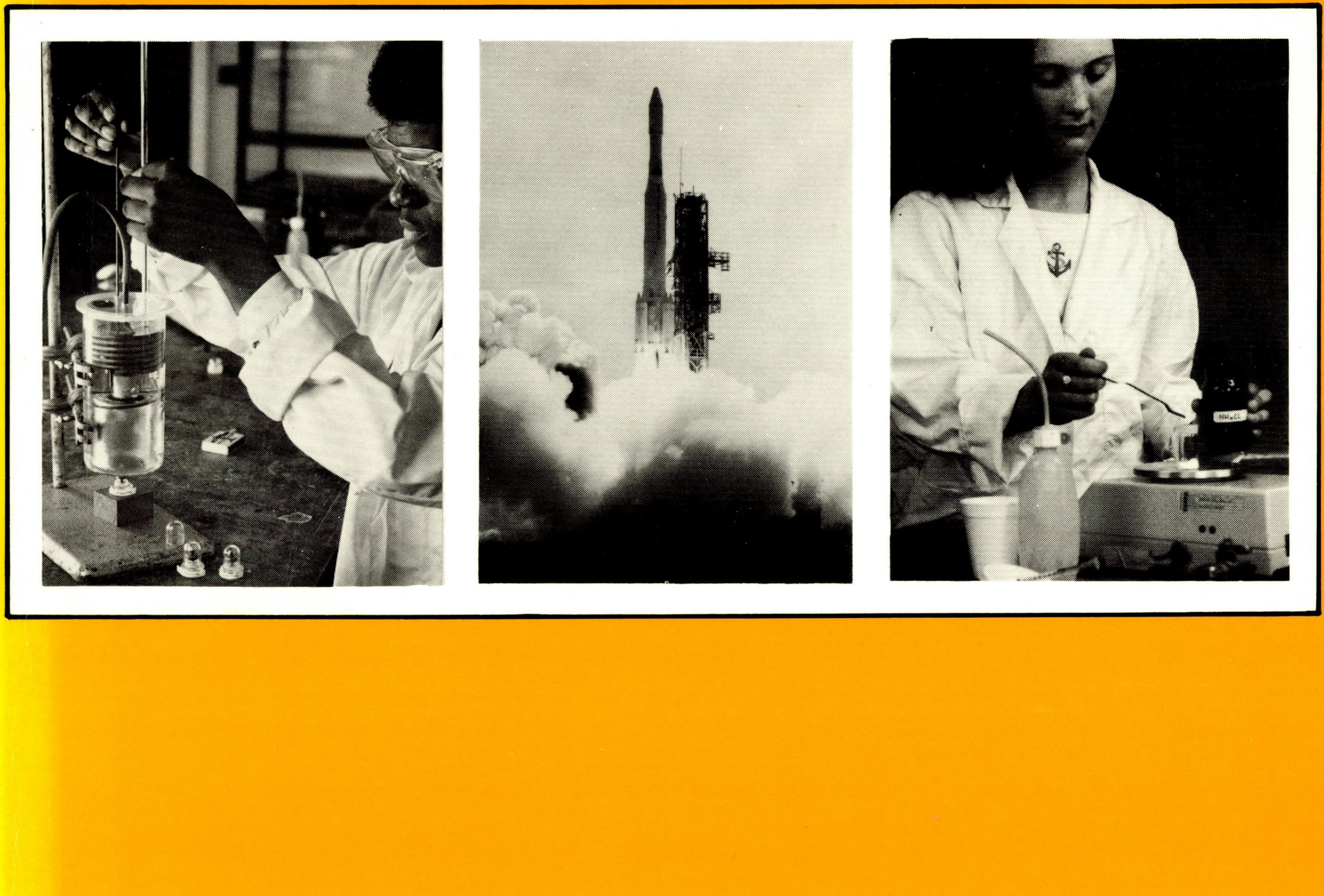
ILPAC

UNIT S3

INDEPENDENT LEARNING PROJECT FOR ADVANCED CHEMISTRY

Chemical Energetics



Periodic Table of the Elements

I	II											III	IV	V	VI	VII	O
						1 H 1.0											2 He 4.0
3 Li 6.9	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 99.0	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
87 Fr 223.0	88 Ra 226.0	89 Ac 227.0															

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.1	93 Np (237)	94 Pu 239.1	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

A value in brackets denotes the
mass number of the most stable isotope.

UNIT

S3

Chemical Energetics

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PREFACE

This volume is one of twenty Units produced by ILPAC, the Independent Learning Project for Advanced Chemistry, written for students preparing for the Advanced Level examinations of the G.C.E. The Project has been sponsored by the Inner London Education Authority and the materials have been extensively tested in London schools and colleges. In its present revised form, however, it is intended for a wider audience; the syllabuses of all the major Examination Boards have been taken into account and questions set by these boards have been included.

Although ILPAC was initially conceived as a way of overcoming some of the difficulties presented by uneconomically small sixth forms, it has frequently been adopted because its approach to learning has certain advantages over more traditional teaching methods. Students assume a greater responsibility for their own learning and can work, to some extent, at their own pace, while teachers can devote more time to guiding individual students and to managing resources.

By providing personal guidance, and detailed solutions to the many exercises, supported by the optional use of video-cassettes, the Project allows students to study A-level chemistry with less teacher-contact time than a conventional course demands. The extent to which this is possible must be determined locally; potentially hazardous practical work must, of course, be supervised. Nevertheless, flexibility in time-tabling makes ILPAC an attractive proposition in situations where classes are small or suitably-qualified teachers are scarce.

In addition, ILPAC can provide at least a partial solution to other problems. Students with only limited access to laboratories, for example, those studying at evening classes, can concentrate upon ILPAC practical work in the laboratory, in the confidence that related theory can be systematically studied elsewhere. Teachers of A-level chemistry who are inexperienced, or whose main discipline is another science, will find ILPAC very supportive. The materials can be used effectively where upper and lower sixth form classes are timetabled together. ILPAC can provide 'remedial' material for students in higher education. Schools operating sixth form consortia can benefit from the cohesion that ILPAC can provide in a fragmented situation. The project can be adapted for use in parts of the world where there is a severe shortage of qualified chemistry teachers. And so on.

A more detailed introduction to ILPAC, with specific advice both to students and to teachers, is included in the first volume only. Details of the Project Team and Trial Schools appear inside the back cover.

LONDON 1983

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Thanks are due to the following examination boards for permission to reproduce questions from past A-level papers:

Oxford Delegacy of Local Examinations;

Level One Test 7(1977)

University of London Entrance and School Examination Council;

Exercise 16 (L 1979), 20(L 1981), 31(N 1978), 39(L 1980)

Level One Test 1(L 1979), 2(L 1982), 3(L 1975), 4(N 1974), 5(N 1978)

End of Unit Test 1(L 1978), 2(L 1976), 3(N 1980), 4(L 1980), 5(N 1977),
6(N 1979), 7(N 1979), 8(N 1974), 9(N 1980), 10(N 1980),
11(L 1974), 12(L 1981), 13(L 1977), 14(L 1980).

Welsh Joint Education Committee;

Exercise 30(1977), 34(1976), 35(1978)

Where answers to these questions are included, they are provided by ILPAC and not by the examination boards.
Questions from papers of other examining boards appear in other Units.

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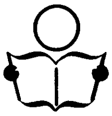
SYMBOLS USED IN ILPAC UNITS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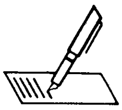
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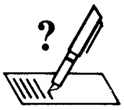

Test

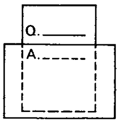
A 'A' Level question

A part 'A' Level part question

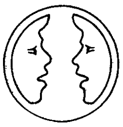
S A 'A' Level question Special paper

W Worked example

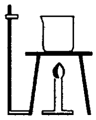
✓ Teacher-marked exercise



Revealing exercise


Discussion

C Computer programme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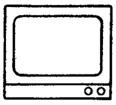
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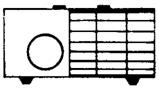
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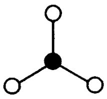
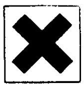

Model-making

INTERNATIONAL HAZARD SYMBOLS


Harmful


Toxic


Radioactive


Flammable


Explosive


Corrosive


Oxidising

INTRODUCTION

All chemical reactions involve energy changes. For example, your school or college is heated by burning natural gas, oil, coal or coke, either close at hand or in a power station; you have probably noticed a rise in temperature when an acid reacts with an alkali in a test-tube; the metabolism of food releases energy that is needed to 'drive' other vital reactions in your body.

The study of energy changes is an important part of chemistry. Fundamental to the study of energetics is the law of conservation of energy, which states that energy is neither created nor destroyed, but can be converted from one form to another. Such transformations account for heat from the burning of coal being able to turn a turbine to generate electricity, and the changes in potential energy and kinetic energy when a ball is thrown up into the air.

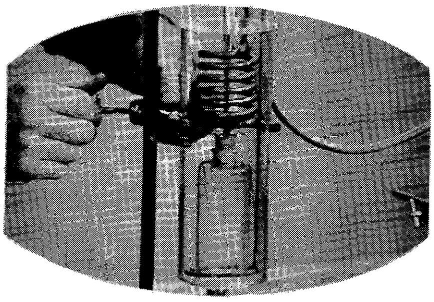
In this Unit, we are particularly concerned with the transformation of chemical energy (energy stored in every chemical substance) into heat energy, and vice versa. By the end of the Unit you should have some understanding of the relationship between chemical energy and chemical bonds.

In Level One, we extend many of the ideas of energetics from your pre-A-level course and introduce Hess's law, an application of the law of conservation of energy, which enables you to calculate some energy changes that cannot be measured directly. We also show you how the energy (enthalpy) changes associated with chemical reactions are used to discuss the stability of substances and the likelihood of those reactions occurring spontaneously.

In Level Two, we look more closely at the energetics of bond formation in both covalent and ionic substances. To enable you to predict more reliably the possibility of a reaction occurring, we introduce you to two more thermodynamic quantities, free energy and entropy, and show how they are related to enthalpy.

There are six experiments in this Unit, but you may not have time to do them all. Three are in Level One, two in Level Two and one in an appendix.

There is an ILPAC video-programme designed to accompany this Unit. It is not essential, but you should try to see it at the appropriate time if it is available.



Using a heat of combustion apparatus

PRE-KNOWLEDGE

Before you start work on this Unit, you should be able to:

(1) do simple calculations of reacting mass based on chemical equations;

(2) define 'heat capacity' and 'specific heat capacity';

(3) calculate the heat capacity of an object of uniform composition (e.g. all glass, all copper, all solution) using the relationship:

	HEAT CAPACITY	=	MASS	×	SPECIFIC HEAT CAPACITY
usual units:	kJ K^{-1}		kg		kJ kg^{-1} K^{-1}
	(or J K^{-1}	or	g		or J g^{-1} K^{-1})

(4) calculate the heat gained or lost by an object (i.e. its change in heat energy) when its temperature changes, using the relationship:

	HEAT GAIN OR LOSS	=	HEAT CAPACITY	×	TEMPERATURE CHANGE
usual units:	kJ		kJ K^{-1}		K

(5) solve simple simultaneous equations in x and y.

PRE-TEST

To find out whether you are ready to start Level One, try the following test, which is based on the pre-knowledge items. You should not spend more than 40 minutes on this test. Hand your answers to your teacher for marking.

PRE-TEST

1. What mass of lead would be obtained on complete reduction of 1.60 g of lead(IV) oxide by hydrogen?

   $PbO_2(s) + 2H_2(g) \rightarrow Pb(s) + 2H_2O(g)$ (4)

2. From the equation

   $CuSO_4(s) + 100H_2O(l) \rightarrow CuSO_4(aq,100H_2O)$

   calculate the masses of copper sulphate and water required to prepare the solution from 0.025 mol of the solid. (4)

3. State, in your own words, what you understand by the terms:

   (a) heat capacity of an object;

   (b) specific heat capacity of a substance. (4)

4. When one mole of concentrated sulphuric acid is carefully added to sufficient water to make 1 dm^3 of solution, the temperature of the solution rises by 17 °C. Calculate the increase in heat energy of the solution. You may assume in your calculation that the specific heat capacity of the mixture is the same as that of water, 4.2 $kJ\ kg^{-1}\ K^{-1}$, and that 1 dm^3 of water weighs 1 kg. (2)

5. A copper can (calorimeter) of mass 60 g containing 100 g of water was heated by a spirit lamp till the temperature of the water rose by 10°C. Calculate the heat energy transferred from the flame to the calorimeter and contents.

   (Specific heat capacities: water, 4.18 $kJ\ kg^{-1}\ K^{-1}$
   copper, 0.38 $kJ\ kg^{-1}\ K^{-1}$) (4)

6. Solve the simultaneous equations:

   $$3x + 2y = 16$$
   $$2x + y = 9$$ (2)

(Total 20 marks)

LEVEL ONE

We start this Unit by defining some important terms used in the study of energetics, sometimes called thermodynamics. The subject was developed in the nineteenth century, so some of the words may seem strange. They will, of course, eventually form an integral part of your scientific vocabulary.

BASIC IDEAS

When you read your text-books, you may find it assumed that certain terms and ideas are familiar to you. In the following sections, we briefly describe and define them to aid your reading.

Objectives. When you have finished these sections, you should be able to:

(1) distinguish between system and surroundings;
(2) describe a process as exothermic or endothermic;
(3) describe in principle how enthalpy changes are measured;
(4) quote the standard conditions for thermodynamic processes.

System and surroundings

In your study of energetics (and, later, of chemical equilibrium), you must define the region or particular quantity of matter of interest. This is called the system. Two examples are:

(a) one in which no reaction is taking place; e.g. 25 g of potassium bromide under different physical conditions:

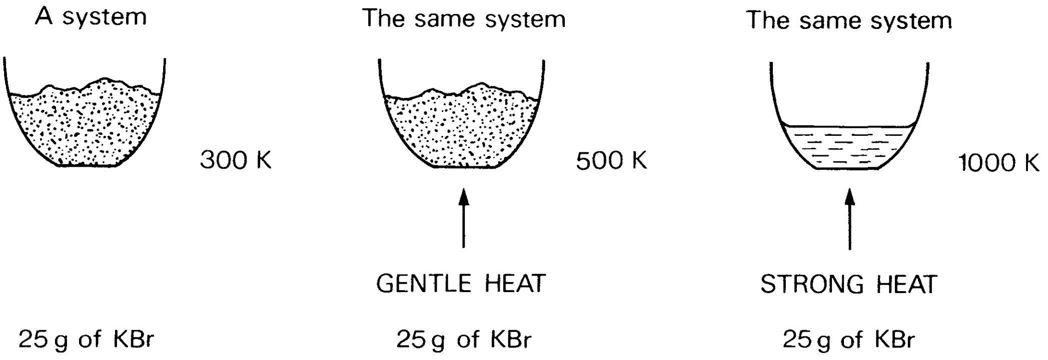
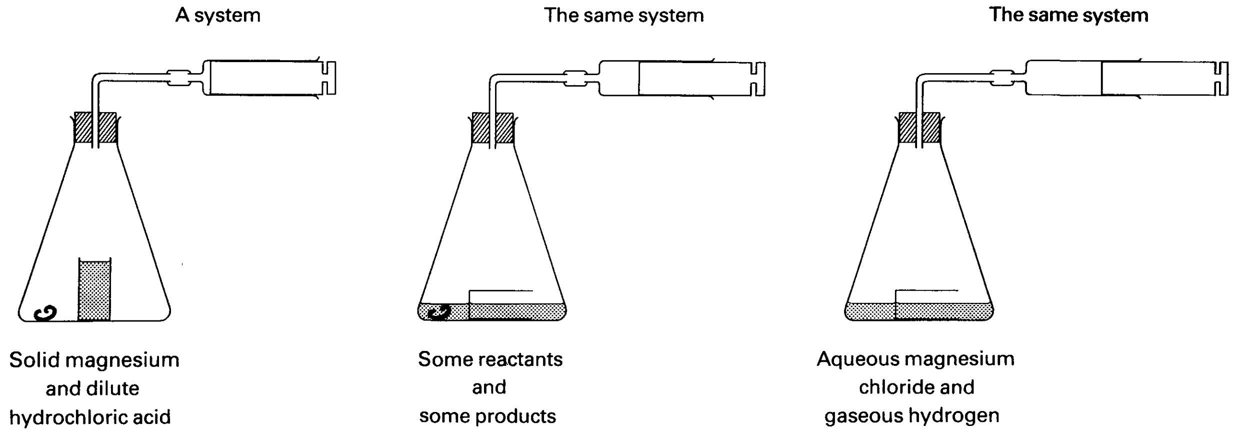


Fig. 1. The same system under different conditions.

(b) one in which reaction could take place, or is taking place, or has taken place; e.g. stoichiometric amounts of magnesium and hydrochloric acid:



Solid magnesium and dilute hydrochloric acid

Some reactants and some products

Aqueous magnesium chloride and gaseous hydrogen

Fig. 2. A system in which a reaction occurs.

The surroundings are everything other than the system. In certain instances it is important to specify whether the container (e.g. the crucible in Fig. 1 or the flask and syringe in Fig. 2) is to be considered part of the system or part of the surroundings.

The symbol Δ (Greek letter 'delta')

In science and mathematics we use the symbol Δ to indicate an increase in a quantity; for example, an increase in temperature from 295 K to 300 K may be referred to as ΔT, where

$$\Delta T = T\text{ (final)} - T\text{(initial)}$$

$$= 300\text{ K} - 295\text{ K} = 5\text{ K}$$

A negative value of ΔT implies a decrease in temperature. However, you may find the symbol Δ used to refer to a change in a quantity, X, in such a way that both increase and decrease are positive. But remember, the strict definition of ΔX is

$$\Delta X = X\text{ (final)} - X\text{ (initial)}$$

Exothermic and endothermic changes

An exothermic change is one in which stored chemical energy is converted to heat energy. We often say that 'heat is given out' (the prefix 'ex-' means 'out' - as in 'exit') or 'heat is released' or 'heat is evolved'. This heat energy very often increases the temperature of the system, and then is transferred to the surroundings as the temperature returns to normal. You are familiar with exothermic changes such as the burning of fuel and the condensation of water vapour (this is why steam can cause more severe scalding than water at the same temperature).

Conversely, an endothermic change is one in which heat energy is converted to chemical energy. Heat energy is absorbed, and this can cause a fall in temperature of the system unless heat is transferred from the surroundings. You are familiar with endothermic changes such as dissolving ammonium chloride in water or frying an egg.

Enthalpy (symbol *H*)

The enthalpy of a substance, sometimes called its heat content, is an indication of its total energy content. We shall not attempt to define enthalpy formally, and we cannot measure it, but we can measure enthalpy changes and these are very useful.

A simple analogy may be helpful here: if you are out walking in the hills you probably do not worry much about your height above sea level, but it is easy to tell whether you are going up or down, and information on differences in height is very useful in planning your journey.

Enthalpy change, ΔH

There are two main ways in which the enthalpy of a system can change. One is by a change in temperature corresponding to a change in heat energy; for instance, 25 g of water at 70°C has greater enthalpy than 25 g of water at 50°C. The other is by a change in chemical energy, or stored energy; for instance, 25 g of water vapour at 100°C has greater enthalpy than 25 g of liquid water at 100°C.

In each of these cases, it is possible to measure ΔH by measuring the heat energy input required to make the change.

In chemical reactions, both types of enthalpy change are likely to occur, but in order to focus attention on chemical energy we usually measure enthalpy changes between reactants and products which are at the same temperature.

Changes in pressure and volume also have some bearing on the way we describe energy changes, as we now show.

The constant pressure process

Consider the reaction between magnesium and hydrochloric acid:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Assume that the reaction is carried out in the apparatus in Fig. 3 under the laboratory conditions shown.

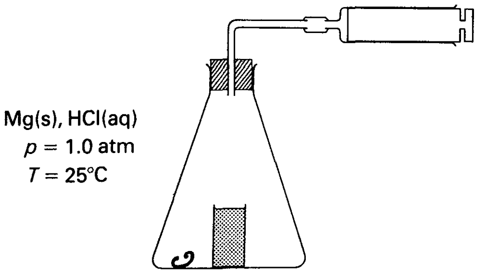


Fig. 3.

We allow the two to react, and immediately after reaction we have the situation shown in Fig. 4, where the temperature has increased due to heat energy released in the reaction.

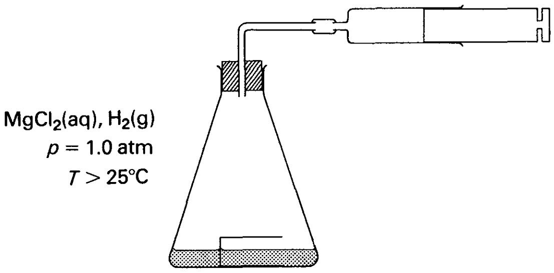


Fig. 4.

Then we let the system cool back to room temperature (25°C). Its final state is described in Fig. 5.

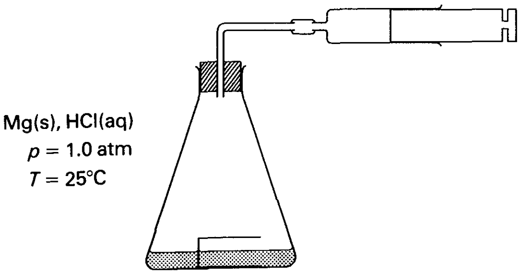


Fig. 5.

Notice that both before and after the reaction the temperature and pressure are the same but the volume is different.

If we measure all the heat transferred between system and surroundings in order to return the system to 25°C, this is the enthalpy change for the reaction.

Most reactions you study are carried out at constant pressure, but sometimes you may consider a process where the pressure may vary because the volume is kept constant.

The constant volume process

We can perform this same reaction at constant volume in a very strong flask. Again, we assume a set of initial conditions and let the substances react as before. After an intermediate state when all the magnesium has reacted and the temperature is greater than 25°C, the system cools back to 25°C, but the pressure is higher than before. The process is shown in Fig. 6.

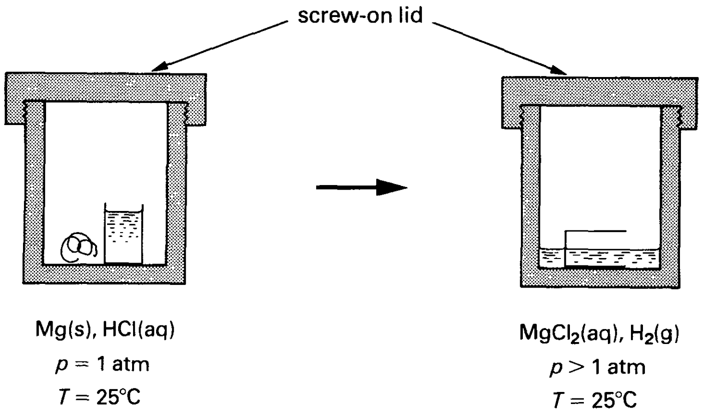


Fig. 6. Chemical reaction at constant volume.

The heat energy transferred between system and surroundings is <u>not</u> quite the same as the enthalpy change, ΔH: it is a true measure of the change in internal energy, ΔU. In many cases, there is very little difference between ΔH and ΔU. In Appendix 2, we show the relation between enthalpy change and internal energy change. Ask your teacher if you should study this.

All of the reactions you perform in the laboratory are constant pressure processes because they take place in open beakers, test-tubes and flasks. Therefore we concentrate on enthalpy changes, especially those which occur under certain standard conditions.

Standard enthalpy change, $\Delta H^\ominus$

For the basis of comparison and tabulation of data, a set of standard conditions has been arbitrarily defined for thermodynamics; the enthalpy change for a reaction which occurs at a pressure of 101325 N m^{-2} (1 atm) and 298 K (25 °C) is called the standard enthalpy change and is indicated by the symbol $\Delta H^\ominus$ (298 K). Usually, however, the '298 K' is omitted. If the temperature is other than this, it is indicated.

Now that we have given a rather lengthy introduction to enthalpy change, you should see what your text-books have to say on the subject. Look in the index under enthalpy change or heat of reaction. (Note that the terms 'enthalpy change', 'energy change', and 'heat' are often used interchangeably in this context.) You should then be able to do the following exercises.

Exercise 1 State the temperature, pressure and concentration which are the thermodynamic standard conditions.

(Answer on page 86)

Exercise 2 (a) Classify the following changes as exothermic or endothermic:

(i) Sodium hydroxide dissolves in water and the temperature of the solution rises.

(ii) Ammonium chloride dissolves in water and the temperature of the surroundings drops.

(iii) Hydrogen and oxygen combine explosively to form water.

(iv) Liquid water condenses to ice at 0°C.

(v) Liquid nitrogen (boiling point = 77 K) boils spontaneously at room temperature.

(b) Explain why $\Delta H^\ominus$ has a negative value for an exothermic reaction and a positive value for an endothermic reaction.

(Answers on page 86)

It is very convenient to link values of standard enthalpy change with chemical equations, which we now consider.

Thermochemical equations

A thermochemical equation summarises the information needed in the study of energetics - it gives the amounts, measured in moles, of reactants and products, and also tells the quantity of energy involved. One such equation is given below. It summarises these facts: when two moles of hydrogen react with one mole of oxygen to produce two moles of liquid water, with both the initial and final states at 298 K and 1 atm, 572 kJ of heat energy are released.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \quad \Delta H^\ominus = -572 \text{ kJ mol}^{-1}$$

Notice the use of the symbol $^\ominus$ to indicate standard conditions. If half the amounts are used, then the energy is halved also.

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l); \quad \Delta H^\ominus = -286 \text{ kJ mol}^{-1}$$

Notice that in both examples, the unit for standard enthalpy change is kJ mol^{-1}. You can consider that the term 'per mole' refers to all the amounts specified in the equation. You may find it useful to think of the term 'per mole' as referring to 'a mole of equation' if, as in the two examples, the stoichiometric coefficients are not all unity.

It is important to include the state symbols (e.g. g, l, s, aq) because the energy change depends on the state of the substance. If the water produced were not allowed to condense, then we would write a thermochemical equation with a different value of the enthalpy change;

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g); \quad \Delta H^\ominus = -484 \text{ kJ mol}^{-1}$$

Another useful way to summarise thermochemical data is to use energy level diagrams.

Energy-level diagrams

An energy-level diagram drawn to scale provides a way to visualise the relative enthalpies of substances in a reaction (or process).

Objectives. When you have finished this section, you should be able to:

(5) relate thermochemical equations to energy-level diagrams;

(6) use an energy-level diagram to calculate enthalpy change.

We introduce energy level diagrams by a Worked Example.

W

Worked Example Consider the two thermochemical equations:

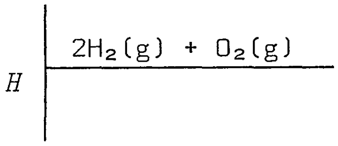
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g); \quad \Delta H^\ominus = -484 \text{ kJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \quad \Delta H^\ominus = -572 \text{ kJ mol}^{-1}$$

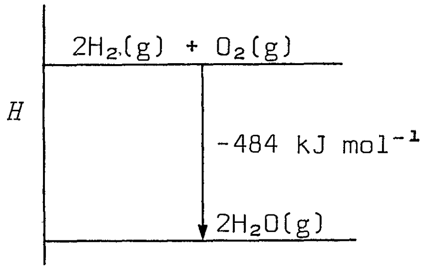
Draw an energy level diagram to represent both of these changes.

Solution

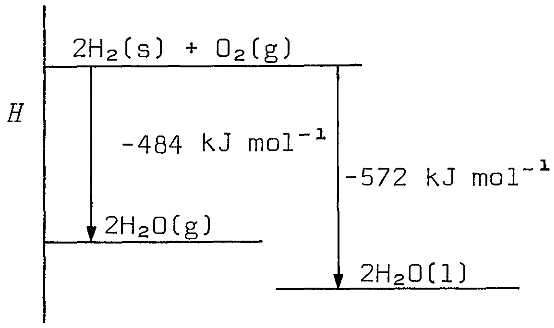
1. We plot enthalpy vertically and specify the scale. Here let 1 cm = 200 kJ mol^{-1}. Draw a horizontal line to represent the enthalpy of the reactants. It is quite proper to do this even though we do not know where zero enthalpy is.



2. Measure the distance downward corresponding to the release of 484 kJ mol^{-1} of energy and drawn another horizontal line to indicate the enthalpy of 2 mol of gaseous water. The arrow shows the direction of change, as does the negative sign.



3. Measure the distance downward from the first line corresponding to the release of 572 kJ mol^{-1} of energy and draw a third horizontal line to show the enthalpy of 2 mol of liquid water.



Now try the next exercise based on this diagram.

Exercise 3 How much heat is released when one mole of steam condenses to one mole of liquid water? Write a thermochemical equation summarising this information.

(Answer on page 86)

The next exercises emphasise the use of thermochemical equations and energy level diagrams.

Exercise 4 When one mole of graphite is burned completely in oxygen to produce carbon dioxide, 394 kJ of heat is evolved whereas, when diamond is similarly burned, 396 kJ is evolved.

(a) Write thermochemical equations summarising this information.

(b) Draw an energy level diagram comparing the combustion of diamond and graphite.

(c) What is the enthalpy change for the conversion of graphite into diamond?

(Answers on page 86)

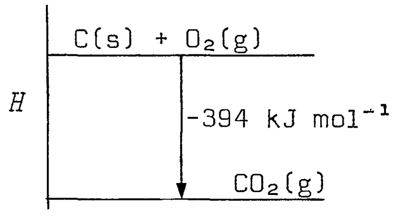
Exercise 5 Draw energy level diagrams for the following reactions:

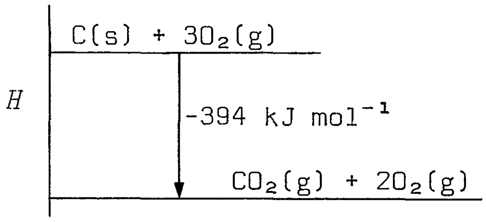
(a) $C(s) + 2S(s) \rightarrow CS_2(l)$; $\Delta H^\ominus = +88$ kJ mol^{-1}

(b) $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$; $\Delta H^\ominus = -152$ kJ mol^{-1}

(Answers on page 86)

Exercise 6 The two energy level diagrams below refer to the complete combustion, under standard conditions, of 1 mol of carbon when mixed with different amounts of oxygen.





Explain why the two additional moles of oxygen do not affect the enthalpy change.

(Answer on page 86)

Since the enthalpy change in the last exercise refers to combustion, it is sometimes called enthalpy change of combustion or, more simply, heat of combustion. Enthalpy changes for other types of reaction may be named in a similar way.

Labelling enthalpy changes

In order to tabulate numerical values of standard enthalpy change, certain types of reaction and their enthalpy changes are labelled. For example, standard enthalpy change of formation (symbol: $\Delta H^{\ominus}_{f}$); standard enthalpy change of combustion (symbol: $\Delta H^{\ominus}_{c}$) and standard enthalpy change of solution (symbol: $\Delta H^{\ominus}_{soln}$). Note that the word 'standard' is sometimes omitted but is always implied by the symbol $^{\ominus}$.

Objectives. When you have finished this section, you should be able to:

(7) define (a) enthalpy change of formation,
(b) enthalpy change of combustion,
(c) enthalpy change of solution;

(8) use your data book to find numerical values of these enthalpy changes;

(9) recognise that the standard enthalpy change of formation of an element is defined as zero.

Look up the definitions of different types of enthalpy change in your text-book(s). Include examples in your notes. Remember that, for example, 'standard enthalpy of combustion' may be shortened to 'enthalpy of combustion' or even 'heat of combustion'.

To see if you can apply these definitions, do the next two exercises.

Exercise 7 (a) Select the specific term(s) which describe the enthalpy changes in the following reactions:

(i) $C_2H_5OH(l) + 3\,O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

(ii) $CuSO_4(s) + 100H_2O(l) \rightarrow CuSO_4(aq, 100H_2O)$

(iii) $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

(iv) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

(v) $S(s) + O_2(g) \rightarrow SO_2(g)$

(b) Using your data book, list the numerical value of the enthalpy change in each of these reactions.

(Answers on page 86)

Exercise 8 Write complete thermochemical equations showing

(a) the standard heat of combustion of methane, CH_4,

(b) the standard heat of formation of calcium oxide, CaO,

(c) the standard heat of formation of liquid bromine, Br_2,

(d) the standard heat of formation of sodium metal, Na.

(Answers on page 86)

As stated on page 10, the amounts of reactants determine the quantity of heat which is exchanged with the surroundings. The enthalpy change of formation of one mole of water is -285.9 kJ mol^{-1} and for two moles of water it is twice this amount, -571.8 kJ mol^{-1}. To avoid confusion in such cases, an equation should always be written, as in the next two exercises.

Exercise 9 Write thermochemical equations to represent the following reactions at standard conditions:

(a) the combustion of 2.00 mol of calcium;

(b) the formation of 1.00 mol of ammonia from its elements;

(c) the dissolving of 1.00 mol of magnesium chloride in 500 mol of water;

(d) the combustion of 1.00 mol of ethane, C_2H_6.

(Answers on page 86)

Exercise 10 (a) Write a thermochemical equation showing that when 1.00 mol of carbon burns completely in oxygen, 394 kJ of heat are liberated.

(b) Calculate the enthalpy change on complete combustion of

(i) 10.0 mol of carbon, (iii) 18.0 g of carbon.

(ii) 0.25 mol of carbon,

(c) What mass of carbon would have to be burned to produce

(i) 197 kJ, (ii) 1000 kJ?

(Answers on page 87)

For convenience, we can use a shorthand notation. For example, "the standard enthalpy change of formation of water is -286 kJ mol^{-1}" can be represented as $\Delta H^{\ominus}_{f}\,[H_2O(l)] = -286$ kJ mol^{-1}.

Similarly, for the standard heat of combustion of hydrogen we can write $\Delta H^{\ominus}_{c}\,[H_2(g)] = -286$ kJ mol^{-1}.

Now that you understand what enthalpy changes are, we consider practical ways of measuring them.

EXPERIMENTAL DETERMINATION OF ENTHALPY CHANGE

In discussing enthalpy changes earlier, we spoke of heat transfers to the surroundings and of being able to measure them. In practice, it is much easier to measure the enthalpy change of a reaction using a calorimeter in which the system is insulated from the surroundings. For an exothermic reaction, the energy which would otherwise be given to the surroundings results in an increase in the temperature of the system.

If the maximum temperature change of the system is recorded and if the heat capacity of the system is known, it is easy to calculate the quantity of heat which would have to be taken from the system in order to restore it to its initial temperature. This quantity of heat is the enthalpy change.

For an endothermic reaction, the temperature of the system would drop, but again the enthalpy change can be calculated from the temperature change if the heat capacity of the system is known.

There are several types of insulated calorimeter you can use for simple experiments, as illustrated in Fig. 7. These calorimeters insulate the system from the surroundings so that all energy changes occur within the system. The energy exchanged with the surroundings is usually small enough to be ignored.

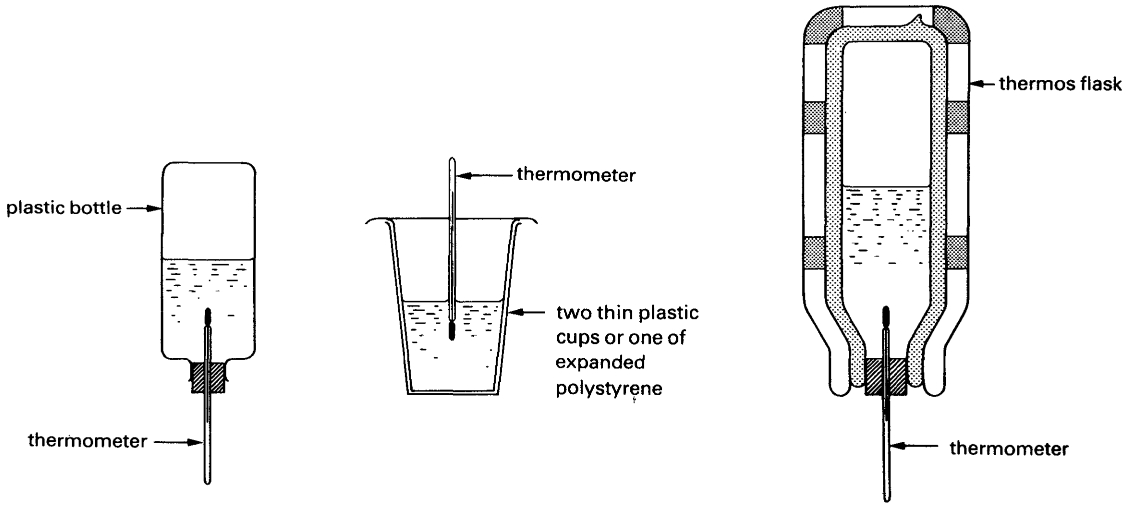


Fig. 7. Various insulated calorimeters.

Before you begin Experiment 1, we give a Worked Example showing how the enthalpy change of reaction can be calculated from experimental data.

W

Worked Example An excess of zinc powder was added to 50.0 cm^3 of 0.100 M $AgNO_3$ in a polystyrene cup. Initially, the temperature was 21.10°C and it rose to 25.40°C. Calculate the enthalpy change for the reaction:

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

Assume that the density of the solution is 1.00 g cm^{-3} and its specific heat capacity is 4.18 kJ kg^{-1} K^{-1}. Ignore the heat capacity of the metals.

Solution

1. Since the polystyrene cup is an insulator and its heat capacity is almost zero, you can assume that no energy is exchanged between system and surroundings. All the chemical energy released in the reaction is transformed into heat energy which raises the temperature of the solution. The total energy change in the system is zero, so you can write:

$$\begin{bmatrix}\text{enthalpy change, } \Delta H\text{, due} \\ \text{to reaction (at constant } T\text{)}\end{bmatrix} + \begin{bmatrix}\text{change in heat} \\ \text{energy of solution}\end{bmatrix} = 0$$

Since $\begin{bmatrix}\text{change in heat} \\ \text{energy of solution}\end{bmatrix} = \begin{bmatrix}\text{mass x specific heat capacity} \\ \text{x temperature change}\end{bmatrix} = mc_p{}^{*}\ \Delta T$

you can now write: $\Delta H + mc_p\Delta T = 0$

$$\therefore\ \Delta H = -mc_p\Delta T = -\frac{50.0}{1000}\text{ kg} \times 4.18\text{ kJ kg}^{-1}\text{ K}^{-1} \times 4.30\text{ K} = -0.899\text{ kJ}$$

*c_p is the symbol commonly used for specific heat capacity. The 'p' refers to constant pressure conditions (as does ΔH).

2. The value -0.899 kJ is the enthalpy change for the amounts used in the experiment. To obtain a value for the enthalpy change of reaction, compare the amounts used in the experiment with the amounts shown in the equation:

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + Ag(s)$$

1 mol 2 mol

The amount of silver ion used = 0.0500 dm^3 x 0.100 mol dm^{-3} = 5.00×10^{-3} mol

$\therefore$ the enthalpy change using 2 mol of Ag^+

$$= -0.899\text{ kJ} \times \frac{2.00\text{ mol}}{5.00 \times 10^{-3}\text{ mol}} = -360\text{ kJ}$$

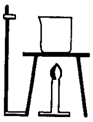
3. Now write the complete thermochemical equation:

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + Ag(s):\ \Delta H = -360\text{ kJ mol}^{-1}$$

Strictly speaking, you should not write $\Delta H^{\ominus}$ in this case because the conditions of the experiment were not standard, but the values of ΔH and $\Delta H^{\ominus}$ would be very close.

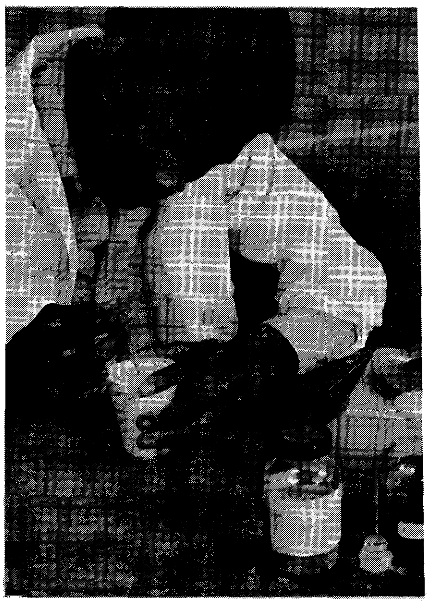
Note that enthalpy changes related to equations, which include all standard enthalpy changes, have the unit kJ mol^{-1}.

Now you can do an experiment which is similar to the one described in the worked example.



EXPERIMENT 1

Determining an enthalpy change of reaction



Aim

The purpose of this experiment is to determine the enthalpy change for the displacement reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Introduction

By adding an excess of zinc powder to a measured amount of aqueous copper (II) sulphate, and measuring the temperature change over a period of time, you can then calculate the enthalpy change for the reaction.

Requirements

safety spectacles
pipette, 25 cm^3
pipette filler
polystyrene cup with lid
copper(II) sulphate solution, 1.00 M $CuSO_4$ - ☠
weighing bottle
spatula
zinc powder
balance
thermometer, 0-100°C (0.1° graduations)
watch or clock with second hand

Procedure

1. Pipette 25.0 cm^3 of the copper(II) sulphate solution into a polystyrene cup. ☠
2. Weigh about 6 g of zinc powder in the weighing bottle. Since this is an excess, there is no need to be accurate.
3. Put the thermometer through the hole in the lid, stir and record the temperature to the nearest 0.1°C every half minute for 2½ minutes.
4. At precisely 3 minutes, add the zinc powder to the cup.
5. Continue stirring and record the temperature for an additional 6 minutes to complete Results Table 1.

Results Table 1

Time/min	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Temperature/°C							-			
Time/min	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
Temperature/°C										

Calculations

1. Plot the temperature (y-axis) against time (x-axis).
2. Extrapolate the curve to 3.0 minutes to establish the maximum temperature rise as shown in Fig. 8.

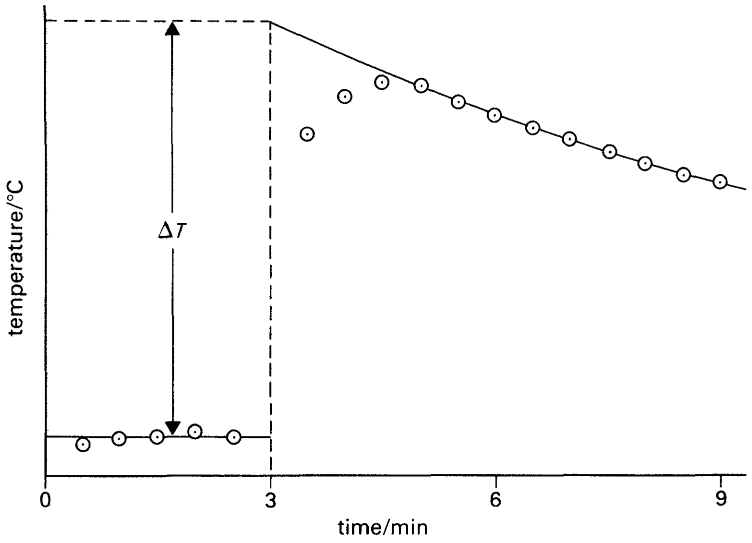


Fig. 8.

3. Calculate the enthalpy change for the quantities used, making the same assumptions as in the preceding exercise.
4. Calculate the enthalpy change for one mole of Zn and $CuSO_4$(aq), and write the thermochemical equation for the reaction.

(Specimen results on page 87)

Questions

1. Compare your result with the accepted value of -217 kJ mol^{-1} by calculating the percentage error in your answer:

$$\text{error} = \frac{\text{experimental value - accepted value}}{\text{accepted value}} \times 100\%$$

2. List some possible reasons for any difference between your value and the accepted value.
3. Why do you think the temperature increases for a few readings after adding the zinc? (Hint: it does not increase if more zinc is used or if the powder is very finely divided.)

(Answers on page 87)

Now we look at another type of enthalpy change.

Measuring an enthalpy change of solution

When substances dissolve, the enthalpy change depends on the relative amounts of solute and solvent. Before you do the next experiment, we give a Worked Example to illustrate the calculations.

<u>Worked Example</u> When 0.85 g of anhydrous lithium chloride, LiCl, was added to 36.0 g of water at 25.0°C in a polystyrene cup, the final temperature of the solution was 29.7°C. Calculate the enthalpy change of solution for one mole of lithium chloride.

W

<u>Solution</u>

1. In problems involving heat of solution, the amount of solvent is important so calculate the ratio: amount of LiCl/amount of H_2O. Then you can write the correct equation describing the process for one mole of the salt.

$$\text{amount of LiCl} = \frac{m}{M} = \frac{0.85\ \text{g}}{42.4\ \text{g mol}^{-1}} = 0.020\ \text{mol}$$

$$\text{amount of } H_2O = \frac{m}{M} = \frac{36.0\ \text{g}}{18.0\ \text{g mol}^{-1}} = 2.00\ \text{mol}$$

$$\therefore \quad \frac{\text{amount of LiCl}}{\text{amount of } H_2O} = \frac{0.020}{2.00} = \frac{1}{100}$$

2. Write the equation:

$$LiCl(s) + 100H_2O(l) \rightarrow LiCl(aq,100H_2O)$$

3. Calculate the enthalpy change for the amounts used in the experiment:

$$\left[\begin{array}{l}\text{enthalpy change, } \Delta H,\\ \text{on dissolving LiCl,}\end{array}\right] + \left[\begin{array}{l}\text{change in heat energy}\\ \text{of the solution}\end{array}\right] = 0$$

$$\text{or} \quad \Delta H + mc_p\Delta T = 0$$

$$\therefore \quad \Delta H = -mc_p\Delta T = -\frac{36.0}{1000}\ \text{kg} \times 4.18\ \text{kJ kg}^{-1}\ \text{K}^{-1} \times 4.7\ \text{K} = -0.70\ \text{kJ}$$

(Note that although the mass of the solution is greater than 36.0 g (36.85 g) its specific heat capacity is slightly <u>less</u> than 4.18 kJ kg^{-1} K^{-1}. The error arising from considering only the water in this type of calculation is therefore small.)

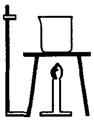
4. Scale up to the amounts shown in the equation, as in the last worked example:

$$\Delta H = -0.70\ \text{kJ} \times \frac{1\ \text{mol}}{0.020\ \text{mol}} = -35\ \text{kJ}$$

5. Write the complete thermochemical equation:

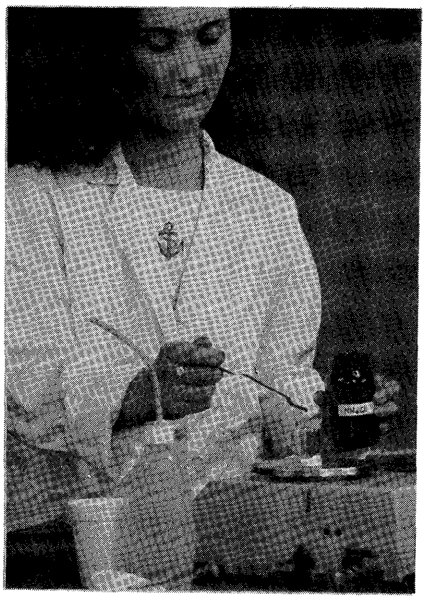
$$LiCl(s) + 100H_2O(l) \rightarrow LiCl(aq,100H_2O); \qquad \Delta H_{soln} = -35\ \text{kJ mol}^{-1}$$

You can use this method of calculation in the next experiment.



EXPERIMENT 2

Determining an enthalpy change of solution



Aim

The purpose of this experiment is to determine the enthalpy change for the process

$$NH_4Cl(s) + 100H_2O(l) \rightarrow NH_4Cl(aq, 100H_2O)$$

Introduction

Because this is a planning experiment, we give fewer details and instructions than you have been used to. It is, of course, very similar to Experiment 1, but you need not plot a temperature/time graph because the maximum temperature change occurs very rapidly.

Requirements

Make a list of requirements including the masses and amounts needed; show the list to your teacher or technician.

Procedure

Work this out for yourself and keep an accurate record.

Results

1. Tabulate your results in an appropriate form.
2. Calculate the enthalpy change of solution for the thermochemical equation in the aim.

(Specimen results on page 88)

Question

Compare your result with the accepted value of +16.4 kJ mol^{-1}. Suggest reasons for any difference.

(Answer on page 88)

Some enthalpy changes cannot be measured easily by direct experiment. However, you can often calculate them from the results of other experiments by using Hess's law, which we now consider.

HESS'S LAW

Hess's law (sometimes called Hess's law of constant heat summation) is a corollary to the law of conservation of energy. We use Hess's law to calculate enthalpy changes which cannot be measured directly.

Objectives. When you have finished this section, you should be able to:

(10) state Hess's law;

(11) apply Hess's law in the calculation of enthalpy changes which cannot be determined experimentally.

Study the section of your text-book which deals with Hess's law. Note down a statement of the law which you can remember and follow through an example of its application.

It is not possible to measure the enthalpy change for the reaction

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$$

directly in a calorimeter because it represents an incomplete combustion which cannot be controlled. However, it is possible to measure the enthalpy change for the complete combustion of both graphite and carbon monoxide, and we can calculate the heat of formation of carbon monoxide from these results. We illustrate Hess's law by showing this calculation, using an energy level diagram, in a Worked Example.

Worked Example Calculate the standard enthalpy change for the reaction

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g),$$

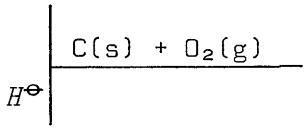
given the following information:

$$C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H^\ominus = -394\ \text{kJ mol}^{-1}$$

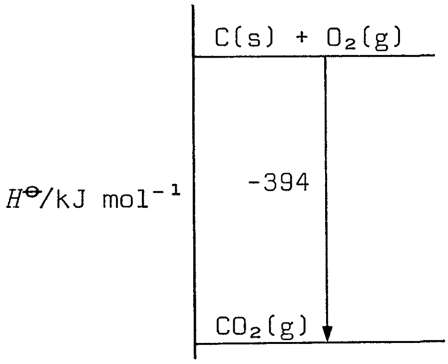
$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g); \quad \Delta H^\ominus = -283\ \text{kJ mol}^{-1}$$

Solution

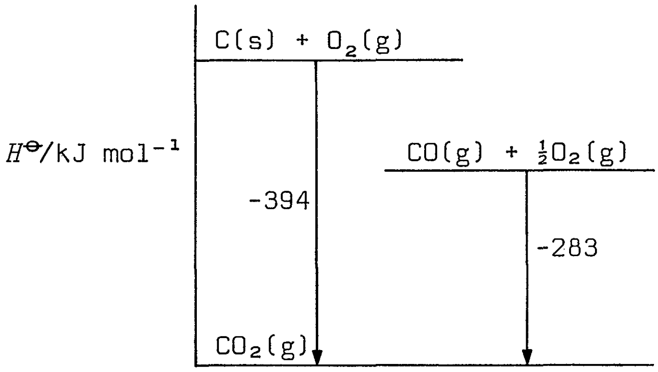
1. Draw an energy level diagram to summarise the information given. Start by drawing a line to represent the enthalpy of 1 mol of graphite and 1 mol of oxygen at standard conditions.



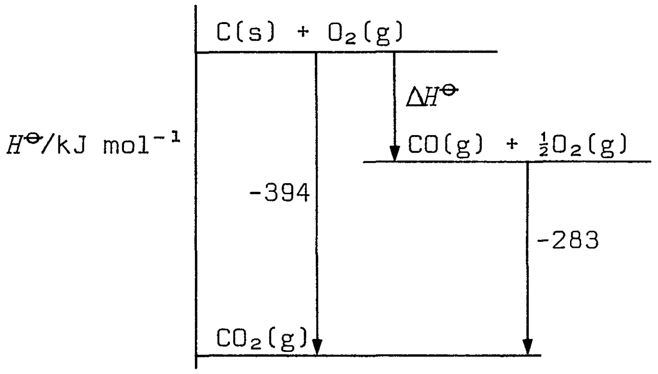
2. The combustion of 1 mol of graphite produces CO_2 and releases 394 kJ. Show this on the energy-level diagram (not necessarily to scale):



3. Now consider the combustion of CO, which gives the same product, 1 mol of CO_2. The energy released is 283 kJ mol^{-1}. Show this on the diagram:



4. The gap between the two upper lines represents the heat of formation of carbon monoxide. Show this on the diagram:



5. So you have two routes to the formation of CO_2. One is represented by the heat of formation of $CO_2(g)$ and the other by the sum of two processes: the heat of formation of CO(g) plus the heat of combustion of CO(g). Hess's law states that the energy changes for the two routes are equal and you can see that this must be so from the energy level diagram. Thus:

$$-394 \text{ kJ mol}^{-1} = \Delta H_f^\ominus [CO(g)] + (-283 \text{ kJ mol}^{-1})$$

$$\therefore \Delta H_f^\ominus [CO(g)] = (-394 + 283) \text{ kJ mol}^{-1} = \boxed{-111 \text{ kJ mol}^{-1}}$$

An energy level diagram establishes clearly the validity of Hess's law, but for solving problems, you may find it simpler to use an alternative method based on energy cycles.

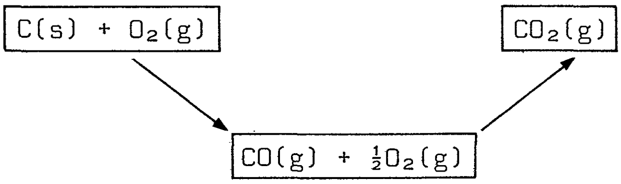
Use of energy cycles

An energy cycle simply shows two different routes between initial and final states, without reference to energy levels. We illustrate this by using the same example as before and showing two routes for the production of CO_2.

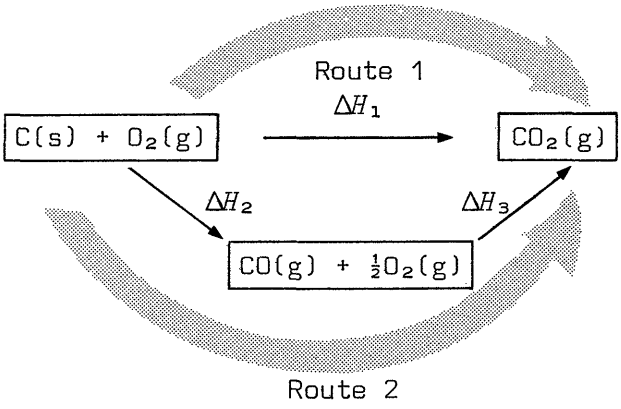
1. First represent the direct combination of elements:

$$\boxed{C(s) + O_2(g)} \longrightarrow \boxed{CO_2(g)}$$

2. Write the two-step process:



3. Hess's law tells us that the enthalpy change via one route ('route 1') must equal the enthalpy change via the two-step route ('route 2').



$\therefore \quad \Delta H_1 = \Delta H_2 + \Delta H_3$

4. Calculate the unknown by substituting the known values:

$$\Delta H_2 = \Delta H_1 - \Delta H_3$$

$$\therefore \quad \Delta H_f^\ominus[CO(g)] = -394 \text{ kJ mol}^{-1} - (-283 \text{ kJ mol}^{-1}) = \boxed{-111 \text{ kJ mol}^{-1}}$$

Both energy cycles and energy level diagrams are very useful in solving problems. In the next exercise you use both methods: be careful to distinguish between the two. In an energy level diagram, the arrows should be drawn vertically, and preferably to scale, to represent both direction and extent of enthalpy change. In an energy cycle, the arrows simply indicate a change from one state to another, and to avoid confusion we suggest you do not use vertical arrows in energy cycles.

Exercise 11 Calculate the standard enthalpy change for the reaction

$$2NO_2(g) \rightarrow N_2O_4(g)$$

given the thermochemical equations:

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g); \quad \Delta H^\ominus = +33.2 \text{ kJ mol}^{-1}$$

$$N_2(g) + 2O_2(g) \rightarrow N_2O_4(g); \quad \Delta H^\ominus = +9.2 \text{ kJ mol}^{-1}$$

(a) by drawing an energy-level diagram;

(b) by drawing an energy cycle.

(Answers on page 88)

In the next exercise, you use and justify yet another way of applying Hess's law.

Exercise 12 Two of the possible methods of preparing a solution of ammonium chloride containing 1.00 mol of NH_4Cl in 200 mol of H_2O are summarised in the thermochemical equations below:

Method 1

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s); \quad \Delta H^\ominus = -175.3 \text{ kJ mol}^{-1}$

$NH_4Cl(s) + 200H_2O(l) \rightarrow NH_4Cl(aq, 200H_2O) \quad \Delta H^\ominus = +16.3 \text{ kJ mol}^{-1}$

Method 2

$NH_3(g) + 100H_2O(l) \rightarrow NH_3(aq, 100H_2O); \quad \Delta H^\ominus = -35.6 \text{ kJ mol}^{-1}$

$HCl(g) + 100H_2O(l) \rightarrow HCl(aq, 100H_2O); \quad \Delta H^\ominus = -73.2 \text{ kJ mol}^{-1}$

$NH_3(aq, 100H_2O) + HCl(aq, 100H_2O) \rightarrow NH_4Cl(aq, 200H_2O); \quad \Delta H^\ominus = -50.2 \text{ kJ mol}^{-1}$

(a) Add the equations in Method 1, and simplify the result.

(b) Add the equations in Method 2, and simplify the result.

(c) How does this illustrate Hess's law?

(d) Draw an energy level diagram and an energy cycle.

(Answers on page 88)

We usually use the energy cycle method in the solutions we provide to exercises because it is the most general, but you may prefer to add equations as in Exercise 12. You should always be able to justify your method by means of an energy level diagram.

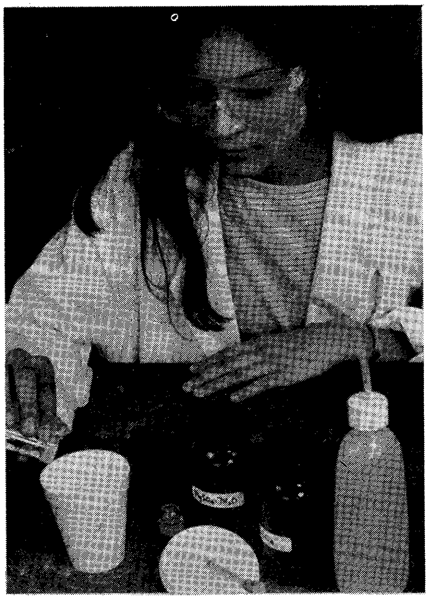
In Experiment 3, you apply Hess's law to a reaction for which the enthalpy change cannot be measured directly - the hydration of magnesium sulphate, $MgSO_4$. The method and apparatus are very similar to those you used in Experiments 1 and 2.

In Appendix 3, we have included a similar experiment, the determination of the heat of hydration of copper(II) sulphate, $CuSO_4$. However, it is necessary to use a vacuum flask calorimeter, and both the practical work and the calculation are a little more difficult.

Ask your teacher which of these experiments you should do.

EXPERIMENT 3

Using Hess's law



Aim

The purpose of this experiment is to determine the enthalpy change for the reaction

$$MgSO_4(s) + 7H_2O(l) \rightarrow MgSO_4{\cdot}7H_2O(s)$$

Introduction

It is impossible to measure the enthalpy change for this reaction directly because the process cannot be controlled. However, you can calculate this enthalpy change by measuring the enthalpy change of solution for the two solids:

$$MgSO_4(s) + 100H_2O(l) \rightarrow MgSO_4(aq,100H_2O)$$

$$MgSO_4{\cdot}7H_2O(s) + 93H_2O(l) \rightarrow MgSO_4(aq,100H_2O)$$

We suggest that you use 0.0250 mol of each salt, so we have calculated, from the equations, the required masses of each salt and water.

Requirements

safety spectacles
2 weighing bottles
spatula
magnesium sulphate (anhydrous), $MgSO_4$
access to balance
2 polystyrene cups and lids
distilled water
teat pipette
thermometer (0° to 50°C)
magnesium sulphate-7-water, $MgSO_4{\cdot}7H_2O$

Procedure

A. Heat of solution of $MgSO_4(s)$

1. Weigh 3.01 g of $MgSO_4$ to the nearest 0.01 g into a clean, dry weighing bottle. Record, in a copy of Results Table 2, the masses of weighing bottle empty and with contents, unless your balance has a reliable taring device.
2. Similarly, weigh 45.00 g of H_2O to the nearest 0.01 g into a polystyrene cup.
3. Put the thermometer through the hole in the lid and measure the temperature of the water. Record this in Results Table 2.
4. Carefully transfer the $MgSO_4$ into the water, stir gently with the thermometer, and record the maximum temperature.

B. Heat of solution of $MgSO_4 \cdot 7H_2O$

5. Weigh 6.16 g of $MgSO_4 \cdot 7H_2O$ to the nearest 0.01 g into a clean, dry weighing bottle.

6. Weigh 41.85 g of H_2O to the nearest 0.01 g into a polystyrene cup.

7. Measure and record the temperature change associated with dissolving the $MgSO_4 \cdot 7H_2O$

Results Table 2

	$MgSO_4$	$MgSO_4 \cdot 7H_2O$
Mass of weighing bottle		
Mass of weighing bottle + salt		
Mass of salt	3.01 g	6.16 g
Mass of polystyrene cup		
Mass of polystyrene cup + water		
Mass of water	45.00 g	41.85 g
Initial temperature		
Final temperature		

Calculations

1. From the data in Results Table 2, calculate the enthalpy change of solution for one mole of $MgSO_4$. Assume c_p = 4.18 kJ kg^{-1} K^{-1}.
2. Similarly, calculate the enthalpy change of solution for one mole of $MgSO_4 \cdot 7H_2O$
3. By means of an energy cycle, calculate the enthalpy change for the reaction:

$$MgSO_4(s) + 7H_2O(l) \rightarrow MgSO_4 \cdot 7H_2O$$

(Specimen results on page 89)

Questions

1. Plot the results on an energy-level diagram.
2. Why is it not necessary to plot a temperature/time graph as you did in Experiment 1?
3. Compare your result with the accepted value of -104 kJ mol^{-1}. Suggest reasons for any difference.

(Answers on page 89)

Now we look at another application of Hess's law.

Calculating heat of formation from heat of combustion

As you will see later, it is particularly useful to list enthalpy change of formation for compounds. However, most compounds cannot be formed directly from the elements, so it is impossible to measure these enthalpy changes in a calorimeter.

One of the most useful applications of Hess's law is in calculating heat of formation from heats of combustion, which can be measured directly.

Objectives. When you have finished this section, you should be able to:

(12) calculate $\Delta H^\ominus_f$ of a compound from values of $\Delta H^\ominus_c$ for the compound and for its constituent elements.

We illustrate the calculation by a Worked Example, but to help you follow it you should read the section in your text-book on this topic, paying particular attention to the explanation of the calculation procedure.

Worked Example Calculate the standard enthalpy of formation of ethane, C_2H_6, given:

$$C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H^\ominus = -394 \text{ kJ mol}^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l); \quad \Delta H^\ominus = -286 \text{ kJ mol}^{-1}$$

$$C_2H_6(g) + 2\tfrac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l); \quad \Delta H^\ominus = -1560 \text{ kJ mol}^{-1}$$

Solution

1. Starting with the reaction for which you want to calculate $\Delta H^\ominus_f$, begin to construct an energy cycle:

$$\boxed{2C(s) + 3H_2(g)} \xrightarrow{\Delta H_1} \boxed{C_2H_6(g)}$$

2. Put in the combustion reactions:

$$\begin{tikzcd}
\boxed{2C(s) + 3H_2(g) + 3\tfrac{1}{2}O_2(g)} \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & \boxed{C_2H_6(g) + 3\tfrac{1}{2}O_2(g)} \arrow[dl, "\Delta H_3"] \\
& \boxed{2CO_2(g) + 3H_2O(l)} &
\end{tikzcd}$$

Note that the inclusion of $3\tfrac{1}{2}O_2(g)$, which is necessary for the combustions, makes no difference to ΔH_1 (see Exercise 6).

3. Use Hess's law to equate the enthalpy changes.

$$\Delta H_2 = \Delta H_1 + \Delta H_3$$

or $$\Delta H_1 = \Delta H_2 - \Delta H_3$$

4. Substitute numerical values for ΔH_2 and ΔH_3.

$$\begin{aligned}
\Delta H_2 &= 2 \times \Delta H^\ominus_c[C(s)] + 3 \times \Delta H^\ominus_c[H_2(g)] \\
&= 2 \times (-394 \text{ kJ mol}^{-1}) + 3 \times (-286 \text{ kJ mol}^{-1}) \\
&= (-788 - 858 \text{ kJ mol}^{-1}) = -1646 \text{ kJ mol}^{-1} \\
\Delta H_3 &= \Delta H^\ominus_c[C_2H_6(g)] = -1560 \text{ kJ mol}^{-1} \\
\therefore \quad \Delta H_1 &= \Delta H_2 - \Delta H_3 \\
&= -1646 \text{ kJ mol}^{-1} - (-1560 \text{ kJ mol}^{-1}) = \boxed{-86 \text{ kJ mol}^{-1}}
\end{aligned}$$

Now try the next two exercises to test your understanding of this application of Hess's law.

<u>Exercise 13</u> Calculate the standard enthalpy change of formation of carbon disulphide, CS_2, given that

$\Delta H^\ominus_f\,[CO_2(g)] = -393.5\ \mathrm{kJ\ mol^{-1}}$,

$\Delta H^\ominus_f\,[SO_2(g)] = -296.9\ \mathrm{kJ\ mol^{-1}}$,

$\Delta H^\ominus_c\,[CS_2(l)] = -1075.2\ \mathrm{kJ\ mol^{-1}}$.

(Answer on page 89)

<u>Exercise 14</u> Calculate the standard enthalpy change of formation of the following compounds:

(a) ethane, C_2H_6

(b) ethanol, C_2H_5OH

(c) methylamine, CH_3NH_2

Hint: For part (c) assume that when CH_3NH_2 burns, nitrogen is released as $N_2(g)$.

(Answers on page 89)

Having shown you how enthalpy changes of formation can be calculated, we now consider what use can be made of the values.

Uses of standard enthalpy changes of formation

In your data book you will find lists of enthalpy changes of formation for both organic and inorganic compounds. Many of the values have been calculated from experimental results in ways similar to those we have described; now you learn how to use them.

<u>Objectives</u>. When you have finished this section you should be able to:

(13) use standard enthalpy changes of formation to calculate the standard enthalpy change for a reaction.

Standard enthalpy changes of formation can be used to calculate the enthalpy changes in a reaction. The fact that we can predict the enthalpy change for any reaction is vitally important, for instance, to chemical engineers when planning chemical plant. They need to know how much heat will be generated or absorbed during the course of a particular reaction and make adequate provision for extremes of temperature in their designs.

Read the section of your text-book which describes the calculation paying particular attention to the derivation of the expression:

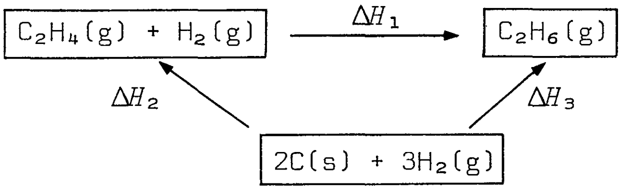
$$\Delta H^\ominus_{\mathrm{reaction}} = \Sigma\Delta H^\ominus_f\ (\mathrm{products}) - \Sigma\Delta H^\ominus_f\ (\mathrm{reactants}),$$

where the symbol Σ meants 'the sum of'.

You should now be able to work through the following Revealing Exercise, which is in the form of a series of short questions and answers.

We often use a Revealing Exercise to illustrate a concept or explain a calculation which involves many steps. You should cover the page with a sheet of paper and move it down to the first horizontal line across the page. Write an answer to the question which is above the line and then move the sheet down to the next horizontal line. Compare your answer with ours and then answer the next question. You should find each step very simple.

Consider the energy cycle:



Q1. Identify two routes for the conversion of C_2H_4 and H_2 to C_2H_6

A1. Route 1. Direct combination.

Route 2. (i) Decomposition of C_2H_4 to the elements, followed by
(ii) formation of C_2H_6 from the elements.

Q2. Write down the enthalpy changes for each route.

A2. Route 1. ΔH_1

Route 2. $-\Delta H_2 + \Delta H_3$

Q3. Why does ΔH_2 have a negative sign?

A3. ΔH_2 refers to the formation of C_2H_4 from elements; $-\Delta H_2$ refers to the change in the opposite direction.

Q4. Apply Hess's law to obtain an expression for ΔH_1 in terms of ΔH_2 and ΔH_3.

A4. $\Delta H_1 - -\Delta H_2 + \Delta H_3$ or

$\Delta H_1 = \Delta H_3 - \Delta H_2$

Q5. How would you obtain values for ΔH_2 and ΔH_3?

A5. Look up $\Delta H_f^{\ominus}$ [$C_2H_4(g)$] and $\Delta H_f^{\ominus}$ [$C_2H_6(g)$].

Q6. Why is it not necessary to look up $\Delta H_f^{\ominus}$ [$H_2(g)$]?

A6. $\Delta H_f^{\ominus}$ for elements in their standard states is, by definition, zero - since it refers to a change between identical states, i.e. no change at all!

Q7. Rewrite the expression in A4, using symbols for heats of formation.

A7. $\Delta H_1 = \Delta H_f^\ominus[C_2H_6(g)] - \Delta H_f^\ominus[C_2H_4(g)]$

Q8. Show that this is a particular case of the general expression

$$\Delta H_r = \Sigma\Delta H_f^\ominus[\text{products}] - \Sigma\Delta H_f^\ominus[\text{reactants}]$$

A8. $\Sigma\Delta H_f^\ominus[\text{products}] = \Delta H_f^\ominus[C_2H_6(g)]$

$\Sigma\Delta H_f^\ominus[\text{reactants}] = \Delta H_f^\ominus[C_2H_4(g)] + \Delta H_f^\ominus[H_2(g)]$

$= \Delta H_f^\ominus[C_2H_4(g)] + 0$ (see A6)

$= \Delta H_f^\ominus[C_2H_4(g)]$

$\therefore\ \Delta H_1 = \Sigma\Delta H_f^\ominus[\text{products}] - \Sigma\Delta H_f^\ominus[\text{reactants}]$

$= \Delta H_f^\ominus[C_2H_6(g)] - \Delta H_f^\ominus[C_2H_4(g)]$

Q9. Use your data book to calculate a value for ΔH_1.

A9. $\Delta H_1 = \Delta H_f^\ominus[C_2H_6(g)] - \Delta H_f^\ominus[C_2H_4(g)]$

$= -84.6\ \text{kJ mol}^{-1} - (+52.3\ \text{kJ mol}^{-1}) = -136.9\ \text{kJ mol}^{-1}$

You can apply the same procedure to any reaction. However, once you have understood the derivation of the expression

$$\Delta H_r^\ominus = \Sigma\Delta H_f^\ominus[\text{products}] - \Sigma\Delta H_f^\ominus[\text{reactants}]$$

you can use it to solve problems without drawing an energy cycle, as we show in a Worked Example.

W

Worked Example Calculate the standard enthalpy change for the reaction

$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$$

using only standard heat of formation data.

Compound	$\Delta H_f^\ominus$/kJ mol^{-1}
$H_2S(g)$	-20.6
$SO_2(g)$	-296.9
$H_2O(l)$	-285.9

Solution

1. Write an equation, leaving room to put the value of $\Delta H_f^\ominus$ under each formula.

$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$$

2. Calculate the standard enthalpy change of formation for the amount specified in the equation for each substance. In this equation, 2 mol of $H_2O(l)$ are produced.

$2\ \Delta H_f^\ominus\ [H_2O(l)] = -571.8\ \text{kJ mol}^{-1}$

Similarly, for $H_2S(g)$, $2\ \Delta H_f^\ominus\ [H_2S(g)] = -41.2\ \text{kJ mol}^{-1}$

and for $SO_2(g)$, $\Delta H_f^\ominus\ [SO_2(g)] = -296.9\ \text{kJ mol}^{-1}$

Because $\Delta H_f^\ominus$ for all elements is zero, no value appears for sulphur.

3. Put these values under the compounds to which they refer.

	$2H_2S(g)$ +	$SO_2(g)$ →	$3S(s)$ +	$2H_2O(l)$
$\Delta H_f^\ominus/\text{kJ mol}^{-1}$	-41.2	-296.9	0	-571.8

4. Add the values for the products.

$\Sigma\Delta H_f^\ominus$ [products] = 0 - 571.8 = -571.8 kJ mol^{-1}

Add the values for the reactants.

$\Sigma\Delta H_f^\ominus$ [reactants] = (-41.2 - 296.9)kJ mol^{-1} = -338.1 kJ mol^{-1}

5. Subtract:

$$\Delta H_r = \Sigma\Delta H_f^\ominus\,[\text{products}] - \Sigma\Delta H_f^\ominus\,[\text{reactants}]$$
$$= [-571.8 - (-338.1)]\ \text{kJ mol}^{-1} = \boxed{-233.7\ \text{kJ mol}^{-1}}$$

Now try some examples for yourself. Be very careful about positive and negative signs.

Exercise 15 Calculate the standard enthalpy changes for the following reactions. Obtain values of $\Delta H_f^\ominus$ from your data book.

(a) $CH_3OH(l) + 1\frac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

(b) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

(c) $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

(d) $2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$

(Answers on page 90)

Exercise 16 The standard enthalpies of formation ($\Delta H_f^\ominus$) at 298 K for a number of compounds are, in kJ mol^{-1}:

$CH_4(g)$ - 75; $H_2O(g)$ - 242; $CO(g)$ - 110

Calculate the enthalpy change for the reaction:

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

(Answer on page 90)

Another important use of enthalpy changes of formation is the prediction of the relative stabilities of compounds. However, it is important to clarify what we mean by the word 'stability', which we do in the next section.

ENERGETIC AND KINETIC STABILITY

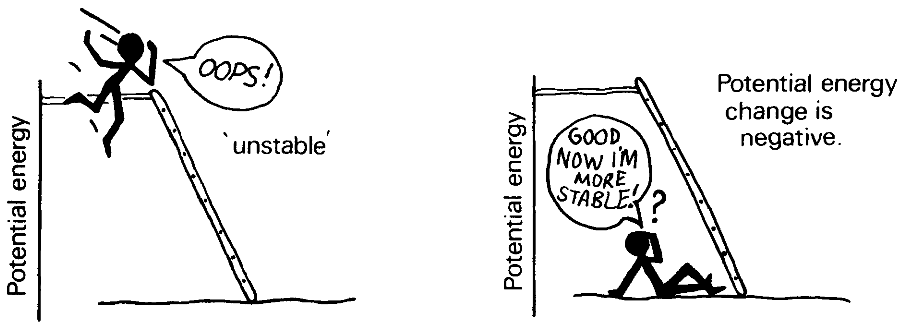


Fig. 9.

We can discuss the stability of the man at the top of the ladder (Fig. 9) in two different ways. He is unstable in that if he misses his footing or is pushed, he would fall to the ground. He is liable to fall from a position of high potential energy to one of lower potential energy. We can therefore say that his position is one of energetic instability.

However, if he stands carefully, he can stay at the top of the ladder indefinitely. The rate at which he actually falls to the ground is then zero, even though we might expect him to fall by consideration of energy levels. The word 'kinetic' refers to the rate of a process; thus, we can say that the man is kinetically stable.

Objectives. At the end of this section, you should be able to:

(14) distinguish between kinetic and energetic (thermodynamic) stability;

(15) describe compounds as stable or unstable with respect to specified substances, using the enthalpy change of reaction.

Read the appropriate section in your text-book, looking for other examples of kinetic and energetic stability to clarify the concepts. (You may find the term thermodynamic stability used for energetic stability.) Look also for the way in which stability may be inferred from values of enthalpy change so that you can do the following exercises.

Exercise 17 (a) Would you expect a compound with a negative value of $\Delta H_f^{\ominus}$ to be stable or unstable? Explain your answer.

(b) Draw an energy level diagram showing the enthalpy change of formation of $H_2O_2(l)$.

(c) Calculate the enthalpy change for the reaction:

$$H_2O_2(l) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

Show this on the same energy-level diagram.

(d) Comment on the energetic stability of $H_2O_2(l)$.

(Answers on page 90)

Exercise 18 Comment on the thermodynamic stability of NO(g). Base your answer on the two equations:

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g); \quad \Delta H^{\ominus} = 90 \text{ kJ mol}^{-1}$$

$$NO(g) + \tfrac{1}{2}O_2(g) \rightarrow NO_2(g); \quad \Delta H^{\ominus} = -74 \text{ kJ mol}^{-1}$$

(Answer on page 90)

Exercise 19 Comment on the stability of ethyne, C_2H_2, relative to the elements and relative to benzene, C_6H_6.

$$3C_2H_2(g) \xrightarrow{\text{catalyst}} C_6H_6(l)$$

(Answer on page 90)

Exercise 20 The standard enthalpy of formation at 298 K of carbon dioxide, CO_2, is -394 kJ mol^{-1} whilst that of carbon monoxide, CO, is -110 kJ mol^{-1}.

(a) State precisely what is meant by standard enthalpy of formation.

(b) (i) Calculate the enthalpy change for the reaction:

$$CO_2(g) \rightarrow CO(g) + \tfrac{1}{2}O_2(g)$$

(ii) Are these oxides of carbon thermodynamically stable or unstable with respect to carbon and oxygen? Explain.

(Answers on page 90)

The exercises you have just done suggest that you can predict whether a particular reaction can occur or not simply by calculating $\Delta H^{\ominus}$. Although this is a useful idea, you have to be careful in applying it, as we now show.

Using $\Delta H^{\ominus}$ values to predict the direction of change

Just as we would expect the man to fall off the ladder if he were given a push, we might expect any reaction which has a negative value for its enthalpy change to proceed spontaneously. It may not happen, of course, if the system is kinetically stable. Such a system is

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l); \quad \Delta H^{\ominus} = -286 \text{ kJ mol}^{-1}$$

Hydrogen and oxygen can stay mixed for years with no sign of reaction. But in the presence of a spark (similar to a 'push' causing the man to fall from the ladder) the reaction proceeds explosively.

However, there are reactions with positive values of $\Delta H^{\ominus}$ which also proceed spontaneously; e.g.

$$6SOCl_2(l) + FeCl_3{\cdot}6H_2O(s) \rightarrow FeCl_3(s) + 6SO_2(g) + 12HCl(g);$$

$$\Delta H^{\ominus} = +1271 \text{ kJ mol}^{-1}$$

Your teacher may be able to demonstrate this for you.

Conversely, there are some reactions with negative values of $\Delta H^\ominus$ which do not proceed spontaneously, even with a 'push' or a catalyst to increase the rate. One example is:

$$N_2(g) + 2\tfrac{1}{2}O_2(g) \rightarrow N_2O_5(s); \quad \Delta H^\ominus = -43.1 \text{ kJ mol}^{-1}$$

And, of course, you know a number of reactions which can go in either direction. These reversible reactions may have positive or negative values of $\Delta H^\ominus$, depending on the way the equation is written.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H^\ominus = -46.0 \text{ kJ mol}^{-1}$$

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g); \quad \Delta H^\ominus = +46.0 \text{ kJ mol}^{-1}$$

Obviously, our 'ladder' analogy, like most analogies, must not be pressed too far - we never expect to see a man fall up a ladder, nor to remain suspended at the top if he is pushed off!

So, it is clear that enthalpy changes alone do not govern the direction in which a reaction can proceed. The quantity we should use is the standard free energy change, $\Delta G^\ominus$, and you will learn more about this later in the course. It is $\Delta G^\ominus$ and not $\Delta H^\ominus$ which is negative for a reaction which goes to completion.

Fortunately, however, $\Delta G^\ominus$ is closely related to $\Delta H^\ominus$ and for most reactions (at 298 K) has similar values. Check this in your data book by looking up values of $\Delta G_f^\ominus$ and $\Delta H_f^\ominus$ - they are usually tabulated in adjacent columns.

Provided $\Delta G_f^\ominus$ values are known, you can calculate $\Delta G^\ominus$ for a reaction just as you calculated $\Delta H^\ominus$. Use the relationship:

$$\Delta G^\ominus = \Sigma\Delta G_f^\ominus\,[\text{products}] - \Sigma\Delta G_f^\ominus\,[\text{reactants}]$$

Exercise 21 Calculate $\Delta G^\ominus$ for the following reactions and compare your answers with the values of $\Delta H^\ominus$ calculated in Exercise 15. Comment on any difference.

(a) $CH_3OH(l) + 1\tfrac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

(b) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

(c) $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

(d) $2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$

(Answers on page 91)

The last exercise illustrates the fact that $\Delta H^\ominus$ is usually a good guide for predicting the relative stabilities of substances and the direction of change. You will often use $\Delta H^\ominus$ for this purpose, but you should remember that it is better to use $\Delta G^\ominus$, if values are available (frequently they are not!).

(Free energy is often called 'Gibbs free energy' after the famous American thermodynamicist, J. Willard Gibbs who first introduced the term - hence the use of the letter G.)

LEVEL ONE CHECKLIST

You have now reached the end of Level One of this Unit. The following is a summary of the objectives in Level One. Read carefully through them and check that you have adequate notes. At this stage you should be able to:

(1) distinguish between system and surroundings;

(2) describe a process as exothermic or endothermic;

(3) describe in principle how enthalpy changes are measured;

(4) quote the standard conditions for thermochemical processes;

(5) relate thermochemical equations to energy-level diagrams;

(6) use an energy level diagram to calculate enthalpy change.

(7) define (a) enthalpy change of formation;
  (b) enthalpy change of combustion;
  (c) enthalpy change of solution;

(8) use your data book to find numerical values of these enthalpy changes;

(9) recognise that the standard enthalpy change of formation of an element is defined as zero;

(10) state Hess's law;

(11) apply Hess's law in the calculation of enthalpy changes which cannot be determined experimentally;

(12) calculate $\Delta H_f^{\ominus}$ for a compound from values of $\Delta H_c^{\ominus}$ for the compound and for its constituent elements;

(13) use standard enthalpy changes of formation to calculate the standard enthalpy change for a reaction;

(14) distinguish between kinetic and energetic (thermodynamic) stability;

(15) describe compounds as stable or unstable with respect to specified substances, using the enthalpy change of reaction.

LEVEL ONE TEST

To find out how well you have learned the material in Level One, try the test which follows. Read the notes below before starting.

1. You should spend about 1 hour on this test.

2. Hand your answers to your teacher for marking.

LEVEL ONE TEST

Questions 1 to 5 are either questions or incomplete statements followed by five suggested answers. Select the best answer in each case.

1. The enthalpy of formation of ethane (C_2H_6) is the enthalpy change represented by

A

A $2C(s) + 6H(g) \rightarrow C_2H_6(g)$

B $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

C $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

D $2C(g) + 6H(g) \rightarrow C_2H_6(g)$

E $2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$

(1)

2. The standard enthalpies of combustion of carbon, hydrogen and methane are -394, -286 and -891 kJ mol^{-1}, respectively.

A

Which one of the following expressions gives the correct value for the enthalpy of formation of methane?

A 394 + (2 x 286) - 891

B -394 - (2 x 286) + 891

C 394 + 286 - 891

D -394 - 286 + 891

E -394 - (4 x 286) + 891

(1)

3. The enthalpy changes for two reactions are given by the equations

A

$2Cr(s) + 1\frac{1}{2}O_2(g) \rightarrow Cr_2O_3(s)$; $\Delta H = -1130$ kJ

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$; $\Delta H = -110$ kJ

What is the enthalpy change, in kJ, for the reaction

$3C(s) + Cr_2O_3(s) \rightarrow 2Cr(s) + 3CO(g)$?

A - 1460 C + 800 E + 1460

B - 800 D + 1020

(1)

4.

A

	$CS_2(l)$	$NOCl(g)$	$CCl_4(l)$	$SO_2(g)$
$\Delta H_f^\ominus$ (298)/kJ mol^{-1}	88	53	-139	-296

From the data above, the value of $\Delta H^\ominus$ (298) in kJ mol^{-1}, for the reaction

$CS_2(l) + 4NOCl(g) \rightarrow CCl_4(l) + 2SO_2(g) + 2N_2(g)$ is

A -1031 B -731 C -431 D 431 E 1031

(1)

5. Some heats of formation, in kJ mol^{-1}, at 298 K are

A

S_8(rhombic) 0, $S_8(g)$ 103, $S(g)$ 274.

What is the heat of atomization of sulphur in kJ mol^{-1}?

A $\frac{103}{8}$ B 103 C 274 D $274 + \frac{103}{8}$ E 274 + 103

(1)

6 (a) Write a thermochemical equation to summarise the following statement.

'When a mole of anhydrous copper(II) chloride (melting point 771 K) is formed from its elements at a temperature of 800 K, and under constant pressure conditions, 210 kJ of heat is evolved.' (3)

(b) Draw an energy level diagram (not to scale) to represent the information given above. (2)

(c) (i) Define standard enthalpy of formation. (2)

(ii) What value is assigned to the standard enthalpy of formation of an element? (1)

(d) (i) Why can the enthalpies of formation of compounds not always be determined by direct experiment? (2)

(ii) State, and briefly explain, the law which allows such enthalpies of formation to be calculated. (3)

7. Calculate $\Delta H^\ominus$ at 25°C for the reaction

A

$H(g) + Br(g) \rightarrow HBr(g)$

from the following data, which refer to 25°C:

$H_2(g) \rightarrow 2H(g); \quad \Delta H^\ominus = +436 \text{ kJ mol}^{-1};$

$Br_2(g) \rightarrow 2Br(g); \quad \Delta H^\ominus = +193 \text{ kJ mol}^{-1};$

$H_2(g) + Br_2(g) \rightarrow 2HBr(g); \quad \Delta H^\ominus = -104 \text{ kJ mol}^{-1}$ (5)

8. (a) Calculate the standard enthalpy of formation of ethanoic acid, $CH_3CO_2H(l)$, from the following data:

A

$\Delta H^\ominus_c$ [graphite] = -394 kJ mol^{-1}

$\Delta H^\ominus_c$ [$H_2(g)$] = -286 kJ mol^{-1}

$\Delta H^\ominus_c$ [$CH_3CO_2H(l)$] = -873.2 kJ mol^{-1} (4)

(b) What can you deduce about the stability of ethanoic acid? (2)

(c) What further information would you need to make a more reliable statement about the stability of ethanoic acid? (2)

9. (a) Use the data in Table 2 to determine $\Delta H^\ominus$ and $\Delta G^\ominus$ for the following reactions

$N_2O_5(s) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$

$N_2O_5(s) \rightarrow N_2O_4(g) + \tfrac{1}{2}O_2(g)$

Table 2

Compound	$\Delta H^\ominus_f$/kJ mol^{-1}	$\Delta G^\ominus_f$/kJ mol^{-1}
$N_2O_5(s)$	-43.1	$+113.8$
$NO_2(g)$	$+33.2$	$+51.3$
$N_2O_4(g)$	$+9.2$	$+97.8$

(6)

(b) Would you expect $N_2O_5(s)$ to be stable? (3)

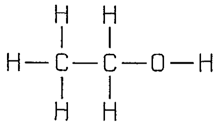
(Total 40 marks)

LEVEL TWO

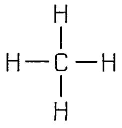
In this level we consider in more detail the energetics of bond formation. First we consider covalent molecules and introduce the idea of an average bond energy; then we consider the energetics of ionic bond formation.

BOND ENERGY TERM

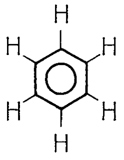
The energy required to break a particular bond depends not only on the nature of the two bonded atoms but also on the environment of those atoms. For instance, not all the C-H bonds in ethanol, C_2H_5OH, are equally strong because the oxygen atom has more influence on those near it than on those further away.

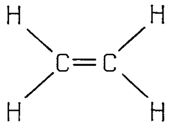


$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$$



$$H-\overset{H}{\underset{H}{C}}-H$$





Similarly, C-H bonds in methane, CH_4, are not quite the same as those in benzene, C_6H_6, or ethane, C_2H_4. Fortunately, however, the differences are small enough for the concept of <u>average</u> bond energy (bond energy term) to be very useful.

<u>Objectives</u>. When you have finished this section, you should be able to:

(16) state what is meant by <u>bond energy term</u> ;

(17) distinguish between <u>bond dissociation energy</u> and bond energy term.

Read about bond energy term (sometimes just called <u>bond energy</u> or <u>average bond energy</u>) in your text-book paying particular attention to the difference between bond energy term and <u>bond dissociation energy</u>. This will help you to do the next two exercises.

<u>Exercise 22</u> Table 3 gives enthalpy changes for four successive dissociation reactions:

Table 3

Reaction	$\Delta H^{\ominus}$/kJ mol^{-1}
$CH_4(g) \rightarrow CH_3(g) + H(g)$	+435
$CH_3(g) \rightarrow CH_2(g) + H(g)$	+444
$CH_2(g) \rightarrow CH(g) + H(g)$	+440
$CH(g) \rightarrow C(g) + H(g)$	+343

(a) Calculate the enthalpy change for the reaction

$$CH_4(g) \rightarrow C(g) + 4H(g)$$

Exercise 22 (cont.)

(b) Calculate the average bond energy of a C-H bond in methane.

(c) What name do we give each of the enthalpy changes in Table 3?

(d) Suggest a reason why each is different.

(Answers on page 91)

Exercise 23 (a) Explain the difference between 'bond energy term' and 'bond dissociation energy'.

(b) Name a molecule for which the bond dissociation energy is the same as the bond energy term.

(Answers on page 91)

We cannot always obtain bond energy terms by the method you have just used because bond dissociation energies are often not known. In the next section we look at another method of calculation.

Calculating bond energy terms

Once again we can use an energy cycle and Hess's law to determine an enthalpy change which cannot be measured directly. We illustrate this method by a Worked Example.

Objective. At the end of this section, you should be able to:

(18) calculate the bond energy term for a molecule using standard heat of formation data and standard enthalpy of atomization data.

The standard enthalpy change of atomization of an element is the enthalpy change in the production of one mole of gaseous atoms from the element in its standard state. For example, it refers to processes such as

$$\mathrm{Na(s)} \rightarrow \mathrm{Na(g)} \quad \text{and} \quad \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{Cl(g)}$$

We deal with the atomization of compounds later.

Worked Example Calculate the C-H bond energy term in methane.

Solution

1. Write the equation for the complete dissociation of methane.

$$\mathrm{CH_4(g)} \rightarrow \mathrm{C(g)} + \mathrm{4H(g)}$$

2. Construct an energy cycle by including the elements in their standard states.

$$\begin{tikzcd}
\boxed{\mathrm{CH_4(g)}} \arrow[rr, "\Delta H_1"] & & \boxed{\mathrm{C(g) + 4H(g)}} \\
& \boxed{\mathrm{C(s) + 2H_2(g)}} \arrow[ul, "\Delta H_2"] \arrow[ur, "\Delta H_3"'] &
\end{tikzcd}$$

Here ΔH_2 is the standard heat of formation of methane, $\Delta H^{\ominus}_{f}$ [$CH_4(g)$]; and ΔH_3 is the standard enthalpy change of atomization of carbon plus four times the standard enthalpy change of atomization of hydrogen; i.e.

$$\Delta H_3 = \Delta H^{\ominus}_{at}\,[C(g)] + 4\,\Delta H^{\ominus}_{at}\,[H(g)].$$

3. Look up these values in your data book:

   $\Delta H^{\ominus}_{f}\,[CH_4(g)] = -74.8\ \mathrm{kJ\ mol^{-1}}$

   $\Delta H^{\ominus}_{at}\,[C(g)] = +715.0\ \mathrm{kJ\ mol^{-1}}$

   $4\,\Delta H^{\ominus}_{at}\,[H(g)] = 4(+218.0\ \mathrm{kJ\ mol^{-1}}) = 872.0\ \mathrm{kJ\ mol^{-1}}$

4. Apply Hess's law

   $\Delta H_2 + \Delta H_1 = \Delta H_3$

5. Substitute the appropriate values and solve for ΔH_1:

   $$\Delta H_1 = \Delta H_3 - \Delta H_2$$
   $$= (715.0 + 872.0 - -74.8)\ \mathrm{kJ\ mol^{-1}} = 1661.8\ \mathrm{kJ\ mol^{-1}}$$

6. This is the energy required to break four bonds. We want to know the average value for one bond.

   $$\therefore \quad \bar{E}(\mathrm{C{-}H}) = \frac{1661.8}{4}\ \mathrm{kJ\ mol^{-1}} = \boxed{415\ \mathrm{kJ\ mol^{-1}}}$$

Now try two similar problems.

Exercise 24 Determine the enthalpy change for the process:

$$H_2S(g) \rightarrow 2H(g) + S(g)$$

and so calculate the bond energy term, $\bar{E}$(H-S).

(Answer on page 91)

Exercise 25 Calculate $\bar{E}$(N-H), given the following data:

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$; $\Delta H^{\ominus} = -46\ \mathrm{kJ\ mol^{-1}}$

$\frac{1}{2}H_2(g) \rightarrow H(g)$; $\Delta H^{\ominus} = +218\ \mathrm{kJ\ mol^{-1}}$

$\frac{1}{2}N_2(g) \rightarrow N(g)$; $\Delta H^{\ominus} = +473\ \mathrm{kJ\ mol^{-1}}$

(Answer on page 91)

Notice that in all these examples and exercises, reactants and products are in the gaseous state. If the substance we are decomposing exists as a liquid in its standard state, it must first be vaporised, and this requires energy.

$$CCl_4(l) \rightarrow CCl_4(g);\quad \Delta H^{\ominus}_{vap}\,[CCl_4(l)] = 30.5\ \mathrm{kJ\ mol^{-1}}$$

Apply this idea in the next exercise.

Exercise 26 Calculate the enthalpy change for the process:

$$CCl_4(g) \rightarrow C(g) + 4Cl(g)$$

and calculate the bond energy term, $\bar{E}$(C-Cl).

(Answer on page 91)

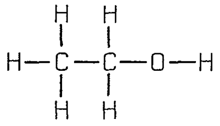
So far you have averaged energies for similar bonds within identical molecules. Now you investigate the validity of assuming that bond energy terms can be applied to similar bonds in different molecules. Start by working out, in the next exercise, what bonds are broken and formed in the combustion of some similar alcohols.

Objectives. When you have finished this section, you should be able to:

(19) describe briefly how the heats of combustion of a series of alcohols can be measured;

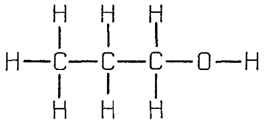
(20) interpret heat of combustion data for a series of alcohols in terms of bonds broken and bonds formed.

Exercise 27 This question concerns the combustion of a number of alcohols. The structural formulae of some of these alcohols and of the other substances involved are:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & O—H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

ethanol

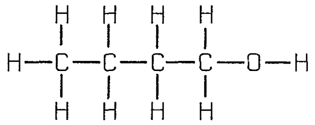


$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & O—H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

propan-1-ol

$O{=}O$

oxygen



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & O—H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

butan-1-ol

$O{=}C{=}O$

carbon dioxide

$H—O—H$

water

Two equations for combustion are:

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$C_3H_7OH(l) + 4\frac{1}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

(a) For the combustion of one mole of each alcohol, calculate (i) the number of bonds of each type broken, (ii) the number of bonds of each type formed, and complete a copy of Table 4.

Table 4

	Bonds broken/mol					Bonds formed	
Alcohol	C—C	C—H	C—O	O—H	O=O	O=C	O—H
ethanol							
propan-1-ol							
butan-1-ol							

(b) What is the difference, in terms of bonds broken and bonds formed, between the combustions of ethanol and propan-1-ol and between the combustions of propan-1-ol and butan-1-ol?

(c) Use your answer to part (b) to complete Table 4 for two more alcohols, pentan-1-ol, $C_5H_{11}OH$, and hexan-1-ol, $C_6H_{13}OH$, which have very similar structural formulae to the others.

(d) Which of the bonds you have identified in part (b) are identical, i.e. bonds between the same atoms in identical molecules, and which are merely similar, i.e. bonds between the same atoms in different molecules?

(e) Would you expect a constant difference in $\Delta H^{\ominus}$ between one alcohol and the next in the list, (i) at a temperature high enough for all reactants and products to be gaseous, (ii) at 298 K?

Hint: the difference in $\Delta H^{\ominus}_{vap}$ between one alcohol and the next is between 1 kJ mol^{-1} and 6 kJ mol^{-1}.

(Answers on page 92)

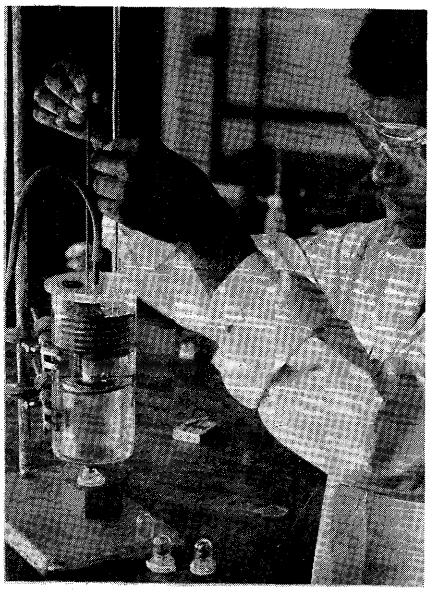
Now you can check your answer to Exercise 27 part (e). You can either obtain the values from your data book or, if your teacher agrees, perform an experiment to determine the heats of combustion of a series of alcohols.

If you are going to do Experiment 4, you will find it helpful to look at the ILPAC video-tape 'Using a heat of combustion apparatus'.

If you are not doing the experiment, go directly to Exercise 28 on page 47.

EXPERIMENT 4

Determining heats of combustion



Aim

The purpose of this experiment is to determine the heats of combustion of a series of similar alcohols from butan-1-ol to octan-1-ol.

Introduction

In this experiment, you burn a measured mass of an alcohol in a spirit lamp and transfer the heat energy released to a calorimeter containing water. From the resulting temperature rise you can calculate the heat of combustion.

In your earlier calorimetric experiments, you assumed that all the heat energy released in a chemical reaction was absorbed by the contents of the calorimeter. You cannot make that assumption in this experiment for two reasons.

1. The heat energy is released in a flame, and although the apparatus is designed to transfer most of the energy to the calorimeter, a significant quantity is lost to the surrounding air.

2. The heat capacity of the calorimeter itself is not so small as to be insignificant compared with the heat capacity of its contents.

You can take account of both these factors by calibrating the apparatus using an alcohol with known heat of combustion.

Requirements

safety spectacles
heat of combustion apparatus
spirit lamp
wood block
retort stand (with 2 clamps and bosses)
Drechsel bottle
filter pump
rubber tubing (for connections to filter pump)
water (at room temperature)
adhesive labels
propan-1-ol, C_3H_7OH
butan-1-ol, C_4H_9OH
pentan-1-ol, $C_5H_{11}OH$
hexan-1-ol, $C_6H_{13}OH$
heptan-1-ol, $C_7H_{15}OH$
octan-1-ol, $C_8H_{17}OH$
(If these alcohols are supplied in separate spirit lamps, you will not need the next two items.)
6 beakers, 50 cm^3
6 teat pipette droppers
Bunsen burner and protective mat
wood splints
tweezers (not plastic-tipped)
balance (preferably capable of weighing to 0.001 g, but 0.01 g will do)
thermometer -5 to -50°C (in 0.1°C)

Hazard warning

The alcohols you will be using are very flammable and can be poisonous by absorption through the skin and lungs. Therefore you MUST:

KEEP THE STOPPERS ON THE BOTTLES WHEN NOT IN USE

KEEP THE BOTTLES AWAY FROM FLAMES

WASH YOUR HANDS AFTER USE (OR WEAR GLOVES)

WEAR SAFETY SPECTACLES

Procedure

A. Determination of the heat capacity of the apparatus

1. Arrange the heat of combustion apparatus (i.e. the calorimeter), the Drechsel bottle, etc., as shown in Fig. 10. Don't use the calorimeter base supplied by the manufacturer but stand the burner on a small block of wood to ensure a good flow of air. Adjust the height of the calorimeter (or the size of the block) so that the top of the spirit lamp is level with the bottom of the calorimeter.

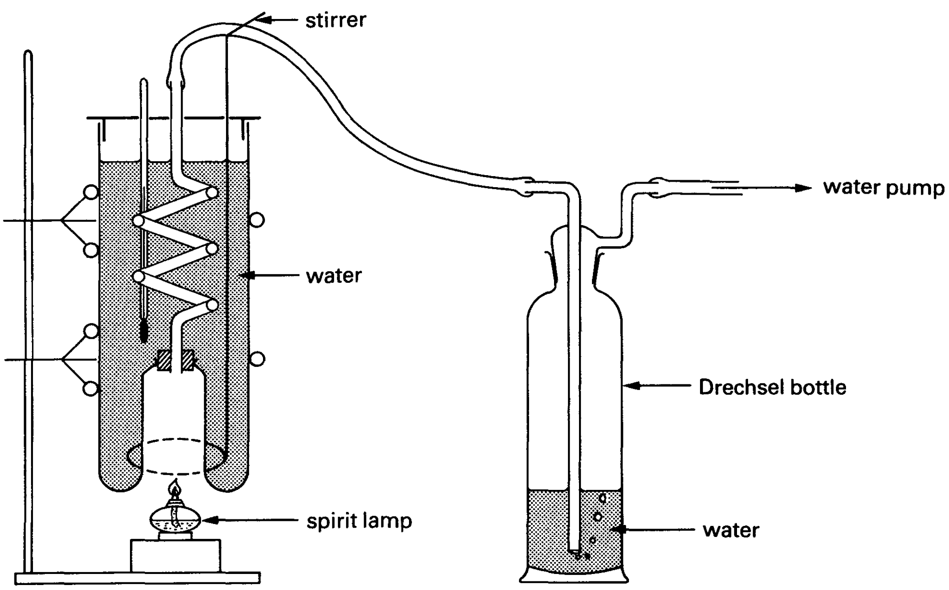


Fig. 10. Heat of combustion apparatus

2. Use water at room temperature (not direct from the tap) to fill the calorimeter to about 1.5 cm below the rim. Mark this level with a label.

3. Pour a little propan-1-ol into a small beaker and use a teat pipette to half-fill the spirit lamp. (This may have been done for you already.) Replace the wick and cap, return any excess alcohol to the bottle, and remove both bottle and beaker to a safe distance from any flame.

4. Turn on the filter pump and adjust the flow of air through the Drechsel bottle to about 3-4 bubbles per second.

5. Stand the spirit lamp away from the calorimeter, and use a wood splint to light it. Adjust the height of the wick, using metal tweezers, to obtain a flame about 1 cm high.

6. Check that the lamp burns satisfactorily for about 15 seconds in position under the calorimeter. If it goes out, either increase the flow of air or adjust the height of the lamp relative to the calorimeter. Once these adjustments have been made, they should not be changed for the rest of the experiment. Extinguish the flame and put on the cap.

7. Weigh the spirit lamp, including the cap, as accurately as possible and record the mass in Results Table 3.

8. Stir the water in the calorimeter and record its temperature, to the nearest 0.1°C.

9. Put the lamp under the calorimeter and light it.

10. Slowly and continuously stir the water in the calorimeter and watch the thermometer. When the temperature has risen by about 10°C, extinguish the flame and immediately replace the cap. Record the maximum temperature of the water.

11. Re-weigh the spirit lamp and cap and record the mass.

12. Without removing the calorimeter from the stand, and holding both together carefully, pour away the water.

13. If you have time, repeat the experiment to increase the accuracy of your calibration. This second run should be much quicker because you should not need to make any adjustments (i.e. start at step 7).
14. Before doing any calculations, repeat the experiment using as many of the other alcohols as you have time for and complete Results Table 4. If you have to use the same spirit lamp, you will have to empty it, rinse it with the new alcohol, and fit a new wick (or dry the old wick). If time is limited, your teacher may suggest that you share your results with other students, or may give you some pre-determined results.

Results Table 3	1st run	2nd run	
Molar mass of propan-1-ol, M			g mol^{-1}
Initial mass of spirit lamp + alcohol, m_1			g
Final mass of spirit lamp + alcohol, m_2			g
Mass of alcohol burned, $m_1 - m_2$			g
Amount of alcohol burned, $n = (m_1 - m_2)/M$			mol
Initial temperature of calorimeter			°C
Final temperature of calorimeter			°C
Temperature change, ΔT			K
$\Delta H_c^\ominus$ [propan-1-ol] (given)	-2017		kJ mol^{-1}
Heat released during the experiment, ΔH $= \Delta H_c^\ominus$ [propan-1-ol] x amount burned $= -2017$ kJ mol^{-1} x n			kJ
Heat required for a rise in temperature of 1 K $= \frac{\Delta H}{\Delta T}$			
$= C$, the calorimeter calibration factor			kJ K^{-1}
Average value of C			kJ K^{-1}

Results Table 4	C_4H_9OH	$C_5H_{11}OH$	$C_6H_{13}OH$	$C_7H_{15}OH$	$C_8H_{17}OH$
Molar mass, M/g mol^{-1}					
Initial mass of lamp/g					
Final mass of lamp/g					
Mass of alcohol burned/g					
Amount burned, n/mol					
Initial temperature/°C					
Final temperature/°C					
Temperature change, ΔT/K					
$\Delta H_c = \frac{C \times \Delta T}{n}$/kJ mol^{-1}					

(Specimen results on page 92)

You can make use of your experimental results in the next exercise.

Exercise 28 (a) Either using your experimental results or $\Delta H^\ominus$ values from your data book, fill in the first column of Table 5.

Table 5

Alcohol	$\Delta H^\ominus_c$/kJ mol^{-1}	Differences /kJ mol^{-1}
propan-1-ol, C_3H_7OH		▨
butan-1-ol, C_4H_9OH		
pentan-1-ol, $C_5H_{11}OH$		
hexan-1-ol, $C_6H_{13}OH$		
heptan-1-ol, $C_7H_{15}OH$		
octan-1-ol, $C_8H_{17}OH$		▨
	Average difference =	

(b) Calculate the differences and fill in the second column. Calculate the average difference in $\Delta H^\ominus_c$.

(c) Do you now think it is reasonable to use average bond energy terms for C-C and C-H in the different alcohols? Explain your answer.

(Answers on page 92)

Having established that a particular kind of bond has a particular quantity of energy associated with it, we can calculate two average bond energies, $\bar{E}$(C-H) and $\bar{E}$(C-C), by solving simultaneous equations.

Determining two bond energy terms simultaneously

Work through the following revealing exercise where we show you how to do this calculation. You need the following information:

butane: $C_4H_{10}(g) \rightarrow 4C(g) + 10H(g)$; $\Delta H^\ominus = +5165$ kJ mol^{-1}

pentane: $C_5H_{12}(g) \rightarrow 5C(g) + 12H(g)$; $\Delta H^\ominus = +6337$ kJ mol^{-1}

Q1. How many bonds are broken in the atomization of butane and pentane?

A1. In butane, 3 C-C bonds and 10 C-H bonds are broken per molecule; in pentane, 4 C-C bonds and 12 C-H bonds are broken per molecule.

Q2. Express the enthalpy changes for the atomization of pentane and butane as the sums of the bond energy terms.

A2. Butane: $3\bar{E}(\text{C-C}) + 10\bar{E}(\text{C-H}) = +5165 \text{ kJ mol}^{-1}$

Pentane: $4\bar{E}(\text{C-C}) + 12\bar{E}(\text{C-H}) = +6337 \text{ kJ mol}^{-1}$

Notice that for a compound, $\Delta H^{\ominus}_{\text{at}}$ refers to one mole of molecules, whereas for an element it refers to one mole of atoms.

Q3. Let $\bar{E}$ (C-C) = x kJ mol^{-1}

$\bar{E}$ (C-H) = y kJ mol^{-1}

and solve these equations simultaneously.

A3. $3x + 10y = 5165$ (1)

$4x + 12y = 6337$ (2)

Multiply equation (1) by 4 and equation (2) by 3 and subtract:

$$\begin{array}{r}12x + 40y = 20660\\ \underline{12x + 36y = 19011}\\ 4y = 1649\end{array} \quad \therefore\ y = 412.25$$

Substitute this value for y into either equation (1) or (2).

$3x + 10(412.25) = 5165$

$3x = 5165 - 4122.5 = 1042.5 \quad \therefore\ x = 347.5$

$\therefore\ \bar{E}(\text{C-C}) = \boxed{347.5 \text{ kJ mol}^{-1}} \qquad \bar{E}(\text{C-H}) = \boxed{412.2 \text{ kJ mol}^{-1}}$

Now that we have shown you how bond energy terms can be obtained we illustrate their use in estimating enthalpy changes in reactions for which there are no experimental data.

Uses of bond energy terms

In order to obtain a bond energy term which can be tabulated and used generally, an average value is taken for a particular type of bond in a large number of compounds. The bond energy terms quoted in your data book should, therefore, not be considered as accurately stating the bond energy in any particular molecular environment. Calculations using bond energy terms can only give approximate answers.

Objectives. When you have finished this section, you should be able to:

(21) use bond energy terms to estimate enthalpy changes that cannot be determined directly.

Using bond energy terms to estimate enthalpy changes

You have already used one method for calculating enthalpy changes that cannot be determined directly, by substituting known enthalpy data into an energy cycle and applying Hess's law. We now show you another method, this time using bond energy terms, in a Worked Example. We remind you that:

BOND BREAKING REQUIRES ENERGY (ENDOTHERMIC)
BOND MAKING RELEASES ENERGY (EXOTHERMIC)

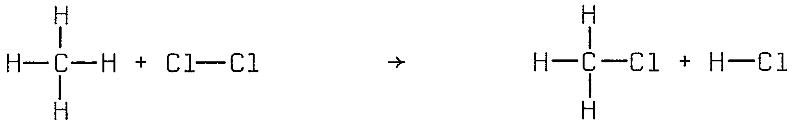
W

Worked Example Use bond energy terms to calculate the enthalpy change for the reaction:

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

Solution

1. Write the equation using structural formulae:



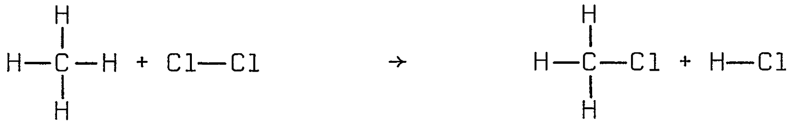
$$\mathrm{H-\overset{H}{\underset{H}{C}}-H + Cl-Cl \rightarrow H-\overset{H}{\underset{H}{C}}-Cl + H-Cl}$$

2. List the bonds broken and bonds made under the equations as shown:

$$\underbrace{\mathrm{H-\overset{H}{\underset{H}{C}}-H + Cl-Cl}} \rightarrow \underbrace{\mathrm{H-\overset{H}{\underset{H}{C}}-Cl + H-Cl}}$$

bonds broken	bonds made
C—H	C—Cl
Cl—Cl	H—Cl

3. Look up the bond energy terms for the bonds broken and made. Add them up as shown, including negative signs for the exothermic bond-making.



$$\mathrm{H-\overset{H}{\underset{H}{C}}-H + Cl-Cl \rightarrow H-\overset{H}{\underset{H}{C}}-Cl + H-Cl}$$

bonds broken	bonds made
$\bar{E}(C\text{-}H) = 435\ kJ\ mol^{-1}$	$-\bar{E}(C\text{-}Cl) = -339\ kJ\ mol^{-1}$
$\bar{E}(Cl\text{-}Cl) = 242\ kJ\ mol^{-1}$	$-\bar{E}(H\text{-}Cl) = -431\ kJ\ mol^{-1}$
Total $= 677\ kJ\ mol^{-1}$	Total $= -770\ kJ\ mol^{-1}$

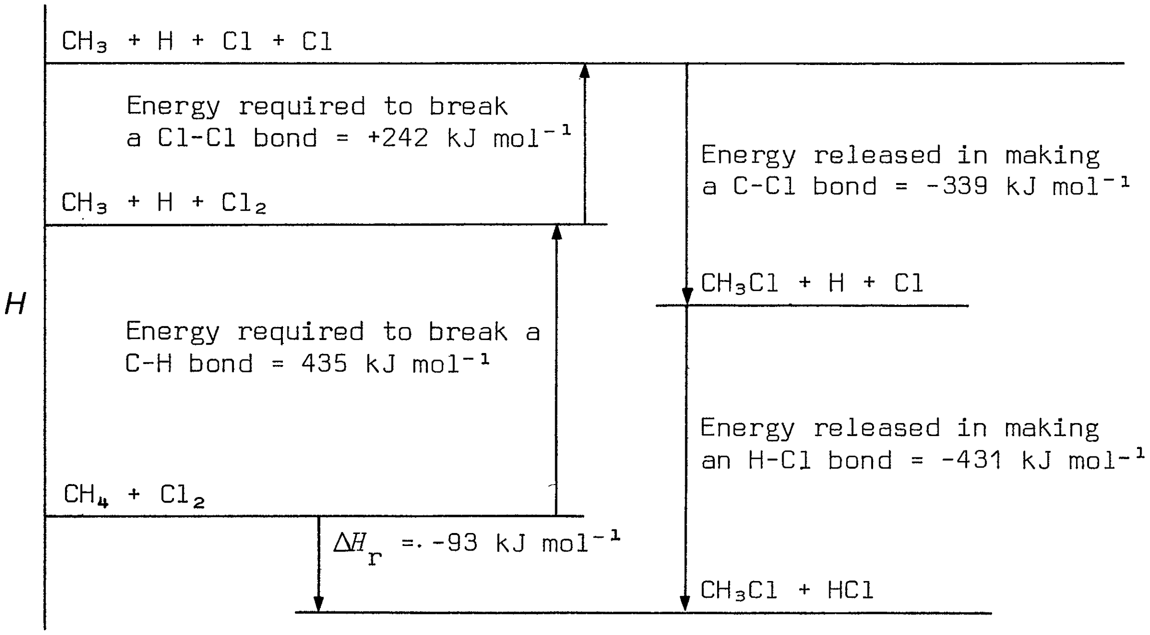
4. Add the values for bond breaking and making (including the correct signs) to obtain the required enthalpy change

$\Delta H = 677\ kJ\ mol^{-1} - 770\ kJ\ mol^{-1} = -93\ kJ\ mol^{-1}$

5. Write the complete thermochemical equation:

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g);\ \Delta H = \boxed{-93\ kJ\ mol^{-1}}$

The following energy level diagram summarises the energy changes during the reaction we have just considered.



Now attempt the following exercises, two of which are A-level questions.

Exercise 29 Use bond energy terms listed in your data book to calculate the enthalpy change for the reactions

(a) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

(b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(Answers on page **92**)

Exercise 30 Some bond energy terms are listed below:

A

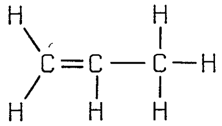
Table 6

Bond	H-H	C-H	C-Br	C–C	C=C	Br-Br
Bond energy /kJ mol^{-1}	436	413	209	346	611	112

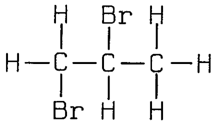
(a) What do you understand by bond energy term?

(b) Using the given data, calculate the enthalpies of formation, from gaseous atoms, of

(i) gaseous propene, (propylene),



(ii) gaseous 1,2-dibromopropane



$$\begin{array}{ccccccc} & & H & & Br & & H \\ & & | & & | & & | \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | \\ & & Br & & H & & H \end{array}$$

(c) Calculate the enthalpy change, $\Delta H^\ominus$, for the reaction:

$CH_2 = CH - CH_3(g) + Br_2(g) \rightarrow CH_2BrCHBrCH_3(g)$

(Answers on page **93**)

Exercise 31 (a) Use the values of bond energy terms contained in your data book to calculate the standard enthalpy change for the reaction:

A

$$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$$

(b) Calculate another value for this standard enthalpy change from heats of formation.

(c) Write a short account of the reasons why the two values you have calculated differ from each other.

(Answers on page 93)

So far in Level Two your work has been confined to covalent compounds. You have seen how to use bond energy terms to calculate the enthalpy change of formation of a molecular compound from its constituent gaseous atoms - an important step in the calculation of $\Delta H^\ominus$ for a reaction. Now we look at energy changes in the formation of ionic compounds.

LATTICE ENERGY

It is often useful to know the heat of formation of an ionic compound from its constituent gaseous ions. The energy value is called the 'lattice energy' of the compound, because ionic bonding always leads to a solid crystal lattice. It provides a measure of the strength of ionic bonds.

Objective. When you have finished this section, you should be able to:

(22) define lattice energy;

$\boxed{\Delta H^\ominus_{lat}}$

The lattice energy of an ionic compound is the enthalpy change which occurs when one mole of it is formed, as a crystal lattice, from its constituent gaseous ions.

This definition of lattice energy always gives a negative sign, e.g.

$$Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s); \quad \Delta H^\ominus_{lat} = -781 \text{ kJ mol}^{-1}$$

If we were considering the energy required to separate the salt into its separate ions then the enthalpy change must have a positive sign:

$$Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g); \quad \Delta H^\ominus_{lat} = +781 \text{ kJ mol}^{-1}$$

You may find that some books quote positive values of lattice energy, but you will not go wrong if you always relate $\Delta H^\ominus$ to the appropriate equation.

Since it is impossible to determine lattice energies directly by experiment we use an indirect method where we construct an energy diagram called a Born-Haber cycle.

Calculating lattice energy using a Born-Haber cycle

The Born-Haber cycle is yet another application of Hess's law but the alternative routes involve more steps than you have used so far.

To construct a Born-Haber cycle you need two enthalpy changes not previously mentioned in this Unit, ionization energy and electron affinity. You should be familiar with ionization energy from ILPAC S2 (Atomic Structure).

$\boxed{\Delta H_i^\ominus}$

The ionization energy of an element is the enthalpy change which occurs when one mole of its gaseous atoms loses one mole of electrons to form one mole of gaseous positive ions, e.g.

$$Na(g) \rightarrow Na^+(g); \quad \Delta H_i^\ominus = +500\ kJ\ mol^{-1}$$

$\boxed{\Delta H_e^\ominus}$

The electron affinity of an element is the enthalpy change which occurs when one mole of its gaseous atoms accepts one mole of electrons to form one mole of gaseous negative ions, e.g.

$$Br(g) + e^- \rightarrow Br^-(g); \quad \Delta H_e^\ominus = -342\ kJ\ mol^{-1}$$

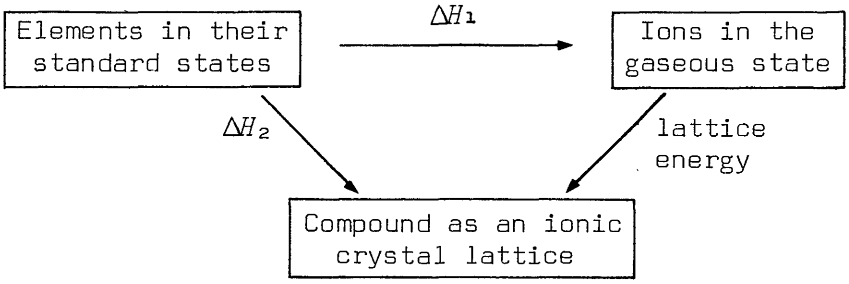
Objectives. When you have finished this section, you should be able to:

(23) construct a Born-Haber cycle for an ionic compound;

(24) use a Born-Haber cycle to calculate the lattice energy for an ionic compound.

Find the section on the Born-Haber cycle in your text-book. Skim through it and then use it to help you with the revealing exercise which follows.

Below is a generalised Born-Haber cycle for an ionic compound.



Q1. Redraw the cycle including the appropriate formulae for the formation of sodium chloride.

A1.

$$\begin{tikzcd}
\boxed{Na(s) + \frac{1}{2}Cl_2(g)} \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & \boxed{Na^+(g) + Cl^-(g)} \arrow[dl, "\text{lattice energy}"] \\
& \boxed{Na^+Cl^-(s)} &
\end{tikzcd}$$

Q2. ΔH_1 is the sum of the energy changes associated with four steps, two for sodium and two for chlorine. Write thermochemical equations for these four steps.

A2. $Na(s) \rightarrow Na(g)$; $\Delta H^\ominus_{at} = +108$ kJ mol^{-1}

$Na(g) \rightarrow Na^+(g)$; $\Delta H^\ominus_{i} = +500$ kJ mol^{-1}

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$; $\Delta H^\ominus_{at} = +121$ kJ mol^{-1}

$Cl(g) + e^- \rightarrow Cl^-(g)$; $\Delta H^\ominus_{e} = -364$ kJ mol^{-1}

Q3. Calculate ΔH_1.

A3. $\Delta H_1 = \Delta H^\ominus_{at}(Na) + \Delta H^\ominus_{i}(Na) + \Delta H^\ominus_{at}(\frac{1}{2}Cl_2) + \Delta H^\ominus_{e}(Cl)$

So $\Delta H_1 = (+108 + 500 + 121 - 364)$ kJ mol^{-1} = +365 kJ mol^{-1}

Q4. What name is given to ΔH_2? Look up a value in your data book.

A4. ΔH_2 is the enthalpy change of formation of sodium chloride.

$\Delta H^\ominus_f[NaCl(s)] = -411$ kJ mol^{-1}

Q5. Insert the values for ΔH_1 and ΔH_2 in the energy cycle.

A5.

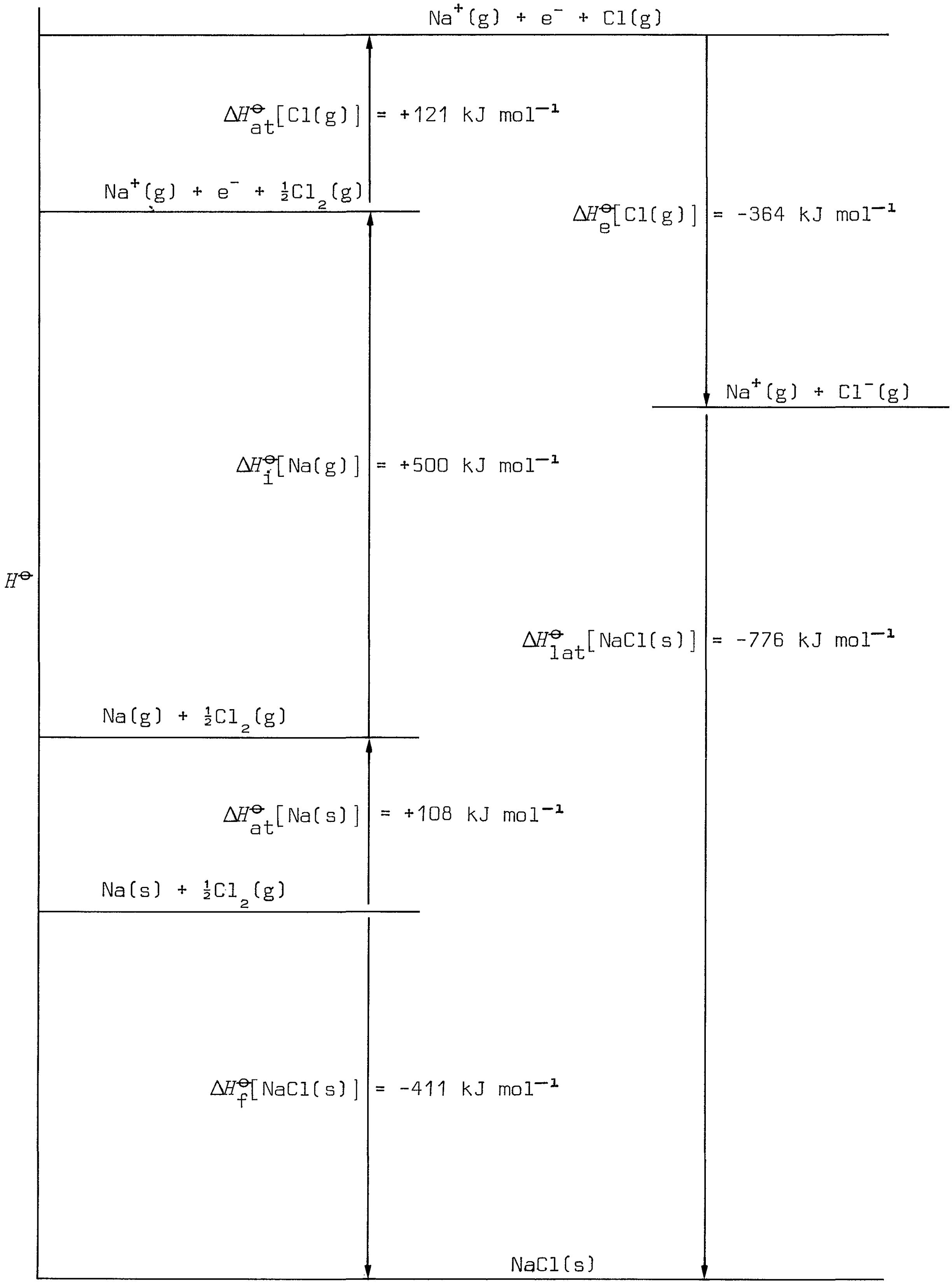
$$\begin{tikzcd}
\boxed{Na(s) + \frac{1}{2}Cl\ (g)} \arrow[rr, "+365\ \text{kJ mol}^{-1}"] \arrow[dr, "-411\ \text{kJ mol}^{-1}"] & & \boxed{Na^+(g) + Cl^-(g)} \arrow[dl, "\text{lattice energy}"] \\
& \boxed{Na^+Cl^-(s)} &
\end{tikzcd}$$

Q6. Use Hess's law to calculate the lattice energy for sodium chloride.

A6. 365 kJ mol^{-1} + lattice energy = -411 kJ mol^{-1}

∴ lattice energy = -411 kJ mol^{-1} -365 kJ mol^{-1} = $\boxed{-776\ \text{kJ mol}^{-1}}$

Born-Haber cycles are often drawn as energy level diagrams. Compare the following energy level diagram with the cycle you drew in the revealing exercise and trace the various steps.



Born-Haber cycle for sodium chloride, drawn approximately to scale.

Note that Born-Haber cycles are frequently not drawn to scale, in order to save time and space. Also, the electrons are not always included in the ionization steps.

Try drawing some Born-Haber cycles for yourself in the following exercises, and use the cycles to calculate some lattice energies.

Exercise 32 Draw a Born-Haber cycle for each of the following ionic compounds, and then calculate their lattice energies. (Note that in sodium hydride, the hydrogen forms a negative ion.) The cycles need not be drawn to scale.

Table 7

		Metal		Non-metal	
Compound	$\Delta H^{\ominus}_{f}$ /kJ mol^{-1}	$\Delta H^{\ominus}_{at}$ /kJ mol^{-1}	$\Delta H^{\ominus}_{i}$ /kJ mol^{-1}	$\Delta H^{\ominus}_{at}$ /kJ mol^{-1}	$\Delta H^{\ominus}_{e}$ /kJ mol^{-1}
KBr (K^+,Br^-)	-392	+ 89	+420	+112	-342
NaH (Na^+,H^-)	- 57	+108	+500	+218	- 72

(Answers on page 93)

Exercise 33 Complete Table 8 and draw Born-Haber cycles to obtain lattice energies. Note that in this example you may have to combine successive values for $\Delta H^{\ominus}_{i}$ and $\Delta H^{\ominus}_{e}$. Also, whereas $\Delta H^{\ominus}_{i}$ is <u>always</u> positive, $\Delta H^{\ominus}_{e}$ may be positive or negative.

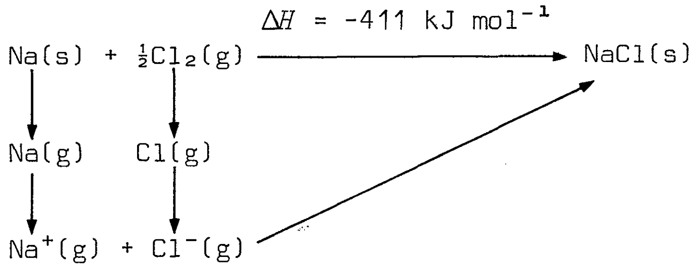
Table 8

		Metal		Non-metal	
Compound	$\Delta H^{\ominus}_{f}$ /kJ mol^{-1}	$\Delta H^{\ominus}_{at}$ /kJ mol^{-1}	$\Delta H^{\ominus}_{i}$ /kJ mol^{-1}	$\Delta H^{\ominus}_{at}$ /kJ mol^{-1}	$\Delta H^{\ominus}_{e}$ /kJ mol^{-1}
$BaCl_2$ $(Ba^{2+},2Cl^-)$	-860	+175	+ 500 +1000	+121	-364
SrO (Sr^{2+},O^{2-})					

(Answers on page 94)

Born-Haber cycles are not used exclusively to calculate lattice energies as the next two exercises illustrate.

Exercise 34



Use the above diagram and the following data to calculate ΔH for the reaction:

$Cl(g) + e^- \rightarrow Cl^-(g)$

$Na(s) \rightarrow Na(g)$; ΔH = 108 kJ mol^{-1}

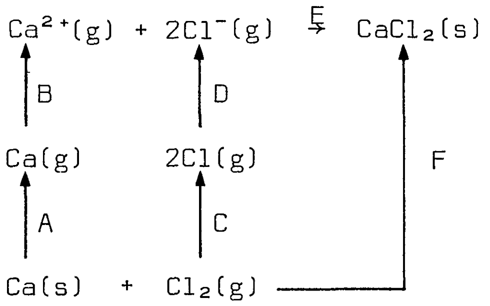
$Na(g) \rightarrow Na^+(g)$; ΔH = 500 kJ mol^{-1}

$\frac{1}{2}Cl(g) \rightarrow Cl(g)$; ΔH = 121 kJ mol^{-1}

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$; ΔH = 776 kJ mol^{-1}

(Answer on page **94**)

Exercise 35 The Born-Haber cycle for the formation of calcium chloride is given below:



A = 177 kJ mol^{-1} C = 242 kJ mol^{-1} F = -795 kJ mol^{-1}

B = 1690 kJ mol^{-1} E = -2197 kJ mol^{-1}

(a) A is the enthalpy change of sublimation (atomization) of solid calcium. Similarly, define the following:

(i) B (ii) C (iii) E (iv) F

(b) Calculate the enthalpy change D.

(Answers on page **94**)

Another use of Born-Haber cycles enables us to discuss the stoichiometry of compounds which might be formed by direct combination.

Lattice energy and stoichiometry

We now use enthalpy data and suitable Born-Haber cycles to predict the formula of a compound.

Objective. When you have finished this section, you should be able to:

(25) predict the stoichiometry of a compound using calculated values of standard enthalpy of formation.

In the exercise which follows, you construct Born-Haber cycles for MgCl, $MgCl_2$, and $MgCl_3$ to determine heats of formation and then decide which would be the most likely formula for magnesium chloride.

Exercise 36 (a) Construct Born-Haber cycles for MgCl, $MgCl_2$ and $MgCl_3$, inserting all the values except $\Delta H^{\ominus}_{f}$. Since experimentally determined lattice energies for MgCl and $MgCl_3$ are not available, use the theoretically calculated values:

$$\Delta H^{\ominus}_{lat}[MgCl] = -753 \text{ kJ mol}^{-1}$$

$$\Delta H^{\ominus}_{lat}[MgCl_3] = -5440 \text{ kJ mol}^{-1}$$

(b) Use the cycles to obtain values for

(i) $\Delta H^{\ominus}_{f}$ [MgCl] (ii) $\Delta H^{\ominus}_{f}$ [$MgCl_2$] (iii) $\Delta H^{\ominus}_{f}$ [$MgCl_3$]

(c) Which of the three compounds MgCl, $MgCl_2$, $MgCl_3$ is/are energetically stable with respect to the elements?

(d) Calculate the enthalpy change for the hypothetical reaction

$$2MgCl(s) \rightarrow MgCl_2(s) + Mg(s)$$

using the $\Delta H^{\ominus}_{f}$ values you calculated in part (b).

(e) Discuss briefly the relative stability of MgCl and $MgCl_2$ in the light of your answer to (d). Does this explain why MgCl is not known?

(Answers on page 94)

To test your understanding of the last section you should do the following teacher-marked exercise which is a question taken from a past A-level examination paper.

✓

Teacher-marked Exercise Use your data book to determine the lattice energy of strontium chloride. Show how you arrive at your answer. A substance of formula $SrCl_3$ does not exist. What further energetics data would you need to explain this fact? Show how you would use the data.

A

In the next section we return to the experimental determination of heat of reaction and show you how to adapt for this purpose the titration method you learned in Unit S1.

THERMOMETRIC TITRATIONS

We now give you another method for determining experimentally the enthalpy change of a reaction, i.e. using the technique of thermometric titration.

Objectives. When you have completed this section you should be able to:

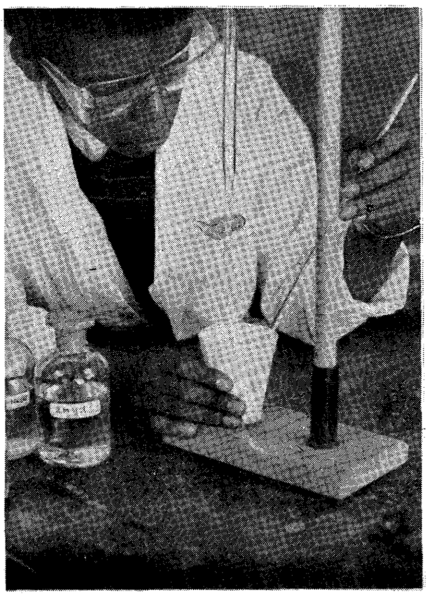
(26) perform a thermometric titration in order to determine the enthalpy change of a reaction;

(27) define standard enthalpy change of neutralization.

In thermometric titrations we make use of the fact that reactions in solution are accompanied by temperature changes, and thus it is possible to follow the course of a reaction using a thermometer. In the next experiment you perform two thermometric titrations.

EXPERIMENT 5

A thermometric titration



Aim

The purpose of this experiment is to determine the concentrations of two acids, hydrochloric acid, HCl, and ethanoic acid, CH_3CO_2H, by thermometric titration; and having done that, to calculate the enthalpy change for each reaction - the enthalpy change of neutralization.

Introduction

You titrate both hydrochloric acid and ethanoic acid in turn with a standardised solution of sodium hydroxide and record the temperatures of the mixtures during the course of the titrations. In each case a plot of temperature against time will enable you to determine the maximum temperature rise, from which you calculate both the concentration of the acid and the enthalpy change of neutralization.

Requirements

safety spectacles
pipette, 50.0 cm^3
pipette filler
expanded polystyrene cup
sodium hydroxide solution, 1 M NaOH (standardised)
thermometer, 0-50°C (in 0.1°C)
burette, 50.0 cm^3
filter funnel, small
hydrochloric acid, ~ 2.0 M HCl
ethanoic acid, ~ 2.0 M CH_3CO_2H

Hazard warning

Sodium hydroxide is very corrosive. Therefore you must:

USE THE PIPETTE FILLER SUPPLIED

WEAR SAFETY SPECTACLES

Procedure

Titration of hydrochloric acid with standard sodium hydroxide solution

1. Using a pipette and filler, transfer 50.0 cm^3 of NaOH solution into the polystyrene cup. Allow to stand for a few minutes.
2. Record the temperature of the solution.
3. From a burette, add 5.0 cm^3 of HCl solution to the cup.
4. Stir the mixture with the thermometer and record its temperature.
5. Add successive 5.0 cm^3 portions of HCl solution stirring the mixture and recording its temperature after each addition.
6. Record your results in a copy of Results Table 5. Stop after the addition of 50.0 cm^3 of acid.

Titration of ethanoic acid with standard sodium hydroxide solution

7. Follow the same procedure as you did for the titration of HCl, except that you use ethanoic acid in the burette. When filling the burette, remember to use correct rinsing procedures. If in doubt, ask your teacher.
8. Record your results in a copy of Results Table 6.

Results Table 5 Titration of hydrochloric acid

Volume added/cm^3	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
Temperature/°C											

Results Table 6 Titration of ethanoic acid

Volume added/cm^3	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
Temperature/°C											

Calculation

1. Plot temperature (y-axis) against volume of acid added (x-axis) for each acid on the same graph.
2. Extend the straighter portions of the curves near the top as shown in Fig. 11. The point at which they meet corresponds to both the volume of acid required for neutralization and to the maximum temperature.

(Specimen results on page 95)

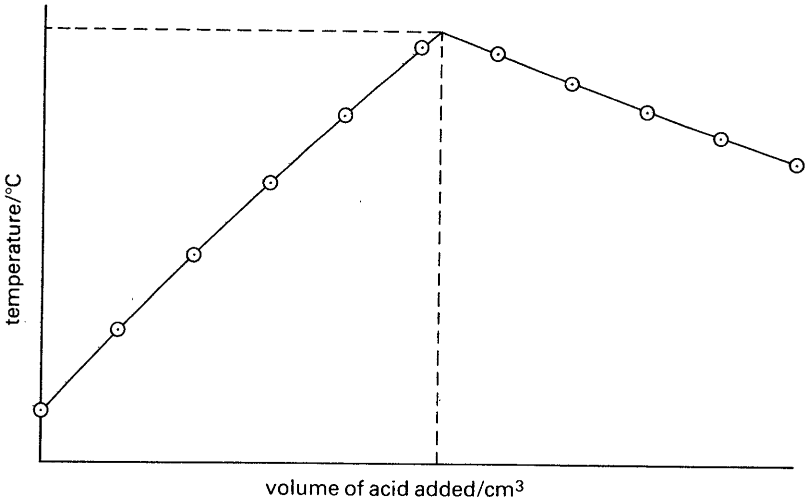


Fig. 11.

3. Calculate the concentration of each of the acids. If necessary, look at your notes in Unit S1: The Mole, to help you.
4. From the maximum temperature rise, determine the quantity of energy released in each titration. Assume that the specific heat capacity of the solutions is the same as that for water, 4.18 kJ kg^{-1} K^{-1} and that the heat capacity of the cup is zero.
5. Calculate the standard enthalpy change of neutralisation for each reaction.

(Specimen results on page 95)

Questions

1. The enthalpy change of neutralization for a very dilute strong acid (i.e. an acid which is completely ionized in solution) reacting with a very dilute strong base is constant at -57.6 kJ mol^{-1} where mol^{-1} refers to one mole of water produced. Why is the value constant?
2. Experimental results for hydrochloric acid are usually a little less negative than -57.6 kJ mol^{-1}. Suggest two reasons for this.
3. Ethanoic acid is a weak acid, i.e. it is not completely ionized in solution. Suggest a reason why the heats of neutralisation for reactions involving weak acids and/or weak bases are always less negative than for strong acids and bases.

(Answers on page 96)

In the final section of this Unit, we take you a little further in your study of free energy change, ΔG, which you first encountered at the end of Level One. Syllabus requirements vary widely in this area; we therefore suggest that, before you start this section, you ask your teacher which parts of it are relevant to your study. While some of the ideas are simple, others are more difficult to grasp; consequently, your teacher may recommend that you spend only a short time on this section now and return to it at a later stage in your course.

THE DIRECTION OF CHANGE

You have already learned that the use of $\Delta H^\ominus$ to predict the stability of substances and the direction of change is useful but not completely reliable. It is $\Delta G^\ominus$ rather than $\Delta H^\ominus$ which is always negative for a reaction which goes to completion. We now show you how $\Delta H^\ominus$ and $\Delta G^\ominus$ are related to each other.

Objectives. When you have finished this section, you should be able to:

(28) state the equation relating $\Delta H^\ominus$ and $\Delta G^\ominus$;

(29) state how the value of $\Delta G^\ominus$ determines the feasibility of a reaction.

Free energy and enthalpy, and also changes in these quantities, are related by the following equations,

$$\boxed{\begin{aligned} G &= H - TS \\ \Delta G &= \Delta H - T\Delta S \\ \Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \end{aligned}}$$

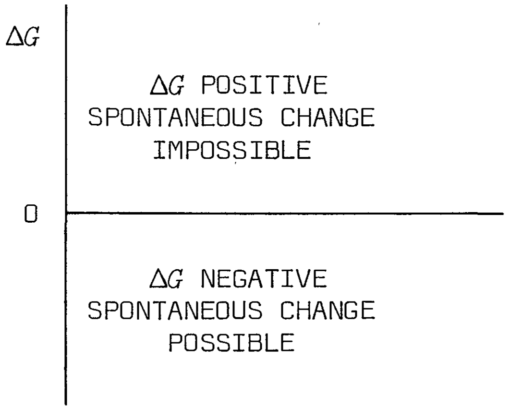
where S is another measurable (or calculable) thermodynamic property called entropy and T is the absolute temperature. Before we discuss entropy. however, we want to be sure that you understand the use of the symbol $^\ominus$ in this context.

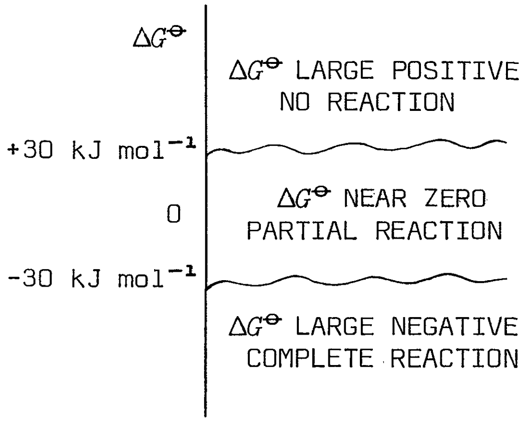
ΔH, ΔG and ΔS refer to any change in a system. For a chemical reaction, this change may involve any amounts of reactants under any conditions and may also be a partial change into a mixture of reactants and products.

$\Delta H^\ominus$, $\Delta G^\ominus$ and $\Delta S^\ominus$ refer only to a complete change in a system from reactants to products as shown in an equation, where reactants and products are at the same standard conditions of temperature, pressure and concentration.

The simple rule that a spontaneous change in a system can only occur if $\Delta G < 0$ is, unfortunately. not always easy to apply because we have to work with tabulated values of $\Delta G^\ominus$. not ΔG. It is not strictly true that spontaneous change can only occur if $\Delta G^\ominus < 0$: it has been shown that although a reaction with a small positive value of $\Delta G^\ominus$ cannot proceed to completion, it can proceed towards an equilibrium mixture of reactants and products, because that change has a negative value of ΔG.

The following diagram shows how the possibility of change is related to values of ΔG and $\Delta G^\ominus$.





The boundary between partial reaction and complete reaction is, of course, not clearly defined. As $\Delta G^{\ominus}$ becomes more negative, reaction favours products more and more until, at values of $\Delta G^{\ominus}$ below about -30 kJ mol^{-1}, it can be regarded as complete.

Similarly, as $\Delta G^{\ominus}$ becomes more positive, reaction favours products less and less until, at values of $\Delta G^{\ominus}$ above about +30 kJ mol^{-1}, it can be regarded as not occurring at all.

You will learn more about incomplete changes, and the significance of the values ±30 kJ mol^{-1}, in the ILPAC Units on equilibrium. At this stage you should simply try to remember the following expressions:

$\Delta G < 0$ spontaneous change possible
$\Delta G^{\ominus} < 0$ reaction possible; products favoured
$\Delta G^{\ominus} < \sim -30$ kJ mol^{-1} complete reaction possible
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

The following sections on entropy will help you to apply them.

Entropy, *S*

The only completely satisfactory definition of entropy is a mathematical one, which you need not concern yourself with at A-level. However, the definition does allow the calculation of absolute values of entropy for any amount of any substance. Non-mathematical definitions are imprecise, but you may find the following statements help you (eventually!) to get some mental picture of entropy.

1. Entropy is an indication of the degree of disorder in a system.
2. Entropy is a measure of the extent to which energy is dispersed.
3. Entropy is a measure of 'sameness', i.e. substances with high entropy are more nearly alike than those with low entropy.

It is a fundamental law of experience that entropy tends to increase in natural processes. Applying this to the three statements gives:

1. Disorder tends to increase.
2. Energy tends to become dispersed.
3. Things that are different tend to become less distinguishable.

Clearly it is possible for us to create order, to localise energy and to separate mixtures, all of which <u>decrease</u> the entropy of a system, but we believe this can only be done at the expense of a greater increase in the entropy of the surroundings. This means that in the passage of any interval of time.

$$\boxed{\Delta S(\text{total}) > 0}$$

You may like to reflect on the philosophical significance of this statement as regards the nature of time and the future of our universe. (Does it mean that we are inexorably moving towards a state of maximum entropy where energy and atoms are totally and randomly dispersed - the so-called 'heat-death'?) However, it is of more relevance to your A-level studies to focus on entropy changes within a defined system. Since

$$\Delta S\text{(total)} = \Delta S\text{(system)} + \Delta S\text{(surroundings)}$$

we can say that

$$\boxed{\Delta S\text{(system)} + \Delta S\text{(surroundings)} > 0}$$

and therefore that, in many cases, ΔS(system) > 0.

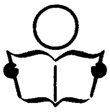
Thus, just as the enthalpy of a reacting system often (but not always) decreases ($\Delta H^\ominus$ negative), so the entropy often increases ($\Delta S^\ominus$ positive).

Objectives. When you have finished this section, you should be able to:

(30) explain, in simple terms, the differences in entropy between solids and liquids, and between liquids and gases;

(31) state whether the standard entropy change for a given reaction is positive or negative.

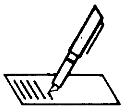
Read about entropy in your text-book(s). Don't worry if you still feel a little uncertain about the nature of entropy. The way you use values of entropy is very simple, and when you have mastered that, you may wish to return to your text-book and also re-read the preceding pages of this Unit.



Now try the next two exercises.

Exercise 37 Does the entropy of a substance increase or decrease when its temperature is raised? Explain your answer.

(Answer on page 96)



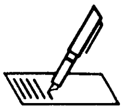
Exercise 38 Look up and record the values of $S^\ominus$ at 298 K for the following substances:

(a) iodine(s) (d) water(l)

(b) bromine(l) (e) water(g)

(c) chlorine(g)

(Answers on page 96)



Whenever you use tables of entropy, you should bear in mind three points.

1. The tabulated entropy values give the entropy of one mole of substance in its standard state.
2. The unit is J K^{-1} mol^{-1} (not kJ K^{-1} mol^{-1}).
3. These are actual entropy values, not entropy changes.

If we can look up entropy values for reactants and products, it is a simple matter to calculate $\Delta S^\ominus$, but first we consider how to predict whether $\Delta S^\ominus$ is positive or negative without reference to tables.

Predicting entropy changes

We consider five examples.

1. $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$

   Gases have much higher values of entropy than solids because they are less ordered and energy is more dispersed. The conversion of gas to solid, as in this example, is therefore accompanied by a large decrease in entropy.

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

   Here there is a large decrease in entropy because three moles of gas form two moles of liquid. Liquids have lower values of entropy because they are more ordered and energy is more localised.

3. $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

   Here there is a decrease in entropy because three moles of gas form two moles and the system becomes more ordered. However, the entropy decrease is not so great as in Example 2.

4. $N_2O_4(g) \rightarrow 2NO_2(g)$

   In this reaction, one mole of gas forms two moles of gas. Therefore, the entropy increases.

5. $H_2O(l) \rightarrow H_2O(g)$

   Here one mole of liquid forms one mole of gas. Therefore, the entropy increases.

To see if you can apply this to an examination question, try the next exercise.

Exercise 39 For each of the following reactions, indicate whether the entropy is likely to increase, decrease or stay the same, explaining your reasoning.

A part

(a) $H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$

(b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(c) $2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$

(Answers on page 96)

You can confirm the predictions made in the examples and in the Exercise by calculating the entropy changes.

Calculating entropy changes

Objective. When you have finished this section, you should be able to:

(32) calculate $\Delta S^{\ominus}$ for a process from tabulated values of $S^{\ominus}$.

Because entropy is a function like enthalpy, we can calculate the entropy change for a process by the relation

$$\Delta S^{\ominus} = S^{\ominus}\,(\text{products}) - S^{\ominus}\,(\text{reactants})$$

We illustrate this by a Worked Example.

Worked Example. Calculate the standard entropy change for the reaction

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$

Solution

1. Look up the value of $S^\ominus$ for each substance, multiply it by the number of moles in the reaction, and put this value under the formula.

	$2Cu(s)$	+	$O_2(g)$	$\rightarrow$	$2CuO(s)$
$S^\ominus$/J K^{-1} mol^{-1}	(2 x 33.3)		(204.9)		(2 x 43.5)

2. Calculate the total entropy of the products.

$$S^\ominus\ [\text{products}] = 2 \times 43.5\ \text{J K}^{-1}\ \text{mol}^{-1} = 87.0\ \text{J K}^{-1}\ \text{mol}^{-1}$$

3. Calculate the total entropy of the reactants.

$$S^\ominus\ [\text{reactants}] = ((2 \times 33.3) + 204.9))\ \text{J K}^{-1}\ \text{mol}^{-1} = 271.5\ \text{J K}^{-1}\ \text{mol}^{-1}$$

4. Calculate the entropy change by subtraction.

$$\Delta S^\ominus = S^\ominus\ [\text{products}] - S^\ominus\ [\text{reactants}] = (87.0 - 271.5)\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$= \boxed{-184.5\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

Now work out some values of $\Delta S^\ominus$ for yourself.

Exercise 40 Calculate $\Delta S^\ominus$ for the reactions in Exercise 39.

(Answers on page 96)

Exercise 41 Predict whether $\Delta S^\ominus$ will be positive or negative for each of the following reactions. In at least one example, check your prediction by calculation.

(a) $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$

(b) $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

(c) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

(d) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

(e) $2C(s) + O_2(g) \rightarrow 2CO(g)$

(Answers on page 96)

Now that you know how to calculate $\Delta S^\ominus$, you can use the value to calculate $\Delta G^\ominus$ in order to see whether or not a reaction is possible.

Using $\Delta S^\ominus$ to calculate $\Delta G^\ominus$

You already know that the standard free energy change, $\Delta G^\ominus$, is related to enthalpy and entropy changes by the equation

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

and that, for a reaction to be possible, $\Delta G^\ominus$ must be substantially negative. We now show you how to predict the feasibility of a reaction by calculating $\Delta G^\ominus$.

Objectives. When you have finished this section, you should be able to:

(33) calculate $\Delta G^\ominus$ for a process given tables of $\Delta H^\ominus$ and $S^\ominus$ values;

(34) use calculated values of $\Delta G^\ominus$ to determine if a process is possible.

We start with a Worked Example.

Worked Example Calculate the standard free energy change, $\Delta G^\ominus$, for the process

W

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

at 25°C, using the following values of standard enthalpy formation and entropy.

Table 9

	$\Delta H_f^\ominus$/kJ mol^{-1}	$S^\ominus$/J K^{-1} mol^{-1}
$CaO(s)$	-636.5	39.7
$Ca(OH)_2(s)$	-986.6	76.1
$H_2O(l)$	-285.9	70.0

Solution

1. Calculate the standard enthalpy change.

$$\Delta H^\ominus = \Delta H_f^\ominus \text{ [products]} - \Delta H_f^\ominus \text{ [reactants]}$$
$$= -986.6 \text{ kJ mol}^{-1} - (-635.5 - 285.9) \text{ kJ mol}^{-1}$$
$$= (-986.6 + 921.4) \text{ kJ mol}^{-1} = -65.2 \text{ kJ mol}^{-1}$$

2. Calculate the standard entropy change.

$$\Delta S^\ominus = S^\ominus \text{ [products]} - S^\ominus \text{ [reactants]}$$
$$= 76.1 \text{ J K}^{-1} \text{ mol}^{-1} - (39.7 + 70.0) \text{ J K}^{-1} \text{ mol}^{-1}$$
$$= (76.1 - 109.7) \text{ J K}^{-1} \text{ mol}^{-1} = -33.6 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0336 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Note the change of unit from J to kJ. This is necessary for the next step.

3. Substitute into the expression for $\Delta G^\ominus$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$
$$= -65.2 \text{ kJ mol}^{-1} - (298 \text{ K} \times 0.0336 \text{ kJ K}^{-1} \text{ mol}^{-1})$$
$$= (-65.2 - 10.0) \text{ kJ mol}^{-1} = \boxed{-75.2 \text{ kJ mol}^{-1}}$$

The negative value of $\Delta G^\ominus$ indicates that at 25°C and 1.00 atm, this reaction can proceed spontaneously (although it may, of course, be slow).

Now try some similar calculations for yourself.

Exercise 42 Calculate the standard free energy change, $\Delta G^\ominus$, accompanying each of the following processes at 25°C.

(a) $2NO(g) + O_2(g) \rightarrow N_2O_4(g)$

(b) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

(c) $H_2O(l) \rightarrow H_2O(g)$

(Answers on page 97)

You may have realised that it would have been simpler to calculate $\Delta G^\ominus$ in the last exercise using the expression you met in Level One.

$$\Delta G^\ominus = \Sigma\Delta G_f^\ominus\,[\text{products}] - \Sigma\Delta G_f^\ominus\,[\text{reactants}]$$

However, the great advantage of using $\Delta H^\ominus$ and $\Delta S^\ominus$ is that you can calculate $\Delta G^\ominus$ at temperatures other than 298 K as we show in the next section.

Temperature and spontaneous processes

You would expect $\Delta G^\ominus$ to vary considerably with temperature because of the form of the equation

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

This variation means that some processes which are not possible at low temperatures become feasible at higher temperatures, and vice versa. For an example, consider the familiar process

$$H_2O(l) \rightarrow H_2O(g)$$

You know that this change does not occur to completion (in a closed system) at 25°C but that it proceeds spontaneously at temperatures above 100°C. This shows that $\Delta G^\ominus$ has very different values at different temperatures.

Note that the variation of $\Delta G^\ominus$ with temperature is quite separate from the fact that an increase in temperature increases the rate of reaction. Remember that thermodynamics tells us nothing at all about how fast a feasible reaction will occur.

Objectives. When you have finished this section, you should be able to:

(35) calculate $\Delta G^\ominus$ for a stated reaction at any temperature;

(36) explain why many endothermic reactions are possible only at high temperatures.

To calculate $\Delta G^\ominus$ at a temperature other than 25 °C we should, strictly speaking, use values of $\Delta H^\ominus$ and $\Delta S^\ominus$ at the appropriate temperature. Fortunately, the variation of $\Delta H^\ominus$ and $\Delta S^\ominus$ with temperature is small enough for us to ignore in this context.

Exercise 43 Calculate $\Delta G^{\ominus}$ (1000 K) for the following reactions and compare with given values of $\Delta G^{\ominus}$ (298 K). State whether or not the reactions are feasible at each temperature.

(a) $2NO(g) + O_2(g) \rightarrow N_2O_4(g)$; $\Delta G^{\ominus}$ (298 K) = -75.6 kJ mol^{-1}

(b) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$; $\Delta G^{\ominus}$ (298 K) = -92.3 kJ mol^{-1}

(c) $H_2O(l) \rightarrow H_2O(g)$; $\Delta G^{\ominus}$ (298 K) = $+8.6$ kJ mol^{-1}

(d) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$; $\Delta G^{\ominus}$ (298 K) = $+130.2$ kJ mol^{-1}
(calcite)

(Answers on page 97)

Exercise 44 (a) In what circumstances can an endothermic reaction take place spontaneously?

(b) Explain why, in the majority of cases, $\Delta H^{\ominus}$ provides an indication of the feasibility of a reaction at 298 K.

(Answers on page 97)

In the rest of your course, you will often use $\Delta H^{\ominus}$ as an indication of the stability of a substance, i.e. to indicate whether a certain reaction is likely to occur. You should now realise that $\Delta G^{\ominus}$ provides a better indication than $\Delta H^{\ominus}$ and should be used if data is available.

In order to consolidate your understanding of the use of $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ as guides to the feasibility of a reaction, your teacher may wish you to attempt the following Teacher-marked Exercise, which is taken from a Special Paper.

✓

Teacher-marked Exercise 'Not all exothermic reactions are spontaneous; some endothermic changes are spontaneous.'

A

Discuss the extent to which a knowledge of the enthalpy change for a reaction is a guide to its ability to proceed.

Illustrate your answer by considering FOUR reactions of varied type, TWO of which are exothermic, and TWO endothermic.

You may wish to consider some or all of the following reactions or others of your own choice.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

LEVEL TWO CHECKLIST

You have now reached the end of this Unit. In addition to what was listed at the end of Level One, you should now be able to:

(16) and (17) state what is meant by bond energy term and bond dissociation energy;

(18) calculate the bond energy term for a molecule using standard heat of formation data and standard enthalpy of atomization data;

(19) and (20) describe briefly how heats of combustion of a series of alcohols can be measured and interpret the results in terms of bond-breaking and bond-making;

(21) use bond energy terms to estimate enthalpy changes that cannot be determined directly;

(22) define lattice energy;

(23) and (24) construct a Born-Haber cycle for an ionic compound and use it to calculate the lattice energy;

(25) predict the stoichiometry of a compound using calculated values of standard enthalpy of formation;

(26) perform a thermometric titration in order to determine the enthalpy change of a reaction;

(27) define standard enthalpy change of neutralisation;

(28) state the equation relating $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$, the standard free energy change;

(29) state how the value of $\Delta G^{\ominus}$ determines the feasibility of a reaction;

(30) explain, in simple terms, the differences in entropy between solids and liquids and between liquids and gases;

(31) state whether the standard entropy change, $\Delta S^{\ominus}$, for a given reaction is positive or negative;

(32) calculate $\Delta S^{\ominus}$ for a process from tabulated values of $S^{\ominus}$;

(33) and (34) calculate $\Delta G^{\ominus}$ for a process from tabulated values of $\Delta H^{\ominus}$ and $S^{\ominus}$, and use it to determine whether a process is feasible;

(35) calculate $\Delta G^{\ominus}$ for a stated reaction at any temperature;

(36) explain why many endothermic reactions are possible only at high temperatures.

Check that you have adequate notes before going on to the End-of-Unit Test.

END-OF-UNIT TEST

To find out how well you have learned the material in this Unit, try the test which follows. Read the notes below before starting.

1. You should spend about $1\frac{1}{2}$ hours on this test.
2. You will need a sheet of graph paper and a data book.
3. Hand your answers to your teacher for marking.

END-OF-UNIT TEST

For questions 1-4, select the best answer from those given, A-E.

1. Which change would have a negative ΔH value?

A

A $Na(s) \rightarrow Na(g)$ D $Cl_2(g) \rightarrow 2Cl(g)$

B $Na(g) \rightarrow Na^+(g)$ E $Cl(g) \rightarrow Cl^-(g)$

C $Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g)$ (1)

2. For the reaction

A

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$, $\Delta H^{\ominus}_{298} = -242$ kJ

the enthalpies of dissociation of hydrogen and oxygen are given by

$H_2(g) \rightarrow 2H(g)$ $\Delta H^{\ominus}_{298} = +436$ kJ mol^{-1}

$O_2(g) \rightarrow 2O(g)$ $\Delta H^{\ominus}_{298} = +500$ kJ mol^{-1}

The bond energy of the O—H bond in water is

A +121 kJ B +242 kJ C +444 kJ D +464 kJ E +589 kJ (1)

3. For which equation is the energy change called the bond energy term of the C—H bond?

A

A $\frac{1}{4}CH_4(g) \rightarrow \frac{1}{4}C(g) + H(g)$ D $\frac{1}{4}CH_4(g) \rightarrow \frac{1}{4}C(s) + \frac{1}{2}H_2(g)$

B $CH_4(g) \rightarrow C(s) + 2H_2(g)$ E $CH_4(g) \rightarrow C(g) + 2H_2(g)$

C $CH_4(g) \rightarrow C(g) + 4H(g)$ (1)

4. The lattice energy of magnesium chloride is numerically equal to the energy change for the reaction

A

A $Mg^{2+}(s) + 2Cl^-(s) \rightarrow MgCl_2(s)$

B $Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(g)$

C $Mg(g) + Cl_2(g) \rightarrow MgCl_2(g)$

D $Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s)$

E $Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow MgCl_2(s)$ (1)

In Questions 5 to 8 inclusive, one, more than one, or none of the suggested responses may be correct. Answer as follows:

A if only 1, 2 and 3 are correct

B if only 1 and 3 are correct

C if only 2 and 4 are correct

D if only 4 is correct

E if some other response, or combination, is correct.

5. The heat of combustion of a liquid may be measured by burning the liquid in a spirit burner and drawing the products of combustion through a copper tube immersed in a calorimeter. A result LOWER than the correct value for the heat of combustion would be obtained if:

A

1 some of the liquid evaporates from the wick of the burner after use but before the final weighing

2 the flame deposits some soot in the calorimeter

3 the temperature of the waste gases leaving the calorimeter is a little above the temperature of the water in the calorimeter

4 some water condenses in the calorimeter (1)

6. Which of the following would be necessary to calculate the value of $\Delta H^{\ominus}_{f}(298)$ for a hypothetical ionic compound consisting of only two elements?

A

1 the lattice energy of the compound

2 the electron affinity of the non-metallic element

3 the ionization energy of the metallic element

4 the heats of hydration of the ions of its elements (1)

7. Which of the following data are necessary to calculate the overall enthalpy change for $\frac{1}{2}Cl_2(g) \rightarrow Cl^-(aq)$?

A

1 the hydration energy of Cl^- ions

2 the electron affinity of chlorine

3 the heat of atomization of chlorine

4 the first ionization energy of chlorine (1)

8. Which of the following experimentally determined quantities requires MORE THAN ONE thermochemical experiment?

A

1 the lattice energy of calcium chloride

2 the heat of formation of methane

3 the energy required to atomise 1 mol of dimethyl ether, $(CH_3)_2O$

4 the heat of combustion of decanol (1)

For questions 9 and 10, choose an answer from A to E as follows:

A Both statements true: second explains first.

B Both statements true: second does not explain first.

C First true: second false.

D First false: second true.

E Both false.

	First statement	Second statement	
9.	The standard enthalpy of formation of a compound has the same numerical value as the enthalpy of atomization of the compound, but is opposite in sign.	The formation of a compound from its elements in their standard states involves the release of an amount of energy equal to the sum of all the bond energy terms in the compound.	A (1)

10. The standard free energy changes of all spontaneously occurring reactions are positive in value.

The standard free energies of the elements in their standard states and at 760 mmHg pressure and 298 K are taken as zero.

A

(1)

11. The following table lists the enthalpy changes of combustion of several monohydric alcohols.

A

Table 10

alcohol	$\Delta H^\ominus_c$/kJ mol^{-1}
methanol	- 715
ethanol	-1367
propan-1-ol	-2017
butan-1-ol	-2675

(a) Draw a plot of $\Delta H^\ominus_c$ against the relative molecular mass of the alcohols. (3)

(b) From your graph estimate a value for the enthalpy change of combustion of pentan-1-ol. (2)

(c) Given $\Delta H^\ominus_f$ [$H_2O(l)$] = -286 kJ mol^{-1} and $\Delta H^\ominus_f$ [$CO_2(g)$] = -394 kJ mol^{-1}, calculate the standard enthalpy change of formation of ethanol. (3)

(d) The enthalpy change of combustion of ethane-1,2-diol is -1180 kJ mol^{-1}. What would you expect the corresponding value for propane-1,3-diol to be? (1)

In the next question you need to know that the structural formula of ethene is $H_2C{=}CH_2$.

12. (a) Define:

A

(i) standard enthalpy of formation;

(ii) standard enthalpy of combustion. (2)

(b) The standard enthalpy changes, in kJ mol^{-1}, of the following reactions refer to a temperature of 298 K

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H^\ominus = -394$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H^\ominus = -286$

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$; $\Delta H^\ominus = -1411$

Calculate the standard enthalpy of formation of ethene, C_2H_4. (4)

(c) If, at 298 K, the enthalpy of sublimation of graphite is 713 kJ mol^{-1} and the bond energy terms H-H and C-H are 436 and 415 kJ mol^{-1} respectively, calculate the C=C bond energy term. (7)

(d) When ethene is burned in oxygen, does the entropy increase, decrease or stay the same? Explain your answer. Assume that the reactants and products are at 298 K. (2)

13. The diagram shows in outline, and not to scale, the 'Born-Haber' cycle for one mole of magnesium oxide. Some of the information has been left out.

A

The relevant data from which the cycle is constructed are:

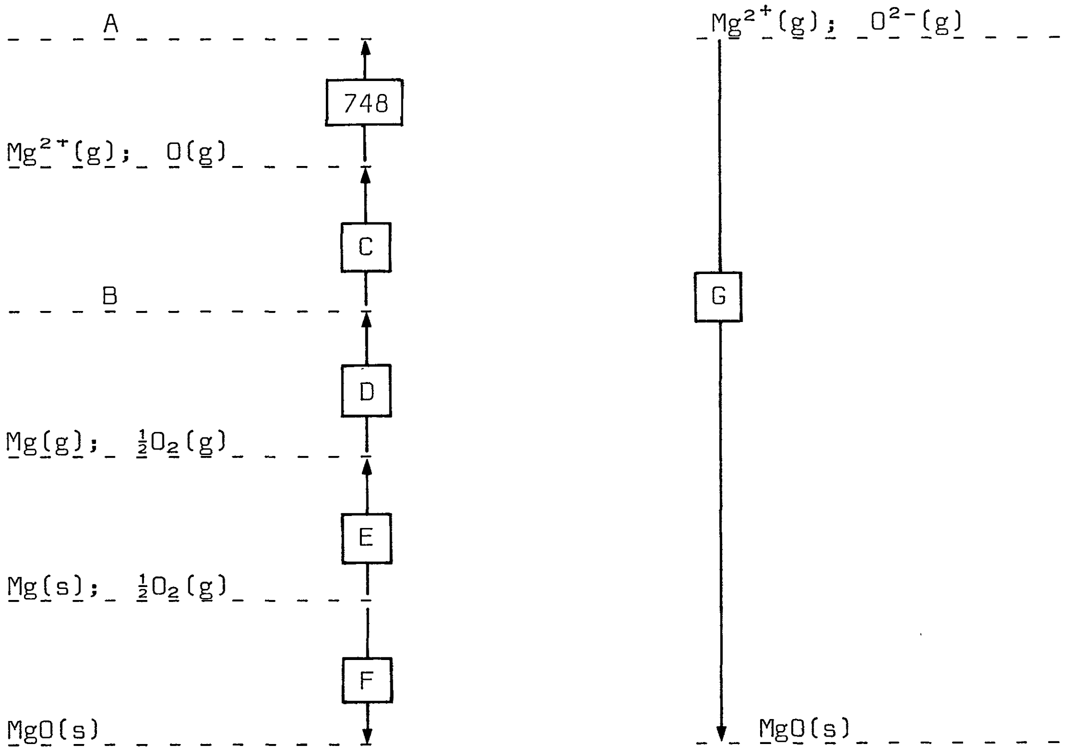
Standard enthalpy of formation of magnesium oxide = -610 kJ mol^{-1}

Sublimation energy of magnesium = +153 kJ mol^{-1}

Sum of first two ionization energies of magnesium = +2178 kJ mol^{-1}

Dissociation energy of oxygen = +250 kJ mol^{-1} (of oxygen atoms formed)

Electron affinity of oxygen (for two electrons gained) = +748 kJ mol^{-1}



(a) Complete the diagram by inserting the appropriate energies in the empty squares and the appropriate formulae on the dotted lines. (7)

(b) State what is meant by the 'lattice energy' of magnesium oxide and compute its value. (5)

14. In an experiment to determine the enthalpy of neutralization of sodium hydroxide with sulphuric acid, 50 cm^3 of 0.40 M sodium hydroxide was titrated, thermometrically, with 0.50 M sulphuric acid. The results were plotted as follows:

A part

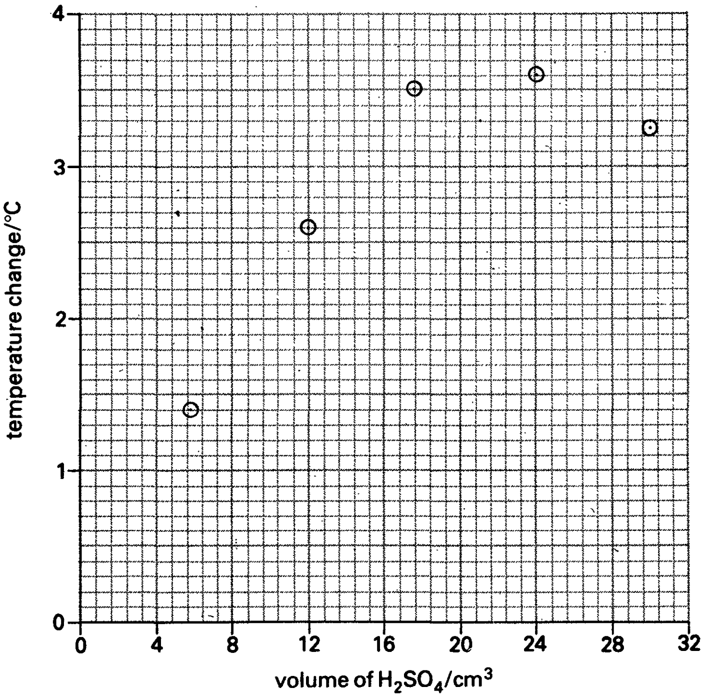


Fig. 12.

(a) Define 'enthalpy of neutralization'. (2)

(b) What is a thermometric titration? (1)

(c) Describe, or draw a labelled diagram of, the apparatus you would use for such a titration. (2)

(d) How do you account for the shape of the graph? (2)

(e) Calculate a value for the enthalpy of neutralization of sodium hydroxide with sulphuric acid. (The specific heat capacity of water is 4.2 J K^{-1} g^{-1}.) What assumptions have you made in your calculations? (5)

15. (a) Calculate the standard entropy change and standard free energy change at 298 K accompanying the following process:

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g); \quad \Delta H^\ominus = -112 \text{ kJ mol}^{-1}$$

given the following table of standard entropy values.

Table 11

Substance	$S^\ominus$/J mol^{-1} K^{-1}
CO(g)	198
COCl (g)	289
Cl_2(g)	233

(5)

(b) Would you expect this reaction to be feasible (i) at 298 K, and (ii) at very high temperatures? (2)

(Total 65 marks)

APPENDIX ONE

THE BOMB CALORIMETER

The apparatus and procedures you used to determine the enthalpy change of combustion in Experiment 4 are capable of giving reasonable but not highly accurate results. For more accurate results a bomb calorimeter is used.

Objective. When you have finished this section, you should be able to:

(37) describe the bomb calorimeter.

For a description of the bomb calorimeter and how it works read your text-book. Look out for the difference in the conditions of pressure between the bomb calorimeter and the enthalpy of combustion apparatus you used in Experiment 4.

Exercise 45 Fig. 13 represents a bomb calorimeter.

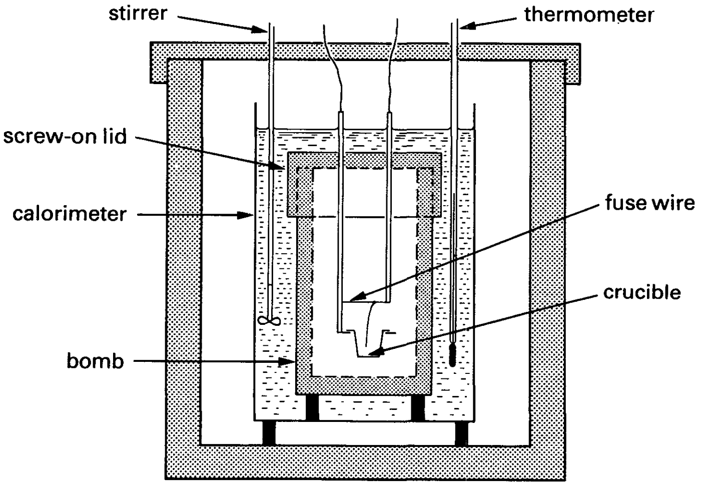


Fig. 13. A bomb calorimeter.

(a) What substance would be put into:

(i) the crucible, (ii) the bomb, (iii) the calorimeter?

(b) How is the combustion initiated?

(c) Why is the energy produced by the complete combustion of one mole of the substance in this apparatus not the same as the enthalpy change of combustion of the substance? (Hint: see page 7 for conditions of pressure for measuring ΔH.)

(Answers on page 98)

Under the conditions of constant volume employed in the bomb, the energy change measured is known as the internal energy change (symbol: ΔU), and not enthalpy change, ΔH. However, the value of ΔU can be converted to ΔH using the expression:

$$\Delta H = \Delta U + \Delta n\ RT$$

where T = average water temperature in the calorimeter

R = gas constant

Δn = increase in number of moles of gases during the reaction

This expression is derived in Appendix Two.

APPENDIX TWO

INTERNAL ENERGY CHANGE, ΔU

The symbol *U* represents a property called the internal energy which, like *H*, has a definite value for a given system in a given state.

Objectives. When you have finished this section, you should be able to:

(38) explain the term internal energy change;

(39) derive the equation relating ΔH to ΔU and use it in calculations.

Consider the same reaction

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

taking place in each set of apparatus shown in Fig. 14. In (a) the tap is open, in (b) it is closed

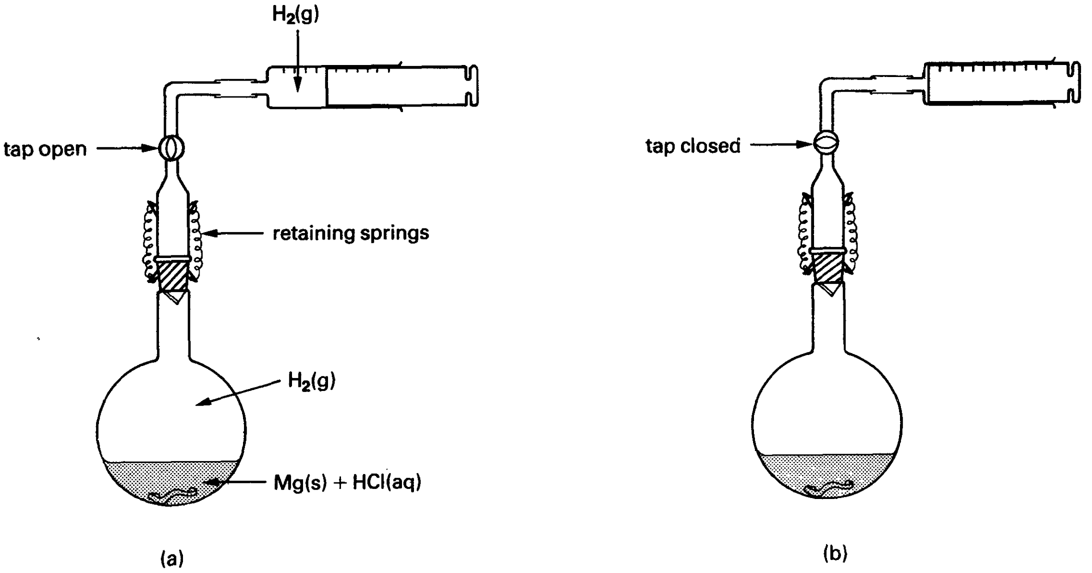


Fig. 14.

Let us suppose that equal amounts of reactants are used in each case, and that it is possible to measure the heat given out to the surroundings in cooling to the original temperature. Do you think the quantities of heat given out in (a) and (b) will be the same? Give this a few moments thought before going on.

In fact, a little more heat will be given out in (b) where the evolved gas is unable to expand into the syringe. The reason is this: in (a) the evolved gas will push the piston of the syringe outwards against the pressure of the atmosphere, i.e. it will do work against the atmosphere; this will use up some of the energy which would otherwise be given out as heat. In (b) the reaction takes place at constant volume, and no work is done against the atmosphere; thus, more energy is available for evolution as heat than in (a).

In (a) the heat given out at constant pressure is called an enthalpy change (symbol: ΔH), an energy change with which you should now be familiar.

In (b) the heat given out at constant volume is called an internal energy change (symbol: ΔU). This is the energy change which is measured in a bomb calorimeter. (See Appendix One.)

The reaction in Fig. 14 was one in which gas is evolved. For a reaction in which gas is used up, the system contracts at constant pressure and, in this case, the atmosphere does work on the system so that the enthalpy change ΔH is numerically greater than the internal energy change ΔU.

Relationship between ΔU and ΔH

The first law of thermodynamics (the law of conservation of energy) states that in any conversion of energy from one form to another, or to heat or to work, no energy is either created or destroyed. (There are many alternative ways of expressing this as you will find when reading different text-books.)

An important consequence of this law is that for a system undergoing a change in its internal energy, the total work and/or heat changes involved must equal the change in internal energy.

This can be expressed as

$$\Delta U = \Delta H - w \text{ .... } (1)$$

where w is the work done by the system against the atmosphere. (w is negative if the atmosphere does work on the system, as in a reaction where gas is used up.)

Note that the difference between ΔH and ΔU is only significant for reactions involving changes in the amounts of gases present. The small volume changes encountered in most other reactions mean that, in elementary work, the difference between ΔH and ΔU may be ignored.

We now show you how we can convert expression (1) into a form which will enable us to calculate ΔU values from given ΔH values and vice versa.

For a reaction taking place at constant (atmospheric) pressure, the work done against atmosphere, w, is given by

$$w = \text{force} \times \text{distance}$$

Dividing and multiplying by area,

$$w = \frac{\text{force}}{\text{area}} \times \text{distance} \times \text{area}$$

$$= \text{pressure} \times \text{volume change} = p\Delta V$$

So, the relationship (1) becomes

$$\Delta U = \Delta H - p\Delta V \text{ .... } (2)$$

Now the pressure, volume and temperature of an amount of gas are related by the ideal gas equation,

$$pV = nRT \;\dots\dots\dots\dots\; (3)$$

where R is the universal gas constant. (You will study this equation further in Unit P1: The Gaseous State.) For a reaction at constant pressure and temperature where the increase in volume is ΔV and the increase in the amount of gas is Δn, equation (3) becomes

$$p\Delta V = \Delta nRT$$

Substituting this expression into equation (2) gives

$$\Delta U = \Delta H - \Delta nRT$$

For the reaction at constant pressure and 298 K:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g); \quad \Delta H^\ominus = -463 \text{ kJ mol}^{-1}$$

$$\Delta n = +1 \text{ mol}, \; T = 298 \text{ K}, \; R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \text{ and } \Delta H = -463 \text{ kJ}$$

$$\therefore \; \Delta U = \Delta H - \Delta nRT = -463 \text{ kJ} - (1 \text{ mol} \times \frac{8.3}{1000} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

$$= (-463 - 2.47) \text{ kJ} = -465 \text{ kJ and } \Delta U^\ominus = \boxed{-465 \text{ kJ mol}^{-1}}$$

Note that even in a reaction involving the production of gas, the difference between $\Delta U^\ominus$ and $\Delta H^\ominus$ is seldom great.

Now try some similar calculations for yourself.

Exercise 46 Calculate $\Delta U^\ominus$ for the reactions:

(a) $BaCO_3(s) \rightarrow BaO(s) + CO_2(g); \quad \Delta H^\ominus = +267 \text{ kJ mol}^{-1}$

(b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \quad \Delta H^\ominus = -92 \text{ kJ mol}^{-1}$

(c) $C_6H_6(l) + 3H_2(g) \rightarrow C_6H_{12}(l); \quad \Delta H^\ominus = -208 \text{ kJ mol}^{-1}$

(Answers on page 98)

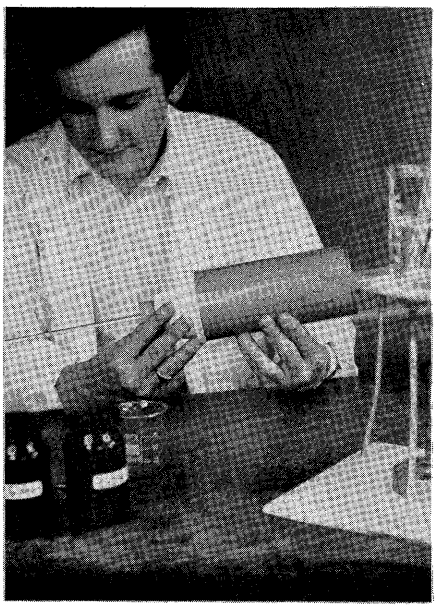
APPENDIX THREE

ANOTHER PRACTICAL APPLICATION OF HESS'S LAW

This determination of an enthalpy change which cannot be measured directly is an alternative to Experiment 3. You use better apparatus, but you need to work more carefully and the calculation is a little more difficult.

EXPERIMENT 6

Using Hess's law



Aim

The purpose of this experiment is to determine the enthalpy change for the reaction

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4{\cdot}5H_2O(s)$$

Introduction

Because $CuSO_4(s)$ is slow to dissolve, and $\Delta H^{\ominus}$ is small, it is best to do this experiment in a vacuum flask. However, the flask has a measurable heat capacity which you must determine before you proceed with the experiment.

To calculate the required enthalpy change, you perform two 'heat of solution' determinations. You should calculate the masses of the salts and water required. Base your calculations on the following equations:

$$CuSO_4(s) + 100H_2O(l) \rightarrow CuSO_4(aq, 100H_2O)$$

$$CuSO_4{\cdot}5H_2O(s) + 95H_2O(l) \rightarrow CuSO_4(aq, 100H_2O)$$

and use 0.025 mol of the appropriate salt in each of the determinations. Show your calculations to your teacher just in case you have made an error which would spoil your laboratory work.

Requirements

safety spectacles
vacuum flask with thermometer fitted
pipette, 50 cm^3
distilled water
2 beakers, 100 cm^3
Bunsen burner, tripod, gauze and bench mat
thermometer, 0-100 °C
access to balance (weighing to nearest 0.01 g)
2 weighing bottles
spatula
anhydrous copper(II) sulphate, $CuSO_4$
copper(II) sulphate-5-water, $CuSO_4{\cdot}5H_2O$, finely ground beforehand

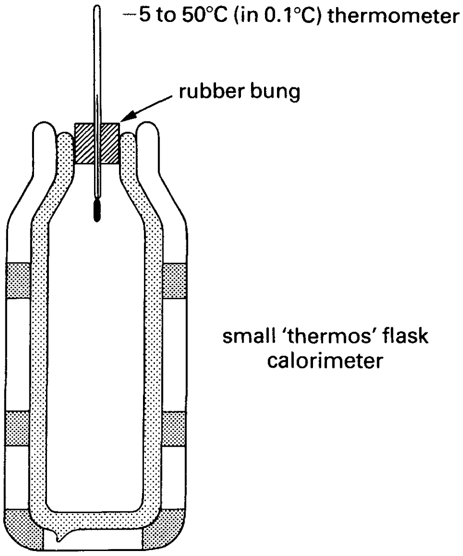


Fig. 15.

Procedure

A. Determination of the heat capacity of the vacuum flask

1. Check that the inside of the vacuum flask is dry and pipette into it 50 cm^3 of distilled water at room temperature.
2. Place the thermometer-fitted bung in position and shake gently. Make sure that the entire inside surface of the flask is wet. To read the steady temperature, hold the bung firmly in and turn the flask on its side so that the water covers the mercury reservoir of the thermometer. Read the steady temperature to the nearest 0.1°C. Leave the bung and thermometer in position.
3. Pipette 50 cm^3 of distilled water into a clean, dry 100 cm^3 beaker and heat it gently till its temperature reaches about 40°C - use a small 0-100°C thermometer. Remove from heat.
4. Use the thermometer from the vacuum flask (with bung still fitted) to gently stir the water in the beaker to ensure its temperature is uniform throughout. Record this temperature to the nearest 0.1°C.
5. Immediately pour all of the warmed distilled water into the vacuum flask, close with bung and thermometer, shake gently and note the steady temperature to the nearest 0.1°C. Remember to wet the inside surface and tilt the flask to read the temperature as before.
6. Complete Results Table 7 and then, if you have time, repeat the procedure. It is good practice to do the determination twice and average the results. Furthermore, because this is the first time you have done such an experiment, the second determination should improve your technique.
7. To make best use of laboratory time, we suggest that you complete parts B and C of the experiment before calculating the heat capacity of the flask.

Results Table 7

Mass of cold water in vacuum flask	g	g
Mass of warm water added	g	g
Initial temperature of flask and cold water	°C	°C
Initial temperature of warm water	°C	°C
Final temperature of flask and mixture	°C	°C

The specific heat capacity of water is 4.18 kJ kg^{-1} K^{-1}.

The density of water is 1.00 g cm^{-3}.

B. Heat of solution of $CuSO_4(s)$

1. Rinse the inside of the vacuum flask with distilled water and drain well.
2. Weigh the calculated quantity of anhydrous copper(II) sulphate ($CuSO_4$), to the nearest 0.01 g, into a clean dry weighing bottle. (Do not keep bottle lids and/or stoppers off longer than is necessary. Why not?)
3. Weigh the appropriate calculated quantity of water, to the nearest 0.1 g, into a dry 100 cm^3 beaker, and then pour this water into the vacuum flask. (If the balance you are using has sufficient overall weighing capacity, you may weigh the water directly into the vacuum flask - why is it better to do this?) Close with bung and thermometer, shake, and note the steady temperature, tilting the flask as before.
4. Remove the bung and thermometer from the vacuum flask and quickly and carefully tip all of the weighed sample of anhydrous copper(II) sulphate into the water. Replace the bung and thermometer, shake to dissolve the salt, and note the temperature once it has become steady. This last step may take up to 15 mins (shaking periodically) because the anhydrous salt is often very slow to dissolve.
5. Complete Results Table 8 and then move on to part C.

Results Table 8

Mass of anhydrous copper(II) sulphate	g
Mass of water	g
Initial temperature of vacuum flask and water	°C
Maximum temperature of vacuum flask and solution	°C

C. Heat of solution of $CuSO_4 \cdot 5H_2O(s)$

Wash out your apparatus and then repeat the procedure in part B using the hydrated salt ($CuSO_4 \cdot 5H_2O$). In this second determination the salt dissolves quickly in step 4 and the final steady temperature will be obtained within half a minute. Complete Results Table 9.

Results Table 9

Mass of copper(II) sulphate-5-water	g
Mass of water	g
Initial temperature of vacuum flask and water	°C
Maximum temperature of vacuum flask and solution	°C

Calculation A (heat capacity of flask)

1. Since the flask is insulated, no heat energy is transferred between system and surroundings (in this case, the flask is part of the system). Therefore you can write:

$$\begin{bmatrix}\text{Change in heat}\\ \text{energy of flask}\end{bmatrix} + \begin{bmatrix}\text{Change in heat}\\ \text{energy of cold water}\end{bmatrix} + \begin{bmatrix}\text{Change in heat}\\ \text{energy of warm water}\end{bmatrix} = 0$$

2. In each case, the change in heat energy = heat capacity x ΔT

   and for the water, heat capacity = mass x specific heat capacity

   = mass x 4.18 $\mathrm{kJ\ kg^{-1}\ K^{-1}}$

3. Substitute values from Results Table 7 into these expressions and so obtain a value for the heat capacity, C, of the flask. Remember that ΔT is positive for the flask and the cold water but negative for the hot water, and also that the mass must be in kg.

Calculations B and C (enthalpy changes)

1. Again, there is no heat energy transfer between system and surroundings so that:

$$\begin{bmatrix}\text{Change in heat}\\ \text{energy of flask}\end{bmatrix} + \begin{bmatrix}\text{Change in heat}\\ \text{energy of contents}\end{bmatrix} + \begin{bmatrix}\text{Enthalpy change}\\ \text{of solution}\end{bmatrix} = 0$$

2. Use this expression and values from Results Tables 8 and 9 to obtain the enthalpy changes for dissolving the weighed amounts of the two salts. Ignore the very small heat capacities of the salts, i.e. use the mass and specific heat capacity of the water in your calculations.
3. Scale up to the amounts shown in the equations.
4. Use Hess's law to calculate the required standard enthalpy change.

(Speciment results and calculations are on page 98)

Questions

1. Suggest a reason why it would be difficult to determine, by direct experiment, $\Delta H^{\ominus}$ for the reaction

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4{\cdot}5H_2O(s)$$

2. Why is it good practice to replace the stoppers/lids of chemical bottles as soon as possible?
3. Why, in step 3 of part B of the experiment, would it better to weigh the water directly into the vacuum flask rather than in a beaker?

(Answers on page 98)

ANSWERS

(Answers to questions from examination papers are provided by ILPAC and not by the Examination Boards.)

Exercise 1

Standard conditions are: T = 298 K (25 °C), p = 1.00 atm, c = 1.00 mol dm^{-3}

Exercise 2

(a) (i) exothermic (iii) exothermic (v) endothermic

(ii) endothermic (iv) exothermic

(b) An increase in any quantity X gives a positive value for ΔX. In an endothermic reaction heat energy must be transferred from the surroundings to the system to maintain constant temperature, i.e. the standard enthalpy ($H^\ominus$) of the system increases and $\Delta H^\ominus$ is positive. Similarly, in an exothermic reaction, the enthalpy of the system decreases and $\Delta H^\ominus$ is negative.

Exercise 3

The energy level diagram shows that

$2H_2O(g) \rightarrow 2H_2O(l)$; $\Delta H^\ominus = -(572 - 484)$ kJ mol^{-1} = -88 kJ mol^{-1}

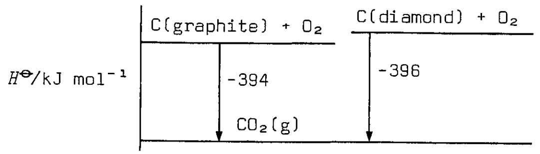
or, for one mole, $\boxed{H_2O(g) \rightarrow H_2O(l);\ \Delta H^\ominus = -44 \text{ kJ mol}^{-1}}$

Exercise 4

(a) C(graphite) + $O_2(g) \rightarrow CO_2(g)$; $\Delta H^\ominus$ = -394 kJ mol^{-1}

C(diamond) + $O_2(g) \rightarrow CO_2(g)$; $\Delta H^\ominus$ = -396 kJ mol^{-1}

(b)



(c) The energy level diagram shows that

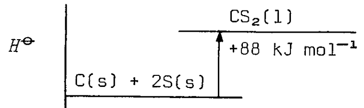
$H^\ominus$(diamond) = $H^\ominus$(graphite) + 2 kJ mol^{-1}

For the reaction C(graphite) → C(diamond),

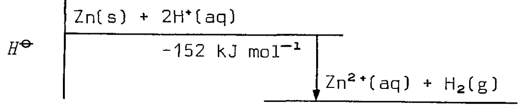
$\Delta H^\ominus = H^\ominus$(diamond) - $H^\ominus$(graphite) = +2 kJ mol^{-1}

Exercise 5

(a)



(b)



Exercise 6

Only those substances which actually take part in the reaction affect the value of $\Delta H^\ominus$. Because enthalpies are additive, for the first diagram we can write:

$\Delta H^\ominus = H^\ominus$(products) - $H^\ominus$(reactants)

$= H^\ominus(CO_2) - H^\ominus(C) - H^\ominus(O_2)$ = -393 kJ mol^{-1}

Similarly, for the second diagram, we can write:

$\Delta H^\ominus = H^\ominus(CO_2) + 2H^\ominus(O_2) - H^\ominus(C) - 3H^\ominus(O_2)$

$= H^\ominus(CO_2) - H^\ominus(C) - H^\ominus(O_2)$ = -393 kJ mol^{-1}

Exercise 7

(a) (i) Enthalpy change of combustion (of ethanol)

(ii) Enthalpy change of solution (of anhydrous copper sulphate)

(iii) Enthalpy change of combustion (of magnesium)
Enthalpy change of formation (of magnesium oxide)

(iv) Enthalpy change of combustion (of hydrogen)
Enthalpy change of formation (of water)

(v) Enthalpy change of combustion (of sulphur)
Enthalpy change of formation (of sulphur dioxide)

(b) (i) $\Delta H^\ominus_c[C_2H_5OH(l)]$ = -1366.7 kJ mol^{-1}

(ii) $\Delta H^\ominus_{soln}[CuSO_4(s)]$ = -67.4 kJ mol^{-1} (see note below)

(iii) $\Delta H^\ominus_c[Mg(s)] = \Delta H^\ominus_f[MgO(s)]$ = -601.7 kJ mol^{-1}

(iv) $\Delta H^\ominus_c[H_2(g)] = \Delta H^\ominus_f[H_2O(l)]$ = -285.9 kJ mol^{-1}

(v) $\Delta H^\ominus_c[S(s)] = \Delta H^\ominus_f[SO_2(g)]$ = -296.9 kJ mol^{-1}

Note that some data books list ΔH_{soln} only at infinite dilution (-73.3 kJ mol^{-1} for $CuSO_4$), and others list only the heat of formation of the solution from water and the elements of the solute (-837.3 kJ mol^{-1} for $CuSO_4$). In the latter case, ΔH_{soln} is obtained by subtracting $\Delta H^\ominus_f$ for the solute, i.e. $\Delta H^\ominus_{soln}[CuSO_4(s)] = \Delta H^\ominus_f[CuSO_4(aq)] - \Delta H^\ominus_f[CuSO_4(s)]$

Exercise 8

(a) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta H^\ominus$ = -890.4 kJ mol^{-1}

(b) $Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$; $\Delta H^\ominus$ = -635.5 kJ mol^{-1}

(c) $Br_2(l) \rightarrow Br_2(l)$; $\Delta H^\ominus$ = 0.0 kJ mol^{-1} (i.e. there is no reaction)

(d) Again $\Delta H^\ominus$ = 0.0 kJ mol^{-1} because there is no reaction.

Remember that the heat of formation of any element in its standard state is zero for the same reason.

Exercise 9

(a) $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$; $\Delta H^\ominus$ = -1271.0 kJ mol^{-1}

(b) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$; $\Delta H^\ominus$ = -46.0 kJ mol^{-1}

(c) $MgCl_2(s) + 500H_2O(l) \rightarrow MgCl_2(aq, 500H_2O)$; ΔH = -152.9 kJ mol^{-1} (see Ex. 7)

(d) $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta H^\ominus$ = -1559.8 kJ mol^{-1}

Exercise 10

(a) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H^{\ominus} = -394\ \text{kJ mol}^{-1}$

(b) (i) Part (a) shows the enthalpy change for 1.00 mol of carbon; for 10.0 mol the enthalpy change is

$$10.0 \times (-394\ \text{kJ mol}^{-1}) = \boxed{-3940\ \text{kJ mol}^{-1}}$$

(ii) For 0.25 mol of carbon

$$\Delta H^{\ominus} = 0.25 \times (-394\ \text{kJ mol}^{-1}) = \boxed{-98.5\ \text{kJ mol}^{-1}}$$

(iii) Amount of carbon $= \frac{m}{M} = \frac{18.0\ \text{g}}{12.0\ \text{g}}\ \text{mol}^{-1} = 1.5\ \text{mol}$

$$\therefore \Delta H = 1.5\ \text{mol} \times (-394\ \text{kJ mol}^{-1}) = \boxed{-591\ \text{kJ mol}^{-1}}$$

(c) (i) You may be able to see at a glance that 197 is half 394, so that the amount of carbon is $\frac{1}{2}$ mol and the mass is 6 g. Otherwise, since the quantity of heat depends directly on the amount of carbon burned;

$$\frac{1.00\ \text{mol of C}}{-394\ \text{kJ}} = \frac{x\ \text{mol of C}}{-197\ \text{kJ}}$$

$$\therefore x = \frac{197}{394} = 0.500$$

$$\therefore \text{mass of carbon} = 0.500\ \text{mol} \times 12.0\ \text{g mol}^{-1} = \boxed{6.00\ \text{g}}$$

(ii) $$\frac{1.00\ \text{mol of C}}{-394\ \text{kJ}} = \frac{y\ \text{mol of C}}{-1000\ \text{kJ}}$$

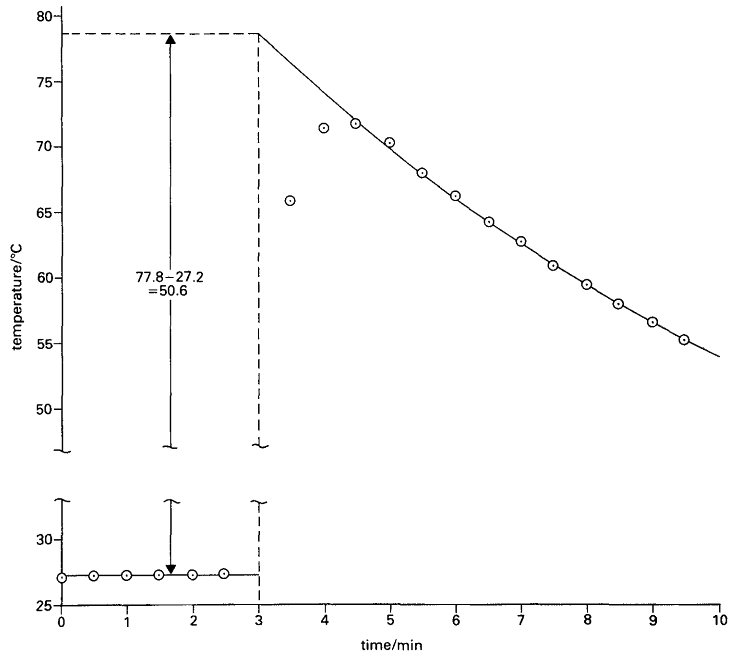
$$\therefore y = \frac{1000}{394} = 2.54$$

$$\therefore \text{mass of carbon} = 2.54\ \text{mol} \times 12.0\ \text{g mol}^{-1} = \boxed{30.5\ \text{g}}$$

Experiment 1 Specimen results and calculation

Results Table 1

Time/min	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Temperature/°C	27.0	27.0	27.2	27.2	27.2	27.2	-	66.0	71.4	71.8
Time/min	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
Temperature/°C	70.2	68.0	66.2	64.4	62.8	61.0	59.5	58.0	56.6	55.1



$$\begin{bmatrix}\text{enthalpy change due to}\\ \text{reaction (at constant } T)\end{bmatrix} + \begin{bmatrix}\text{change in heat}\\ \text{energy of solution}\end{bmatrix} = 0$$

i.e. $\Delta H + mc_p\Delta T = 0$

$$\therefore \Delta H = -mc_p\Delta T = -0.0250\ \text{kg} \times 4.18\ \text{kJ kg}^{-1}\ \text{K}^{-1} \times 50.6\ \text{K} = \boxed{-5.29\ \text{kJ}}$$

Amount of Cu^{2+} used $= cV = 1.00\ \text{mol dm}^{-3} \times 0.0250\ \text{dm}^{-3} = 0.0250\ \text{mol}$

Scaling up to the amount in the equation, 1 mol,

$$\Delta H = -5.29\ \text{kJ} \times \frac{1}{0.0250} = \boxed{-212\ \text{kJ}}$$

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq); \quad \Delta H^{\ominus} = -212\ \text{kJ mol}^{-1}$$

Experiment 1. Questions

1. $$\text{Error} = \frac{(-212 - -217)\ \text{kJ mol}^{-1}}{-217\ \text{kJ mol}^{-1}} \times 100 = \frac{+5}{-217} \times 100 = -2.3\%$$

2. (a) There is some heat loss from the polystyrene cup.
   (b) The heat capacity of the solution is not precisely 4.18 kJ kg^{-1} K^{-1}
   (c) The density of the solution is not precisely 1.00 g dm^{-3}.
   (d) The heat capacities of the metals were ignored.
   (e) The thermometer has a small but measurable heat capacity.

3. *The reaction takes a few minutes to complete because the copper first precipitated shields some of each zinc particle from the* Cu^{2+}.

Experiment 2. Specimen results and calculations

Suitable amounts are 0.0500 mol of NH_4Cl and 5.00 mol of H_2O.

Then mass of NH_4Cl = 53.4 g mol^{-1} x 0.500 mol = 2.67 g

and mass of H_2O = 18.0 g mol^{-1} x 5.00 mol = 90.0 g

ΔT = final temperature - initial temperature = 22.7 °C - 24.5 °C = -1.8 K

$$\begin{bmatrix}\text{enthalpy change on}\\ \text{dissolving } NH_4Cl\end{bmatrix} + \begin{bmatrix}\text{change in heat}\\ \text{energy of solution}\end{bmatrix} = 0$$

$$\Delta H \quad + \quad mc_p\Delta T \quad = \quad 0$$

$\therefore \Delta H = -mc_p\Delta T = -(0.090 \text{ kg} \times 4.18 \text{ kJ kg}^{-1} \text{K}^{-1} \times (-1.8 \text{ K})) = +0.68 \text{ kJ}$

Scaling up from 0.050 mol to 1 mol,

$$\Delta H = +0.68 \text{ kJ} \times \frac{1}{0.050} = +14 \text{ kJ}$$

$NH_4Cl(s) + 100H_2O(l) \rightarrow NH_4Cl(aq,100H_2O)$; $\Delta H^\ominus = \boxed{+14 \text{ kJ mol}^{-1}}$

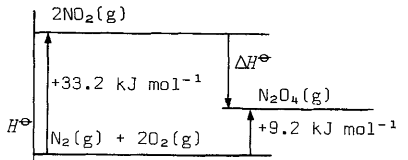
Note that only two significant figures are justified here because ΔT is small.

Experiment 2. Question

Results are usually lower than 16.4 kJ mol^{-1}, largely because some heat energy enters the system to increase the final temperature a little. It is difficult to measure a small temperature change accurately and an error of only 0.1°C changes the result by almost 1 kJ mol^{-1}. Also, we have made the usual assumptions about heat capacities of the polystyrene cup (= 0), thermometer (= 0) and solution (= water).

Exercise 11

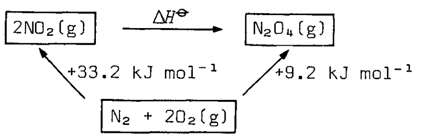
(a)



+33.2 kJ mol^{-1} = +9.2 kJ mol^{-1} + ($-\Delta H^\ominus$)

$\therefore \Delta H^\ominus$ = (9.2 - 33.2) kJ mol^{-1} = $\boxed{-24.0 \text{ kJ mol}^{-1}}$

(b)



+33.2 kJ mol^{-1} + $\Delta H^\ominus$ = +9.2 kJ mol^{-1}

$\therefore \Delta H^\ominus$ = (9.2 - 33.2) kJ mol^{-1} = $\boxed{-24.0 \text{ kJ mol}^{-1}}$

Exercise 12

(a) $NH_3(g) + HCl(g) + NH_4Cl(s) + 200H_2O(l)$

$\rightarrow NH_4Cl(s) + NH_4Cl(aq,200H_2O)$; $\Delta H^\ominus$ = (-175.3 + 16.3)kJ mol^{-1}

$NH_3(g) + HCl(g) + 200H_2O(l) \rightarrow NH_4Cl(aq,200H_2O)$; $\Delta H^\ominus$ = -159.0 kJ mol^{-1}

(b) $NH_3(g) + 100H_2O(l) + HCl(g) + 100H_2O(l) + NH_3(aq,100H_2O) + HCl(aq,100H_2O)$

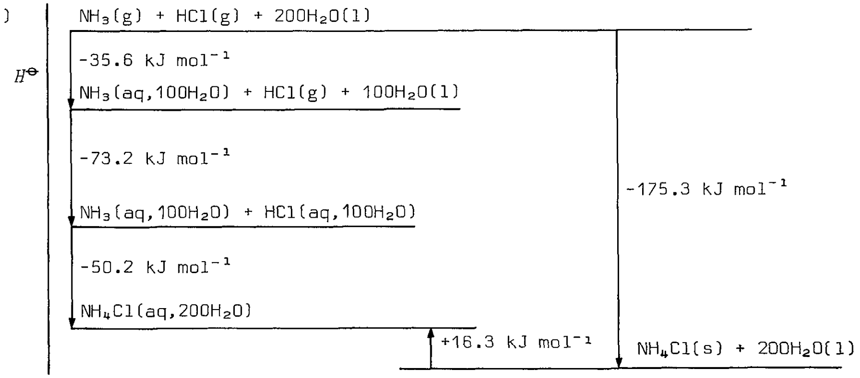
$\rightarrow NH_3(aq,100H_2O) + HCl(aq,100H_2O) + NH_4Cl(aq,200H_2O)$;

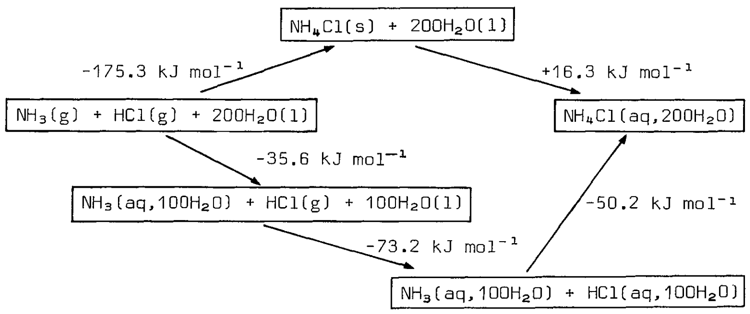
$\Delta H^\ominus$ = (-35.6 - 73.2 - 50.2)kJ mol^{-1}

$NH_3(g) + HCl(g) + 200H_2O(l) \rightarrow NH_4Cl(aq,200H_2O)$; $\Delta H^\ominus$ = -159.0 kJ mol^{-1}

(c) The enthalpy change for the overall process is the same by either Method 1 or Method 2.

(d)





Experiment 3. Specimen results and calculations

Results Table 2

	$MgSO_4$	$MgSO_4\cdot 7H_2O$
Mass of weighing bottle	12.91 g	13.42 g
Mass of weighing bottle and salt	15.92 g	19.58 g
Mass of salt	3.01 g	6.16 g
Mass of polystyrene cup	2.10 g	2.36 g
Mass of polystyrene cup and water	47.10 g	44.21 g
Mass of water	45.00 g	41.85 g
Initial temperature	24.1 °C	24.8 °C
Final temperature	35.4 °C	23.4 °C

1. $\Delta H = -mc_p\Delta T = -(0.0450 \text{ kg} \times 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1} \times 11.3 \text{ K}) = -2.12 \text{ kJ}$

   Scaling up, $\Delta H = -2.12 \text{ kJ} \times \frac{1 \text{ mol}}{0.0250 \text{ mol}} = -84.8 \text{ kJ}$

   Thus $MgSO_4(s) + 100H_2O(l) \rightarrow MgSO_4(aq,100H_2O)$; $\Delta H^\ominus = \boxed{-84.8 \text{ kJ mol}^{-1}}$

2. $\Delta H = -mc_p\Delta T = -(0.04185 \text{ kg} \times 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1} \times (-1.4 \text{ K}) = +0.24 \text{ kJ}$

   Scaling up, $\Delta H = +0.24 \text{ kJ} \times \frac{1 \text{ mol}}{0.0250 \text{ mol}} = +9.6 \text{ kJ}$

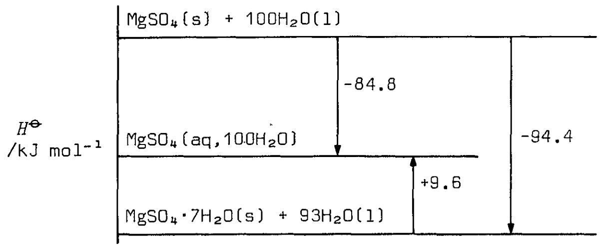
   Thus $MgSO_4\cdot 7H_2O(s) + 93H_2O(l) \rightarrow MgSO_4(aq,100H_2O)$; $\Delta H^\ominus = \boxed{+9.6 \text{ kJ mol}^{-1}}$

3. $$\begin{tikzcd}
\boxed{93H_2O(l)} + \boxed{MgSO_4(s) + 7H_2O(l)} \arrow[rr, "\Delta H^\ominus"] \arrow[dr, "\Delta H_1"'] & & \boxed{MgSO_4\cdot 7H_2O(s)} + \boxed{93H_2O(l)} \arrow[dl, "\Delta H_2"] \\
& \boxed{MgSO_4(aq,100H_2O)} &
\end{tikzcd}$$

   $\Delta H^\ominus = \Delta H_1 - \Delta H_2 = (-84.8 - 9.6) \text{ kJ mol}^{-1} = \boxed{-94.4 \text{ kJ mol}^{-1}}$

Experiment 3. Questions

1.



2. The maximum temperature change is much smaller and occurs more quickly.

3. Error $= \frac{-94.4 - (-104.0)}{104.0} \times 100 = -9.2\%$

   In addition to the usual assumptions about zero heat transfer between system and surroundings, and the heat capacities of the solutions, impurities in the salts may also affect the results. The anhydrous salt may not be totally free of water, and the hydrated salt may have absorbed extra water.

Exercise 13

$$\begin{tikzcd}
\boxed{3O_2(g)} + \boxed{C(s) + 2S(g)} \arrow[rr, "\Delta H^\ominus_f"] \arrow[dr, "\Delta H_1"'] & & \boxed{CS_2(l)} + \boxed{3O_2(g)} \arrow[dl, "\Delta H^\ominus_c"] \\
& \boxed{CO_2(g) + 2SO_2(g)} &
\end{tikzcd}$$

$\Delta H^\ominus_f[CS_2(l)] + \Delta H^\ominus_c[CS_2(l)] = \Delta H_1$

$\Delta H_1 = \Delta H^\ominus_f[CO_2(g)] + 2\Delta H^\ominus_f[SO_2(g)]$

$\therefore \Delta H^\ominus_f[CS_2(l)] = \Delta H^\ominus_f[CO_2(g)] + 2\Delta H^\ominus_f[SO_2(g)] - \Delta H^\ominus_c[CS_2(l)]$

$= (-393.5 + 2(-296.9) + 1075.2) \text{ kJ mol}^{-1}$

$\Delta H^\ominus_f[CS_2(l)] = \boxed{+87.9 \text{ kJ mol}^{-1}}$

Exercise 14

(a)
$$\begin{tikzcd}
\boxed{3\tfrac{1}{2}O_2(g)} + \boxed{2C(s) + 3H_2(g)} \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & \boxed{C_2H_6(g)} + \boxed{3\tfrac{1}{2}O_2(g)} \arrow[dl, "\Delta H_3"] \\
& \boxed{2CO_2(g) + 3H_2O(l)} &
\end{tikzcd}$$

$\Delta H_1 + \Delta H_3 = \Delta H_2$ or $\Delta H_1 = \Delta H_2 - \Delta H_3$

$\Delta H_2 = 2\Delta H^\ominus_f[CO_2(g)] + 3\Delta H^\ominus_f[H_2O(l)]$

$= (2(-393.5) + 3(-285.9)) \text{ kJ mol}^{-1} = -1644.7 \text{ kJ mol}^{-1}$

$\Delta H_3 = \Delta H^\ominus_c[C_2H_6(g)] = -1559.8 \text{ kJ mol}^{-1}$

$\therefore \Delta H_1 = (-1644.7 - (-1559.8)) \text{ kJ mol}^{-1} = \boxed{-84.9 \text{ kJ mol}^{-1}}$

(b)
$$\begin{tikzcd}
\boxed{3O_2(g)} + \boxed{2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g)} \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & \boxed{C_2H_5OH(l)} + \boxed{3O_2(g)} \arrow[dl, "\Delta H_3"] \\
& \boxed{2CO_2(g) + 3H_2O(l)} &
\end{tikzcd}$$

$\Delta H_2 = 2\Delta H^\ominus_f[CO_2(g)] + 3\Delta H^\ominus_f[H_2O(l)]$

$= (2(-393.5) + 3(-285.9)) \text{ kJ mol}^{-1} = -1644.7 \text{ kJ mol}^{-1}$

$\Delta H_3 = \Delta H^\ominus_c[C_2H_5OH(l)] = -1366.7 \text{ kJ mol}^{-1}$

$\Delta H_1 = \Delta H_2 - \Delta H_3 = (-1644.7 - (-1366.7)) \text{ kJ mol}^{-1} = \boxed{-278 \text{ kJ mol}^{-1}}$

(c)
$$\begin{tikzcd}
\boxed{2\tfrac{1}{4}O_2(g)} + \boxed{C(s) + 2\tfrac{1}{2}H_2(g) + \tfrac{1}{2}N_2(g)} \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & \boxed{CH_3NH_2(g)} + \boxed{2\tfrac{1}{4}O_2(g)} \arrow[dl, "\Delta H_3"] \\
& \boxed{CO_2(g) + 2\tfrac{1}{2}H_2O(l) + \tfrac{1}{2}N_2(g)} &
\end{tikzcd}$$

$\Delta H_2 = \Delta H^\ominus_f[CO_2(g)] + 2\tfrac{1}{2}\Delta H^\ominus_f[H_2O(l)]$

$= (-393.5 + 2\tfrac{1}{2}(-285.9)) \text{ kJ mol}^{-1} = -1108.3 \text{ kJ mol}^{-1}$

$\Delta H_3 = \Delta H^\ominus_c[CH_3NH_2(g)] = -1079.9 \text{ kJ mol}^{-1}$

$\Delta H_1 + \Delta H_3 = \Delta H_2$

$\therefore \Delta H_1 = \Delta H_2 - \Delta H_3 = (-1108.3 - (-1079.9)) \text{ kJ mol}^{-1} = \boxed{-28.4 \text{ kJ mol}^{-1}}$

Exercise 15

(a) $CH_3OH(l) + 1\frac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H_f^\ominus/\text{kJ mol}^{-1}$ -238.9 0 -393.5 $-2(285.9)$

$\Delta H^\ominus = (-571.8 - 393.5 -(-238.9))\ \text{kJ mol}^{-1} = \boxed{-726.4\ \text{kJ mol}^{-1}}$

(b) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

$\Delta H_f^\ominus/\text{kJ mol}^{-1}$ $-2(110.5)$ 0 $-2(393.5)$

$\Delta H^\ominus = (-787.0 -(-221.0))\ \text{kJ mol}^{-1} = \boxed{-566.0\ \text{kJ mol}^{-1}}$

(c) $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

$\Delta H_f^\ominus/\text{kJ mol}^{-1}$ -812.5 -348.0 -393.5

$\Delta H^\ominus = (-393.5 -348.0 -(-812.5))\ \text{kJ mol}^{-1} = \boxed{+71.0\ \text{kJ mol}^{-1}}$

(d) $2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$

$\Delta H_f^\ominus/\text{kJ mol}^{-1}$ 0 -822.2 0 -1675.7

$\Delta H^\ominus = (-1675.7 -(-822.2))\ \text{kJ mol}^{-1} = \boxed{-853.5\ \text{kJ mol}^{-1}}$

[The very large quantity of heat released is sufficient to melt the iron produced and other iron in contact with the reaction mixture. This is the basis of the 'Thermit' process which is still sometimes used to weld steel rails *in situ* on railway tracks.]

Exercise 16

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

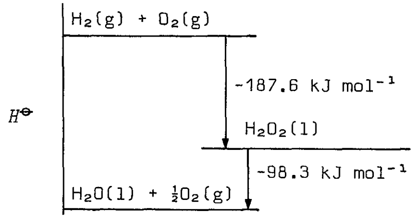
$\Delta H_f^\ominus/\text{kJ mol}^{-1}$ -75 -242 -110 0

$\Delta H^\ominus = (-110 -(-242) -(-75))\ \text{kJ mol}^{-1} = \boxed{+207\ \text{kJ mol}^{-1}}$

Exercise 17

(a) A compound with a negative value of $\Delta H_f^\ominus$ is likely to be stable with respect to decomposition to its elements because that process involves an increase in enthalpy. However, such a substance may be unstable with respect to some other reaction, e.g. combustion, or decomposition to another compound.

(b)



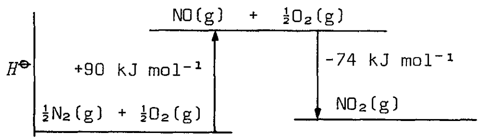
(c) $H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$

$\Delta H_f^\ominus/\text{kJ mol}^{-1}$ -187.6 -285.9 0

$\Delta H^\ominus = -285.9 + 187.6\ \text{kJ mol}^{-1} = \boxed{-98.3\ \text{kJ mol}^{-1}}$

(d) $H_2O_2(l)$ is energetically (thermodynamically) stable with respect to its elements; i.e. it will not spontaneously decompose into hydrogen and oxygen. However, $H_2O_2(l)$ is thermodynamically unstable with respect to water and oxygen and will spontaneously decompose to give these products.

Exercise 18



NO(g) in the presence of O_2 is unstable and the two gases react to form NO_2. NO(g) is also unstable relative to the elements and would be expected to decompose spontaneously. However, this reaction is kinetically slower, so the reaction to form NO_2 occurs.

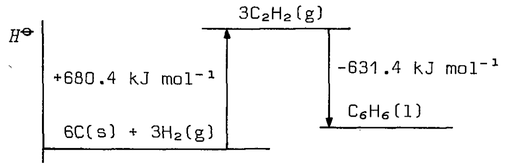
Exercise 19

First calculate $\Delta H^\ominus$ for the reaction:

$3C_2H_2(g) \rightarrow C_6H_6(l)$

$\Delta H_f^\ominus/\text{kJ mol}^{-1}$ $+3(226.8)$ $+49$

$\Delta H^\ominus = (49.0 - 680.4)\ \text{kJ mol}^{-1} = -631.4\ \text{kJ mol}^{-1}$



C_2H_2 is energetically unstable with respect to both benzene and its elements. The faster reaction is the one which will occur.

Exercise 20

(a) The standard enthalpy of formation is the increase in enthalpy that occurs when one mole of the compound is formed from its constituent atoms, all substances being in their standard states at 298 K (25°C) and 1.00 atm.

(b) (i) $CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$

$\Delta H_f^\ominus/\text{kJ mol}^{-1}$ -394 -110 0

$\Delta H^\ominus = -110 + 394\ \text{kJ mol}^{-1} = \boxed{+284\ \text{kJ mol}^{-1}}$

(ii) Both of the oxides are thermodynamically stable relative to carbon and oxygen because they both have negative heats of formation. Decomposition to the elements would therefore involve an <u>increase</u> in enthalpy.

Exercise 21

(a)

$$\begin{array}{lcccc} & CH_3OH(l) + 1\tfrac{1}{2}O_2(g) & \rightarrow & CO_2(g) + 2H_2O(l) \\ \Delta G_f^{\ominus}/\text{kJ mol}^{-1} & -166.7 \quad 0 & & -394.4 \quad -2(237.2)\end{array}$$

$\Delta G^{\ominus} = (-394.4 - 474.4 - (-166.7))\ \text{kJ mol}^{-1} = \boxed{-702.1\ \text{kJ mol}^{-1}}$

$(\Delta H^{\ominus} = -726.4\ \text{kJ mol}^{-1})$

(b)

$$\begin{array}{lccc} & 2CO(g) + O_2(g) & \rightarrow & 2CO_2(g) \\ \Delta G_f^{\ominus}/\text{kJ mol}^{-1} & -2(137.3) \quad 0 & & -2(394.4)\end{array}$$

$\Delta G^{\ominus} = (-788.8 - (-274.6))\ \text{kJ mol}^{-1} = \boxed{-514.2\ \text{kJ mol}^{-1}}$

$(\Delta H^{\ominus} = -566.0\ \text{kJ mol}^{-1})$

(c)

$$\begin{array}{lccc} & ZnCO_3(s) & \rightarrow & ZnO(s) + CO_2(g) \\ \Delta G_f^{\ominus}/\text{kJ mol}^{-1} & -731.4 & & -318.2 \quad -394.4\end{array}$$

$\Delta G^{\ominus} = (-318.2 - 394.4 - (-731.4))\ \text{kJ mol}^{-1} = \boxed{+18.8\ \text{kJ mol}^{-1}}$

$(\Delta H^{\ominus} = +71.0\ \text{kJ mol}^{-1})$

(d)

$$\begin{array}{lccc} & 2Al(s) + Fe_2O_3(s) & \rightarrow & 2Fe(s) + Al_2O_3(s) \\ \Delta G_f^{\ominus}/\text{kJ mol}^{-1} & 0 \quad -741.0 & & 0 \quad -1582.4\end{array}$$

$\Delta G^{\ominus} = (-1582.4 - (-741.0))\ \text{kJ mol}^{-1} = \boxed{-841.0\ \text{kJ mol}^{-1}}$

$(\Delta H^{\ominus} = -853.5\ \text{kJ mol}^{-1})$

In these examples (and many others) the values of $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ are not greatly different and the use of $\Delta H^{\ominus}$ values to predict the feasibility of reactions would give the correct result.

Note, however, that this only applies to standard conditions, especially $T = 298$ K. ZnO reacts with CO_2 at 298 K, whereas $ZnCO_3$ decomposes readily at higher temperatures. You will see how $\Delta G^{\ominus}$ varies with temperature later in the Unit.

Exercise 22

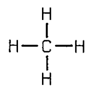
(a) Adding the reactions in Table 3 gives the overall reaction:

$CH_4(g) \rightarrow C(g) + 4H(g);\ \Delta H = \boxed{+1662\ \text{kJ mol}^{-1}}$

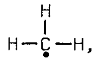
(b) $\bar{E}(\text{C–H}) = \dfrac{1662\ \text{kJ mol}^{-1}}{4} = \boxed{416\ \text{kJ mol}^{-1}}$

(c) Each step represents a bond dissociation energy.

(d) Each bond dissociation energy is different because the environment in each step is different; i.e. the C–H bond broken in



is different from the ones broken in



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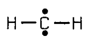
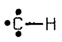


and



Exercise 23

(a) Bond energy term is an average value for a given type of bond whereas bond dissociation energy refers to a specific bond in a specific compound.

(b) Any diatomic molecule; e.g. Cl_2, HBr, CO.

Exercise 24

$$\begin{tikzcd} \boxed{H_2S(g)} \arrow[rr, "\Delta H_1"] & & \boxed{2H(g) + S(g)} \\ & \boxed{H_2(g) + S(s)} \arrow[ul, "\Delta H_2"] \arrow[ur, "\Delta H_3"'] & \end{tikzcd}$$

$\Delta H_3 = 2\Delta H_{at}^{\ominus}[H(g)] + \Delta H_{at}^{\ominus}[S(s)] = (2(218.0) + 238.1)\text{kJ mol}^{-1} = 674.1\ \text{kJ mol}^{-1}$

$\Delta H_2 = \Delta H_f^{\ominus}[H_2S(g)] = -20.6\ \text{kJ mol}^{-1}$

$\Delta H_1 = -\Delta H_2 + \Delta H_3 = (20.6 + 674.1)\ \text{kJ mol}^{-1} = 694.7\ \text{kJ mol}^{-1}$

$\therefore\ \bar{E}(\text{H–S}) = \dfrac{694.7}{2}\ \text{kJ mol}^{-1} = \boxed{347.4\ \text{kJ mol}^{-1}}$

Exercise 25

$$\begin{tikzcd} \boxed{NH_3(g)} \arrow[rr, "\Delta H_1"] & & \boxed{N(g) + 3H(g)} \\ & \boxed{\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)} \arrow[ul, "\Delta H_2"] \arrow[ur, "\Delta H_3"'] & \end{tikzcd}$$

$\Delta H_3 = \Delta H_{at}^{\ominus}[N(g)] + 3\Delta H_{at}^{\ominus}[H(g)] = (473 + 3(218))\text{kJ mol}^{-1} = 1127\ \text{kJ mol}^{-1}$

$\Delta H_2 = -46\ \text{kJ mol}^{-1}$

$\therefore\ \Delta H_1 = -\Delta H_2 + \Delta H_3 = (46 + 1127)\ \text{kJ mol}^{-1} = 1173\ \text{kJ mol}^{-1}$

$\bar{E}(\text{N–H}) = \dfrac{1173}{3}\ \text{kJ mol}^{-1} = \boxed{391\ \text{kJ mol}^{-1}}$

Exercise 26

$$\begin{tikzcd} \boxed{CCl_4(g)} \arrow[rr, "\Delta H_1"] & & \boxed{C(g) + 4Cl(g)} \\ & \boxed{C(s) + 2Cl_2(g)} \arrow[ul, "\Delta H_2"] \arrow[ur, "\Delta H_3"'] & \end{tikzcd}$$

$\Delta H_2 = \Delta H_f^{\ominus}[CCl_4(l)] + \Delta H_{vap}^{\ominus}[CCl_4(l)] = (-135.5 + 30.5)\ \text{kJ mol}^{-1}$

$= -105.0\ \text{kJ mol}^{-1}$

$\Delta H_3 = \Delta H_{at}^{\ominus}[C(g)] + 4\Delta H_{at}^{\ominus}[Cl(g)] = (715.0 + 4(121.1))\text{kJ mol}^{-1} = 1199.4\ \text{kJ mol}^{-1}$

$\Delta H_1 = -\Delta H_2 + \Delta H_3 = (105.0 + 1199.4)\ \text{kJ mol}^{-1} = 1304.4\ \text{kJ mol}^{-1}$

$\therefore\ \bar{E}(\text{C–Cl})\quad \dfrac{1304.4}{4}\ \text{kJ mol}^{-1} = \boxed{326\ \text{kJ mol}^{-1}}$

Exercise 27

(a) Table 4

(c)

Alcohol	Bonds broken/mol					Bonds formed	
	C—C	C—H	C—O	O—H	O═O	C═O	O—H
ethanol	1	5	1	1	3	4	6
propan-1-ol	2	7	1	1	4½	6	8
butan-1-ol	3	9	1	1	6	8	10
pentan-1-ol	4	11	1	1	7½	10	12
hexan-1-ol	5	13	1	1	9	12	14

(b) Bonds broken - 1(C—C), 2(C—H) and 1½(O═O)

Bonds formed - 1(C═O), 2(O—H)

(d) The O═O bonds are identical because they are all in oxygen molecules: the C═O bonds are identical because they are all in CO_2 molecules: the O—H bonds are identical because they are all in H_2O molecules. However, the C—C bonds and the C—H bonds are not identical because they are in different, though similar, molecules.

(e) (i) The difference in $\Delta H^\ominus_c$ should be almost constant, assuming that the bond energies for C—C and C—H are almost constant in different alcohols.

(ii) The difference in $\Delta H^\ominus_c$ at 298 K should be nearly constant, but slight variations will occur due to the variations in $\Delta H^\ominus_{vap}$.

Experiment 4. Specimen results and calculations

Results Table 3

	1st run	2nd run	
Molar mass of propan-1-ol, M	60.1	60.1	g mol^{-1}
Initial mass of spirit lamp + alcohol, m_1	13.112	12.083	g
Final mass of spirit lamp + alcohol, m_2	12.083	11.034	g
Mass of alcohol burned, $m_1 - m_2$	1.029	1.049	g
Amounts of alcohol burned, $n = (m_1 - m_2)/M$	0.0171	0.0175	mol
Initial temperature of calorimeter	21.7	21.4	°C
Final temperature of calorimeter	33.2	33.0	°C
Temperature change, ΔT	11.5	11.6	K
Heat released during the experiment $= \Delta H^\ominus_c$ [propan-1-ol] x amount burned, n	34.5	35.3	kJ
Heat required to raise temperature by 1 K $= \dfrac{-2017 \text{ kJ} \times n}{\Delta T}$ = calibration factor, C	-3.00	-3.04	kJ K^{-1}
Mean value of C		-3.02	kJ K^{-1}

Results Table 4 above right.

Results Table 4	C_4H_9OH	$C_5H_{11}OH$	$C_6H_{13}OH$	$C_7H_{15}OH$	$C_8H_{17}OH$
Molar Mass m/g mol^{-1}	74.1	88.2	102.2	116.2	130.2
Initial mass of lamp/g	13.691	12.820	13.571	13.679	13.909
Final mass of lamp/g	12.642	12.023	12.668	12.794	13.175
Mass of alcohol burned/g	1.049	0.797	0.903	0.885	0.734
Amount burned, n/mol	0.0142	0.00904	0.00884	0.00762	0.00564
Initial temperature/°C	21.5	21.0	21.7	21.4	22.0
Final temperature/°C	33.5	30.0	33.1	32.2	32.1
Temperature change, ΔT/K	12.0	9.0	11.4	10.8	10.1
$\Delta H^\ominus_c = \dfrac{C \times \Delta T}{n}$ /kJ mol^{-1}	-2552	-3007	-3895	-4280	-5408

Exercise 28

(a) Table 5

(b)

Alcohol	$\Delta H^\ominus_c$/kJ mol^{-1}	Differences /kJ mol^{-1}
propan-1-ol	-2017	
butan-1-ol	-2675	658
pentan-1-ol	-3323	648
hexan-1-ol	-3976	653
heptan-1-ol	-4623	647
octan-1-ol	-5280	657

Average difference in $\Delta H^\ominus_c$ for adjacent pairs $= \frac{3263}{5} = \boxed{653 \text{ kJ mol}^{-1}}$

(c) It is reasonable to use average bond energy terms for C—C and for C—H in different alcohols, because the heat of combustion data show that the bond dissociation energies do not differ by more than a few kJ mol^{-1}. The difference in heat of combustion between adjacent alcohols in the list is made up from O═O, C═O and O—H bond energies which are constant; from $\Delta H^\ominus_{vap}$ difference, which is almost constant; and from C—C and C—H bond energies which must therefore also be nearly constant.

Exercise 29

(a) $H_2(g) + Cl_2(g) \rightarrow 2H{-}Cl(g)$

Bonds broken: $\bar{E}(H{-}H) + \bar{E}(Cl{-}Cl) = (436 + 242)$ kJ mol^{-1} = 678 kJ mol^{-1}

Bonds made: $-2\bar{E}(H{-}Cl) = -2(431)$ kJ mol^{-1} = -862 kJ mol^{-1}

$\therefore \Delta H = (678 - 862)$ kJ mol^{-1} = $\boxed{-184 \text{ kJ mol}^{-1}}$

(b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Bonds broken: $\bar{E}(N{\equiv}N) + 3\bar{E}(H{-}H) = (945 + 3(436))$ kJ mol^{-1} = 2253 kJ mol^{-1}

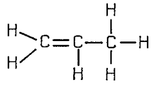
Bonds formed: $-6\bar{E}(N{-}H) = -6(389)$ kJ mol^{-1} = -2334 kJ mol^{-1}

$\Delta H = (2253 - 2334)$ kJ mol^{-1} = $\boxed{-81 \text{ kJ mol}^{-1}}$

Exercise 30

(a) Bond energy term is the average value for the dissociation of a particular type of bond.

(b) (i) $6H(g) + 3C(g) \rightarrow$



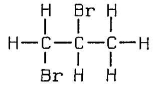
Bonds formed: 6C—H; $-6\bar{E}(C—H) = -6(413\ kJ\ mol^{-1}$

1C—C; $-\bar{E}(C—C) = -611\ kJ\ mol^{-1}$

1C—C; $-\bar{E}(C—C) = -346\ kJ\ mol^{-1}$

$\therefore \Delta H = -(6(413) + 611 + 346)\ kJ\ mol^{-1} = \boxed{-3435\ kJ\ mol^{-1}}$

(ii) $3C(g) + 6H(g) + 2Br(g) \rightarrow$



$H—CH_2—CHBr—CHBr... $ (g)

Bonds formed: 6C—H; $-6\bar{E}(C—H) = -6(413\ kJ\ mol^{-1})$

2C—Br; $-2\bar{E}(C—Br) = -2(209\ kJ\ mol^{-1})$

2C—C; $-2\bar{E}(C—C) = -2(346\ kJ\ mol^{-1})$

$\therefore \Delta H = -(6(413) + 2(209) + 2(346)\ kJ\ mol^{-1} = \boxed{-3588\ kJ\ mol^{-1}}$

(c)

$$\begin{tikzcd}
\boxed{CH_2{=}CH—CH_3(g) + Br_2(g)} \arrow[rr, "\Delta H_1"] & & \boxed{CH_2BrCHBrCH_3(g)} \\
& \boxed{3C(g) + 6H(g) + 2Br(g)} \arrow[ul, "\Delta H_2"] \arrow[ur, "\Delta H_3"'] &
\end{tikzcd}$$

$\Delta H_2 = -3435\ kJ\ mol^{-1} - \bar{E}(Br—Br) = (-3435 - 193)\ kJ\ mol^{-1} = -3628\ kJ\ mol^{-1}$

$\Delta H_1 = -\Delta H_2 + \Delta H_3 = (3628 + (-3588))\ kJ\ mol^{-1} = \boxed{-40\ kJ\ mol^{-1}}$

Exercise 31

(a)

$$\begin{tikzcd}
\boxed{C_2H_6(g) + Cl_2(g)} \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & \boxed{C_2H_5Cl(g) + HCl(g)} \arrow[dl, "\Delta H_3"] \\
& \boxed{2C(g) + 6H(g) + 2Cl(g)} &
\end{tikzcd}$$

$\Delta H_2 = \bar{E}(C—C) + 6\bar{E}(C—H) + \bar{E}(Cl—Cl)$

$= (346 + 6(413) + 242))kJ\ mol^{-1} = 3066\ kJ\ mol^{-1}$

$\Delta H_3 = \bar{E}(C—C) + 5\bar{E}(C—H) + \bar{E}(C—Cl) + \bar{E}(H—Cl)$

$= (346 + 5(413) + 339 + 431)kJ\ mol^{-1} = 3181\ kJ\ mol^{-1}$

$\Delta H_1 = \Delta H_2 - \Delta H_3 = (3066 - 3181)\ kJ\ mol^{-1} = \boxed{-115\ kJ\ mol^{-1}}$

Or, more simply,

$$\begin{tikzcd}
\boxed{C_2H_6(g) + Cl_2(g)} \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & \boxed{C_2H_5Cl(g) + HCl(g)} \arrow[dl, "\Delta H_3"] \\
& \boxed{C_2H_5(g) + H(g) + 2Cl(g)} &
\end{tikzcd}$$

$\Delta H_2 = \bar{E}(C—H) + \bar{E}(Cl—Cl) = (413 + 242)\ kJ\ mol^{-1} = 655\ kJ\ mol^{-1}$

Exercise 31 (cont.)

$\Delta H_3 = \bar{E}(C—Cl) + \bar{E}(H—Cl) = (339 + 431)kJ\ mol^{-1} = 770\ kJ\ mol^{-1}$

$\Delta H_1 = \Delta H_2 - \Delta H_3 = (655 - 770)kJ\ mol^{-1} = \boxed{-115\ kJ\ mol^{-1}}$

(b) $C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$

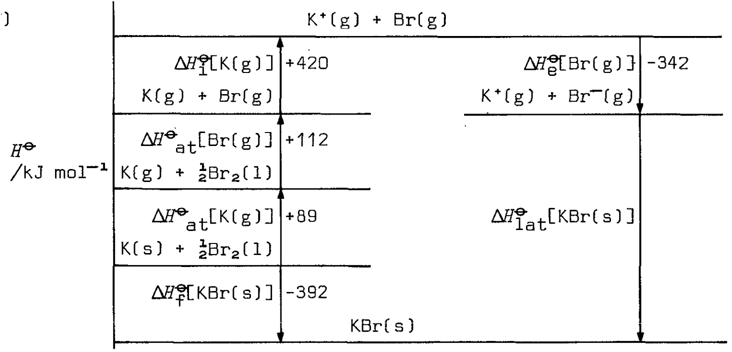
$\Delta H^\ominus_f/kJ\ mol^{-1}$ -84.6 0 -136.5 -92.3

$\Delta H^\ominus = (-136.5 - 92.3 - (-84.6))kJ\ mol^{-1} = \boxed{-144.2\ kJ\ mol^{-1}}$

(c) The bond energy terms $\bar{E}(C—H)$ and $\bar{E}(C—Cl)$ used in the first calculation are average values and are not quite the same as the bond dissociation energies for the particular compounds C_2H_6 and C_2H_5Cl. If the bond dissociation energies were known and used in the calculation they would give a more accurate result, much closer to $-144.2\ kJ\ mol^{-1}$. Even then, however, the two answers might not quite agree because there is some uncertainty in data book values for $\Delta H^\ominus_f$ and bond dissociation energies.

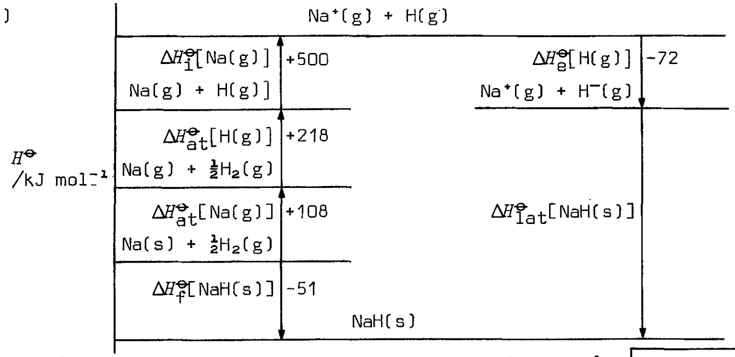
Exercise 32

(a)



$\Delta H^\ominus_{lat}[KBr(s)] = -[392 + 89 + 112 + 420 - 342]kJ\ mol^{-1} = \boxed{-671\ kJ\ mol^{-1}}$

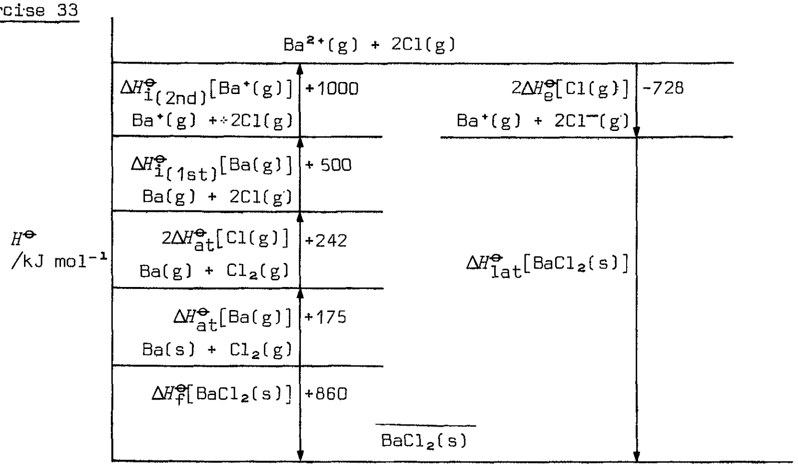
(b)



$\Delta H^\ominus_{lat}[NaH(s)] = -[57 + 108 + 218 + 500 - 72]kJ\ mol^{-1} = \boxed{-811\ kJ\ mol^{-1}}$

Exercise 33

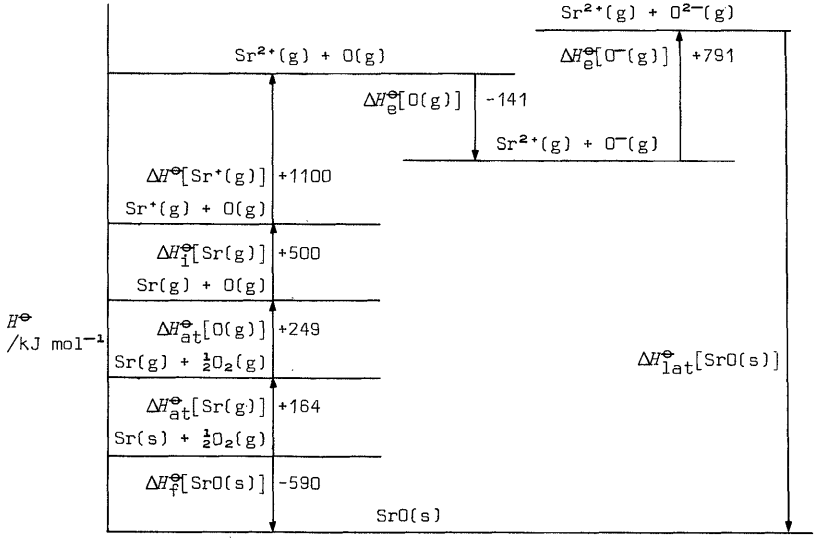
(a)



$\Delta H^\ominus_{lat}[BaCl_2(s)] = -(860 + 175 + 242 + 500 + 1000 - 728)$ kJ mol^{-1}

$= \boxed{-2049 \text{ kJ mol}^{-1}}$

(b)



$\Delta H^\ominus_{lat}[SrO(s)] = -(590 + 164 + 249 + 550 + 1100 - 141 + 791)$ kJ mol^{-1}

$= \boxed{-3303 \text{ kJ mol}^{-1}}$

Exercise 34

$$\begin{tikzcd}
Na(s) + \arrow[d, "108"] & \frac{1}{2}Cl_2(g) \arrow[r, "-411"] \arrow[d, "121"] & NaCl(s) \\
Na(g) \arrow[d, "500"] & Cl(g) \arrow[d, "x"] & \\
Na^+(g) + & Cl^-(g) \arrow[uur, "-776"'] &
\end{tikzcd}$$

All values in kJ mol^{-1}

$-411 = 108 + 500 + 121 + x - 776$

$\therefore x = -411 - 108 - 500 - 121 + 776 = -364$

and $\Delta H^\ominus = \boxed{-364 \text{ kJ mol}^{-1}}$

Exercise 35

(a) (i) B is the sum of the first and second ionization energies of calcium.

(ii) C is twice the enthalpy change of atomization of chlorine.

(iii) E is the lattice energy of $CaCl_2(s)$.

(iv) F is the enthalpy change of formation of $CaCl_2(s)$.

(b) F = A+B+C+D+E

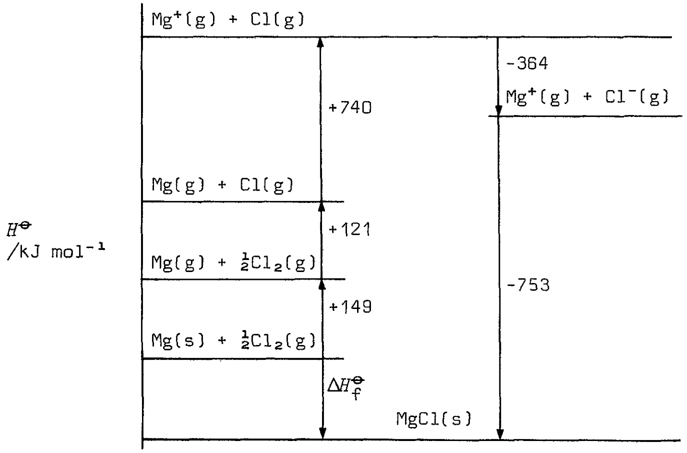
$\therefore$ D = F-A-B-C-E = (-795 - 177 - 1690 - 242 + 2197) kJ mol^{-1}

$= \boxed{-707 \text{ kJ mol}^{-1}}$

(This is twice the electron affinity of chlorine.)

Exercise 36

(a) MgCl



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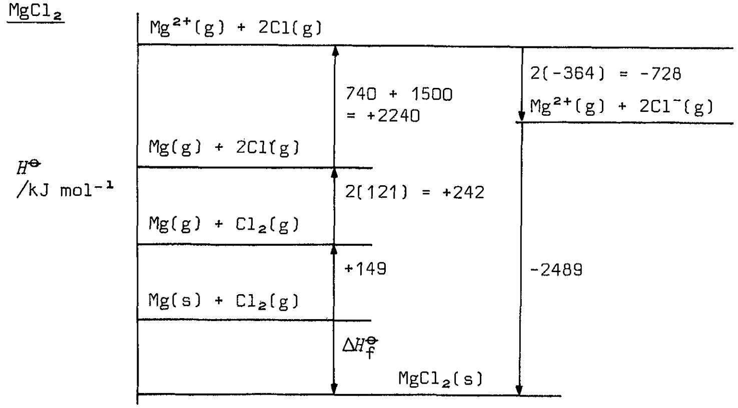
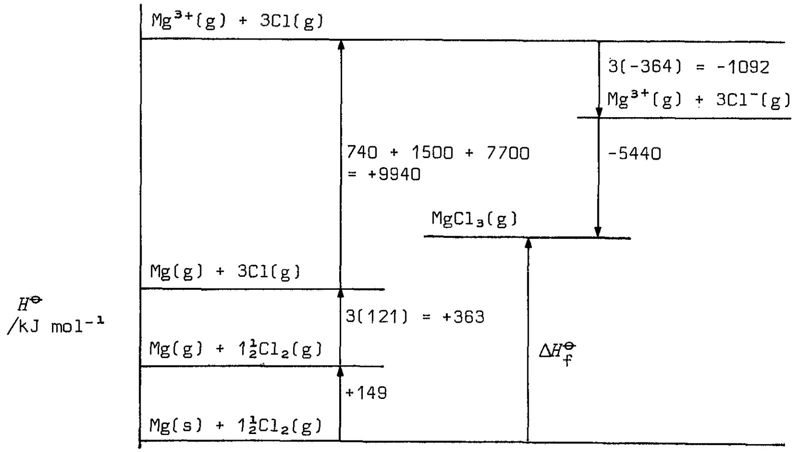
Exercise 36 (cont.)

MgCl$_2$



MgCl$_3$



(b) $\Delta H_f^\ominus$[MgCl] = (149 + 121 + 740 - 364 - 753)kJ mol^{-1} = $\boxed{-107 \text{ kJ mol}^{-1}}$

$\Delta H_f^\ominus$[MgCl$_2$] = (149 + 242 + 2240 - 728 - 2489)kJ mol^{-1} = $\boxed{-586 \text{ kJ mol}^{-1}}$

$\Delta H_f^\ominus$[MgCl$_3$] = (149 + 363 + 9940 - 1092 - 5440)kJ mol^{-1} = $\boxed{+3920 \text{ kJ mol}^{-1}}$

(c) MgCl and MgCl$_2$ are both energetically stable with respect to the elements, but MgCl$_2$ is more stable than MgCl.

(d)

	2MgCl(s)	→	MgCl$_2$(s) +	Mg(s)
$\Delta H_f^\ominus$/kJ mol^{-1}	-214		-586	0

$\Delta H^\ominus$ = $\Sigma\Delta H_f^\ominus$[products] - $\Sigma\Delta H_f^\ominus$[reactants]

= (-586 + 214)kJ mol^{-1} = $\boxed{-372 \text{ kJ mol}^{-1}}$

(e) MgCl is unstable relative to MgCl$_2$ and Mg. This explains why MgCl is unknown; as soon as it forms, it would be converted into MgCl$_2$ and Mg.

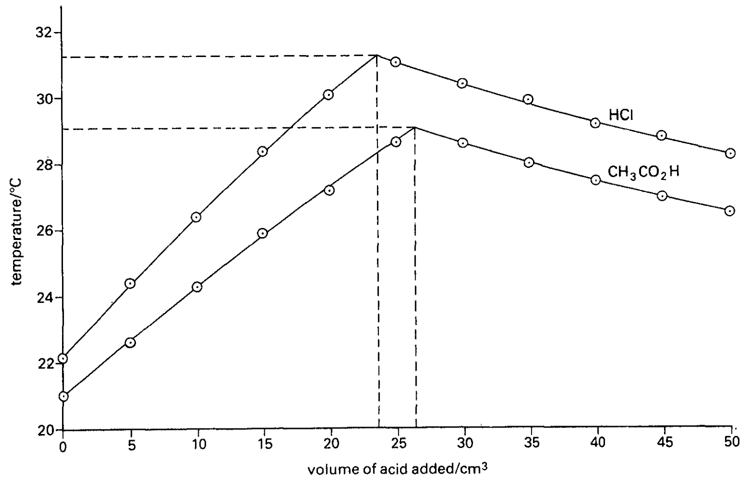
Experiment 5. Specimen results and calculation

Results Table 5. Titration of hydrochloric acid

Volume added/cm^3	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
Temperature/°C	22.2	24.4	26.4	28.4	30.1	31.1	30.4	29.9	29.2	28.8	28.2

Results Table 6. Titration of ethanoic acid

Volume added/cm^3	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
Temperature/°C	21.0	22.6	24.3	25.9	27.2	28.7	28.6	28.0	27.5	27.0	26.5



3. (a) HCl(aq) + NaOH(aq) → NaCl(aq) + H$_2$O(l)

Amount of HCl = amount of NaOH

$c \times \frac{23.5}{1000}$ dm^3 = 1.00 mol dm^{-3} × $\frac{50.0}{1000}$ dm^3

∴ c = 1.00 mol dm^{-3} × $\frac{50.0}{23.5}$ = $\boxed{2.13 \text{ mol dm}^{-3}}$

(b) CH$_3$CO$_2$H(aq) + NaOH(aq) → CH$_3$CO$_2$Na(aq) + H$_2$O(l)

Amount of CH$_3$CO$_2$H = amount of NaOH

∴ $c \times \frac{26.5}{1000}$ dm^3 = 1.00 mol dm^{-3} × $\frac{50.0}{1000}$ dm^3

∴ c = 1.00 mol dm^{-3} × $\frac{50.0}{26.5}$ = $\boxed{1.89 \text{ mol dm}^{-3}}$

(Continued on next page.)

4. Volume of mixture when reaction is complete = (50.0 + 23.5)cm^3 = 73.5 cm^3

ΔT = (31.3 - 22.2)K = 9.1 K

$\Delta H = -mc_p\Delta T$ = -0.0735 kg x 4.18 kJ kg^{-1} K^{-1} x 9.1 K = -2.80 kJ

Amount of NaOH used = cV = 1.00 mol dm^{-3} x 0.0500 dm^3 = 0.0500 mol

Scaling up to 1 mol, ΔH = 2.80 kJ x $\frac{1}{0.0500}$ = -56.0 kJ

$\therefore$ HCl(aq) + NaOH(aq) → NaCl(aq) + H_2O(l); $\Delta H^\ominus$ = $\boxed{-56.0 \text{ kJ mol}^{-1}}$

(b) Volume of mixture when reaction is complete = (50.0 + 26.5)cm^3 = 76.5 cm^3

ΔT = (29.1 - 21.0)K = 8.1 K

$\Delta H = -mcp\Delta T$ = -0.0765 kg x 4.18 kJ kg^{-1} K^{-1} x 8.1 K = -2.59 kJ

Scaling up to 1 mol, ΔH = -2.59 kJ x $\frac{1}{0.0500}$ = 51.8 kJ

$\therefore$ CH_3CO_2H(aq) + NaOH(aq) → CH_3CO_2Na(aq) + H_2O(l);

$\Delta H^\ominus$ = $\boxed{-51.8 \text{ kJ mol}^{-1}}$

Experiment 5. Questions

1. The enthalpy change of neutralization for completely ionized acids and bases is constant because the reaction is the same in every case.

   H^+(aq) + OH^-(aq) → H_2O(l)

2. Some heat is lost from the reaction mixture. The specific heat capacity of the mixture is not precisely 4.18 kJ kg^{-1} K^{-1}.
3. The enthalpy change of neutralization for incompletely ionized acids and/or bases is less negative because some energy is required to complete the ionization before the reaction between hydrogen ion and hydroxide ion can occur.

Exercise 37

Entropy increases as temperature rises. The molecules acquire more energy, and there are therefore more ways of sharing the total energy between the molecules - this is what is meant by saying that the substance becomes more disordered. If the temperature rise is sufficient to cause a change in state (i.e. melting or vaporization) there is a considerable increase in disorder and, therefore, in entropy.

Exercise 38

(a) $S^\ominus[I_2(s)]$ = 117 J K^{-1} mol^{-1} ($S^\ominus[I(s)]$ = 58.4 kJ mol^{-1})

$S^\ominus[Br_2(l)]$ = 151.6 J K^{-1} mol^{-1}

$S^\ominus[Cl_2(g)]$ = 233.0 J K^{-1} mol^{-1}

$S^\ominus[H_2O(l)]$ = 70.0 J K^{-1} mol^{-1}

$S^\ominus[H_2O(g)]$ = 188.7 J K^{-1} mol^{-1}

Exercise 39

(a) Decrease. Two moles of gas form one mole thereby decreasing the disorder.

(b) Decrease. Four moles of gas form two moles thereby decreasing the disorder.

(c) Increase. Two moles of solid produces two moles of another solid plus one mole of a gas.

Exercise 40

(a)

	H_2(g) +	C_2H_4(g) →	C_2H_6(g)
$S^\ominus$/J K^{-1} mol^{-1}	130.6	219.5	229.5

$\Delta S^\ominus$ = {229.5 - (130.6 + 219.5)} J K^{-1} mol^{-1} = $\boxed{-120.6 \text{ J K}^{-1} \text{ mol}^{-1}}$

(b)

	N_2(g) +	$3H_2$(g) →	$2NH_3$(g)
$S^\ominus$/J K^{-1} mol^{-1}	191.4	3 x 130.6	2 x 192.5

$\Delta S^\ominus$ = {385.0 - (191.4 + 391.8)} J K^{-1} mol^{-1} = $\boxed{-198.2 \text{ J K}^{-1} \text{ mol}^{-1}}$

(c)

	$2NaNO_3$(s) →	$2NaNO_2$(s) +	O_2(g)
$S^\ominus$/J K^{-1} mol^{-1}	2 x 116.3	2 x 120.5	204.9

$\Delta S^\ominus$ = (204.9 + 241.0 - 232.6) J K^{-1} mol^{-1} = $\boxed{+213.3 \text{ J K}^{-1} \text{ mol}^{-1}}$

Exercise 41

(a) Negative. $\Delta S^\ominus$ = {289 - (198 + 223)} J K^{-1} mol^{-1} = $\boxed{-132 \text{ J K}^{-1} \text{ mol}^{-1}}$

(b) Positive. $\Delta S^\ominus$ = {(2 x 70.0) + 204.9 - (2 x 102)} J K^{-1} mol^{-1} = $\boxed{+140.9 \text{ J K}^{-1} \text{ mol}^{-1}}$

(c) Negative. $\Delta S^\ominus$ = {(2 x 213.6) + 70.0 - 219.5 - (3 x 204.9)} J K^{-1} mol^{-1} = $\boxed{-337.0 \text{ J K}^{-1} \text{ mol}^{-1}}$

(d) Positive. $\Delta S^\ominus$ = {(2 x 82.7) + (3 x 204.9) - (2 x 143.0)} J K^{-1} mol^{-1} = $\boxed{+494.1 \text{ J K}^{-1} \text{ mol}^{-1}}$

(e) Positive. $\Delta S^\ominus$ = {(2 x 197.9) - (2 x 5.7) - 204.9} J K^{-1} mol^{-1} = $\boxed{+179.5 \text{ J K}^{-1} \text{ mol}^{-1}}$

Exercise 42

(a)

	$2NO(g)$ +	$O_2(g)$ →	$N_2O_4(g)$
$\Delta H_f^\ominus$/kJ mol^{-1}	2 x 90.4	0	9.2
$S^\ominus$/J K^{-1} mol^{-1}	2 x 210.5	204.9	304.2

$\Delta H^\ominus$ = (9.2 - 180.8 - 0)kJ mol^{-1} = -171.6 kJ mol^{-1}

$\Delta S^\ominus$ = (304.2 - 421 - 204.9)J K^{-1} mol^{-1} = -321.7 J K^{-1} mol^{-1}

= -0.322 kJ K^{-1} mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ = -171.6 kJ mol^{-1} -(298 K x (-0.322 kJ K^{-1} mol^{-1}))

= $\boxed{\text{-75.6 kJ mol}^{-1}}$

(b)

	$NH_3(g)$ +	$HCl(g)$ →	$NH_4Cl(s)$
$\Delta H_f^\ominus$/kJ mol	-46.0	-92.3	-315.5
$S^\ominus$/J K^{-1} mol^{-1}	192.5	186.7	94.6

$\Delta H^\ominus$ = (-315.5 -(-46.0 - 92.3))kJ mol^{-1} = -177.2 kJ mol^{-1}

$\Delta S^\ominus$ = (94.6 - 186.7 - 192.5)J K^{-1} mol^{-1} = -284.6 J K^{-1} mol^{-1}

= -0.285 kJ K^{-1} mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ = -177.2 kJ mol^{-1} -(298 K x (-0.285 kJ K^{-1} mol^{-1}))

= $\boxed{\text{-92.3 mol}^{-1}}$

(c)

	$H_2O(l)$ →	$H_2O(g)$
$\Delta H_f^\ominus$/kJ mol^{-1}	-285.9	-241.8
$S^\ominus$/J K^{-1} mol^{-1}	70.0	188.7

$\Delta H^\ominus$ = (-241.8 - (-285.9))kJ mol^{-1} = +44.1 kJ mol^{-1}

$\Delta S^\ominus$ = (188.7 - 70.0)J K^{-1} mol^{-1} = 118.7 J K^{-1} mol^{-1} = 0.119 kJ K^{-1} mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ = 44.1 kJ mol^{-1} - (298 K x 0.119 kJ K^{-1} mol^{-1})

= $\boxed{\text{8.6 kJ mol}^{-1}}$

Exercise 43

(a) As in Exercise 42, $\Delta H^\ominus$ = -171.6 kJ mol^{-1} and $\Delta S^\ominus$ = -0.322 kJ K^{-1} mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ = -171.6 kJ mol^{-1} - (1000 K x (-0.322 kJ K^{-1} mol^{-1}))

= (-171.6 + 322)kJ K^{-1} mol^{-1} = $\boxed{\text{+150 kJ mol}^{-1}}$

This reaction is feasible at 298 K ($\Delta G^\ominus$ negative) but not at 1000 K ($\Delta G^\ominus$ positive).

(b) As in Exercise 42, $\Delta H^\ominus$ = -177.2 kJ mol^{-1} and $\Delta S^\ominus$ = -0.285 kJ K^{-1} mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ = -177.2 kJ mol^{-1} - (1000 K x (-0.285 kJ K^{-1} mol^{-1}))

= (-177.2 + 285)kJ mol^{-1} = $\boxed{\text{+108 kJ mol}^{-1}}$

This reaction is feasible at 298 K but not at 1000 K

(c) As in Exercise 42, $\Delta H^\ominus$ = +44.1 kJ mol^{-1} and $\Delta S^\ominus$ = +0.119 kJ K^{-1} mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ = 44.1 kJ mol^{-1} - (1000 K x 0.119 kJ K^{-1} mol^{-1})

= (44.1 - 119)kJ mol^{-1} = $\boxed{\text{-75 kJ mol}^{-1}}$

At 298 K water vaporises only to a small extent ($\Delta G^\ominus$ small and positive) but at 1000 K vaporisation is complete ($\Delta G^\ominus$ substantially negative).

(d)

	$CaCO_3(s)$ →	$CaO(s)$ +	$CO_2(g)$
$\Delta H_f^\ominus$/kJ mol^{-1}	-1206.9	-635.5	-393.5
$S^\ominus$/J K^{-1} mol^{-1}	92.9	39.7	213.6

$\Delta H^\ominus$ = (-635.5 - 393.5 + 1206.9)kJ mol^{-1} = 177.9 kJ mol^{-1}

$\Delta S^\ominus$ = (213.6 + 39.7 - 92.9)J K^{-1} mol^{-1} = 160.4 J K^{-1} mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ = 177.9 kJ mol^{-1} - (1000 K x 0.1604 kJ K^{-1} mol^{-1})

= (177.9 - 160.4)kJ mol^{-1} = $\boxed{\text{+17.5 kJ mol}^{-1}}$

This reaction is not feasible at 298 K ($\Delta G^\ominus$ substantially positive) but can proceed to an equilibrium mixture of reactants and products at 1000 K ($\Delta G^\ominus$ small and positive).

Exercise 44

(a) An endothermic reaction can take place spontaneously if there is an increase in entropy ($\Delta S^\ominus$ positive) and if the product $T\Delta S^\ominus$ is greater than $\Delta H^\ominus$. In these circumstances, $\Delta G^\ominus$ ($= \Delta H^\ominus - T\Delta S^\ominus$) will be negative. This is more likely if (i) $\Delta H^\ominus$ is small, (ii) $\Delta S^\ominus$ is large (e.g. much gas formed) and (iii) T is large.

(b) In most reactions $\Delta S^\ominus$ is very small so that $T\Delta S^\ominus$ at 298 K is much smaller numerically than $\Delta H^\ominus$. $\Delta G^\ominus$ will then have almost the same value as $\Delta H^\ominus$, which therefore indicates the feasibility of the reaction.

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \simeq \Delta H^\ominus \text{ if } T\Delta S^\ominus \text{ is small}$$

Exercise 45

(a) (i) the substance for which the heat of combustion is being determined,
(ii) oxygen at high pressure, (iii) water.

(b) The combustion is started by passing a current through a wire in contact with the substance in the crucible. The wire heats the sample which then burns in the oxygen.

(c) The energy produced by burning one mole of substance in constant volume conditions is the change in internal energy, ΔU, rather than the change in enthalpy, ΔH.

Exercise 46

(a) $\Delta n = +1$ mol

$\Delta U = \Delta H - \Delta nRT = +267\ \text{kJ} - (1\ \text{mol} \times 8.31 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K})$

$= (+267 - 2.47)\text{kJ} = 265\ \text{kJ} \quad \therefore \Delta U^{\ominus} = \boxed{265\ \text{kJ mol}^{-1}}$

(b) $\Delta n = -2$ mol

$\Delta U = \Delta H - \Delta nRT = -92\ \text{kJ} - (-2\ \text{mol} \times 8.31 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K})$

$= (-92 + 5.0)\text{kJ} = -87\ \text{kJ} \quad \therefore \Delta U^{\ominus} = \boxed{-87\ \text{kJ mol}^{-1}}$

(c) $\Delta n = -3$ mol

$\Delta U = \Delta H - \Delta nRT = -208\ \text{kJ} - (-3\ \text{mol} \times 8.31 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K})$

$= (-208 + 7.4)\text{kJ} = -201\ \text{kJ} \quad \therefore \Delta U^{\ominus} = \boxed{-201\ \text{kJ mol}^{-1}}$

Experiment 6. Specimen results and calculations

Results Table 7

Mass of cold water in vacuum flask	50.0 g	50.0 g
Mass of warm water added	50.0 g	50.0 g
Initial temperature of flask and cold water	23.1 °C	23.5 °C
Initial temperature of warm water	41.3 °C	45.2 °C
Final temperature of flask and mixture	31.0 °C	33.0 °C

$$\begin{bmatrix}\text{Change in heat}\\ \text{energy of flask}\end{bmatrix} + \begin{bmatrix}\text{Change in heat energy}\\ \text{of cold water}\end{bmatrix} + \begin{bmatrix}\text{Change in heat energy}\\ \text{of warm water}\end{bmatrix} = 0$$

(1) $C \times (31.0 - 23.1)\text{K} + 0.0500\ \text{kg} \times 4.18\ \text{kJ kg}^{-1}\ \text{K}^{-1} \times (31.0 - 23.1)\text{K}$
$+ 0.0500\ \text{kg} \times 4.18\ \text{kJ kg}^{-1}\ \text{K}^{-1} \times (41.3 - 31.0)\text{K} = 0$

$(C \times 7.9\ \text{K}) + (1.65\ \text{kJ}) + (-2.15\ \text{kJ}) = 0$

$\therefore C = \dfrac{(2.15 - 1.65)\ \text{kJ}}{7.9\ \text{K}} = 0.063\ \text{kJ K}^{-1}$

(2) $(C \times 9.5\ \text{K}) + (1.99\ \text{kJ}) + (-2.55\ \text{kJ}) = 0$

$\therefore C = \dfrac{(2.55 - 1.99)\ \text{kJ}}{9.5\ \text{K}} = 0.059\ \text{kJ K}^{-1}$

Mean value of $C = \boxed{0.061\ \text{kJ K}^{-1}}$

(Continued above right.)

Experiment 6. (continued)

Results Table 8

Mass of anhydrous copper(II) sulphate (0.025 mol)	3.99 g
Mass of water (0.025 x 100 mol)	45.0 g
Initial temperature of vacuum flask and water	22.5 °C
Maximum temperature of vacuum flask and water	27.5 °C

$$\begin{bmatrix}\text{Change in heat}\\ \text{energy of flask}\end{bmatrix} + \begin{bmatrix}\text{Change in heat}\\ \text{energy of contents}\end{bmatrix} + \begin{bmatrix}\text{Enthalpy change}\\ \text{of solution}\end{bmatrix} = 0$$

$(0.061\ \text{kJ K}^{-1} \times 5.0\ \text{K}) + (0.0450\ \text{kg} \times 4.18\ \text{kJ kg}^{-1}\ \text{K}^{-1} \times 5.0\ \text{K}) + \Delta H = 0$

$0.305\ \text{kJ} + 0.941\ \text{kJ} + \Delta H = 0 \quad \therefore \Delta H = -1.25\ \text{kJ}$

Scaling up to 1 mol, $\Delta H = -1.25\ \text{kJ} \times \dfrac{1}{0.025} = -50\ \text{kJ}$

$\therefore CuSO_4(s) + 100H_2O(l) \rightarrow CuSO_4(aq, 100H_2O); \quad \Delta H^{\ominus} = \boxed{-50\ \text{kJ mol}^{-1}}$

Results Table 9

Mass of copper(II) sulphate-5-water (0.0250 mol)	6.24 g
Mass of water (0.025 x 95 mol)	42.75 g
Initial temperature of vacuum flask and water	23.0 °C
Minimum temperature of vacuum flask and solution	21.8 °C

$$\begin{bmatrix}\text{Change in heat}\\ \text{energy of flask}\end{bmatrix} + \begin{bmatrix}\text{Change in heat}\\ \text{energy of contents}\end{bmatrix} + \begin{bmatrix}\text{Enthalpy change}\\ \text{of solution}\end{bmatrix} = 0$$

$0.061\ \text{kJ K}^{-1} \times (-1.2\ \text{K}) + \left(0.04275\ \text{kg} \times 4.18\ \text{kJ kg}^{-1}\ \text{K}^{-1} \times (-1.2\ \text{K})\right) + \Delta H = 0$

$-0.0732\ \text{kJ} + (-0.214\ \text{kJ}) + \Delta H = 0 \quad \therefore \Delta H = +0.287\ \text{kJ}$

Scaling up to 1 mol, $\Delta H = +0.287\ \text{kJ} \times \dfrac{1}{0.025} = +11\ \text{kJ}$

$\therefore CuSO_4{\cdot}5H_2O(s) + 95H_2O(l) \rightarrow CuSO_4(aq, 100H_2O); \quad \Delta H^{\ominus} = \boxed{+11\ \text{kJ mol}^{-1}}$

$$\begin{tikzcd}
\boxed{95H_2O(l)} + \boxed{CuSO_4(s) + 5H_2O(l)} \arrow[r, "\Delta H^{\ominus}"] \arrow[dr, "\Delta H_1"'] & \boxed{CuSO_4{\cdot}5H_2O(s)} + \boxed{95H_2O(l)} \arrow[d, "\Delta H_2"] \\
& \boxed{CuSO_4(aq, 100H_2O)}
\end{tikzcd}$$

$\Delta H^{\ominus} = \Delta H_1 - \Delta H_2 = -50\ \text{kJ mol}^{-1} - 11\ \text{kJ mol}^{-1} = \boxed{-61\ \text{kJ mol}^{-1}}$

Experiment 6. Questions

1. The reaction would be extremely slow (even with excess water as in the experiment you have done, it was quite slow).
2. Replacing lids and stoppers prevents moisture being absorbed from the air (especially important for anhydrous copper sulphate). Also, stoppers left off can be exchanged by mistake causing contamination of the contents when eventually replaced.
3. It is impossible to transfer all the weighed quantity from a beaker to the flask.

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The following schools and colleges took part in the trials of the Independent Learning Project for Advanced Chemistry. The Inner London Education Authority wishes to thank the teachers in these schools and their students for their help.

Abbey Wood School
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Elliott School
Eltham Hill School
Ensham School
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Highbury Grove School
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I6 Selected p-Block Elements

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