_{12(g)}$ + $8O_{2(g)}$ → $5CO_{2(g)}$ + $6H_2O_{(g)}$ $\qquad$ ΔH = ?

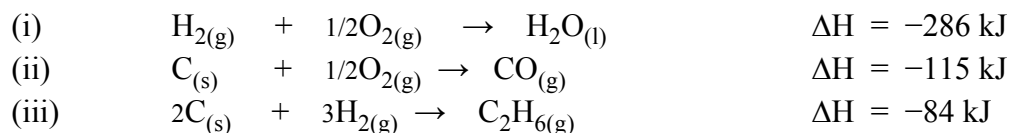**(5 marks)**
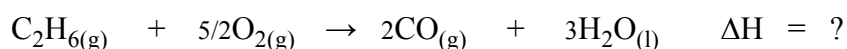
Q4. The energy required to break the covalent bonds between oxygen atoms in hydrogen peroxide (H_2O_2) is 146 kJ mol^{-1} whereas the energy required to break the bonds between oxygen atoms in oxygen gas (O_2) is 497 kJ mol^{-1}. Account for the difference between these values.

<div align="right">(3 marks)</div>

Q5. Given the following standard heats of formation:

(i) $H_{2(g)}$ + $1/2O_{2(g)}$ → $H_2O_{(l)}$ $\Delta H = -286$ kJ

(ii) $C_{(s)}$ + $1/2O_{2(g)}$ → $CO_{(g)}$ $\Delta H = -115$ kJ

(iii) $2C_{(s)}$ + $3H_{2(g)}$ → $C_2H_{6(g)}$ $\Delta H = -84$ kJ

Find the heat of reaction for the **incomplete** combustion of ethane as shown in the equation:

$$C_2H_{6(g)} \;+\; 5/2O_{2(g)} \;\rightarrow\; 2CO_{(g)} \;+\; 3H_2O_{(l)} \qquad \Delta H \;=\; ?$$
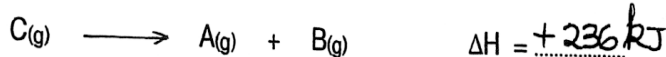
<div align="right">(6 marks)</div>

Q6. Why is a fuel such as petrol often regarded as having "energy stored in its bonds"? Explain carefully.

THERMOCHEMISTRY TEST 2

20A
16B
12C

Q1. Consider the equation: $A_{(g)} + B_{(g)} \longrightarrow C_{(g)} + 236\ kJ$

(i) Rewrite the *reverse* equation using ΔH notation. i.e. (4 marks)

$$C_{(g)} \longrightarrow A_{(g)} + B_{(g)} \qquad \Delta H = \underline{+236\ kJ}$$

(ii) Which has the higher heat content, C or (A + B)? $\underline{(A+B)}$

(2 marks)

Q2. A sample of anthracite coal of mass 7.36 g is burnt in air and the energy released is used to heat 1255 mL of water initially at 22.0°C. After complete combustion of the coal, the water temperature has risen to 62.0°C.

(i) How much energy has been absorbed by the water?

$$Q = \{mass\ H_2O)(\Delta T)(4.18)\}\ J$$
$$= 1255 \times 40.0 \times 4.18\ J$$

$$\underline{Energy = 210\ kJ}$$

(2 marks)

(ii) The coal sample used is known to have a heating value of 37.4 kJ per gram. What is the % efficiency of the heat transfer process in this case? Show your workings.

$$Heat\ released\ by\ coal = (37.4 \times 7.36)\ kJ$$
$$= 275\ kJ$$
$$\therefore\ \%\ Efficiency = \left(\frac{210}{275} \times 100\right) = 76.2\ \%$$

(2 marks)

Q3. Consider the following bond energies:

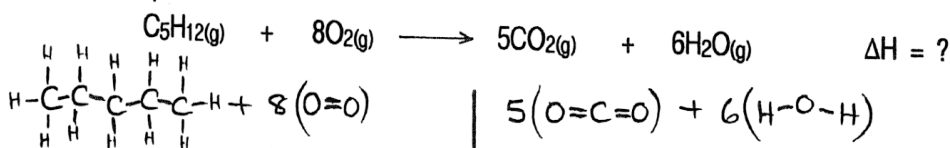|			
O=O	497 kJ/mole	C-C	348 kJ/mole
C-H	412 kJ/mole	O-H	463 kJ/mole
C=O	743 kJ/mole		

Calculate the heat of reaction for the complete combustion of pentane in accordance with the equation:

$$C_5H_{12(g)} + 8O_{2(g)} \longrightarrow 5CO_{2(g)} + 6H_2O_{(g)} \qquad \Delta H = ?$$

H-C-C-C-C-C-H + 8(O=O) | 5(O=C=O) + 6(H-O-H)

Bonds Broken   ∴ kJ REQD. | Bonds Formed   ∴ kJ released

$4 \times (C-C) \Rightarrow 4 \times 348 = 1392$ | $10 \times (C=O) \Rightarrow 10 \times 743 = 7430\ kJ$

$12 \times (C-H) \Rightarrow 12 \times 412 = 4944$ | $12 \times (H-O) \Rightarrow 12 \times 463 = 5556\ kJ$

$8 \times (O=O) \Rightarrow 8 \times 497 = 3976$

∴ Total energy reqd. = 10312 kJ | ∴ Total energy released = 12986 kJ
(*) | (**)

Thus comparing * & ** we see that a net energy release of 2674 kJ occurs

ie Heat of reaction = $\underline{\Delta H = -2674\ kJ}$ (5 marks)

Q4. The energy required to break the covalent bonds between oxygen atoms in hydrogen peroxide (H_2O_2) is 146 kJ/mole whereas the energy required to break the bonds between oxygen atoms in oxygen gas (O_2) is 497 kJ/mole. Account for the difference between these values.
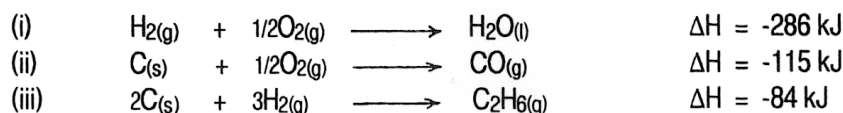
Hydrogen peroxide involves a SINGLE oxygen/oxygen bond whereas O_2 gas has a DOUBLE bond ie

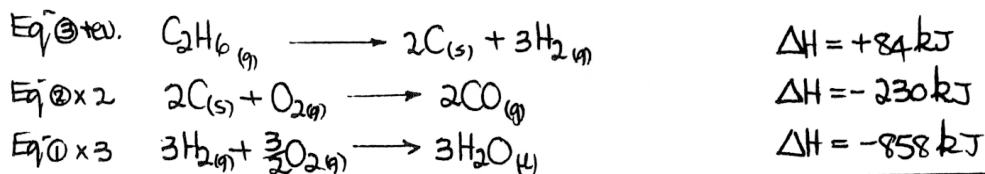H_2O_2 is $H-O-O-H$ and O_2 is $O=O$

The double bond is much stronger than the single

∴ requires a larger amount of energy to break!

(3 marks)

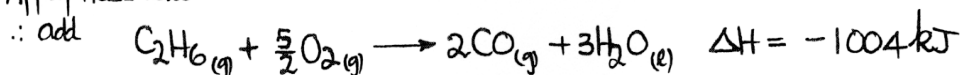Q5. Given the following standard heats of formation:

(i) $H_{2(g)}$ + $1/2O_{2(g)}$ ⟶ $H_2O_{(l)}$ ΔH = -286 kJ
(ii) $C_{(s)}$ + $1/2O_{2(g)}$ ⟶ $CO_{(g)}$ ΔH = -115 kJ
(iii) $2C_{(s)}$ + $3H_{2(g)}$ ⟶ $C_2H_{6(g)}$ ΔH = -84 kJ

Find the heat of reaction for the **incomplete** combustion of ethane as shown in the equation:

$$C_2H_{6(g)} + 5/2O_{2(g)} \longrightarrow 2CO_{(g)} + 3H_2O_{(l)} \qquad \Delta H = ?$$

Eq ③ rev. $C_2H_{6(g)} \longrightarrow 2C_{(s)} + 3H_{2(g)}$ $\Delta H = +84\,kJ$

Eq ② x 2 $2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$ $\Delta H = -230\,kJ$

Eq ① x 3 $3H_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow 3H_2O_{(l)}$ $\Delta H = -858\,kJ$

Apply Hess' Law
∴ add $C_2H_{6(g)} + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{(g)} + 3H_2O_{(l)}$ $\Delta H = -1004\,kJ$

∴ $\Delta H = -1004\,kJ$

(6 marks)

Q6. Why is a fuel such as petrol often regarded as having "energy stored in its bonds"? Explain carefully.

In petrol the (C-C) & (C-H) bonds are comparatively weak & require a small input of energy to break (ΔH_1)

The new bonds that then form (C=O) & (O-H) are quite strong ∴ large amounts of energy is released (ΔH_2)

∴ The net effect is energy is released ($\Delta H_2 > \Delta H_1$)

∴ Fuels "store" energy which can be released! (4 marks)