A STUDY OF TEACHING METHODS IN TERTIARY CHEMICAL EDUCATION

by

Frederick Percival, B.Sc.

A Thesis submitted in part fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Glasgow

Chemistry Department
July, 1976

A STUDY OF TEACHING METHODS IN TERTIARY CHEMICAL EDUCATION

A study of the aims and objectives of courses in science (but more particularly chemistry) at tertiary level has been carried out. Trends in thought have been traced historically over the past fifty years, with particular emphasis being placed on current opinions on the importance of non-cognitive outcomes of chemistry courses, and the broader educational potential of chemistry, apart from purely vocational considerations. An analysis of the strengths and weaknesses of traditional and more novel teaching methods in tertiary education has been made, and the aims and objectives of chemistry courses have been related to the methods through which they can best be achieved.

A range of self-instructional and simulation techniques have been surveyed together with a critical assessment of measurement procedures which have been devised to measure both cognitive and non-cognitive changes in students as a result of using such teaching techniques.

The chemistry courses at a typical tertiary establishment have been examined, and teaching materials produced to complement and supplement present teaching procedures.

A series of audio visual programs utilising tapes, workbooks, models and a construction kit has been produced on Transition Metal Chemistry. Many of the concepts involved are of a three dimensional nature with which the lecture, in isolation, cannot cope adequately. Assessment of the short and longer term effects of the programs has been reported.

To /

To achieve the broader educational aims of an education in chemistry, three simulation exercises have been produced. Each exercise has been written in a different simulation style, and each has been directed at different undergraduate levels. The content and rationale for each exercise has been described, along with the results of evaluations of each exercise using a range of assessment procedures.

Suggestions for further work have been proposed which are considered not only logical progressions from this work, but essential if the potential contribution of chemistry to the general education and development of the individual is to be fully realised.

CONTENTS

Appendix /

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to the supervisors of this work, Professor D.W.A. Sharp and Dr. A.H. Johnstone, for their guidance and assistance throughout this research. I am particularly indebted to Dr. Johnstone whose advice and encouragement proved a constant and invaluable inspiration.

My thanks are also due to Mr. Norman Reid, for many valuable discussions, the students of Glasgow University and of other educational institutions in Britain who co-operated in the assessment of teaching material produced for this thesis, and the S.S.R.C. for a post-graduate award.

Finally, I would like to thank Mrs. Moira Carter for preparing the typescript.

ABSTRACT

A study of the aims and objectives of courses in science (but more particularly chemistry) at tertiary level has been carried out. Trends in thought have been traced historically over the past fifty years, with particular emphasis being placed on current opinions on the importance of non-cognitive outcomes of chemistry courses, and the broader educational potential of chemistry, apart from purely vocational considerations. An analysis of the strengths and weaknesses of traditional and more novel teaching methods in tertiary education has been made, and the aims and objectives of chemistry courses have been related to the methods through which they can best be achieved.

A range of self-instructional and simulation techniques have been surveyed together with a critical assessment of measurement procedures which have been devised to measure both cognitive and non-cognitive changes in students as a result of using such teaching techniques.

The chemistry courses at a typical tertiary establishment have been examined, and teaching materials produced to complement and supplement present teaching procedures.

A series of audio visual programs utilising tapes, workbooks, models and a construction kit has been produced on Transition Metal Chemistry. Many of the concepts involved are of a three dimensional nature with which the lecture, in isolation, cannot cope adequately. Assessment of the short and longer term effects of the programs has been reported.

To achieve the broader educational aims of an education in chemistry, three simulation exercises have been /

been produced. Each exercise has been written in a different simulation style, and each has been directed at different undergraduate levels. The content and rationale for each exercise has been described, along with the results of evaluations of each exercise using a range of assessment procedures.

Suggestions for further work have been proposed which are considered not only logical progressions from this work, but essential if the potential contribution of chemistry to the general education and development of the individual is to be fully realised.

CHAPTER 1

OBJECTIVES IN SCIENCE TEACHING

CHAPTER 1

OBJECTIVES IN SCIENCE TEACHING

1.1 Developments Before the Mid-Sixties

Much of the current thought on science education at the tertiary and indeed secondary level, is concerned with which desired skills, habits, attitudes and modes of thinking the products of that education should possess in addition to purely factual knowledge.

However, a survey of the literature reveals that such consideration of the broader objectives of science teaching is not new. In 1933, Noll(1) stressed the acquisition of sound thinking habits which were fundamental to scientific activities. He concluded that an education in science should produce a scientific attitude which was described by the following habits of thought:-

(a) accuracy in all observations;
(b) intellectual honesty;
(c) open-mindedness;
(d) suspended judgements;
(e) looking for true cause and effect relationships;
(f) criticism, including self criticism.

Noll conceded that the list was not complete, but presented it as an ideal to be borne in mind by science teachers at all levels.

The Science Masters' Association (S.M.A.)(2) in 1938 listed specific features with which science teachers should be concerned. Several categories were mentioned the first of which contained a list of objectives related to the acquisition of 'scientific information and knowledge'. The second category, however /

however, was concerned with the development of scientific modes of thought and included many features which bore a close relationship to those mentioned by Noll, e.g.

(a) ability to use scientific knowledge to explain facts of ordinary life;
(b) capacity to distinguish between facts and hypotheses;
(c) isolation of relevant facts from a complex situation;
(d) ability to apply generalizations to new problems;
(e) ability to draw reasonable generalizations from experimental data.

Mention was made of a further category, namely 'the application of scientific knowledge to socially desirable ends', and the report recommended that more emphasis be laid on the latter two categories stating that objectives under the first category ('scientific knowledge and information') usually presented no particular difficulties for science teachers and examiners.

Frutchley and Tyler(3) had reached similar conclusions a year before the S.M.A. report when they suggested the desirable outcomes of a scientific course. These could be split into categories of objectives similar to those in the S.M.A. report. However, other objectives were mentioned such as 'the ability to present effective oral and written reports' and 'a habit of co-operation with others' both of which imply an emphasis on the development of communication skills. In 1945, Kesslar(4) produced a list of the elements of scientific method as a summary of scientific objectives. The list, derived following a literature survey and subsequent vetting by research scientists at the University of Michigan, was compiled with the needs of University students in mind. Most of the headings were, in fact, essentially what had emerged from the studies listed above.

During /

During the years from 1945 to 1955, most published articles on the objectives of science teaching contained lists of objectives which were subsets of those objectives mentioned previously - the precise subset being dependent upon which aspect of science the author(s) considered important. For example Heil, Kambly, Mainardi and Weisman(5) stressed the development of understanding in the context of the methods of science and knowledge of facts, while Burmester(6) in 1952 placed the emphasis on the ability to think scientifically with consequent importance attached to the recognition of problems, hypotheses, and the ability to interpret data. Dunning,(7) in contrast, was particularly interested in the development of critical thinking and produced a list of related objectives.

In 1954 Dressel and Mayhew(8) reported on research sponsored by the American Council on Education into science objectives and seven specific objectives were formulated, namely:-

(a) to apply scientific knowledge to new problems and situations;
(b) to read and evaluate articles of a scientific nature;
(c) to understand the point of view with which a scientist approaches problems;
(d) to analyse scientific data summarized in maps, tables, curves, charts and graphs;
(e) to understand the role, importance and limitations of science in the modern world;
(f) to revise judgements in the light of appropriate evidence;
(g) to recognise the need for additional scientific knowledge in a situation, and be able to acquire it.

A similarity /

A similarity between this and previously mentioned reports is the stress laid on the broader aspects of science courses in addition to knowledge of the basic subject matter.

In 1961, the Science Masters' Association(9) separated objectives in science teaching into groups of objectives which could be attained at various stages during secondary school. Thus, a major difference became apparent from the former statement of the S.M.A. (twenty-three years previously), in that objectives were to some extent tied to levels of student development, i.e. all objectives cannot be developed equally at all levels. Although many of the objectives listed are similar to those in the 1938 report, others such as 'the use of simple descriptive English' underline the growing appreciation of the need to develop communication skills.

Lewis(10) in reviewing much of the previous work on objectives in science teaching, pointed out the general trends towards the increasing acknowledgement that science is an essential part of the modern world, resulting in the growing importance of communication skills and the need to relate scientific phenomena to everyday life. Lewis also noted the increasing emphasis on objectives other than the memorization of factual knowledge, although the distinction between acquisition of information, and the application and evaluation of that information is important. However, little evidence of these broader objectives being embodied in science courses was found, and Lewis concluded that the reason for this was that 'factual knowledge is easier to test'.

1.2 Developments Since the Mid-Sixties

Broadly speaking, a factor which distinguishes the /

the last decade from previous decades is that some of the broader objectives of science teaching, similar to those mentioned in Chapter 1.1, are beginning to be more widely accepted, and even included in some science courses. As Beard(11) has stated:-

> " ... investigations have proceeded from emphasis on subject matter alone to consideration of differences between students' abilities, personalities and circumstances ... and, from planning curricula around subject headings, to specifying objectives in terms such as skills, knowledge, and attitudes which students should attain."

This trend is illustrated if one looks at the aims of the Nuffield Science Teaching Project(12) which in 1966 re-appraised the place of science in education. The emphasis was changed from the short-term remembering of specific facts to an approach which, hopefully, would instil in students a long-lasting commitment to approach everyday problems scientifically. It was also hoped to develop a critical attitude of mind and encouragement was given to teachers to emphasise the personal commitment of the scientist, the importance of the disciplined guess, the logical argument, and the readiness to make 'apparently unwarranted jumps' while knowing how to check their validity.

Another example of broader objectives being incorporated in secondary science education occurs in a report made to the Consultative Committee on the Curriculum of the Scottish Education Department in 1969.(13) The report stated objectives more specifically than its Nuffield equivalent and many are phrased in such a way as to suggest that a course in science should produce attitudinal changes, e.g.

(a) awareness of the inter-relationship of the different /

different disciplines of science;

(b) awareness of the relationship of science to other aspects of the curriculum;

(c) awareness of the contribution of science to the economic and social life of the community;

(d) interest and enjoyment in science;

(e) an objectivity in observation and in assessing observations;

(f) an interest and a willingness to participate in science-related leisure pursuits;

(g) a willingness to conform to, and an interest in propagating sensible rules for safety and good health for the sake of the community as well as the individual;

(h) an interest and a willingness to participate in conservation of the natural environment;

(i) an interest in gathering information about science through all the media of communication.

As with the 1961 Science Masters' Association report (Chapter 1.1), these objectives are separated into groups to be attained at different stages during secondary school. For the list above, objectives (a) - (e) are for pupils of the first two years of secondary school while objectives (f) - (i) are for pupils in years three and four of secondary school, in addition to the preceding five objectives.

The report obviously reflects the increasing awareness of the importance of attitudinal objectives in modern education.

There is much evidence for the trend away from considering science, and in particular chemistry, as a purely vocational and factual subject. Goodall(14) in summarising a joint British/American symposium on Chemical Education highlighted this drift and suggested that chemistry could be used as the vehicle for the development of judgement, and skills of oral and written communication. /

communication. Wolke(15) echoed this argument and called for more appreciation of the social, economic and aesthetic contributions of chemistry to everyday life rather than merely the regurgitation of 'dry' equations.

At tertiary level Holliday and Maskill(16) have produced a list of 'desired skills' of a graduate in chemistry. This list contains many skills which are related to the objectives listed in Chapter 1.1, but others are added. Similar course objectives have been mentioned elsewhere by Beard(17) and Holliday.(18) Hughes, Poller and Slade(19) outlined broad aims of chemistry teaching under the headings of knowledge, skills and attitudes, while Holliday, Hughes and Maskill(20) suggested more aims and objectives in university chemistry teaching and described how these were applied to an undergraduate chemistry course at Liverpool University. Yet another list containing seventeen broad aims and objectives of chemistry courses was given by Billing.(21)

Obviously, the above lists of desired skills/objectives/aims cover much common ground as all are related to the outcomes of tertiary chemistry courses apart from basic lower cognitive skills such as recall of specific facts. Therefore, to avoid repetition, the list below entitled 'Desired Skills of the Chemist" has been compiled after consideration of the suggestions in the articles referred to in the previous paragraph.

"<u>Desired Skills of the Chemist</u>"

The potential graduate in chemistry should possess the following abilities:-

(a) to argue logically;
(b) to see flaws in arguments and hypotheses;
(c) to identify problems and devise means for solving them;
(d) /

(d) to make and defend decisions;
(e) to make decisions on incomplete information;
(f) to make compromises;
(g) to obtain relevant information;
(h) to see interconnections within the subject;
(i) to realise the existence of interconnections across subject barriers;
(j) to co-operate in discovery;
(k) to write and speak fluently and grammatically;
(l) to teach others in public;
(m) to work to a budget;
(n) to apply a precise, scientific approach to problems;
(o) to appreciate the limitations of science in solving some problems;
(p) to use a library efficiently;
(q) to read and summarise a scientific paper critically and efficiently in both written and verbal form;
(r) to realise that the scientific literature may sometimes be misleading;
(s) to realise the hazards of lack of thoroughness in scientific work;
(t) to spot key facts among less relevant data;
(u) to discriminate between fact and opinion;
(v) to appreciate the value of historical lessons in chemistry and chemical research;
(w) to participate in social relationships within small groups;
(x) to exercise empathy.

This list, although by no means exhaustive, gives some indication of the skills currently thought important for chemistry students. This list does not include any of the lower cognitive or psychomotor skills more commonly associated with chemistry courses, although such skills are also of extreme importance to the graduate in chemistry. However, much time and effort is spent in higher /

in higher education in teaching the lower cognitive and psychomotor skills through the media of lectures and laboratories. Often skills such as the twenty-four listed above are not consciously taught in universities, although it is perhaps hoped that they 'rub-off' on the students during their courses. This point will be further discussed in Chapter 2.3.

1.3 Classification of Educational Objectives

Scientific objectives can be split into three categories - cognitive, affective (attitudinal) and psychomotor objectives. Possibly the most important contribution to the classification of objectives - and not one limited to the scientific field - was that provided by Bloom in his 'Taxonomy of Educational Objectives' in the cognitive domain in 1956(22) and in the affective domain in 1964.(23) Bloom's work has proved very influential in educational thought due to the growing conviction among educators that not only is it important to lay down broad educational objectives but also, if possible, to break these down further into more specific objectives phrased in behavioural terms (Mager(24)) and arranged in a system of classification which, although perhaps artificial, allows a greater degree of operational specificity.

Cognitive domain

The taxonomy applied to the cognitive domain has been used extensively in the testing of cognitive objectives in many school subjects, and it is possible that its full impact on the educational practices associated with teacher training, curriculum planning, and testing and evaluation has still to be realised.

Bloom /

Bloom split the cognitive domain into six major categories as follows:-

(1) KNOWLEDGE, including (a) knowledge of specifics (i.e. the recall of relatively isolated pieces of information);
    (b) knowledge of the ways of dealing with specifics;
    and (c) knowledge of general principles.

(2) COMPREHENSION, representing the lowest level of understanding, i.e. when one knows and can make use of the material communicated without necessarily relating it to other material, or seeing it in all its implications.

(3) APPLICATION, abstracting from a particular situation and applying the abstraction in other ways.

(4) ANALYSIS, involving the breakdown of material into its constituent parts including,
    (a) analysis of elements;
    (b) analysis of relationships.

(5) SYNTHESIS, involving the combination of elements to form a structured whole.

(6) EVALUATION, representing judgements (quantitative and qualitative) about the extent to which the material satisfies evidence or criteria. This includes,
    (a) judgements in terms of internal evidence;
    (b) judgements in terms of external evidence.

On a cautionary note, however, it should be noted that attempts to validate the taxonomy have proved inconclusive.

In 1966, /

In 1966, Kropp, Stocker and Bastow(25) in discussing possible ways of attempting to validate the cognitive taxonomy, suggested that the four basic assumptions made by Bloom should be investigated. The assumptions are:-

(a) all processes stipulated are cognitive;
(b) the progression of categories from knowledge to evaluation is hierarchical according to complexity of the process;
(c) the hierarchy of categories is cumulative, i.e. any given category consists of the processes stipulated by all lower level categories;
(d) the mental processes designated are all learned behaviours.

Kropp et al further proposed that attempts to answer the following four questions may prove fruitful:-

(a) Is the taxonomy inclusive of <u>all</u> cognitive processes?
(b) Are all processes listed cognitive?
(c) Is the taxonomy hierarchical?
(d) Are the categories cumulative?

Stedman,(26) in 1973, produced the first real evidence to challenge the taxonomy. Although Stedman appreciated the worth of a formal classification of objectives, he was worried by the fact that almost twenty years after the publication of the cognitive taxonomy, Bloom's four basic assumptions had not yet been empirically validated, and he stated that a major deficiency of the taxonomy was 'a dearth of statistical support'.

In his research, Stedman investigated Bloom's assumptions that the first four cognitive levels of the taxonomy of educational objectives are arranged hierarchically, and that the hierarchy is cumulative.

Mental ability and motivation scores were used to /

to divide one hundred and forty-four high school students into six blocks. A 93-frame program in genetics was administered, and on the completion of the program, the students took a 28-item post-test that had scores for the cognitive levels of knowledge, comprehension, application and analysis. Results indicated that no significant differences existed in performance between knowledge and comprehension questions or in performance between application and analysis questions. A significant difference was found beyond the 0.0005 level however, between comprehension and application. Significant differences between comprehension and application were consistent across levels of mental ability and motivation, and this consistency was maintained for a lack of significant differences between knowledge and comprehension or application and analysis. Stedman concluded that:-

(a) the assumption that the hierarchy of categories is cumulative is possibly in error;

(b) the assumption that the categories of the taxonomy are hierarchically arranged is acceptable only if the hierarchy is viewed as progressing unevenly from low cognitive levels to higher cognitive levels. The cognitive processes involved in moving from comprehension to application appear to be different from those between knowledge and comprehension or between application and analysis.

These conclusions, although tentative, do imply a potential weakness in the assumptions underlying the taxonomy of educational objectives. It would, however, be rash to generalise too widely from the above conclusions, and Stedman himself pointed out potential weaknesses in his research design. The relatively small number of items used to evaluate each of the four cognitive /

cognitive levels, and the use of programmed materials in genetics both served to restrict the generalising power of the conclusions. A further weakness of Stedman's research was that only four out of the six cognitive categories were investigated, and this must also restrict the scope of the conclusions.

However, the differences between comprehension and application are striking enough to warrant more detailed and specific research, the results of which have still to be reported.

Despite the above reservations on its validity, the taxonomy still has value in that it provides a formalised classification in an area where formalisation is difficult. For instance, it will be noted that many of the desirable objectives of science courses listed in Chapters 1.1 and 1.2 can be fitted into the categories of application, analysis, synthesis and evaluation, although in tertiary science education, the media of lectures and laboratories are probably best suited to fulfil lower-order cognitive objectives in the categories of knowledge and comprehension.

Affective domain

Other objectives of science courses listed earlier (e.g. a commitment to approach problems scientifically) involve attitudes as well as the learning and manipulation of concepts and facts. This area, called the 'affective domain' has been categorized by Bloom et al(23) in ascending hierarchical order as follows:-

(1) RECEIVING, awareness of, and willingness to receive certain stimuli such as aesthetic factors of a subject;

(2) RESPONDING, implies active attention at a low level; taking an interest;

(3) /

(3) VALUING, perceiving phenomena as having worth and revealing behaviour consistent with this attitude;

(4) ORGANISATION, conceptualization of values and ordered relationships between values;

(5) CHARACTERISATION, organisation of values into a total and consistent philosophy.

Lewy(27) attempted empirical validation of the taxonomy at the levels of receiving, responding, valuing and organisation. He concluded that empirical referents for the constructs of the Affective Taxonomy could be both directly observed in human behaviour and defined in terms of a particular category of the model. It was further claimed that the hierarchical structure of these referents corresponded to that claimed by the model.

It should be noted, however, that only four categories of the Affective Domain were considered, and Lewy's procedure involved a degree of subjectivity.

The suitability of various teaching methods in tertiary education to teach different levels of cognitive and affective objectives will be discussed in Chapter 2.

1.4 Education through Chemistry?

It has been noted in previous sections that there is some evidence of a trend away from factually-orientated science courses in favour of courses to develop broader desired skills and attitudes in students. In no science subject is this trend more apparent than in chemistry where there have been several calls recently for education through chemistry rather than education in chemistry, i.e. using chemistry as the vehicle /

the vehicle for developing skills in communication, problem-solving, critical reading etc., in addition to teaching and developing desired attitudinal tracts. Those who take this view believe that it is possible to educate students to take their place in society, through the medium of chemistry.

Arguments on this emotive issue inevitably revolve around the basic question, "What is the role of science in education?" The argument that chemistry is a vocational subject and that chemistry should be used as a training for professional chemists is difficult to defend except perhaps with Honours students at university. At Glasgow University for instance, the students studying first year chemistry number over five hundred, on average, while an average Honours class consists of about thirty-five students. Even with students studying chemistry to Honours level, most of the specific facts 'crammed' for the final examinations are probably soon forgotten, and even if they are not, much of the factual knowledge gained is likely to become redundant well within the lifetime of the student.

In calling for more broadly based chemistry courses, Greenwood(28) has criticised the inward view of many chemistry courses, and argues that -

> "science and science education have an obligation at all levels not only to impart the thrill of discovery and the intellectual satisfaction of rational explanation, but also to discuss the implications of its findings, so that young people can be alerted to the problems facing society, gain an understanding of their nature, and feel involved in finding solutions."

Greenwood went on to suggest that the aims of chemistry courses should be -

"not /

> "not only the training of specialist chemists, but also the education of scientifically knowledgeable students whose understanding of chemistry will inform their thinking on important issues, and enrich the quality of their lives."

Such proposals may prove over-ambitious but do reflect current modes of thought.

Lord James(29) in calling for education through chemistry argued that the subject has the potential to fit a person not merely to be a professional chemist but to hold his own in other disciplines and cultural life. He claimed, bitterly, that in many chemistry courses students have been offered 'the latest detergent, rather than an intellectual adventure'.

Further indications of present feelings were echoed by the Association for Science Education(30) who argued that the main aim of science teaching must be to develop effective decision-making in students through practical experience of problem solving, which should also encourage the students to make value judgements. This approach changes the emphasis from teaching knowledge for its own sake to a consideration of practical problems in which the issue of the 'right answer' may not be relevant as there are often several possible solutions to a problem, each of which may be judged on merit according to the value systems of those concerned.

Thring(31) in agreeing with this, argued that such an approach was essential in developing attitudes such as self-awareness, autonomy and responsibility essential to a student's future role in a complex and changing society.

Holliday(18) who also called for a broader education through /

through chemistry, stated that chemistry courses must be relevant to all concerns of mankind whether social, economic or philosophical. However, Holliday believed that priority must be given to the development of communication skills in order to achieve relevance, and refers to a 'Science Communication' course at Liverpool University which was introduced to help develop such skills.

An interesting piece of research reported by Hadden, Handy and Johnstone(32) investigated a few of the affective objectives which were listed as the desired outcomes of a science course at school level. The level of attainment of these objectives was compared for science and non-science pupils. In most cases the science pupils accomplished a better level of achievement on tests designed to measure the attitude. However, as the authors have pointed out, this does not necessarily mean that science courses are inculcating these desirable attitudes - it may be that such attitudes are already inherent in science pupils and are merely confirmed by their selection of science subjects. Nevertheless, if it is demonstrated that science courses can be effective in developing desired skills and attitudes in students, there is surely a case for changing the emphasis of science courses so that they can do so even more effectively.

CHAPTER 2

THE SUITABILITY OF METHODS IN TERTIARY CHEMISTRY EDUCATION TO ACHIEVE DESIRED EDUCATIONAL OBJECTIVES

CHAPTER 2

THE SUITABILITY OF METHODS IN TERTIARY CHEMISTRY EDUCATION TO ACHIEVE DESIRED EDUCATIONAL OBJECTIVES

2.1 Traditional Methods

(a) The lecture

In science subjects, the traditional teaching methods at tertiary level have long been lectures, laboratories and to a lesser extent, tutorials. Of these three methods, the lecture is still predominant in most establishments of tertiary education. Surprisingly little of scientific value is known about the lecture, and opinions about the pros and cons of lectures are usually voiced more loudly than the results of controlled empirical investigations.

The opinion of the Hale Report(33) in 1964 was that the lecture could effectively fulfill a three-fold function, namely:-

(1) to convey information;
(2) to promote thought;
(3) to change attitudes;

Most of the available evidence however, indicates that while lectures may be reasonably efficient at transmitting information, they are relatively ineffective at promoting thought or changing attitudes, due mainly to the fact that in the lecture situation the student is normally passive.

(1) Effectiveness of lectures in conveying information

In comparing the effectiveness of lectures to other /

other teaching methods with regard to their ability to transmit information, Dubin and Taveggia,(34) in 1968, reviewed ninety-one studies which compared lectures with other teaching methods on one or more measures of 'course content'. Most of the measures were objective tests of the multiple-choice, true/false, or sentence completion type used in course examinations, and were tests of factual knowledge. Other teaching methods used in the comparison included individual reading, televised programmes, audiotapes, individual laboratory work, projects, films, seminars and various discussion methods.

The majority of studies indicated no significant difference between lectures and other modes of teaching in their abilities to convey information, and those that did show a difference were fairly evenly balanced either way. Data for lectures compared with programmed learning was not included as there were few programs which provided a practical alternative to a lecture course at that time. McKeachie(35) emphasised the review findings of Dubin and Taveggia by stating that a host of research reports in this area remained unpublished because there were no significant differences to report. On the basis of this evidence, it appears that, with the possible exception of programmed learning, the lecture is as effective as other methods for transmitting information, but not more effective. However, it is not recommended that discussion methods should be used primarily to teach information. They are expensive in staff time, and the one significant comparison Dubin and Taveggia obtained was that unsupervised reading is superior to discussion for the acquisition of information.

(2) Effectiveness of lectures in promoting thought

The second of the Hale Report's assertions, namely that /

that lectures can be used to stimulate thought, finds little supporting evidence in the literature. Bligh(36) in summarizing twenty-six different comparisons between lectures and more active teaching methods, mainly discussion methods, found that twenty-one of the studies concluded that more active methods stimulate thought better than the lecture method, the remaining five studies showing no significant difference.

The probable reason for the advantage of discussion methods in developing thinking skills is simply that the student is being placed in an active situation where he has to think and respond, compared to his relatively passive role in lectures. Evidence of this was obtained by Bloom(37) in 1953 when he used an interview technique to analyse how students spent their time during the lectures compared to discussions. During discussions, students spent significantly more time engaged in synthesizing information, solving problems and significantly less time engaged in passive and irrelevant thoughts. Bloom claimed the results are reasonably valid because although the method was subjective, the sample was large.

(3) Effectiveness of lectures in changing attitudes

The third assertion of the Hale Report, namely that lectures can be effective in changing attitudes again finds little support from research findings. Bligh(36) summarized twenty-five studies which compared lectures with other teaching methods, taking attitudes towards the subject matter as the criterion. Only one study favoured the lecture method, with nine showing no significant difference. Bligh warned, however, that this cannot be taken as conclusive evidence as the total number of lectures and discussion tutors was small compared to the number of uncontrolled personality variables which must have been involved. In general, however, it /

it would appear that lectures are not as effective as more active methods for changing attitudes.

From the above argument, it seems that lectures are best suited to teach information including the framework of a subject, i.e. the lower cognitive categories of Bloom's taxonomy. Lectures also have a use in defining the scope of a course. It might be argued, however, that since the acquisition of information is basic to all the other Bloom categories (assuming the taxonomy to be hierarchical) a test of factual knowledge may, if only indirectly, be a measure of the attainment of Bloom's 'higher-order' objectives, but experimental studies by Tyler(38) and Stedman(26) in American schools and universities have shown that the correlation between knowledge and application of that knowledge is usually very small. The evidence suggests that higher-order objectives may have to be 'taught for' directly - and they are not the inevitable by-products of instruction. Research by Hoare and Revans(39) has suggested that another factor involved in the attainment of Bloom's 'higher-order' objectives may be intelligence.

(b) Laboratories

The traditional functions of laboratories in tertiary science education include the development of psychomotor skills and the reinforcement of theory by, for example, providing experimental evidence for work covered in lectures. Other 'higher-order' cognitive objectives and skills in communication, critical thinking, library use and problem solving may be developed in the laboratory if appropriate experimental work such as project work or open-ended experiments is undertaken.

The laboratory situation is also capable of developing some of the affective objectives mentioned in Chapter 1, such as 'a commitment to safety' and 'a commitment to accuracy'.

Too /

Too often, however, the full potential of laboratory work is lost due to a 'cook-book' approach, requiring little or no understanding and original thought on the part of the students.

(c) Tutorials

Tutorials can be useful for developing communication and problem solving skills. Very often however, the topic and general direction of a tutorial session is uninspiring, and the tutorial is then in danger of becoming a mini-lecture, almost totally dominated by the tutor. The success of the tutorial system is often dependent on the teaching skill of the tutor, and few staff in universities or colleges are trained in small group teaching skills. This lack of skill is reflected by Broadley's account(40) of tutorial methods which, he claimed, often lead to silence, upon which the tutor 'begins to talk frequently, and feels compelled to fill the gap of silence by giving a mini-lecture, as it is sometimes called. But this defeats the purpose of the tutorial which is actively to engage the student in discussion'.

2.2 Other Methods

To support, and in some cases replace, traditional methods in tertiary science teaching, new methods have been introduced over the past few years in an attempt to attain those objectives and skills to which more traditional methods are not well suited. In some educational institutions, the newer methods have completely superseded the old although the lecture and laboratory still remain the backbone of science courses in most universities in Britain.

Mention will be made of non-traditional teaching techniques /

techniques within two broad categories of teaching methods, namely (a) self-instructional methods, and (b) discussion methods.

(a) Self-instructional methods

Systematic instruction in the absence of a teacher can range from something as simple as unsupervised reading of a text-book, to the technological complexity of computer aided learning. One aspect which all self-instructional media have in common is that they can allow students to proceed through the learning material at their own pace, and can often involve the student in a good deal of active participation. This is in marked contrast to the lecture situation where the student is cast as the passive listener, and the rate of instruction is paced by the lecturer as there is usually very little feedback from the class during a lecture to help him adjust his pace. This aspect of the lecture probably leads to the creation of a learning spectrum amongst the students (especially in large classes of varying ability). This 'learning spectrum' can range from students who completely understand everything the lecturer has said, to students who are totally lost. The majority of the class will lie at various points between these two extremes. This problem is one which only self-paced learning methods can hope to alleviate.

(1) Programmed learning

The most common self-instructional method used in education (apart from text-books) is probably programmed learning. At present, programmed learning is used in universities and colleges to a modest extent. Billing(41) has defined programmed learning as 'a systematically designed and structured set of materials or events through which the student achieves defined learning objectives', and has listed the following basic components of the approach:-

(i) Specification of broad aims and more detailed objectives in advance;
(ii) Construction of a test which will measure how far students attain the objectives;
(iii) Design and construction of materials and situations from which the student will attempt to achieve the objectives;
(iv) Validation of these materials by means of trials with students;
(v) Revision of the materials on the basis of the trials.

The construction of self-instructional programs is very flexible and may use the media of audiotapes, printed pages, slides, film loops, models, overlays, actual samples etc., in many combinations.

There are also several general styles which programmed materials can follow, the two most commonly used being linear and branching programs.

(i) Linear programs were first developed by Skinner.(42) The learning process proceeds in a sequence of steps (frames) directed towards desired goals. In this type of program, there is only one path which the student can take through the sequence of frames.
(ii) Branching programs were first used by Crowder.(43) In such programs, there are several routes through the frames, due to the provision of 'remedial loops' which are designed to rectify common misconceptions.

Programmed learning materials have been used in some establishments to replace lecture courses, while in others their role has been complementary to the lecture. In both these functions, the method has usually been used to enable students to gain 'mastery' of /

of desired factual material. 'Mastery' usually involves students performing above some arbitrarily set level (often 80%) in a subsequent test.

Experimental studies on the efficiency of programmed learning indicate that programs are at least as effective as lectures for teaching factual information,(44)(45) while Owen, Hall, Anderson and Smart(46) have claimed that programs are better than lectures for less able students. Stavert and Wingate(47) and Teather(48) confirmed these findings, and further suggested that programs take as little as two-thirds of the time for average students to efficiently cover the same ground as a lecture. Research into the optimum length of programmed material by Barrington(49) suggested that individual programs should last no longer than twenty-five minutes.

(2) Keller plan

Self-instructional methods have completely replaced lectures in some educational institutions, the best known personalised system of instruction being Keller Plan courses, which are a form of independent learning originally developed by F.S. Keller(50) of Columbia University. Having received a prescribed set of objectives, students work largely on their own, and at their own pace, from units of various self-instructional materials, each unit often representing one week's work. When the student feels he has mastered a given unit, i.e. feels he can satisfy all the objectives, he presents himself for a test which he must pass before going on to the next unit. Although some experiments have claimed that students learn information better, work harder and find the Keller approach more interesting than normal courses,(51)(52)(53)(54) and Linder and Whitehurst(55) concluded that consistently favourable student opinions towards Keller Plan courses are not due to a 'novelty' effect, other workers such as /

as Bent,(56) Hendrick(57) and Young(58) were less satisfied, claiming that results were not appreciably improved although both staff and students were working harder. Emerson(59) also had reservations about the method arguing that 'mastery' of information in each unit is attained at the expense of the development of Bloom's higher objectives (cognitive and affective) and that Keller plan students may be getting 'more training than education'. However, this need not be the case if programmed materials are less heavily relied on, and used only to fulfil the objectives to which they are best suited, namely lower cognitive skills.

The construction and assessment of a series of self-instructional programs on transition metal chemistry are described in Chapter 4. These programs were designed to complement a lecture course given to first year chemistry undergraduates at Glasgow University.

(b) Discussion methods

Intuitively, at least, it would appear likely that, of all the teaching methods so far discussed in tertiary science education, active discussion methods offer the greatest potential for the development of the broader objectives of science teaching such as communication skills, problem solving skills, decision making skills, critical thinking skills and attitudinal change. Courses involving an increased amount of student involvement were recommended in 1972 by Beard,(60) who suggested that discussion and co-operative work in small groups should occupy a significant proportion of teaching time. Examples of such methods are becoming increasingly common. A course with similar objectives to Liverpool University's course in 'Science Communication' (Chapter 1.4) has been developed at Surrey University by Elton.(61) In this course, discussion /

discussion groups read and critically analyse topical articles from newspapers and journals in both written and oral form. Similar methods to develop skills in communication and critical appraisal have been described by Youmans(62) and Epstein.(63)

Research evidence that even limited group discussion can have an influence on subsequent oral work was obtained by Erskine and Tomkin.(64)

Gaming and simulation techniques

One of the largest growth areas at all levels of education at present is in the field of academic gaming and simulation. The characteristics and possibilities of this field will be discussed at some length, as Chapters 5, 6 and 7 of this thesis describe the development and attempted assessment of teaching materials which are closely related to this subject area, especially the simulation aspect.

Gaming and simulation methods have been used for many decades in such forms as war games in military training, business games in industrial training and flight simulation for training pilots. The first formal use of such techniques in education, however, occurred little more than a decade ago in America, and even more recently in Britain. Most of the work so far has been done in the social sciences, while the potential for games and simulations in the pure sciences has had little or no investigation.

Definitions

The two general components of the field, namely simulations and games have been defined as follows:-

Simulation:- 'The representation of a situation or environment by some analogue, usually /

usually of less complexity and greater convenience and often with a compressed time scale.'

Tansey and Unwin(65)(1969)

'An operating representation of the central features of reality.'

Guetzkow(66) (1963)

'Activities which produce artificial environments or which provide artificial experiences for the participants in the activity.'

McGarvey(67) (1971)

'An on-going representation of reality; it may be an abstracted, simplified or accelerated model of the process.'

Bloomer(68) (1973)

'A means for letting learners experience things that otherwise might remain beyond their imagination, a means to practice skills safely and without embarrassment, and perhaps even discover insight into the problems now plaguing mankind.'

Twelker(69) (1970)

'Simulation = real life - task irrelevant elements'

Twelker(70) (1971)

Game:- 'A simulation situation with an injected element of artificial competition'

Tansey and Unwin(65) (1969)

'Any contest (play) among adversaries (players) operating under constraints (rules) /

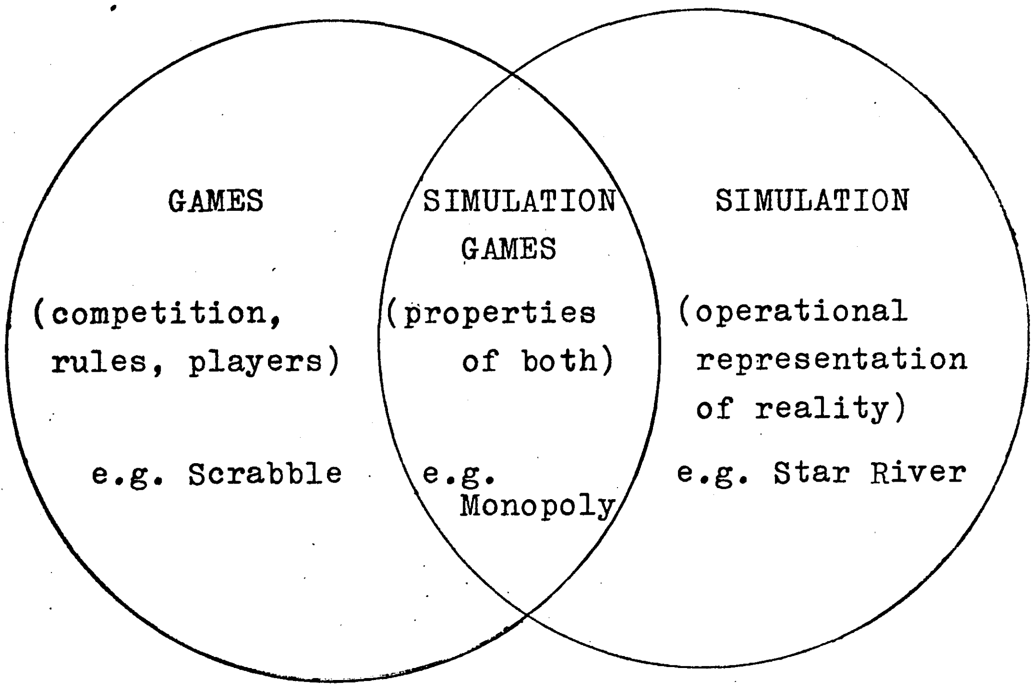
> (rules) for an objective (winning, victory or pay-off)'
>
> Abt(71) (1968)

> 'Something enjoyable, however serious, involving competition for specified objectives and observing rules'
>
> Nesbitt(72) (1956)

> 'A situation when one or more players compete for pay-offs, according to an agreed set of rules'
>
> Bloomer(68) (1973)

Other definitions of games and simulations exist, but most re-state the general features listed above. It appears from the above definitions that simulations are characterized by the inclusion of the essential features of reality and often involve co-operative efforts, while games possess players, rules and the element of competition.

The two concepts of games and simulations are often treated synonymously in the literature, for example Boardman(73) saw no harm in interchanging the words, and Fines(74) exhibited a similar confusion. It should be clear from the definitions given that games and simulations are distinct teaching methods. Bloomer(68) has neatly summarized the situation in the following diagram into which she has introduced the term 'simulation game' to describe activities with characteristics of both games (competition, rules, players) and simulations (operational representations of reality). A reasonably well-known example of each category is also given.



The Relationship between Games and Simulations
(after Bloomer(68) (1973))

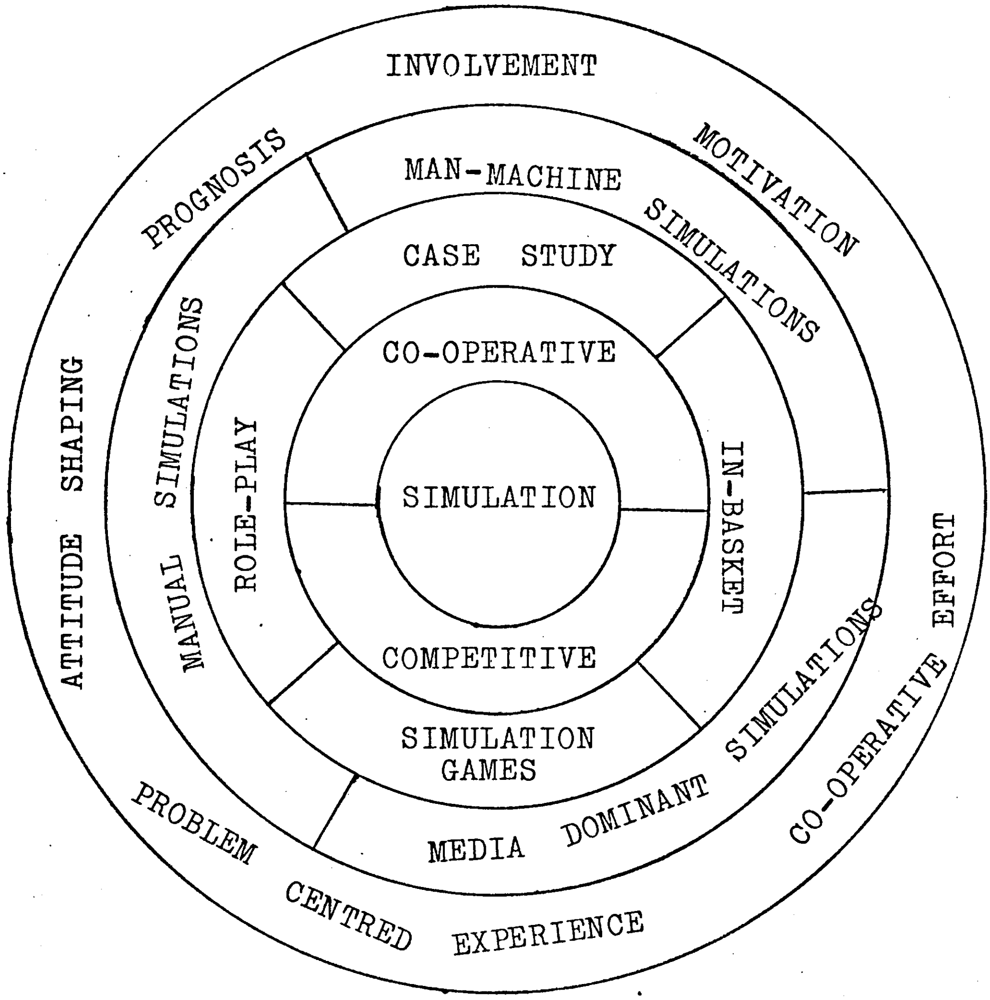
Simulation methods

As Chapters 5, 6 and 7 describe the construction and assessment of materials which are more akin to the category of simulations than games, the remainder of this section will be concerned with the uses and assessment of simulations in education.

It was noted above that simulations are operational representations of reality, often involving a co-operative rather than a competitive approach. Simulation is a technique used for a number of reasons, often because the real life situation, whether it is to be used for concept or skill training, is too complex, difficult or dangerous. In such cases educational models of the situation are designed in which the complexity of the real life situation is reduced, i.e. the 'task-irrelevant elements'(70) are removed.

Tansey /

Tansey,(75) has attempted to summarize some of the aspects of simulation in the diagram below:-



Some Aspects of Simulation

(adapted from P. J. Tansey,(75) 1971)

Apart from simulation games, Tansey makes mention of three other types of simulation, namely (1) case studies, (2) role-play and (3) in-basket exercises.

(1) Case studies have been defined by Walker(76) as 'a study in detail of a particular event, problem or situation'. This all-embracing definition covers a whole spectrum from completely open-ended situations to problems with clearly defined limits. Walker claims that /

that case studies can be divided into three types, (i) problem cases, (ii) illustrative cases and (iii) case histories.

(i) Problem cases are used to teach, train or analyse patterns of behaviour;
(ii) Illustrative cases are used to demonstrate a principle by using a concrete situation;
(iii) Case histories are often a blend of the above two types since a description of a situation, and its outcome enable a student to learn from retrospection of the whole approach.

Claimed aims of case studies include:-(76)

(a) to encourage learning by doing;
(b) to develop generalizations by building up understanding on a framework of experience;
(c) to promote interest and enthusiasm by providing realism;
(d) to introduce a multi-disciplinary approach.

Daniels(77) has claimed that case studies can be of particular value in encouraging students to exercise value judgements and moral evaluations, and often these have to be made with due regard to practical considerations.

(2) Role-playing exercises involve a high level of student involvement. In such exercises, students are put in the position of other people (e.g. a conservationist, an industrial chemist, etc.) and placed in situations in which they have to view possible courses of action from the eyes of the person whose role they have assumed. Intuitively it would appear that role playing simulations could enable students to exercise increased empathy and tolerance.

(3) In-basket exercises are used to introduce problems into a simulated situation. Such exercises are often used /

used in teacher-training for example, to enable students to learn how to cope with classroom situations which may arise at any time.

Claimed benefits of simulation

One of the major reasons for using simulations is that some positive transfer of training will hopefully occur, i.e. students will be able to use skills gained during simulations in other situations. Three types of positive transfer of learning have been described: (i) lateral and (ii) vertical transfer, suggested by Gagné,(78) and (iii) parallel transfer suggested by Twelker.(70)

(i) Lateral transfer involves the application of knowledge gained in one circumstance to a broad variety of new situations at about the same level of complexity;

(ii) Vertical transfer involves the application of subordinate principles to the learning of new principles, possibly at a higher conceptual level;

(iii) Parallel transfer involves the application of the same operation to the same situation as in the instructional condition, but under new conditions.

All three types of transfer may be appropriate to the field of gaming and simulation, depending upon the characteristics and objectives of the material used. It would, however, be difficult to justify the use of simulated materials in education if no transfer of learning occurred.

Tansey(79) has summarized the advantages of simulation in education as being that:-

(a) It motivates the participants;
(b) It uses techniques of co-operation as opposed to competition;
(c) It enables teaching for the long range future to take place even with students who are not highly motivated to learn;
(d) It injects a feeling of realism and relevance into a course;
(e) It enables complex problems to be simplified and so the crucial features are emphasised;
(f) It changes the social conditions under which learning takes place, i.e. the tutor can take a less dominant role than normal;
(g) Decision-making without censure is possible. The student's decision can be discussed in the light of its possible eventualities.

Cruickshank(80) has listed a similar set of advantages for simulations, but has also included:-

(a) Simulations establish a setting wherein theory and practice can be combined;
(b) Simulations are relatively safe in that decisions can be made without physical or psychological harm to either the student or community, although this may detract from the realism aspect.

Bloomer(81) has made similar claims for the simulation method, but has added:-

(a) Simulations are especially useful where objectives include changing students' attitudes and/or where objectives are experiential;
(b) Simulations are useful where multi-disciplinary subject matter has to be integrated and applied to a common, often practical purpose. In such situations the relevance of the exercise is often obvious to the students;

(c) Simulations, especially role-playing exercises, can breed strong identification and empathy.

Evaluation of simulation techniques

Despite the manifold advantages which are often claimed for simulations, as witnessed by the above section, there is a paucity of good experimental evidence to indicate that simulations actually achieve what advocates of the method claim they achieve. However, this lack of evidence does not imply that such claims are unfounded, but reflects more on the inadequacy of current assessment tools to measure the effectiveness of simulation materials. Present instruments for measuring achievement are mainly centred on conventional instructional methods and often measure only knowledge gained. The justification for using simulations, however, is that they are supposed to develop skills in such areas as communication, problem solving and decision making, in addition to possibly changing attitudes and behaviour patterns. Many evaluative attempts in the area of games and simulations have proved inconclusive due to the unsuitability of the assessment device for measuring such skills and attitude changes. Another reason for the lack of conclusive results may lie in the standard of previous research, which has been criticized by several workers in the field.

Many attempted evaluations of simulations have been published, by far the majority of work being American. However, despite the quantity of work, it has been claimed that very few well planned and tight research attempts have been reported.

Fletcher(82), in 1971, and Wentworth and Lewis(83) in 1973, have published useful and critical reviews of research on evaluation of simulations in education.

Fletcher /

Fletcher criticized the approach of many researchers who investigated particular simulations or games, each study employing its own battery of tests to measure different sets of variables. Such approaches made attempts to replicate findings virtually impossible. Among the reasons cited by Fletcher for the low quality of available research were:-

(a) A lack of standardized workable games and simulations;
(b) Simulations varied enormously in objectives, structure and level of sophistication;
(c) Most simulations studied were not adequate models of reality.

Fletcher, however, made little mention of the lack of adequate evaluation methods which would appear to be a major contributing factor to the level of research quality.

Point (b) above is valid criticism only if one is attempting to generalize on the uses of simulations. One of the major attractions of simulation techniques is the very fact that they are so versatile as to be able to vary enormously in objectives and in sophistication.

Wentworth and Lewis were also very critical of much of the research reviewed mainly because of 'inadequate testing procedures and research design, use of unsophisticated statistics, and inability to determine important variables'. Despite their reservations about the standard of much of the work, Wentworth and Lewis concluded from the research which had been done that:-

(a) Simulations do not appear to have any advantage over other methods in teaching content, i.e. the lower /

lower cognitive aspects of learning. If content learning is the major instructional goal, then it appears that other techniques such as lectures, programmed learning or reading may be more effective.

(b) Simulations appear to have a positive influence on student attitudes. However, this may be due to the novelty and quality of each exercise rather than any other factor.

(c) Simulations appear to be influential in encouraging students to become more actively involved in the learning process.

Wentworth and Lewis called for more research of better quality to confirm these tentative conclusions, and to provide solutions to the many unanswered questions which remain about the effects of simulation techniques. They further suggested that a fruitful line of enquiry may be to use observational evaluation instruments to measure identifiable learning behaviours exhibited in simulations and games, arguing that paper and pencil assessment methods have limited measurement capabilities when applied to simulations and games.

Some workers have argued that the worth of simulations and games cannot be expressed by formal evaluations and statistics. Tansey(84) expressed this view in 1973 and Bloomer(85) in 1975 argued that formal measurement of 'input and output' in simulations is often invalid as the so-called 'input and output' is varied, complex and often cannot be specified with certainty, let alone accuracy. In addition, simulations involve complex human interactions which input/output evaluation procedures ignore.

Walford(86) also argued that traditional evaluation methods are often inapplicable to simulations citing the following major objections:-

(a) Simulations usually involve complex mixtures of cognitive and affective intention, and these are not easily specified;

(b) Simulations are often open-ended and therefore unpredictable in outcome.

Reasons such as these have been instrumental in a trend towards subjective approaches to simulation evaluation,(87) and while Taylor(88) has called for better methods of assessment for simulations, he has suggested that, in the absence of a highly developed evaluation science, subjective opinions should not go unheeded.

On validity of evaluation methods, Shubik(89) has criticised the small amount of attention paid to sorting out different simulation uses and the corresponding slow development of a range of assessment and evaluation criteria relevant to particular uses. This degree of discrimination could lead to the construction of more evaluation procedures which could then be applied to the particular objectives under consideration in individual simulations.

From the above account of evaluation procedures in gaming and simulations, it is apparent that research in this area is still in its infancy, possibly due to a combination of (a) the diversity of thought on the direction of evaluation, (b) the poor quality of much of the previous evaluation research and, (c) the difficulty of devising assessment tools where attitude and broader skill changes are involved.

Evaluation procedures which are at present available will be discussed further in Chapter 4.

2.3 Matching Methods with Objectives

From the evidence presented in Chapter 1, it could /

could be argued that some of the skills desired of a student studying chemistry could be broadly classified under the following headings:-

(a) Lower cognitive skills - involving the ability to retain specific knowledge and to apply it in various circumstances. Such skills are included in Bloom's categories of knowledge, comprehension and possibly application.

(b) Psychomotor skills - involving dexterity in handling chemical apparatus allied to other laboratory skills.

(c) Communication skills - involving the ability to clearly impart information to others in both oral and written form, and to enter into critical discussion with one's peers.

(d) Decision making skills - involving the ability to make balanced decisions on matters where there may be several conflicting views or factors. A decision may have to be made on the grounds of ambiguous or incomplete information, but once a decision has been made a student should be able to defend it in the face of disagreement from his peers.

(e) Problem solving skills - involving the ability to tackle new situations in a scientific fashion. Included in this category are skills in identifying, isolating and controlling variables so that multi-variable situations can be tackled. Another basic aspect is the ability to identify relevant information which may often be included amongst irrelevant data.

(f) Library skills - involving the ability to search for and find required information efficiently. Also included are skills in reading and precising scientific papers, discriminating between fact and speculation and the development of a healthy scepticism /

sceptiсism towards the written word.

(g) Inter-personal skills - involving skills in dealing with other people and the ability to co-operate in a group to work efficiently on a common task.

Most of the objectives of science teaching mentioned in Chapter 1 can be accommodated under one or more of the above headings. Skills involving Bloom's higher cognitive objectives of analysis, synthesis and evaluation fall mainly into categories (c), (d), (e), (f) and (g) above, but some of the objectives of science teaching including some which could be placed under the headings of communication or inter-personal skills are difficult to list under any of Bloom's cognitive or affective categories.

In addition to the seven headings given above, a further much quoted aim of chemistry courses is the 'development of desirable scientific attitudes'. This aspect of science education is extremely difficult as, not only are the scientific attitudes thought 'desirable' subjectively chosen and open to disagreement, but the extent, if any, to which scientific attitudes can be developed either by the specific inclusion of affectively-orientated material in science courses or in conjunction with the seven 'scientific skills' listed above is, as yet, unknown.

The strengths and weaknesses of some of the methods used in tertiary science education have already been discussed in this Chapter. Table 2-1 summarizes the suitability of lectures, laboratories, tutorials and programmed learning to develop the seven skills of the chemistry student listed at the start of this section, in addition to desired attitudinal traits.

Lect- /

	Lectures	Laboratories	Tutorials	Programmed Learning
Lower cognitive skills	✓	(✓)	✓	✓
Psychomotor skills		✓		
Communication skills			(✓)	
Decision making skills				
Problem solving skills		(✓)	(✓)	(✓)
Library skills		(✓)		
Inter-personal skills		(✓)		
Desired Attitudinal traits		(✓)		

Table 2-1 Suitability of certain teaching methods to develop desired skills and attitudes

From the argument presented previously, the lecture method is a useful, but not the only, method for teaching lower cognitive skills. The method is, however, not well suited for teaching the other six skills in Table 2-1 or for changing attitudes. The main drawback of the lecture situation is that the student is passive, and the development of the other skills and attitudes demand the student to be active.

The laboratory situation is obviously suited to developing psychomotor skills and may have some potential in developing problem-solving, inter-personal, and library skills, especially if open-ended work or projects are involved. The laboratory may also develop some of the desirable attitudinal objectives related to safety and accuracy. However the potential to develop such skills and attitudes is often ignored, and students are given pre-planned experiments with a set /

set of explicit instructions on how to proceed. This more usual laboratory approach leads only to a development of manipulative skill, and to some familiarity with materials.

The other major traditional teaching method in universities, the tutorial, is also potentially useful in developing problem solving and communication skills. This is possible because in the tutorial situation, the student is supposed to be active. Often, however, he is not. As discussed earlier, the tutorial has a habit of becoming a mini-lecture, almost totally dominated by the tutor. In such cases, only increased understanding of previously covered lecture work is possible (lower cognitive skills) and the chance to develop other skills is lost.

Programmed learning and other self-instructional techniques have much value in teaching for lower cognitive objectives, but the method is unsuitable for any of the other skills, except perhaps problem solving which programmed learning may be able to develop to a limited extent.

It is possible that if only the traditional methods of teaching are applied in tertiary science education, universities run the risk of directing all their efforts towards developing lower cognitive and psychomotor skills, and leaving the development of the broader skills and the formation of 'desirable attitudes' to chance, in the hope that they will 'rub off' on the students during their course. This opinion is not only groundless, as the evidence so far discussed suggests that the broader skills have to be 'taught-for' and are not the inevitable by-products of instruction, but also potentially harmful to the student who will probably be required to use these skills long after most of the detailed scientific knowledge has been forgotten.

CHAPTER 3

INTRODUCTION TO MATERIALS PRODUCED AND ASSESSMENT METHODS AVAILABLE

CHAPTER 3

INTRODUCTION TO MATERIALS PRODUCED AND ASSESSMENT METHODS AVAILABLE

3.1 Materials Produced

(a) Simulation materials

In order to make a conscious effort to develop some of the broader skills of science discussed in Chapter 2.3, and hence reduce some of the shortcomings of the traditional undergraduate chemistry course, some specific simulation-type exercises were produced. These exercises were deliberately designed to fill some of the gaps left by more traditional instructional methods, as illustrated in Table 2-1, p. 43. It has already been pointed out in the previous chapter that simulation exercises may be effective in developing communication, inter-personal, decision making and problem solving skills, and may also have possibilities in the area of attitude change. An important advantage which simulations have over more traditional methods is that they can be made to involve a large amount of student activity.

Three such exercises have been constructed, the objectives, content and assessment of each will be discussed in later chapters.

The three exercises are:-

1. Proteins as Human Food - a discussion exercise, designed to develop lower cognitive, inter-personal, decision making, but above all, communication skills. This exercise will be discussed in Chapter 5.

2. Polywater - a case history to develop communication and library skills. The exercise uses cognitive /

cognitive chemical skills already possessed by the students, and will be discussed in detail in Chapter 6.

3. <u>What Happens when the Gas runs out .... ?</u> - a problem case study involving problem solving, decision making, communication and interpersonal skills. This exercise will be discussed in Chapter 7.

Each of these exercises was intentionally written in a different style. Cowan(90) has argued that academic games and simulations can be classified into standard forms, and having decided upon which standard form is suitable for a given purpose, the task of compiling an exercise is made substantially easier. It is hoped that the three alternative styles adopted may prove the basis of other simulations, using different subject matter. Cowan has claimed that the basic structure of a simulation or game is virtually unrelated to its content, and that once a standard form for a particular type of simulation has been established, the simulation 'can be readily changed from one subject field to another with a minimum of creative effort'. However, a simulation user must be aware of the specific educational objectives desired, as the standard form of a simulation is strongly related to the type of objectives to which that form may be directed, so that 'the transfer of a standard form from one field to another depends on the compatability of the educational objectives in both fields'.

(b) <u>Self-instructional materials</u>

In addition to the work on simulation materials, it was felt that a certain section of a traditional chemistry course would benefit from the production of self-instructional programs which could be used in conjunction with the lecture course. The course on transition /

transition metal chemistry given to first year undergraduates at Glasgow University includes three-dimensional and other concepts of a cognitive nature with which the lecture, in itself, cannot cope adequately.

This complementary series of five programs, which employs a tape/workbook/model approach, is discussed in Chapter 4.

3.2 Available Assessment Procedures

It has been mentioned that the simulation exercises devised were intended to develop in students skills in communication, decision-making, problem solving, library use, and inter-personal relationships, in addition to assisting the development of desired attitudinal traits.

The self-instructional material produced was primarily concerned with the attainment of cognitive objectives.

Cognitive assessment procedures

The assessment procedures in common use are concerned almost entirely with the attainment of cognitive objectives, e.g. knowledge gained; such procedures include:-

(1) Essay-type questions

Within one question, this procedure tries to test knowledge, reasoning, written communication skills, creative thinking and interpretation (including interpretation of the implied objectives of the setter). All of these skills are interwoven in a complex matrix and much is left to the judgement of the marker, since it is usually extremely difficult to tease apart these skills and mark them independently. This results in low reliability and low validity even when marking schemes /

schemes are given.

(2) Objective items

Types of objective items include multiple choice, multiple completion, classification sets, situation sets and reason assertion. Such items usually test at Bloom's cognitive levels of knowledge, comprehension and application. Advantages of objective methods include absolute reliability, easy statistical analysis and wide coverage of desired subject matter. They may, however, have low validity.

(3) Unique answer questions

In such questions the student must supply the answer rather than select from a set of choices. As the answer is unique the questions can be scored reliably. Large subject matter coverage is possible and different skills can be examined individually.

In the teaching materials produced for this thesis, assessment of the attainment of purely cognitive objectives was usually done by means of multiple choice objective items, although in some cases unique answer questions were employed.

Non cognitive assessment procedures

The simulation materials produced were concerned with the development of broader scientific skills and desired attitudinal traits rather than with purely cognitive outcomes, although such outcomes were bound up in them. It was mentioned in Chapter 2.2, p. 37, that, at present, evaluation methods to measure the educational outcomes and effectiveness of simulation materials are not well developed, and traditional assessment methods are often inappropriate.

The suitability of assessment techniques is further restricted /

restricted by the necessity of having procedures which are simple in application, acceptable to students, and as valid and reliable as possible. Such conditions limit the choice to methods which could be broadly classified under two headings:- (a) observational techniques and (b) self-reporting techniques.

(a) Observational techniques

When certain attitudinal objectives are involved or when development of communication skills is a major aim of an exercise, direct observation of individual or group behaviour can be of use in monitoring achievement. Closed circuit television or simply recording on audio-tape the activities in a group session, can act as a permanent record of an exercise so that subsequent analysis of the session can be attempted. The analysis can be in the form of simply noting the numbers and pattern of communications within a group or may reach the complexity of providing insight into the social psychology of groups and the personalities of group members. The latter can be attempted if the system of Interaction Process Analysis(91), developed by R.F. Bales, is adopted. There are, however, difficulties associated with Bales' method, and training and practice in its use are required if it is to be used successfully.

(b) Self-reporting techniques

Several such techniques have been devised, several of which are discussed below.

(i) The Thurstone scale(92) which was first developed in 1929, involves the collection of a large number of statements expressing some attitude to a topic under consideration. A number of 'judges' (at least 25) then rate the statements in one of nine categories ranging from extremely favourable to extremely hostile, and /

and a score from 1 to 9 is assigned to each statement according to how favourable the judges feel each statement is. A person completing the scale selects only those statements which most closely represent his attitude to the topic in question, and is them given an 'attitude score' which is the median or mean score of the items selected.

The disadvantages of this attitude assessment technique lie largely in its cumbersome and tedious organisation, the fact that scale values are influenced by the attitudes of the judges, and that an individual's final score hides information on the <u>patterns</u> of attitudes expressed.

(ii) <u>Likert scales</u>(93), developed in 1932, are much simpler to devise and administer. Essentially a Likert rating scale consists of a list of statements, and the person answering has to make a judgement on every statement, often selecting one response from a number of degrees of agreement and disagreement. The number of points on the scale depends on the requirements of the setter, although the provision of an even number of possibilities makes it impossible for students to take refuge repeatedly in a completely neutral category.

As with Thurstone scales, it is statistically unwise to add together scores for separate statements on a Likert scale to obtain an overall attitude score. This may only be done if the statements are measuring the same dimension and if the frequency of responses from agree to disagree form a normal distribution, which is extremely difficult to obtain in practice.

It should, however, be possible to use Likert-type scales to recognise variations in attitudes and opinions by comparing students' responses to individual statements in a test administered before and after a teaching /

teaching unit designed to modify such opinions.

(iii) The Semantic Differential technique first developed by Osgood, Suci and Tannenbaum(94) in 1957, has been used as a tool for various types of assessment to measure connotations of any given concept for an individual. Word pairs of antonyms such as valuable/worthless and interesting/boring are joined by a seven point scale from +3 to -3 including zero.

The method assumes that the word pairs are opposites, but this assumption may not always be valid as different words may have different meanings to individual students. A major advantage of the method is that it is very rapid to construct and complete.

Hadden(95) has pointed out that rating scales such as +3 to -3 or 1 to 5, not only in semantic differential techniques but also in other assessment techniques, are often statistically groundless, and if used, are a basic fault of such techniques. This is because the scores are on ordinal and not interval scales, e.g. a person who 'strongly agrees' with given statement and is given a score of 3, does not necessarily agree three times more strongly than a person who 'slightly agrees' with the statement and is given a score of 1. Such scores provide only an indication of the relative strength of opinions or attitudes between different people. A further criticism has been that adverbs such as extremely, very, fairly, slightly, etc. do not mean the same to all people, and hence the interval between, say, 'slightly interesting' and 'fairly interesting' on a rating scale may not be the same as the interval between 'fairly interesting' and 'very interesting' to some students.

(iv) Situational techniques were first described by Handy and Johnstone(96) in 1973, and have recently been used /

used by Hadden.(95) Such techniques attempt to assess the modes of thought and scientific attitudes of students, as compared to their attitudes to science. Students are involved in tackling a problem or situation which in itself need not be of a scientific nature, but which requires students to think scientifically to solve it, for example by controlling variables. Such situations involve students using the 'broader skills' of a science education such as problem solving and decision making skills and rely little on previous lower cognitive skills.

Although little work has so far been done on the use of this technique, it would intuitively appear that they should have a reasonably high validity compared to the rather artificial assessment procedures discussed in (i), (ii) and (iii). One problem may be that the method is cumbersome, and questions may be difficult and time-consuming to construct and apply.

(v) Rating objectives by means of a grid in which the objectives of an exercise are listed and the student asked to indicate whether each objective has been 'well achieved' through to 'not achieved at all' has been reported by Vesper and Adams(97) in addition to other workers. The rating is usually done on a five-point scale, but variations are possible. Most of the statistical criticisms levelled at other rating scales discussed also apply to this method if responses are scored on an ordinal scale. However, this method may prove useful in some cases where no other suitable technique exists for assessing the achievement of certain objectives, or as a check on the validity of other measures.

Assessment of simulation materials

Each of the above techniques for assessing confidence, attitudes, opinions and the broader skills of science has /

has certain drawbacks, and no single technique is the best in all situations. It is probably most profitable to use a multi-media assessment approach using alternative methods as a check on the validity of other measures and to identify if a pattern of responses is evident, although a score on one scale cannot be directly compared to a score on another.

In the three simulation exercises discussed in Chapters 5, 6 and 7 a combination of Likert, semantic differential, situational, objective rating, objective multiple choice and observation techniques were used to assess their educational value - the precise subset of techniques being dependent upon the type of objectives and skill being assessed. The reasons for the particular choice of assessment approaches for individual exercises will be discussed in the relevant chapters.

CHAPTER 4

SELF-INSTRUCTIONAL PROGRAMS ON TRANSITION METAL CHEMISTRY

CHAPTER 4

SELF-INSTRUCTIONAL PROGRAMS ON TRANSITION METAL CHEMISTRY

4.1 Introduction

The first year chemistry course at the University of Glasgow includes a series of eight lectures which provide an introduction to transition metal chemistry. This lecture course is the basis of work done in subsequent years on transition metal chemistry, so it is of particular importance that students obtain 'mastery' of the topic in their first year.

All of the objectives of the course on transition metal chemistry belonged to Bloom's lower cognitive categories and it has been argued in Chapter 2.3 that the lecture method can adequately achieve such objectives. However, for this particular part of the course, it was felt that the lecture method alone was insufficient, the major disadvantage being that a grasp of three-dimensional concepts was necessary to fully understand much of the topic. It is impossible, however, to communicate efficiently three-dimensional ideas to large groups of students in a lecture situation since, beyond a few yards, even the best three-dimensional models appear two-dimensional to the students.
The scale of the problem is illustrated by the fact that over 250 students attend each chemistry lecture in the first year at Glasgow.

Other, more general drawbacks of the lecture situation have been discussed in Chapter 2, and include:-

1. Little feedback can be obtained from the students;
2. The rate of presentation is controlled by the lecturer;
3. Students are passive in lectures;
4. /

4. Students have little opportunity to review or consolidate their learning.

It has also been demonstrated by Johnstone and Percival(98) that attention declines with time during a lecture and that breaks in student attention are equivalent to times of inferior learning. Thus material taught towards the end of a lecture, or during a break in a student's attention, has less chance of being assimilated by the student. This research has also indicated that student attention patterns improve if a variety of teaching methods are used in a lecture.

To complement the lecture in achieving the lower cognitive objectives associated with the first year transition metal chemistry course, it was decided to construct a series of self-instructional programs which would be self-paced and employ three-dimensional models and a 'construction kit' with which a student could build and study structures for himself. A further advantage of producing self-instructional materials on transition metal chemistry is that, not only could the students use the material to complement the lecture course, but the programs could also be used for revision before examinations and before subsequent study of more advanced transition metal chemistry in the second and third years of the chemistry course.

4.2 Design of the Self-Instructional Materials

As the material was required to supplement a lecture course, and not to provide an alternative for it, the programs were designed to aid the students achieve 'mastery' of some of the objectives of the lecture course.

The content of the programs was based on the lecture content, but laid more emphasis on aspects of /

of the topic which could not be taught effectively by lecture, and little or no emphasis on some other aspects which were adequately dealt with in the lecture situation. The content of the material was decided upon in collaboration with the lecturers involved in the course and with due regard to the course objectives.

Since a great deal of the material on transition metals was suitable for discussion and description, and often required the use of models, it was decided that 'traditional' written programmed material was inappropriate. Each of the programs involved the use of a workbook which was divided into 'frames' with some basic material given in each frame. Sufficient space was left in each frame for a student to add his own notes if required, and to answer questions posed in the program.

Provision of a workbook served to keep the students active during the course of each program, and also acted as a permanent record of the program as students were allowed to keep their workbooks. In each program, the workbook was accompanied by a taped commentary provided in cassette form, while three of the five programs involved the use of models and a construction kit, and one involved a series of overlays to help illustrate a certain point. The media used in the programs were relatively cheap and easy to produce and could be easily altered or reproduced if required.

The programs were of a 'linear' type,(42) and were made available to students immediately after the relevant section of the course had been covered in lecture form.

4.3 Objectives of the Programs

The parts of the transition metal chemistry course which /

which were thought would benefit from a programmed treatment involving tapes, workbooks and models were gathered under five headings, each of which provided a basis for an individual program. The five programs were entitled:-

Program 1 : The Language of Transition Metal Chemistry;
Program 2 : Naming Co-ordination Compounds and Complex Ions;
Program 3 : Symmetry and Isomerism in Transition Metal Complexes;
Program 4 : Crystal Field Theory;
Program 5 : Colour and Magnetic Properties in Transition Metal Chemistry.

The objectives of each program were made known to the students both at the start of the workbook and the taped commentary, as research has indicated that student achievement is enhanced if the student has prior knowledge of the behavioural objectives of a unit of work.(99)

The objectives of each program, phrased in behavioural terms, are given below.

<u>Program 1</u> On completion of this program, a student should be able to:-

1. point out the position of the transition elements in the periodic table, and realise which ones are concerned with the filling of d sub-shells and which with the filling of f sub-shells;
2. define the term "oxidation state", and appreciate that a characteristic feature of transition metals is that they can possess a variety of oxidation states;
3. recognise that an element is a transition element, given its electronic configuration;
4. write down the electronic configuration of a transition /

transition element in a given oxidation state;

5. define the terms "coordination compound" and "complex ion", in transition metal chemistry;
6. define the term "ligand" in transition metal chemistry;
7. appreciate that certain ligands can interact with a central transition metal ion via more than one bonding site;
8. define the terms uni-, bi-, tri-, tetra-, penta- and hexa- dentate ligands;
9. given the oxidation of a metal in a complex ion and the ligands present, write down the resultant charge on the complex ion;
10. define the terms "inner coordination sphere" and "outer coordination sphere" of a transition metal ion;
11. state some of the methods available to "count" the number of ions present in a coordination compound, and also the method used to estimate the number of free chloride ions present in a coordination compound;
12. define the term "coordination number" of a transition metal ion, and write down the coordination number of a transition metal in a given complex ion.

Program 2 On completion of this program, a student should be able to:-

1. correctly name a coordination compound or complex ion, given its molecular formula;
2. conversely, given the name of a coordination compound or complex ion, write down its molecular formula.

Program 3 On completion of this program a student should be able to:-

1. define what is meant by an octahedral complex, and realise that such complexes can be represented in /

in several equivalent ways;

2. define the term "isomer" in transition metal chemistry;
3. define what is meant by the cis or trans arrangement of ligands in octahedral transition metal complexes;
4. define "geometric isomer" and "chiral isomer" and be able to distinguish between the two;
5. given the molecular formula of a transition metal complex, draw any geometric isomers and chiral isomers which may be possible in the complex.

Program 4 On completion of this program, a student should be able to:-

1. draw the shapes of the five individual d orbitals, paying particular attention to their orientation in space;
2. define the term "degenerate orbitals";
3. explain what is meant by the term "spherical approximation";
4. explain the effect of the spherical approximation upon the energy level of a set of five d orbitals compared to their energy level in the free ion;
5. explain the splitting of the five d orbitals in an octahedral ligand field to give three t_{2g} orbitals at a lower energy level than in the spherical approximation and two eg orbitals at a higher energy level than in the spherical approximation;
6. define the term "crystal field splitting energy", Δo.

Program 5 On completion of this program, the student should be able to:-

1. explain why most transition element compounds are coloured;
2. state the factors affecting the size of Δo - the crystal field splitting energy - in octahedral transition /

transition metal complexes;
3. define high spin and low spin complexes;
4. draw the d electron configuration for both high spin and low spin complexes of a transition metal ion with a given number of d electrons;
5. state the two factors which influence whether a transition metal complex is in a high spin or low spin situation;
6. define the terms "paramagnetic", "diamagnetic" and "ferromagnetic";
7. write down the expected magnetic moment, in Bohr magnetons, of a complex with a given number of unpaired electrons.

4.4 Design of Individual Programs

Program 1

Purpose: to introduce the basic terminology and vocabulary of transition metal chemistry, much of which was required in subsequent programs.

Materials: 18 frame workbook (p. 87)
24 minute taped commentary (p. 99)

Program 2

Purpose: to enable students to gain mastery of the well defined rules for naming transition metal complexes and coordination compounds.

Materials: 11 frame workbook (p. 111)
16 minute taped commentary (p. 116)

Program 3

Purpose: to introduce symmetry and isomerism in transition metal chemistry and to enable mastery /

mastery of other three-dimensional relationships.

Materials: 13 frame workbook (p. 123)
20 minute taped commentary (p.130)
9 models (photographs included in appended tape script)
Construction kit (photograph on p.132)

The construction kit enabled students to make ball and stick models and isomers of certain octahedral transition metal complexes, and hence study three-dimensional relationships. Uni-dentate ligands were represented by single balls, while bi-dentate ligands were represented by two balls attached together by means of a suitably sized spring.

Program 4

Purpose: to develop crystal field theory, requiring a grasp of three-dimensional concepts, with particular reference to the shape and orientation in space of the five d orbitals.

Materials: 9 frame workbook (p. 140)
17 minute taped commentary (p. 145)
2 models (photographs included in appended tape script)
Overlays

Program 5

Purpose: to use crystal field theory to explain the phenomena of colour and magnetic properties in transition metal chemistry.

Materials: 14 frame workbook (p. 153)
20 minute taped commentary (p. 161)
2 models (photographs included in appended tape script).

Organisation /

Organisation

Three sets of materials and the necessary hardware for each program were made available in the science self-teaching laboratory. The programs could be used by students at any time without compulsion. Although it was suggested that students should work through programs 1 to 5 sequentially, it was possible for students to select individual programs to attempt to rectify particular weaknesses.

Students were encouraged to work through each program at their own pace and, if necessary, use any program any number of times.

4.5 Assessment of Programs

The evaluation of the effectiveness of the programs was done in two ways:-

(a) A diagnostic assessment of the programs was designed to show up weaknesses or misleading parts, and to assess the 'mastery' value of the material.

(b) A comparison of the subsequent performance on a transition metal chemistry question set in a formal degree examination was made between students who completed relevant programs and those who attempted none of the programs.

(a) Diagnostic assessment of the programs

It was decided that any form of test had to be concise, quick for the student to do, and that the same test should be used for pre- and post- assessment, otherwise differences may have been due to different tests. Objective test items were used to fulfil these criteria. The items used in each test were related to the objectives of the program(s) which were being evaluated. The objectives of each program are listed in /

in Chapter 4.3 (p. 59-62).

Programs 1, 2 and 3 were evaluated by individual tests while programs 4 and 5 together were evaluated by a single test since the objectives of the programs were closely related. Items were scored by awarding 1 mark for a correct response and 0 for an incorrect or omitted response, and were answered on a computer card to enable easier analysis. Pre-test items were answered on pink cards while post-test items were answered on yellow cards.

Students were encouraged not to guess by the provision in each item of a 'don't know' option.

Differences in the performance of individual students were not studied, but changes in the overall performance in individual items were analysed, and the results related to the objectives and efficiency of the programs. This was done as the tests were designed to be diagnostic of the programs and not of the students.

An attitude questionnaire was attached to each post-test to obtain a general indication of ease, interest and value of individual programs, in addition to the time spent on each program. Space was also available for any further comments the student wished to make.

The programs were assessed over the two sessions 1973-74 and 1974-75. Unfortunately, in both sessions the lecture course in transition metals was not completed until less than four weeks before the degree examination in first year chemistry, so there was little time available for students to use the later programs in the series. However, a sufficient number of students attempted each program for a valid assessment to be made. Only students who completed both pre- and post-test for a particular program were used in the item analysis.

The combined totals of students for the two sessions who attempted both pre- and post-tests for any particular program are given below:-

	Students (both tests)	Students (one test only)
Test 1 (Program 1)	133	44
Test 2 (Program 2)	136	21
Test 3 (Program 3)	92	28
Test 4 (Programs 4 and 5)	57	24

In addition to the numbers listed above, several students completed programs without attempting either the pre- or post-test. This was obvious from the number of workbooks used. The results for the two sessions were combined as it was assumed that no major differences existed in the chemical ability of the students studying first year chemistry in two consecutive years. The lecture course and the lecturers were identical in both years.

Item analysis for test 1 (Program 1)

The test, which contained eight objective items, can be found in the appendix on p. 171.

The frequency of responses for options A, B, C, D and E for questions 1 to 8 in test 1 are given in Table 4-1 for 133 matched pairs of pre- and post-tests.

	ITEM							
Option	1	2	3	4	5	6	7	8
A	7 (3)	39 (10)	4 (1)	2 (0)	4 (1)	9 (1)	*91 (131)	37 (4)
B	*67 (105)	7 (0)	17 (4)	*104 (129)	70 (15)	4 (1)	7 (0)	14 (2)
C	46 (22)	*78 (122)	*93 (127)	3 (1)	*35 (116)	9 (2)	9 (2)	*36 (123)
D	6 (3)	3 (1)	10 (1)	10 (3)	3 (1)	*86 (129)	8 (0)	11 (4)
E	7 (0)	6 (0)	9 (0)	14 (0)	21 (0)	25 (0)	18 (0)	35 (0)
Facility Value	.50 (.79)	.59 (.92)	.70 (.95)	.78 (.97)	.26 (.87)	.65 (.97)	.68 (.98)	.27 (.92)
Difference in Facility Values	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%

Table 4-1 Item by Item Analysis for Test 1 (Program 1) (133 students)

* indicates the correct response for each item (i.e. the key).

Post-test figures are bracketed below pre-test figures.

(The facility value is the proportion of students who had the correct response for the item.)

Differences in pre- and post-test facility values were tested for significance using the following formula(100) -

$$Z = \frac{P_1 - P_2}{\sigma_{P_1 - P_2}} \qquad \text{where } \sigma_{P_1 - P_2} = \sqrt{pq\left(\frac{1}{N_1} + \frac{1}{N_2}\right)}$$

P_1 , P_2 = sample proportions

N_1 , N_2 = sample sizes

$$p = \frac{N_1P_1 + N_2P_2}{N_1 + N_2}$$

$q = 1 - p$

In Test 1 all differences between pre- and post-test facility values were significant above the 1% level. As the program, and hence the pre-test, was done after the lecture course, the measured differences were a direct result of using the program, so it would appear that the objectives of program 1 were being achieved.

One possible weakness of program 1 was indicated from the responses to item 1, in that in the post-test over 16% of the students failed to appreciate that elements with incomplete f shells of electrons are classified as transition elements.

Further analysis of Test 1 involved an examination of student responses in pre- and post-test, and the results are given in Table 4-2.

ITEM	1	2	3	4	5	6	7	8
Right → Right	65	70	91	102	35	84	91	33
Right → Wrong	2	0	2	2	0	2	0	3
Wrong → Right	34	38	17	13	64	21	22	57
Wrong → Wrong	25	11	4	2	13	1	2	5
Don't know → Right	6	6	8	14	17	24	18	33
Don't know → Wrong	1	0	1	0	4	1	0	2
Facility Value (Pre) (Post)	.50 (.79)	.59 (.92)	.70 (.95)	.78 (.97)	.26 (.87)	.65 (.97)	.68 (.98)	.27 (.92)

Table 4-2 Pre/Post Response Comparison for Test 1 (133 students)

It would appear that, with the possible exception of the point made about f shells that no serious misconceptions were apparent in program 1.

Item analysis for Test 2 (Program 2)

This test which contained five objective items can be found in the appendix on p. 173.

The item by item analysis and the pre/post test comparison for Test 2 are given in Table 4-3 and Table 4-4, respectively.

	ITEM				
Option	1	2	3	4	5
A	3 (0)	96* (134)	53 (0)	33 (8)	16 (2)
B	71 (17)	4 (0)	45* (132)	7 (3)	89* (130)
C	45* (117)	10 (0)	6 (1)	7 (0)	10 (3)
D	7 (2)	14 (2)	9 (3)	76* (125)	5 (1)
E	10 (0)	12 (0)	23 (0)	13 (0)	16 (0)
Facility Value	.33 (.86)	.71 (.98)	.33 (.97)	.56 (.92)	.65 (.96)
Difference in Facility Values	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%

Table 4-3 Item by Item Analysis for Test 2 (Program 2)(136 students)

ITEM	1	2	3	4	5
Right → Right	57	95	43	70	88
Right → Wrong	0	1	2	6	1
Wrong → Right	52	27	66	44	27
Wrong → Wrong	17	1	2	3	4
Don't know → Right	8	12	23	11	15
Don't know → Wrong	2	0	0	2	1
Facility Value					
(Pre)	.33	.71	.33	.56	.65
(Post)	(.86)	(.98)	(.97)	(.92)	(.96)

Table 4-4 Pre/Post Response Comparison for Test 2 (136 students)

In general, program 2 would appear to be reasonably satisfactory in terms of achieving the objectives of the program, namely the mastery of the nomenclature system in transition metal chemistry.

The biggest single misconception appeared to be in the order in which ligands should be named (item 1). 12½% of the students continued to list the ligands alphabetically without regard to whether the ligands were charged or uncharged.

All differences between pre- and post-test facility values were significant at the 1% level.

Item analysis for Test 3 (Program 3)

This test contained eight objective items related to the objectives of the program, and is appended on p. 175.

The item by item analysis is given in Table 4-5, while the pre/post-test comparison is summarised in Table 4-6.

	ITEM							
Option	1	2	3	4	5	6	7	8
A	3 (1)	7 (2)	$\overset{*}{24}$ (82)	2 (0)	1 (1)	$\overset{*}{39}$ (74)	20 (13)	11 (4)
B	1 (0)	1 (1)	33 (10)	$\overset{*}{25}$ (81)	13 (1)	7 (10)	$\overset{*}{19}$ (52)	12 (1)
C	8 (0)	11 (2)	9 (0)	14 (7)	$\overset{*}{42}$ (85)	11 (4)	16 (11)	$\overset{*}{26}$ (78)
D	$\overset{*}{78}$ (91)	$\overset{*}{56}$ (87)	1 (0)	14 (3)	11 (4)	14 (4)	10 (16)	7 (9)
E	2 (0)	17 (0)	25 (0)	37 (1)	25 (0)	21 (0)	27 (0)	26 (0)
Facility Value	.85 (.99)	.60 (.95)	.26 (.89)	.27 (.88)	.45 (.93)	.42 (.80)	.20 (.56)	.28 (.85)
Difference in Facility Values	Sig. 5%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%

Table 4-5 Item by Item Analysis for Test 3 (Program 3) (92 students)

ITEM	1	2	3	4	5	6	7	8
Right → Right	78	55	24	23	40	38	16	22
Right → Wrong	0	1	0	2	2	1	3	4
Wrong → Right	11	17	39	29	23	21	23	26
Wrong → Wrong	1	2	4	1	2	11	23	4
Don't know → Right	2	15	19	29	23	15	13	30
Don't know → Wrong	0	2	6	8	2	6	14	6
Facility Value (Pre) (Post)	.85 (.99)	.60 (.95)	.26 (.89)	.27 (.88)	.45 (.93)	.42 (.80)	.20 (.56)	.28 (.85)

Table 4-6 Pre/Post Response Comparison for Test 3 (92 students)

For this test, all differences between pre- and post-test were significant at the 1% level except for item 1, where the difference was significant at the 5% level, due to the high facility value in the pre-test.

Items 3, 6, 7 and 8 each contained at least one distracter which collected between 10% and 18% of the responses. The reason for this was probably that each of these items involved the students thinking three-dimensionally without the aid of models. Item 7 was particularly poorly done in the post-test (facility value 0.56) with 23 of the students continuing to select a wrong answer and a further 14 students who were 'don't knows' in the pre-test selected the wrong answer in the post-test. In addition, each distracter attracted over /

over 12% of the students. The reason for this relatively poor performance in item 7 was probably that, not only did the question require students to be able to visualize structures written in two dimensional form as three-dimensional, but an additional process of mentally 'rotating' the structure was involved. In all other items, this additional 'mental rotation' process was not required, and the post-test facility values did not fall below 0.80, indicating reasonable mastery in general.

Item analysis for Test 4 (Programs 4 and 5)

As the objectives of programs 4 and 5 were closely related, both programs were assessed by means of one test containing 7 objective items. This test is appended on p. 178.

Items 1, 2 and 3 are directly related to program 4 on crystal field theory, while items 4, 5, 6 and 7 are concerned with program 5 on colour and magnetic properties in transition metal compounds, which were explained in terms of crystal field theory.

An item by item analysis is contained in Table 4-7 while pre/post test response comparison is given in Table 4-8.

	ITEM						
Option	1	2	3	4	5	6	7
A	1 (1)	22* (56)	3 (1)	10 (3)	8 (4)	7 (2)	17* (51)
B	24 (0)	8 (1)	32* (56)	8 (6)	4 (1)	3 (0)	4 (1)
C	22* (55)	7 (0)	2 (0)	12* (46)	25* (51)	6 (1)	3 (1)
D	5 (1)	5 (0)	9 (0)	7 (2)	4 (1)	20* (53)	4 (2)
E	5 (0)	15 (0)	11 (0)	20 (0)	16 (0)	21 (1)	30 (1)
Facility Value	.39 (.96)	.39 (.98)	.56 (.98)	.21 (.81)	.44 (.89)	.35 (.93)	.30 (.89)
Difference in Facility Values	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%	Sig. 1%

Table 4-7 Item by Item Analysis for Test 4 (Programs 4 and 5)

(57 students)

ITEM	1	2	3	4	5	6	7
Right→ Right	22	22	31	11	24	19	15
Right→ Wrong	0	0	1	1	1	1	1
Wrong→ Right	29	19	14	19	13	15	10
Wrong→ Wrong	1	1	0	6	3	1	1
Don't know→ Right	4	15	11	16	14	19	26
Don't know→ Wrong	1	0	0	4	2	2	3
Facility Value (Pre) (Post)	.39 (.96)	.39 (.98)	.56 (.98)	.21 (.81)	.44 (.89)	.35 (.93)	.30 (.89)

Table 4-8 Pre/Post Response Comparison for Test 4 (57 students)

All differences in facility value between pre- and post-tests were significant at the 1% level. In no item did the facility value fall below 0.80 in the post-test.

In only one item (item 4) did over 10% of the students select any one distracter in the post-test. The fact that more highly charged transition metal ions produce large crystal field splitting energies in complex ions does not appear to have been fully appreciated by some students as the numbers selecting distracter B in item 4 dropped only slightly. This may be due to lack of emphasis in the program.

In every item in every test, significant improvements were noted between pre- and post-test. Apart from /

from the effect of the programmed material, a further factor involved in this improvement may be that doing a pre-test before the instruction enhanced the learning. Research done by Hartley$^{(101)}$ supports this view. It is possible that doing a pre-test may emphasise the designer's objectives in the mind of the student, and the student may learn from the program with particular reference to the pre-test items.

Attitudes to programs 1, 2, 3, 4 and 5

On completion of each post-test, the students were asked to indicate how useful, easy and interesting they found the program(s) just completed. In addition they were asked to note approximately how long they took to complete each program. A similar assessment method was used by Hogg$^{(102)}$ at Aberdeen in part evaluation of programmed learning materials in chemistry.

Results are given in Table 4-9. Not all the students who completed the pre- or post-test completed the questionnaire, and vice versa. Consequently the numbers of students assessing each program vary slightly from the numbers discussed previously.

PROGRAMS	1	2	3	4	5
Length of Program	24 mins.	16 mins.	20 mins.	17 mins.	20 mins.
No. of students	91	106	69	50	50
Extremely valuable	18 (19.8%)	28 (26.4%)	15 (21.7%)	11 (22%)	12 (24%)
Very useful	53 (58.2%)	50 (47.2%)	26 (37.7%)	23 (46%)	34 (68%)
Satisfactory	18 (19.8%)	28 (26.4%)	24 (34.8%)	16 (32%)	4 (8%)
Not very useful	2 (2.2%)	0 (-)	4 (5.8%)	0 (-)	0 (-)
A complete waste of time	0 (-)	0 (-)	0 (-)	0 (-)	0 (-)
Much too easy	0 (-)	1 (0.9%)	0 (-)	0 (-)	0 (-)
Too easy	11 (12.1%)	7 (6.6%)	0 (-)	1 (2%)	0 (-)
Reasonably easy	78 (85.7%)	93 (87.7%)	18 (26.1%)	36 (72%)	33 (66%)
A little difficult	2 (2.2%)	5 (4.7%)	45 (65.2%)	12 (24%)	16 (32%)
Very difficult	0 (-)	0 (-)	6 (8.7%)	1 (2%)	1 (2%)
Very interesting	11 (12.1%)	17 (16%)	4 (5.8%)	7 (14%)	7 (14%)
Interesting	49 (53.8%)	43 (40.6%)	27 (39.1%)	29 (58%)	34 (68%)
Satisfactory	27 (29.7%)	42 (39.6%)	28 (40.6%)	12 (24%)	8 (16%)
Dull	2 (2.2%)	4 (3.8%)	5 (7.2%)	2 (4%)	1 (2%)
Tedious	2 (2.2%)	0 (-)	5 (7.2%)	0 (-)	0 (-)
Took less than 15 mins.	6 (6.6%)	11 (10.4%)	0 (-)	0 (-)	0 (-)
Took 15-20 mins.	10 (11%)	26 (25.4%)	4 (5.8%)	11 (22%)	3 (6%)
Took 20-25 mins.	13 (14.3%)	30 (28.3%)	8 (10.1%)	18 (36%)	15 (30%)
Took 25-30 mins.	26 (28.6%)	32 (30.2%)	10 (14.5%)	9 (18%)	19 (38%)
Took over 30 mins.	36 (39.6%)	7 (6.6%)	48 (69.6%)	12 (24%)	13 (26%)

Table 4-9 Attitudes to Programs 1 to 5

In general, it would appear from Table 4-9 that the programs were favourably received by the students. Program 3 seems to be the one which the students found most difficult and most tiring. Students also generally spent longer on program 3 than on the other programs. It is probably not coincidental that program 3 laid most emphasis on three-dimensional relationships, which the student had to master by means of models and the construction kit.

It is significant that there was a wide variation in the times taken to complete each program, indicating that the students were controlling the rate of learning, rather than the learning rate being media controlled.

A further piece of evidence to indicate the potential of programmed learning methods in chemistry was obtained from a questionnaire given to all first year chemistry students in mid May, 1975. When asked which learning activities or situations best suited the student, personally, to learn desired subject material in chemistry the responses were:-

Lectures and lecture notes	(64.4%)
Self-instructional programs	(22.0%)
Text books	(7.8%)
Other methods	(5.8%)

A further question revealed that just over 55% of students had actually used any of the self-instructional programs in chemistry.

(b) Performance of students in degree examination

The diagnostic assessment of these programs indicated that in the short-term, the programs proved useful in enabling students to master the subject matter contained in the programs. However the post-test was usually done immediately after the completion of each program /

program and hence measured short-term recall and comprehension.

It was decided to investigate if the programs had a longer term effect by comparing the performance in a subsequent degree examination of students who had used the programs on transition metal chemistry, with those students who did not use any programs.

First year chemistry students were given the opportunity to use the programs on transition metal chemistry immediately after the lecture course in session 1974-75. The degree examination in June 1975 contained one written question valued at 10 marks on the transition metal course.

Question in written paper

The first year degree examination is divided into two sections. Section A is an objective test containing twenty items, while section B is a written paper containing eight questions, all of which must be attempted.

The content of the question of transition metal chemistry is appended on p.181. The question examined aspects of the course which were covered in programs 1, 2 and 3 of the self-instructional series. It was therefore, decided to compare the performance of students who did at least the first three programs against students who did no programs. Students who covered programs 1 and/or program 2 only were not included in the comparison. From the pre-test and post-test returns, 78 students who did at least the first three programs were identified, of whom 66 sat the degree examination - the remainder gaining exemptions. A further 17 students were identified who had done fewer than three programs. The rest of the class (312 students) were assumed to have studied none of the programs.

The performance /

The performance of the students who studied at least three programs and the performance of those who studied no programs is given in Table 4-10.

Question Students		1	2	3	4	5	6	7 *	8
At least 3 programs (n=66)	MEAN	6.45	3.85	6.62	5.71	1.89	2.00	5.11	4.02
	S.D.	2.55	2.10	2.45	2.61	2.21	1.79	2.96	2.72
No programs (n=312)	MEAN	5.73	3.30	5.75	4.11	2.06	1.22	2.93	3.60
	S.D.	2.63	2.02	2.73	2.88	2.51	1.37	3.24	3.08

* transition metal question

<u>Table 4-10 Performance of Program users and non-program users in all written questions</u>

All scores in Table 4-10 are presented out of a possible 10. In fact, questions 1, 2 and 8 were out of a possible 7, 8 and 15 respectively, but the scores were adjusted to fall into line with the other questions. Question 7 was concerned with transition metal chemistry. Straight comparison between performances in question 7 is invalid as it is obvious from the other scores that those students who used the programs performed generally better than those who did not use the programs, scoring better in 7 out of the 8 questions in the paper. It is disturbing that those who could benefit most from the provision of self-instructional programs were less likely to use them.

In an attempt to relate the scores of non-program users to those of program users, a regression line was calculated. This was then used to predict scores of program-users given the mean scores of non-program users. (Scores for question 7 were not included in the calculation of the regression equation.)

The regression equation was -

$\tilde{Y}$ /

$$\tilde{Y} = 1.119\,X + 0.243$$

where $\tilde{Y}$ = predicted mean score of program users,
X = mean score of non-program users.

The correlation coefficient between mean scores of program and non-program users was calculated - this was $r = 0.968$.

The standard error of estimate ($S_{y.x}$) was also calculated -

$$S_{y.x} = S_y\sqrt{1 - r^2} = 0.493$$

(The standard error of estimate is used in the same manner as a standard deviation is used in a normal distribution.)

From the regression equation, the predicted mean score for question 7 was 3.52 out of 10 for program users, compared to the mean score of 5.11 out of 10 which was actually achieved. This difference is significant above the 0.1% level. Thus those who did at least three programs would appear to have performed significantly better in the transition metal chemistry question than those who attempted no programs. The relative performance of program users and non-program users in the degree examination is summarized in Diagram 4-1.

However, the situation is slightly more complex if one looks at question 7 in more detail. Question 7 (appended on p.181) consisted of two parts. Part (a) involved drawing four geometrical structures for isomers of a chromium (111) complex (Program 3) and naming any one of them (Program 2).

Part (b) involved calculations involving the mole concept, and depended upon the ability of students to remember the atomic weights silver and chlorine in order /

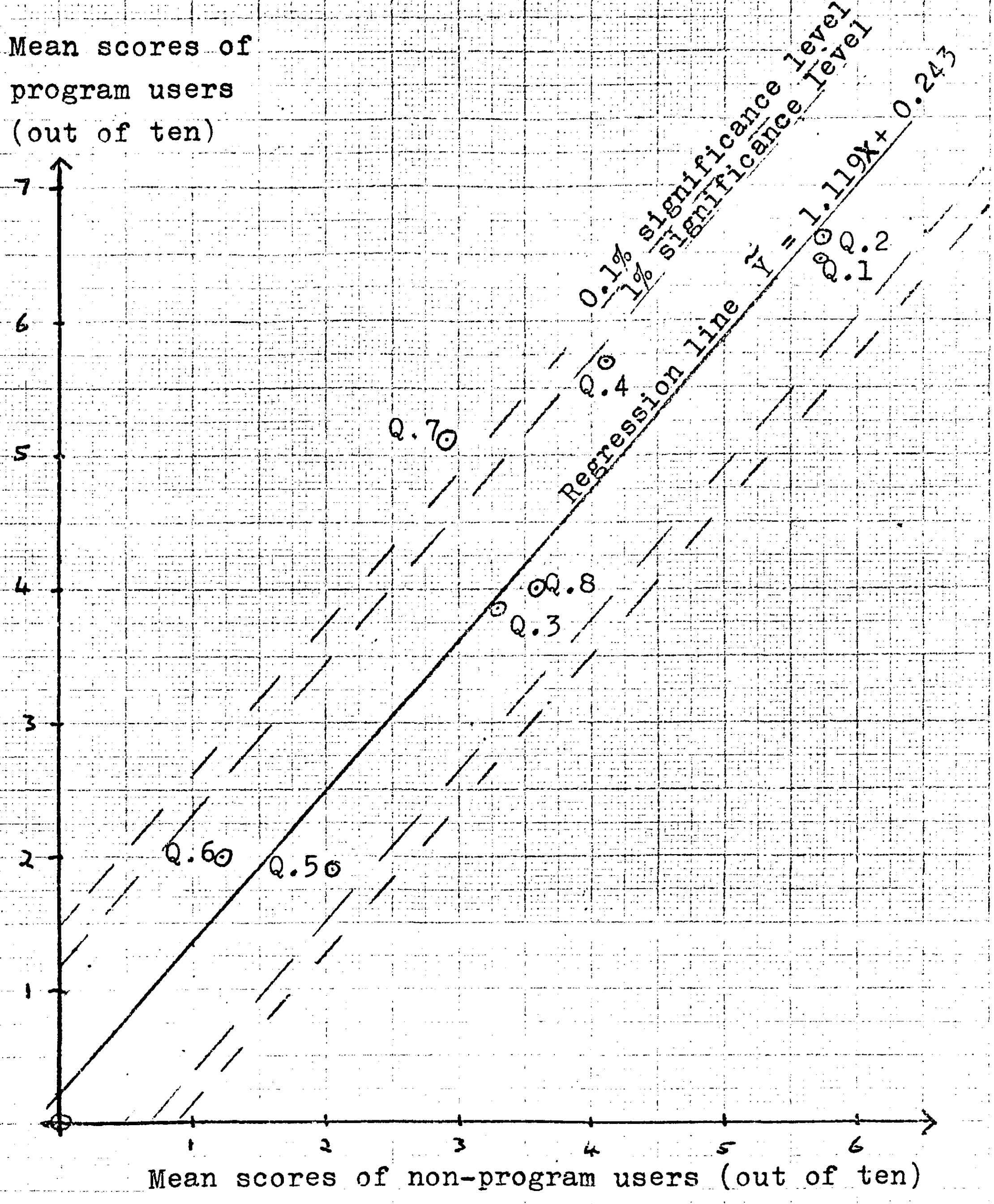


Diagram 4-1 Relative performance of program users and non-program users in 1975 degree examination questions

in order to work out the formula weight of silver chloride.

The breakdown of mean scores in question 7(a) and 7(b) was analysed, and the results summarized in Table 4-11. The scores for parts (a) and (b) have been adjusted to scores out of 10 (they were originally out of 5). The predicted scores for parts (a) and (b) have been calculated from the regression equation.

Question / Students	Actual mean scores (out of ten)			Predicted mean scores (out of ten)		
	7a	7b	7a+b	7a	7b	7a+b
At least 3 programs (n=66)	6.06	4.16	5.11	3.35	3.71	3.52
No programs (n=312)	2.78	3.10	2.93	-	-	-

Table 4-11 Analysis of performances in parts (a) and (b) of question 7

The difference between observed and predicted scores for question 7(a) are significant above the 0.1% level, while the differences for question 7(b) are not significant.

Thus the significant differences between observed and predicted mean scores for question 7 as a whole are almost entirely due to the superior performance in part (a) by those who studied the first three programs on transition metal chemistry. Question 7(a) examined material directly covered in programs 2 and 3. The reason for the lack of significant difference between performances in part (b) is probably due to the fact that students had to know certain molecular weights before attempting the problem which also involved calculations /

calculations using the concept of the mole - a topic not covered in the programs.

Conclusions

It would appear from the diagnostic assessment that few ambiguities exist in the programs, and that the programs enabled students to gain short-term mastery of the topic.

In addition to enhanced short-term recall, the performance in a subsequent degree examination indicated that the programs contributed to longer term retention of the subject matter covered, although the statistical analysis of the degree examination performances was complicated by the fact that students who used the programs tended to have a generally higher ability in chemistry than those students who did not use any programs.

APPENDIX TO CHAPTER 4

TRANSITION METAL CHEMISTRY
WORKBOOK 1

THE LANGUAGE OF TRANSITION METAL CHEMISTRY

OBJECTIVES : As given in Chapter 4.3

Frame 1

THE PERIODIC TABLE

giving atomic number and chemical symbol for each element

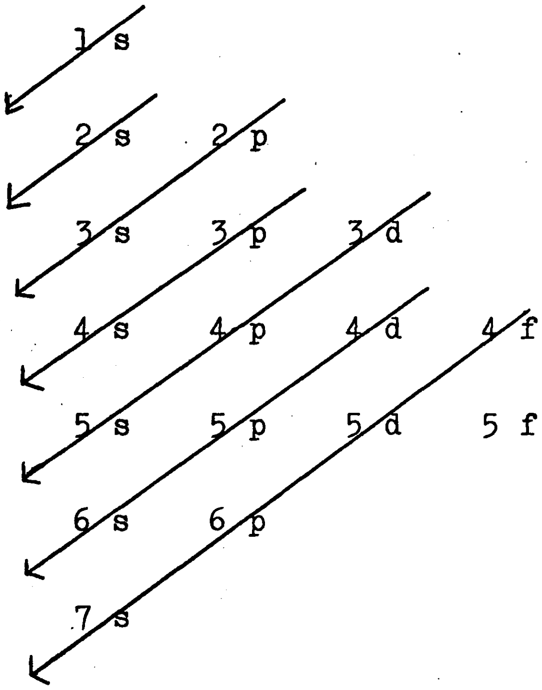
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg						*d* block					13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89† Ac															

f block

* LANTHANONS	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
† ACTINONS	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

We shall consider only d-block elements in this program.

Frame 2



1 s orbital at each energy level

3 p orbitals at each energy level

5 d orbitals at each energy level

7 f orbitals at each energy level

Each orbital can accommodate 2 electrons

Question : What is the electronic configuration of Calcium (atomic no. = 20) ?

Answer :

Frame 3 /

Frame 3

Electronic Configuration of 1st Row Transition Metals

Atomic Number	21	22	23	24	25	26	27	28	29	30
Symbol	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Name	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
Electronic Configuration	$[Ar]3d^1 4s^2$	$[Ar]3d^2 4s^2$	$[Ar]3d^3 4s^2$	$[Ar]3d^5 4s^1$	$[Ar]3d^5 4s^2$	$[Ar]3d^6 4s^2$	$[Ar]3d^7 4s^2$	$[Ar]3d^8 4s^2$	$[Ar]3d^{10} 4s^1$	$[Ar]3d^{10} 4s^2$

where $[Ar] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Discontinuity at Cr and Cu - Filled and half filled d shell effect

Frame 4

Oxidation State

Co (metal) $\xrightarrow{-3e^-}$ Co^{3+} (free ion)

oxidation state : 0 +3

Ni (metal) $\xrightarrow{-2e^-}$ Ni^{2+} (free ion)

oxidation state : 0 +2

Polyatomic Molecules e.g. CuO , $FeCl_3$

Polyatomic Ions e.g. $[Fe(CN)_6]^{4-}$, $[CrO_4]^{2-}$

Assigned oxidation states e.g. $O = -2$, Br, Cl, F, I = -1

$(CN) = -1$, $H = +1$

Question : What is the oxidation state of Fe in $FeCl_3$?

Answer :

Question : What is the oxidation state of Cr in $[CrO_4]^{2-}$?

Answer :

Frame 5

Co $\xrightarrow{-3e}$ Co^{3+} or Co(111)

oxidation state 0 +3

electronic configuration $[Ar]3d^7 4s^2$ $[Ar]3d^6 4s^0$

a d^6 ion

Oxidation state of Fe in $[FeO_4]^{2-}$ ion is +6. (Fe(V1))

Question : /

Question : What is the electronic configuration of Fe(Vl), given that the electronic configuration of Fe in the zero oxidation state is

$$[Ar]3d^{6}4s^{2} \ ?$$

Answer :

Frame 6 /

Frame 6

Variable oxidation states in d block transition metals

Valency shell electron configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
Symbol	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Possible oxidation states	- - 3	- 2 3 4	- 2 3 4 5	1 2 3 4 5 6	- 2 3 4 5 6 7	- 2 3 4 5 6	- 2 3 4	- 2 3 4	1 2 3	- 2 -

e.g. Cobalt : Co(11) , Co(111) or Co(1V)

Manganese
Mn(11) e.g. MnO , $MnCl_2$
⋮
Mn(V11) e.g. Mn_2O_7 , $[MnO_4]^{\ominus}$

Question : What is the oxidation state of manganese in $[Mn(CN)_6]^{3-}$?

Answer :

Question : What is the electronic configuration of manganese in the above oxidation state, given that its electronic configuration is [Ar] $3d^5\ 4s^2$ in the zero oxidation state?

Answer :

Frame 7

$$Co(111) + H_2O \longrightarrow [Co(H_2O)_6]^{3+}$$

A Complex Ion

$$[Co(H_2O)_6]^{3+} + \text{excess } Cl^- \rightarrow [CoCl_6]^{3-}$$

A Complex Ion

Complex ions behave as single ions.

Frame 8

Regard $[Fe(CN)_6]^{4-}$ as $[Fe^{2+} + 6(CN)^-]^{4-}$

$\therefore$ charge on complex ion = +2 - 6 = -4

Question : What is the oxidation state of Fe in $[FeCl_5(H_2O)]^{2-}$?

Answer :

Question : /

<u>Question</u> : What is the value of the charge x on the complex ion $[Ni(NH_3)_3Cl_3]^x$ when Ni(11) is present ?

<u>Answer</u> :

Frame 9

(a) $\underset{\substack{\uparrow \\ \text{counter} \\ \text{ion}}}{(K^+)_4} \quad \underset{\substack{\uparrow \\ \text{complex} \\ \text{ion}}}{[Fe(CN)_6]^{4-}}$ - a coordination compound

(b) $\underset{\substack{\uparrow \\ \text{complex} \\ \text{ion}}}{[Co(NH_3)_6]^{3+}} \quad \underset{\substack{\uparrow \\ \text{counter} \\ \text{ion}}}{(Cl^-)_3}$ - a coordination compound

---

Frame 10

$$\underbrace{[Co(NH_3)_5Cl]}_{\substack{\text{inner} \\ \text{coordination} \\ \text{sphere of} \\ \text{Co(111)}}} \quad \underbrace{Cl_2}_{\substack{\text{outer} \\ \text{coordination} \\ \text{sphere of} \\ \text{Co(111)}}} \quad \text{- a coordination compound}$$

$$\Big\downarrow \text{dissolve}$$

$$\underbrace{[Co(NH_3)_5Cl]^{2+}}_{\substack{\text{inner} \\ \text{coordination} \\ \text{sphere}}} + \underset{\text{free ions}}{2Cl^{\ominus}}$$

K_4 /

$$\underbrace{K_4}_{\substack{\text{outer}\\ \text{coordination}\\ \text{sphere of}\\ \text{Fe(11)}}}\quad \underbrace{[Fe(CN)_6]}_{\substack{\text{inner}\\ \text{coordination}\\ \text{sphere of}\\ \text{Fe(11)}}} \xrightarrow{\text{dissolve}} \underset{\text{Free ions}}{4K^+} + \underbrace{[Fe(CN)_6]}_{\substack{\text{inner}\\ \text{coordination}\\ \text{sphere}}}{}^{4-}$$

Frame 11

$$[Co(NH)_3Cl]\ Cl_2\ \text{(solid)} \xrightarrow{\text{dissolve}} [Co(NH_3)_5\ Cl]^{2+} + 2Cl^{\ominus}$$

3 ions altogether

Number of ions in solution detected by

(a) conductance measurements, or
(b) depression of freezing point.

Number of free chloride ions in solution indicated by titration with silver nitrate ($Ag\ NO_3$).

Total number of chlorines in the coordination compound found by analysis which gives the empirical formula of the compound.

Frame 12

$$\text{(a)}\quad [Fe(CN)_6]^{4-} \quad \text{consider as} \quad [\underset{\underset{\substack{\text{transition}\\ \text{metal ion}\\ \text{Fe(11)}}}{\uparrow}}{Fe^{2+}} + \underset{\underset{\substack{\text{6 cyanide}\\ \underline{\text{ligands}}}}{\uparrow}}{6(CN)^{\ominus}}]^{4-}$$

$$\text{(b)}\quad [\underset{\underset{\text{Pt(1V)}}{\uparrow}}{Pt}\ \underbrace{(NH_3)_4Cl_2}_{\text{6 ligands}}]^{2+}$$

– 4 ammonia ligands
+ 2 chloride ligands

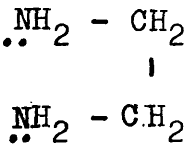
Frame 13

Ligands are Nucleophiles

Charged ligands e.g. $CN^{\ominus}$, $:\ddot{\underset{\cdot\cdot}{Cl}}^{\ominus}$, $:\ddot{\underset{\cdot\cdot}{Br}}^{\ominus}$,

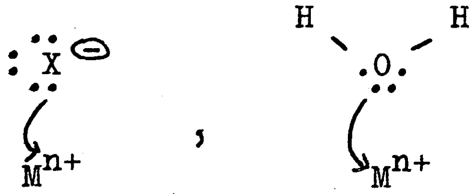
$:\ddot{\underset{\cdot\cdot}{I}}^{\ominus}$, $:\ddot{\underset{\cdot\cdot}{F}}^{\ominus}$, $:\underset{\cdot\cdot}{OH}^{\ominus}$

Uncharged ligands e.g. $H_2\ddot{\underset{\cdot\cdot}{O}}$, $:NH_3$, CO ,



$$\begin{array}{c} \underset{\cdot\cdot}{N}H_2 - CH_2 \\ \qquad\quad | \\ \underset{\cdot\cdot}{N}H_2 - CH_2 \end{array}$$

Nucleophilic attack of ligands e.g.



Question : If a ligand acts as a nucleophile, or electron donor, what is the role of the transition metal ion in this situation ?

Answer :

Frame 14

Monodentate Ligands - "One Toothed"

Examples $:\ddot{\underset{\cdot\cdot}{Cl}}^{\ominus}$, $:\ddot{\underset{\cdot\cdot}{Br}}^{\ominus}$, $CN^{\ominus}$, $:NH_3$, $H_2\ddot{\underset{\cdot\cdot}{O}}$,

$:\underset{\cdot\cdot}{OH}^{\ominus}$, $:\ddot{\underset{\cdot\cdot}{F}}^{\ominus}$, etc.

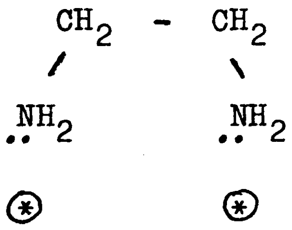
Frame 15 /

Frame 15

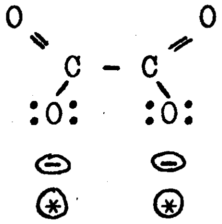
Bidentate Ligands - "Double Toothed"

Examples ethylene diamine (en)

(or 1, 2 diamino ethane)

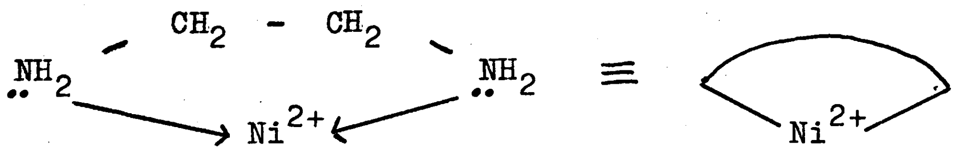


oxalate ion



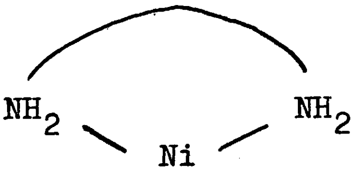
⊛ = potential nucleophilic bonding site

Frame 16



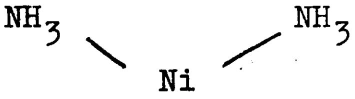
(a)

a chelate

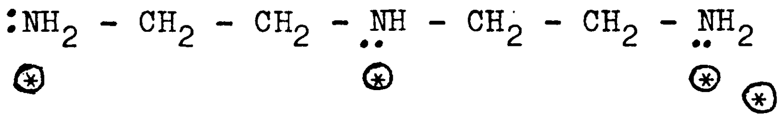


chelate ring

more stable than



Frame 17

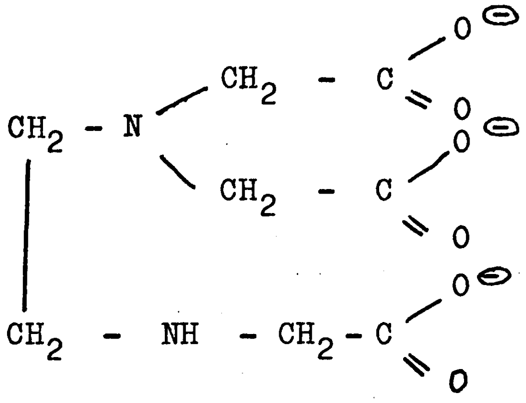


$$:NH_2 - CH_2 - CH_2 - \underset{\cdot\cdot}{N}H - CH_2 - CH_2 - \underset{\cdot\cdot}{N}H_2$$

⊛ = potential nucleophilic bonding site

Diethylene triamine (dien)
- a tridentate ligand

<u>Question</u> : How many potential nucleophilic bonding sites are there in the ethylene diamine triacetate ion ?



The ethylene diamine triacetate ion

<u>Answer</u> :

Frame 18

Coordination Number

		coordination number of transition metal
(a)	$[CoCl_4]^{2-}$	4
(b)	$[Co(NH_3)_5Cl]^{2+}$	6

<u>Question</u> : What is the coordination number of Cr(111) in the $[Cr(en)_2Cl_2]^+$ ion ?

<u>Answer</u> :

TRANSITION METAL CHEMISTRY
Tapéd Commentary for Program 1
THE LANGUAGE OF TRANSITION METAL CHEMISTRY

To gain maximum benefit from this series of five programs, you should use them to reinforce your lecture notes, and not to replace them. You should have a working knowledge of electronic configuration before you start this program.

For this program, all you require is this taped cassette, and Workbook 1. No slides or models are required. During the course of this program, you are occasionally asked to answer a question. When you hear this sound (*), stop the tape and write down your answer in the allotted space in the workbook. You may stop the tape at any time to revise points which you find difficult. Space is provided in the workbook if you wish to take notes from the program.

Objectives for Program 1 : As given in Chapter 4.3.

Frame 1

The transition elements are those elements having filled or partly filled d or f sub shells of electrons. The periodic table in the workbook indicates those elements with filled or partly filled d shells in blue shading, and those with filled or partly filled f shells in red. Altogether, about 60 of the known elements are classified as transition elements and all are metallic in nature.

There are 3 rows of d block transition metals. The 1st, 2nd and 3rd rows are concerned with filling the 3d, 4d and 5d electronic subshells respectively. There are 10 elements in each row as each d subshell can accommodate 10 electrons.

Similarities /

Similarities between transition elements are more marked vertically down a group. Thus, for example, nickel (At. No. 28) shows more chemical resemblance to palladium and platinum than to cobalt or copper.

Elements in the first row of the f block transition elements are called Lanthanons, and are concerned with filling the 4 f electronic subshell, while second row elements in the f block are called the Actinons and involve filling the 5f subshell. Each row contains 14 elements as each f orbital can accommodate 2 electrons and there are 7 f orbitals in a given energy level.

For the remainder of this series of programs we shall confine ourselves to a study of d-block transition metals.

Frame 2

An easy way to remember the order in which electronic orbitals are filled in an element of given atomic number is illustrated in the workbook. Having written down the orbitals as shown, merely follow the arrows downwards to get the order of filling of orbitals. Using this diagram it should be possible to work out the electronic configuration of every element in the periodic table, remembering a filled s orbital contains 2 electrons, a p subshell contains 6 electrons, a d subshell 10 electrons, and an f subshell 14 electrons. In each energy level, there are 3 p orbitals, 5 d orbitals and 7 f orbitals.

Write down the electronic configuration for calcium (At. No. 20). (*)

The answer is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. From the diagram we can see that the 3 d orbitals are next to be filled and this involves the 1st row transition elements.

Frame 3 /

Frame 3

The electronic configuration for the 1st row transition elements are listed here. In each case, the first part of the electronic configuration is the same as that of Argon, so the electronic configurations have been written in a shorthand manner, with only the valency electrons being named. The 3 d shell is steadily filled along the series except at Chromium $3d^5 4s^1$, and Copper $3d^{10} 4s^1$, where there is a slight discontinuity. Here 1 electron is taken from the 4 s orbital and put in the 3 d shell. This is because 3 d and 4 s orbitals are very similar in energy, and an extra stability is obtained when the d shell is exactly half filled with 5 electrons, or full with 10 electrons. More energy is therefore gained from this extra stability than is lost in putting an electron from the 4 s orbital into a 3 d orbital. This is called the filled and half-filled d shell effect.

Frame 4

Ions of transition metals are usually positively charged. The oxidation state of a transition metal can be defined as the positive charge or effective positive charge on the metal ion. It is easy to see that the oxidation states of Co^{3+} and Ni^{2+} are +3 and +2 respectively. However, the situation is slightly more involved when the metal ion is not free but in a polyatomic molecule or ion. Examples of such molecules and ions are given in the workbook. To work out the oxidation state of the metal, in such complexes, we arbitrarily assign oxidation states of -2 to oxygen, -1 to the halogens, +1 to hydrogen etc., i.e. we assign the commonly occuring oxidation state of the ions of these elements.

Thus in CuO (copper oxide), as oxygen is in the -2 oxidation state and as there is no overall charge, copper /

copper must be in the +2 oxidation state.

In the ion $[Fe(CN)_6]^{4-}$, each CN^- or cyanide ion is assigned an oxidation state of -1, and as the overall charge on the ion is -4 the Fe must be in the +2 oxidation state as +2 - 6 = -4.

What is the oxidation state of iron in iron chloride $FeCl_3$? (*)

The answer is that iron is in the +3 oxidation state as each chlorine is assigned -1 oxidation state, so to achieve electron neutrality the iron must be in the +3 oxidation state.

What is the oxidation of chromium in the $[CrO_4]^{2-}$ ion ? (*)

Here the chromium is in the +6 oxidation state.

Each oxygen is assigned an oxidation state of -2 and so 4 oxygens give a total charge of -8. As the overall charge on the ion is only -2, chromium must be in the +6 oxidation state.

Note that in such polyatomic ions as $[CrO_4]^{2-}$, an oxidation state of +6 does not mean that Cr^{6+} ions are present in an ionic lattice, but only that in this ion, having arbitrarily assigned oxygen to have a -2 oxidation state, each chromium has an effective charge of +6.

Frame 5

Consider a transition metal such as cobalt. In the elemental form it is in the zero oxidation state and has a valency electron configuration of $3d^7 4s^2$. If we now look at a cobalt ion in the +3 oxidation state the electronic configuration is now $3d^6 4s^0$. This illustrates an important general feature of transition /

transition metal chemistry which is that when transition metal ions are formed, the s electrons in the valency shell are always lost first, followed by the d electrons. As the s and d electrons are of similar energy d electrons can easily be removed after the s electrons have been removed. The cobalt^{3+} ion is called a d^6 ion, as 6 d electrons are present and no s electrons are left. When writing compounds containing transition metal ions, it is conventional to write the oxidation state of the metal concerned in Roman numerals after the name or chemical symbol of the transition metal concerned. Hence we would write a cobalt $^{3+}$ ion as Co(111) as in the workbook. Iron in the +6 oxidation state is encountered in the $[FeO_4]^{2-}$ ion and we write iron in this oxidation state as Fe(Vl). What would be the electronic configuration of iron in the +6 oxidation state, given that the electronic configuration of the valency shell of iron in the zero oxidation state is $3d^6\ 4s^2$? (*)

The valency shell electronic configuration of iron in a +6 oxidation state would be $3d^2\ 4s^0$, that is, we would have a d^2 ion. Remember that the s electrons in the valency shell are always lost first, followed by the d electrons.

Frame 6

A feature of the d block transition elements is that they exhibit a wide variety of oxidation states. The range of oxidation states for each of the 1st row transition metals is shown in the workbook. Cobalt, for instance, can exist in the +2, +3 or +4 oxidation state. The range of oxidation states is even greater for 2nd and 3rd row d-block transition elements.

In the first row, the widest range of oxidation states is given by manganese, from +2 as in MnO and $MnCl_2$, to +7 as in Mn_2O_7 and the $[MnO_4]^-$ or permanganate /

permanganate ion.

What would be the oxidation state of Mn in the $[Mn(CN)_6]^{3-}$ ion shown in the workbook, and write down the manganese with its oxidation state in Roman numerals. (*)

The oxidation state of Mn is +3 in this complex. Each cyanide group is given an oxidation state of -1, so Mn has to be in the +3 oxidation state to give an overall charge of -3 in the ion. Mn in the +3 oxidation state is written Mn(111).

What is the electronic configuration of Mn in the +3 oxidation state, given that in the zero oxidation state, Mn has the valency shell configuration $3d^5\ 4s^2$? (*)

Mn^{3+} would be a d^3 ion, with electronic configuration $3d^4\ 4s^0$. The s electrons are again lost first as usual.

Frame 7

Transition metal ions such as manganese $^{3+}$, iron $^{2+}$, nickel $^{2+}$, cobalt $^{3+}$ etc. are never found as free ions except in the gas phase. In the liquid or solid phase, transition metal ions become linked to other species and are never found in isolation. For instance if a cobalt (111) compound is dissolved in pure water, a new ion is formed, namely $[Co(H_2O)_6]^{3+}$ in which the water molecules are bound to the transition metal ion. If an excess of chloride ions is now added the species $[CoCl_6]^{3-}$ is formed. The chlorides in this species are not free ions and cannot be detected by any of the conventional tests for chloride ion. Ions such as these are called complex ions and behave as single ions, for example, the $[CoCl_6]^{3-}$ ion behaves as one large anion with a triple negative charge.

Frame 8 /

Frame 8

The resultant charge on a complex ion is the algebraic sum of the charges of the constituent ions or molecules. For example, the complex ion $[Fe(CN)_6]^{4-}$ can be regarded as being made up of one Fe^{2+} ion and 6 CN^- ions although these ions do not behave as individual ions in the complex ion. Thus the resultant charge on the complex ion is $+2 - 6 = -4$ which is what is found.

Consider the complex $[FeCl_5(H_2O)]^{2-}$ in the workbook. Write down the oxidation state of iron in this complex ion. (*) Iron is in the +3 oxidation state here. Each chlorine has a -1 oxidation state and H_2O is uncharged, thus the overall charge of -2 for the complex ion is only possible when Fe(111) is present.

What is the value of the charge x on the complex ion $[Ni(NH_3)_3Cl_3]^x$ when Nickel is in the +2 oxidation state? (*)

Here the overall charge is -1. NH_3 groups are uncharged, but each chlorine has a charge of -1. Thus $x = +2 - 3 = -1$.

Frame 9

In order to ensure overall electrical neutrality, complex ions are always present with counter ions. For example, when the complex ion is negatively charged, as in complex (a) in the workbook, the counter ions are positively charged. When the complex ion is positively charged, negative counter ions are present as in (b).

Such complex compounds are called coordination compounds and consist of an overall electrically neutral arrangement of a complex ion and counter ions. Both examples on the frame are typical coordination compounds.

Frame 10 /

Frame 10

Consider the coordination compound $[Co(NH_3)_5Cl]Cl_2$ shown in the workbook. The chloride ion and 5 NH_3 groups in the complex ion are strongly bound to the metal ion and cannot act as individual ions or molecules. The groups are said to be in the <u>inner coordination sphere</u> or in 1st sphere of influence of the metal ion.

The chloride <u>counter ions</u> can however act as free ions in solution, as these ions are less tightly bound to the cobalt ion and are said to be in the <u>outer</u> coordination sphere of the transition metal, or 2nd sphere of influence.

In the coordination compound $K_4[Fe(CN)_6]$, the 6 cyanide ions are in the inner coordination sphere of the $iron^{2+}$ ion and the 4 potassium ions are in its outer coordination sphere.

Frame 11

As has been stated before, the ions or molecules in the inner coordination sphere of a complex are tightly held to the transition metal and hence cannot be detected chemically. For example, in a solution of the compound shown in the workbook, only 3 ions would be detected using conductance measurements, namely 1 complex ion + 2 free chloride ions. The chloride ion in the complex ion would not be detected by this method. Another method of determining the number of species present in solution, namely depression of freezing point, would also indicate 3 ions present.

Titration with silver nitrate to detect the amount of free chloride ions present would indicate only 2 moles of free chloride ions per mole of coordination compound. The chloride in the complex ion would not be detected. In a case of this sort, the total number of chlorides in the complex would have to be determined by /

by analysis which would give the empirical formula of the compound.

Frame 12

Let us look more closely at complex ions. Complex ion (a) in the workbook can be considered to consist of 1 iron^{2+} ion and 6 cyanide ions. However, in the complex ion, neither the iron ion nor the cyanide ions act as free ions, but rather the complex ion behaves as one large ion. The iron^{2+} ion is the transition metal ion in the complex ion, and we call the other ions or molecules in the complex, such as the cyanide ions in this case, ligands. These ligands are the nearest neighbour ions or molecules to the central metal ion and constitute the inner coordination sphere around the central metal ion. A ligand is therefore any ion or neutral molecule which is bonded to a transition metal in its inner coordination sphere.

Correspondingly a complex ion consists of a transition metal ion surrounded by a series of ligands which need not all be the same as is shown in complex ion (b) in the workbook. Here the Pt^{4+} ion is surrounded by 6 ligands, 4 of which are uncharged ammonia molecules and 2 of which are chloride ions.

Frame 13

A ligand is a donor of electrons or, in other words, a nucleophile. Generally a ligand possesses 1 or more lone pairs of electrons which can be donated to the positively charged transition metal ion. Ligands need not be charged as in the case of cyanide or chloride ions, but may also be uncharged, as in the case of ammonia and water molecules. The important feature of a ligand is that it must have available lone pairs of electrons which it can donate to a metal ion. In this /

In this role, ligands can be regarded as nucleophiles. If the ligand is acting as an electron donor, or nucleophile, what, therefore, can we say is the role of the transition metal ion in this situation? (*)

We can say the metal ion is acting as an electrophile or electron acceptor.

Frame 14

Ligands of the type shown in the workbook are called monodentate ligands. Such ligands have only one position or site at which they can potentially bond to a transition metal ion. We can consider monodentate ligands to be 'one-toothed' ligands.

Frame 15

It is possible to have polydentate or multi-toothed ligands. These ligands have more than one potential bonding site in each molecule or ion. For example, a bidentate ligand has 2 potential bonding sites per molecule and can be considered as a 'double-toothed' ligand.

Examples of bidentate ligands are ethylene diamine or more systematically 1, 2 diamino-ethane, often called 'en' for short, and the oxalate ion.

In ethylene diamine the 2 terminal amine groups each have lone pairs on the nitrogen and there are therefore 2 potential nucleophilic bonding sites per molecule. Similarly in the oxalate ion 2 lone pairs exist on each negatively charged oxygen, so this is also a bidentate ligand.

Frame 16

The ethylene diamine molecule can attack a transition metal ion from both nucleophilic centres to form /

form a ring as shown in figure (a). The shorthand way of drawing an ethylene diamine group attached to a transition metal ion in this way is shown in figure (b). The ring formed by a bidentate ligand attached to a transition metal ion is called a chelate.

These chelate arrangements tend to be more stable than if 2 mono-dentate ligands were attached instead.

A 5 membered chelate ring such as is formed by en is comparable in stability with the 6 membered organic rings.

Frame 17

Diethylene triamine (or dien for short) shown here, is an example of a tridentate or triple toothed ligand. There is a potential nucleophilic bonding site on each nitrogen, in the form of a lone pair of electrons.

How many potential bonding sites are there in the ethylene diamine triacetate ion which is also shown in the workbook? (*)

There are 5 nucleophilic bonding sites in the molecule; 1 at each nitrogen and 1 at each of the three terminal carboxylate groups. Therefore, the ethylene diamine triacetate ion is a pentadentate ligand.

Frame 18

The coordination number of a transition metal ion is the total number of nucleophilic ligand sites which are bonded to the central metal ion in its inner coordination sphere. Note that this is only equal to the number of ligands present when monodentate ligands are involved. A bidentate ligand has 2 nucleophilic sites per molecule, and therefore a metal ion bonded to say 3 bidentate ligands will have a coordination number /

number of 6. Similarly a metal ion surrounded by 1 pentadentate ligand and 1 monodentate ligand in its inner coordination sphere will again have a coordination number of 6, as a pentadentate ligand bonds to the metal in 5 places.

In complex (a) in the workbook, the Co^{2+} ion is surrounded by 4 monodentate ligands and thus has a coordination number of 4. In complex (b) the Co^{3+} ion in the complex is surrounded by 6 monodentate ligands and so has a coordination number of 6.

What is the coordination number of the $chromium^{3+}$ ion in the complex ion $[Cr(en)_2Cl_2]^+$? (*)

The coordination number here is 6. The 2 chlorine ligands are monodentate and so have only one nucleophilic bonding site per molecule, but the bidentate ethylene diamine ligands each have 2 nucleophilic sites per molecule, making a total of 6 nucleophilic bonding sites bonded to the central metal ion.

It is important to remember that the coordination number is not necessarily equal to the number of ligands present, except when all attached ligands are monodentate.

For the remaining programs in this series, only complexes in which the central transition metal ion has a coordination number of 6 in its inner coordination sphere will be considered.

Would you now complete post-test 1 and leave your answer card in the box provided.

END OF PROGRAM

TRANSITION METAL CHEMISTRY
WORKBOOK 2

NAMING COORDINATION COMPOUNDS AND COMPLEX IONS

OBJECTIVES : As given in Chapter 4.3

Frame 1

Rule 1 In a coordination compound the positive ion is named first, followed by the negative ion

Examples :

	Coordination Compound	Positive Ion	Negative Ion
(a)	$K_4[Fe(CN)_6]$	$4K^+$	$[Fe(CN)_6]^{4-}$
(b)	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+}$	$3Cl^{\ominus}$

Frame 2

Rule 2 In a complex ion, the ligands are named in the following order -

1st All negative ligands e.g. $CN^{\ominus}$, $Cl^{\ominus}$, etc.

2nd All uncharged ligands e.g. $:NH_3$, $H_2\ddot{O}:$, etc.

3rd All positive ligands e.g. $:NH_2 - NH_3^{\oplus}$ etc.

Example : (a) $[Co\underbrace{(NH_3)_4}\ \underbrace{ClCN}]$

uncharged ligands ∴ named after the negative ligands	both negative ligands ∴ named first

Question : Which ligands would be named first and which second in the complex ion $[Cr(en)_2Br_2]^{2+}$?

Answer :

Frame 3

Rule 3 Naming of ligands

Negatively charged ligands end in "-o" e.g.

$CN^{\ominus}$	$OH^{\ominus}$	$Cl^{\ominus}$	etc.
cyano	hydroxo	chloro	

Uncharged ligands have no systematic names, e.g.

H_2O	NH_3	$NH_2 - CH_2 - CH_2 - NH_2$
aquo	ammine	ethylene diamine

Positively charged ligands end in "-ium" e.g.

$NH_2 - NH_3^{\oplus}$	($H_2N - NH_2$
hydrazinium	hydrazine)

Frame 4

Rule 4 Ligands of similar charge are listed alphabetically

Examples :

		order of naming		
		1st	2nd	3rd
(a)	$[Co(CN)_5Cl]^{3-}$	chloro	cyano	
(b)	$[Co(en)_2(NH_3)_2]^{3+}$	ammine	ethylene diamine	

Question : What will be the order of naming of ligands in

(c) $[Co(NH_3)_4H_2O\ Cl]^{2+}$?

Answer : ⟶

Frame 5

Number of simple shortnamed ligands present of one type :-

	1	2	3	4	5	6
Prefix used:-	No Prefix	di	tri	tetra	penta	hexa

Number /

Number of complicated long named ligands present of one type :-

	1	2	3
Prefix used:-	No Prefix	bis	tris

e.g. Two ethylenediamine ligands in a complex written as bis (ethylenediamine)

Examples		Way in which ligands are listed
(a)	$[Ni(H_2O)_6]^{2+}$	hexa aquo
(b)	$[Co(en)_2(NH_3)_2]^{3+}$	diammine bis (ethylenediamine)
(c)	$[Co(NH_3)_4H_2O\ Cl]^{2+}$	chloro tetraammine aquo

Question : In what way would you list the ligands in the complex

(d) $[Co(NH_3)_3Cl_2(CN)]$?

Answer : ⟶

Frame 6

Rule 5 The oxidation state of the transition metal in the complex ion must always be stated.
The transition metal in a complex ion is named only after the ligands have been listed.

Examples :	Molecular Formula	Name
(a)	$[Co(NH_3)_6]Cl_3$	hexaammine cobalt (111) chloride
(b)	$[Pt(NH_3)_4Br_2]^{2+}$	dibromotetraammine platinum (1V) cation

---

Frame 7 /

Frame 7

Rule 6 Negatively charged complex ions have the suffix "-ate"

Example	Molecular Formula	Name
(a)	$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (11)
(b)	$[Pt(Cl)_6]^{2-}$	hexachloroplatinate (1V) anion

Question : What is the name of the coordination compound

(c) $K_3[Co(CN)_5Br]$?

Answer : ⟶

Frame 8

Application of Rules

Question : What is the correct name for the coordination compound $[Co(NH_3)_4Cl\ Br]Cl$?

Answer :

Frame 9

Question : Name the complex ion $[Cr(en)_2(H_2O)_2]^{3+}$

Answer :

Frame 10

So far we have been going from molecular formula → name
Now we shall try to go from name → molecular formula

Example /

Example

	Potassium pentachloroaquoferrate (111)
1) Pick out complex ion	pentachloroaquoferrate (111)
2) Write molecular formula of complex ion	$[Fe^{(111)}Cl_5H_2O]^x$ $Fe(111) \quad 5Cl^{\ominus} \rightarrow x$
3) Calculate the overall charge on this ion	$+3 - 5 = -2$
4) Put in the number of counter ions required for electrical neutrality	$K_2[Fe\,Cl_5\,H_2O]$

Frame 11

Question : Write down the molecular formula of cyanopentaammine cobalt (111) chloride

Answer :

TRANSITION METAL CHEMISTRY

Taped Commentary for Program 2

NAMING COORDINATION COMPOUNDS AND COMPLEX IONS

For this program all you require is this taped commentary and Workbook 2. You will be asked questions during the course of this program. When you hear this sound (*), stop the tape, and write the answer in your workbook before restarting the tape.

Space is provided in the workbook if you wish to take notes from the program.

Objectives for Program 2 : As given in Chapter 4.3

Frame 1

In the naming, or in other words, nomenclature, of coordination compounds and complex ions there are several rules which must be observed.

Rule 1 states that, in a coordination compound, the positive ion always is named first, followed by the negative ion. Thus in coordination compound (a) in the workbook, potassium would be named first, followed by the name of the negatively charged complex ion, $[Fe(CN)_6]^{4-}$.

In compound (b), the positively charged complex ion $[Co(NH_3)_6]^{3+}$ would be named first, followed by chloride.

Frame 2

Rule 2 states that when the complex ion is being named, the ligands coordinated to the transition metal in the complex ion are listed in the following order. Firstly, all negatively charged ligands are named, then all neutral ligands are named, and finally all positively charged /

charged ligands are named.

In complex (a) the chloride and cyanide ligands would be named first as these are negatively charged, followed by the ammonia ligands as these are uncharged.

Which ligands would be named first and which second in the complex ion $[Cr(en)_2Br_2]^{2+}$? (*)

The bromide ligands, being negatively charged would be named first, followed by the uncharged ethylene diamine ligands.

Frame 3

When negatively charged ligands are named in complex ions, they are always given the ending -o to replace the ending -ide in the free ion. For example, we talk about chloro ligands in complex ions. Other common negatively charged ligands are cyano, and hydroxo ligands.

Uncharged ligands have no specific ending. For example water ligands are called aquo ligands, while NH_3 ligands are called ammine ligands. Note that ammine is spelled with two m's as in ammonia. Do not confuse ammine ligands with amines met in organic chemistry which have only one m in their spelling. Ethylene diamine ligands are simply called ethylene diamine when named in a complex ion.

Positively charged ligands are uncommon in transition metal chemistry, but when they are encountered, they are given the ending -ium, for example, in the hydrazinium ligand, which is derived from hydrazine.

Frame 4

Rule 4 states that if several different types of ligand are coordinated to a transition metal in a complex ion, then these must be listed alphabetically, while still /

still maintaining rule 2 relating to charge. Thus all negatively charged ligands are named first, in alphabetical order, followed by all uncharged ligands in alphabetical order, followed by any positively charged ligands, again in alphabetical order.

In complex ion (a) two types of negatively charged ligands are present, but as they are named alphabetically, the chloro ligands would be named before the cyano ligands.

Complex ion (b) has no negatively charged ligands and two types of uncharged ligand, which are ammine ligands and ethylene diamine ligands in alphabetical order.

In what order will the ligands be named in complex (c) ? (*)

The order in which the ligands are named is <u>first</u> chloro, <u>second</u> ammine, and <u>third</u> aquo. Negative ligands are always named first, and there is only one type of negative ligand in complex ion (c), namely the chloro ligand. The uncharged ligands are named next, and as there are two types of uncharged ligand in this complex ion, they are named alphabetically, so the ammine ligands are named before the aquo ligand.

<u>Frame 5</u>

The number of each ligand type present in a complex ion is usually indicated by the prefix di, tri, tetra, penta or hexa. If only one ligand of that type is present, no prefix is used.

For more complicated ligands with larger names such as ethylenediamine, diethylenetriamine and ethylene diamine triacetate, prefixes like bis and tris are used to indicate 2 and 3 ligands respectively. The names of these large ligands are always enclosed in brackets /

brackets when a complex is being named, for example if 2 ethylene diamine ligands were present in a complex we would write bis (ethylenediamine) as shown in the workbook.

In example (a) in the workbook, the 6 aquo ligands would be given the prefix hexa, and would be described as hexaaquo. In example (b), the two types of uncharged ligand would be listed alphabetically as diammine bis (ethylenediamine). Note that the name ethylenediamine is bracketed. In example (c) the ligands would be listed as chloro tetraammine aquo. The negatively charged ligand is named first followed by the two uncharged ligands in alphabetical order.

How would you list the ligands in complex (d) ? (*)

The correct way to list them is dichloro cyano triammine. The two types of negative ligand are named alphabetically followed by the 3 uncharged ammine ligands.

Frame 6

Rule 5 states that we must always name the oxidation state of the transition metal in the complex ion. This is denoted in Roman numerals. The name and oxidation state of the metal involved in the complex ion is stated only after the names of the ligands present have been listed.

The coordination compound (a) in the workbook is therefore named hexaammine cobalt (111) chloride. Note that the positive ion, namely the complex ion in case (a), is named first followed by the negative ion.

The complex ion (b) is named the dibromotetraammine platinum (1V) cation. Note that the negative bromo ligands are named before the uncharged ammine ligands.

Frame 7 /

Frame 7

The final rule is rule 6 which states that complex ions which are negatively charged end in -ate. For example, the coordination compound (a) is called

potassium hexacyanoferrate (11)

while the negatively charged complex ion in example (b) is the

hexachloroplatinate (1V) anion.

What is the complete name of the coordination compound (c) ? (*)

It is potassium bromopentacyano cobaltate (111).

The positive ion potassium, is named first, followed by the name of the complex ion. Two types of negative ligand are present which must be named alphabetically. The cobalt is in the +3 oxidation state, as the overall charge on the complex ion is -3 and 6 negatively charged ions are present, so +3 - 6 = -3. As the complex ion is negatively charged, the suffix -ate is added to cobalt.

Frame 8

Now let us try to apply the rules we have learned to a few examples.

Write down the systematic name for the coordination compound shown in the workbook. (*)

It is bromochlorotetraammine cobalt (111) chloride.

The complex ion is positive - hence it is named first. The negatively charged ligands are named first in the complex ion and there are two types of these, namely bromo and chloro in alphabetical order. There are four uncharged ammine ligands, so the prefix tetra is used. The overall charge on the complex ion is +1 as only one negative counter ion is present. As two negatively /

negatively charged ligands are present in the complex ion, the oxidation state of cobalt must be +3, as +3 - 2 = +1. The negative counter ion is the chloride ion and is named last.

Thus the complex is bromochlorotetraammine cobalt (111) chloride.

Frame 9

What is the name of the complex ion shown here? (*)

It is the diaquo bis (ethylenediamine) chromium (111) ion. No negative ligands are present, but two types of uncharged ligands are in the complex ion. The aquo ligands are named first and given the prefix di as there are two of them.

As ethylenediamine is a longer name and a more complicated ligand, the prefix bis is used here and the name ethylene diamine is bracketed. Finally the oxidation state of chromium is +3, as the charge on the complex ion is +3 and no charged ligands are present. No suffix is added to the name of the metal ion when the complex is positively charged or uncharged, and so the ion is called the diaquo bis (ethylene diamine) chromium (111) ion.

Frame 10

As well as naming coordination compounds and complexes given their molecular formula, you should also be able to write down the molecular formula of a coordination compound given its name.

For example, if we are given the name potassium pentachloroaquo ferrate (111), it is possible to write the molecular formula of this compound.

Always start with the complex ion. From the name /

name we know that there is an iron^{3+} ion surrounded by 5 chloro ligands and 1 aquo ligand, so we can write this down.

To find out how many potassium ions are present we require to work out the charge on the complex ion.

We know it is negatively charged as it is named last. The iron is in the +3 oxidation state, and there are 5 negative ligands in the complex ion, so the charge on the ion is +3 - 5 = -2. Thus 2 potassium ions are required for electrical neutrality and we can write down the molecular formula of the complex as $K_2[Fe\ Cl_5\ H_2O]$.

Frame 11

Write down the molecular formula of cyanopenta-ammine cobalt (111) chloride. (*)

The correct formula is $[Co(NH_3)_5\ CN]Cl_2$ written with the complex ion $[Co(NH_3)_5\ CN]$ enclosed in brackets.

Again we start with the complex ion which is positively charged here and is therefore first named. The name implies that the complex ion consists of one cyano ligand and 5 ammine ligands surrounding a cobalt^{3+} ion. To find the number of chloride counter ions, the charge on the complex ion must be worked out. As the cobalt is in the +3 oxidation state, and only 1 negatively charged cyano ligand is present the overall charge on the complex ion is +3 - 1 = +2. Thus 2 chloride ions are required for electrical neutrality making the formula of the compound $[Co(NH_3)_5\ CN]Cl_2$.

Would you now please complete post-test 2 and leave your answer card in the box provided.

END OF PROGRAM

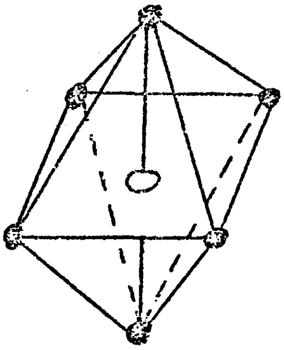
TRANSITION METAL CHEMISTRY
WORKBOOK 3

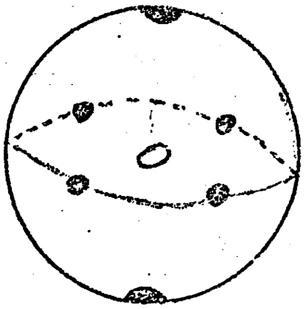
SYMMETRY AND ISOMERISM IN OCTAHEDRAL TRANSITION METAL COMPLEXES

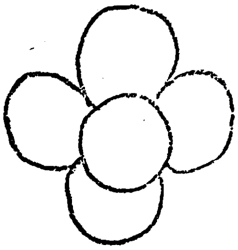
OBJECTIVES : As given in Chapter 4.3

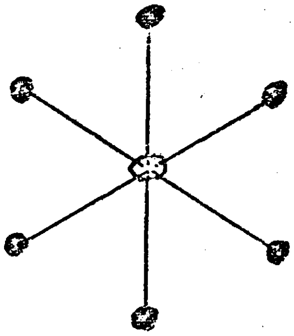
Frame 1

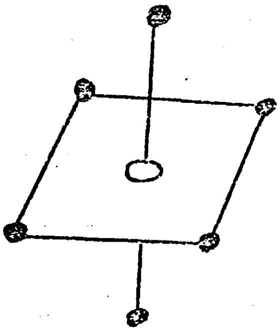
Models of Octahedral Compounds


(1)


(2)


(3)

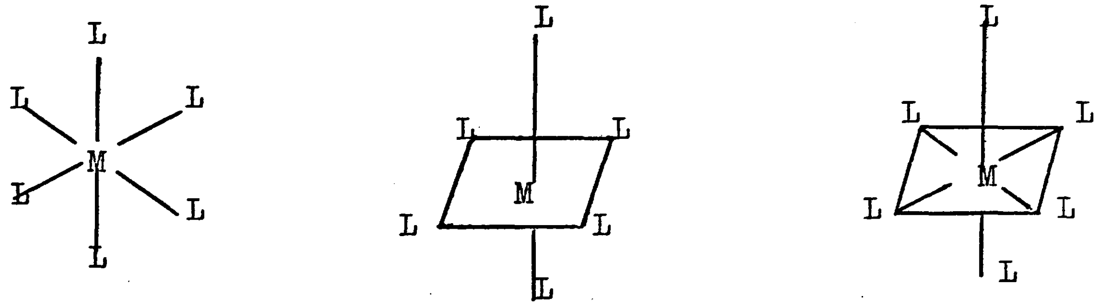

(4)


(5)

All five representations are equivalent.

Frame 2

Methods of Drawing Octahedral Complexes



(a) (b) (c)

M=metal ion; L=ligand

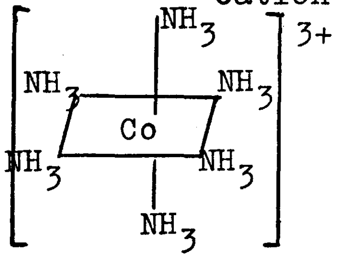
All three representations are equivalent. Only method (b) will be used in future.

Frame 3

Isomers - Non superimposable structures having the same molecular formula

(a) $[Co(NH_3)_6]^{3+}$

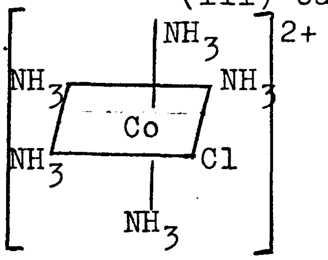
hexaammine cobalt (111) cation



No isomers possible

(b) $[Co(NH_3)_5Cl]^{2+}$

chloropentaammine cobalt (111) cation



Question : Are there any isomers possible in the above complex ion?

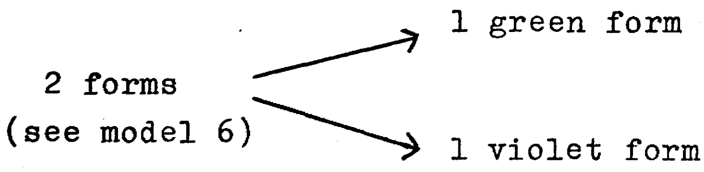
Answer :

Frame 4 /

Frame 4

$[Co(NH_3)_4Cl_2]^+$

dichlorotetraammine cobalt (111) cation



Question : Draw isomers of this complex ion.

Answer :

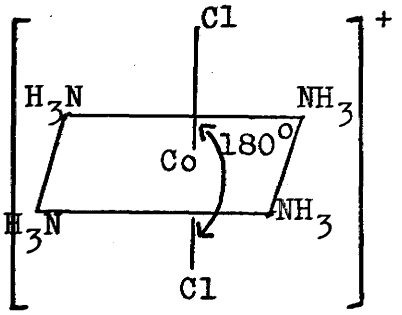
Frame 5

$[Co(NH_3)_4Cl_2]^+$

dichlorotetraammine cobalt (111) cation

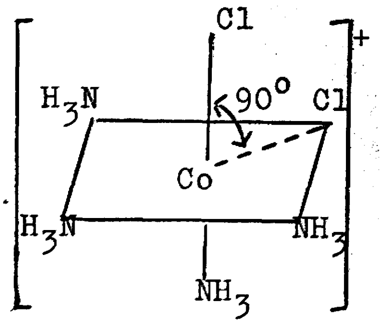
Isomers are

(a)



trans isomer
(green)

(b)



Cis isomer
(violet)

Isomers (a) and (b) are geometric isomers.

Frame 6

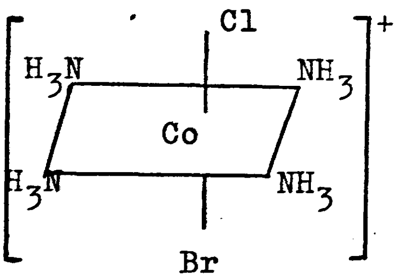
$[Co(NH_3)_4Cl\ Br]^+$

bromochlorotetraammine cobalt (111) cation

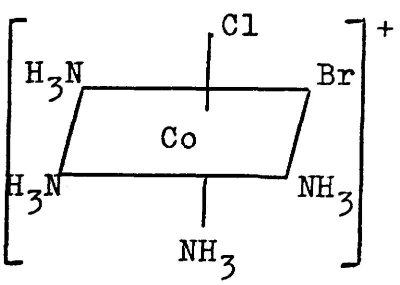
2 geometric isomers

(a) /

(a)



(b)



<u>trans isomer</u>

<u>cis isomer</u>

<u>Question</u> : Are there any more possible isomers?

<u>Answer</u> :

Frame 7

$Co(NH_3)_3\ Cl_2\ Br$

bromodichlorotriammine cobalt (111)

<u>Question</u> : Draw possible geometric isomers for the above complex.

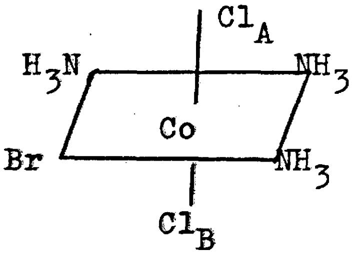
<u>Answer</u> :

Frame 8

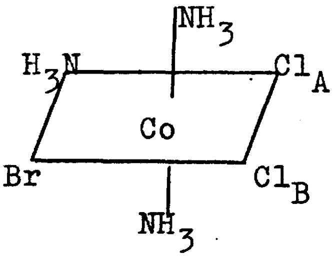
$Co(NH_3)_3\ Cl_2\ Br$

bromodichlorotriammine cobalt (111)

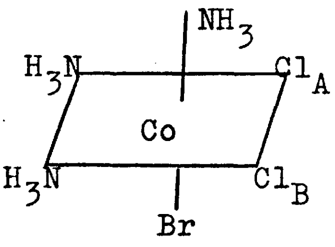
<u>3</u> geometric isomers are possible



(a)



(b)



(c)

Cl-Cl relationship /

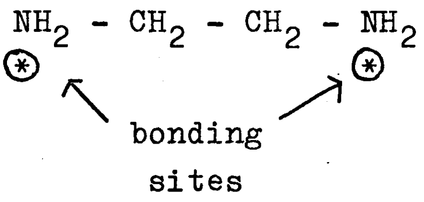
Cl-Cl relationship	trans	cis	cis
Cl_A-Br relationship	cis	trans	cis
Cl_B-Br relationship	cis	cis	cis

Frame 9

$[Co(en)_3]^{3+}$

tri (ethylene diamine) cobalt (111) ion

where en = ethylene diamine
(or 1,2 diamine ethane)



$NH_2 - CH_2 - CH_2 - NH_2$

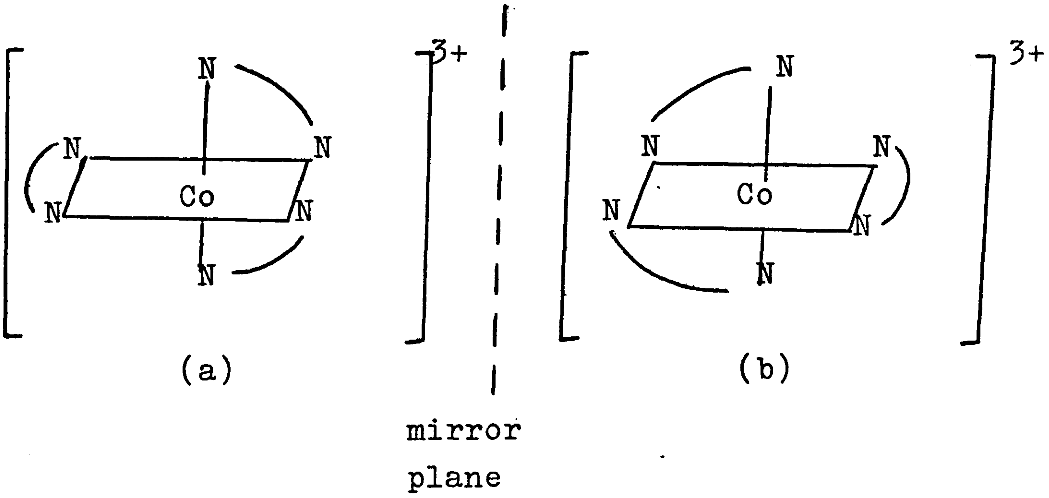
(bidentate ligand)

Question : Is it possible to superimpose model 7a upon model 7b ?

Answer :
- - - - -

Question : Are models 7a and 7b mirror images of each other?

Answer :
- - - - -



(a) and (b) are chiral isomers or enantiomers - non-superimposable mirror images.

Frame 10

$[Cr(en)_2\ Cl_2]^+$

dichlorobis (ethylene diamine) chromium (111) cation

3 forms → 1 green form

3 forms → 2 violet forms

(see model 9)

Question : Explain these 3 forms in terms of geometric and chiral isomerism. Draw the structures of the isomers below.

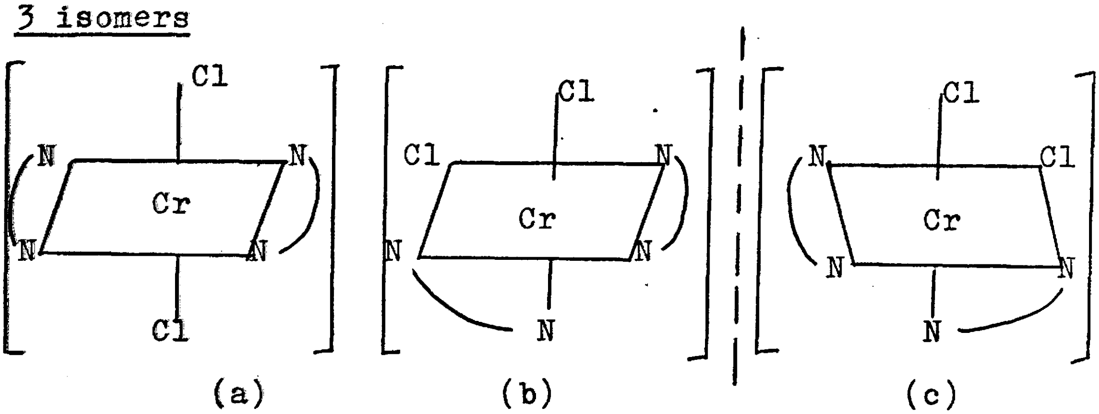
Answer :

Frame 11

$[Cr(en)_2Cl_2]^+$

dichloro bis (ethylene diamine) chromium (111) cation

3 isomers



(a) (green)

(b) (violet)

mirror plane

(c) (violet)

Cl-Cl relationship : trans cis cis

(b) and (c) are enantiomers

Frame 12 /

Frame 12

$[Co(en)(NH_3)_2\ Cl_2]^+$

dichlorodiammine (ethylene diamine) cobalt (111) ion

Question : Draw all possible geometric and chiral isomers of the above complex ion.

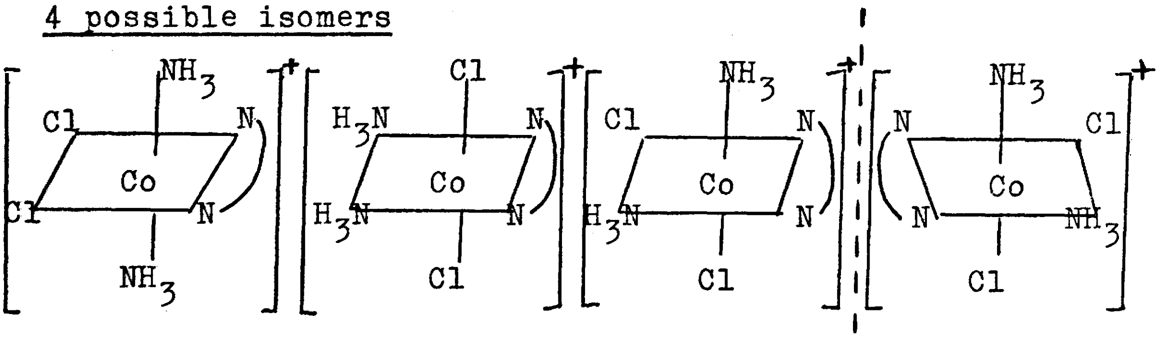
Answer :

Frame 13

$[Co(en)(NH_3)_2\ Cl_2]^+$

dichlorodiammine (ethylene diammine) cobalt (111) ion

4 possible isomers



(1) (2) (3a) mirror plane (3b)

	(1)	(2)	(3a)	(3b)
NH_3-NH_3 relationship :	trans	cis	cis	cis
Cl-Cl relationship :	cis	trans	cis	cis

TRANSITION METAL CHEMISTRY
Taped Commentary for Program 3

SYMMETRY AND ISOMERISM IN OCTAHEDRAL TRANSITION METAL COMPLEXES

For this program, in addition to this tape and Workbook 3, you require models 1 to 9 and the construction kit.

During the program, you are frequently asked to answer a question, examine a model or use the construction kit. While performing these tasks, always stop the tape after hearing this sound. (*)

You are also free to stop the tape at any time to go over points which you did not understand.

Objectives for Program 3 : As given in Chapter 4.3

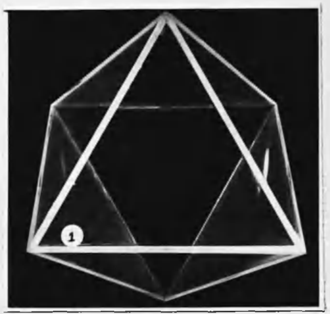
Frame 1

Program 1 in this series introduced some of the terms frequently met in transition metal chemistry, and established the types of ligands encountered in transition metal complexes, while program 2 dealt with the naming of coordination compounds and complex ions.

We now turn our attention to the symmetry of these transition metal complexes, where the central metal ion has a coordination number of 6, that is, there is a total of 6 ligand nucleophilic coordinating sites bonded to the metal ion in its inner coordination sphere. Complexes with a coordination number of 6 are octahedral in shape, with the ligands sitting at the 6 corners of an octahedron.

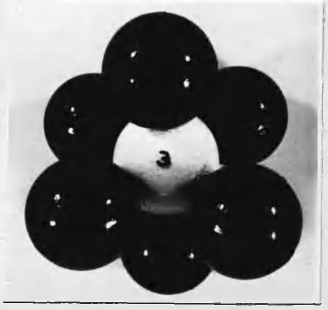
Before considering individual examples of octahedral complexes, let us first review some of the common methods /

methods of representing these complexes. These representations are illustrated by models 1 to 5, and the corresponding diagrams 1 to 5 in the workbook. Model 1 and diagram 1 represent a regular octahedron. An octahedron has 8 faces, but only 6 corners, and the 6 nucleophilic coordinating sites of the ligands involved in the complex, can be considered to be situated at each of the 6 corners with the metal ion in the centre. All 6 positions are equivalent both chemically and geometrically.

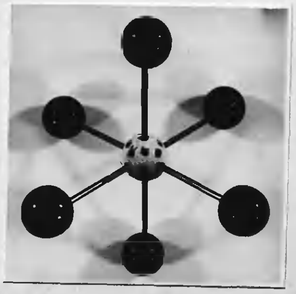


Model 2 and diagram 2 show the 6 ligands placed equidistantly around the surface of a sphere. Again this represents an octahedral complex with a metal ion at the centre surrounded by 6 indistinguishable positions where the ligand bonding sites are placed.

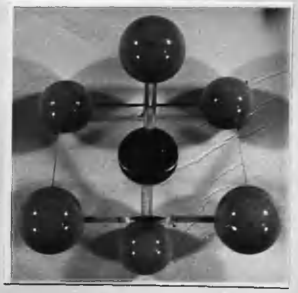
Model 3 and diagram 3 are probably closest to the real situation, and represent 6 ligand sites placed equidistantly around a central metal ion. This situation is, however, difficult to represent pictorially.



Model 4 and diagram 4 is an extension to model 3 and diagram 3. This simple ball and stick representation allows for a less crowded metal ion so that one may see geometric relationships more easily.

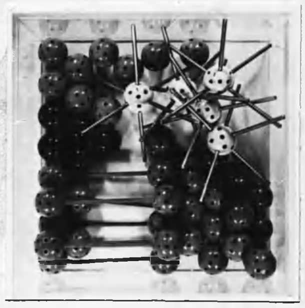


Model 5 and diagram 5 show the metal ion at the centre of a square with 4 ligand sites at each corner, as well as 1 above and 1 below the plane of the square. All metal-ligand distances are equal and hence all the ligand sites are equivalent.



All 5 representations are merely different ways of showing exactly the same thing - namely an octahedral complex with 6 completely equivalent ligand sites surrounding a central metal ion.

All future octahedral models used in this program will be of the ball and stick type as illustrated by model 4. The construction kit is designed so that you can build ball and stick octahedral complexes for yourself. You should recognise however, that any of the other model types would be equally valid.



Construction Kit

Frame 2

Diagrams (a), (b) and (c) in the workbook represent 3 of the common ways of drawing octahedral complexes. In all cases the distance between the central metal ion and each ligand site is equal and therefore each ligand site is equivalent. In all future diagrams in this program diagrams of type (b) will be used, but all 3 are equally valid.

Frame 3

In transition metal complexes, structures with the same molecular formula, but differing in the arrangement of ligands around the central metal ion such that one structure cannot be superimposed atom for atom upon the other, are called isomers.

First consider a transition metal ion surrounded by 6 monodentate ligands in its inner coordination sphere.

When all 6 ligands are the same, as in the hexaammine cobalt (111) cation shown in figure (a) in the workbook /

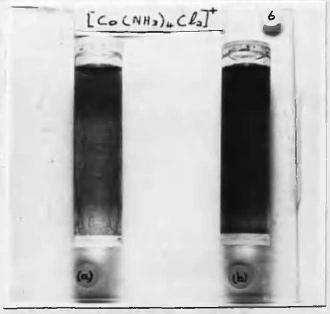
workbook, there are obviously no isomers possible as all 6 ligand positions are equivalent.

If one ammine ligand is replaced by a ligand of a different type, for example a chloro ligand, we obtain a complex such as the chloro pentaammine cobalt (111) cation shown in figure (b). Build a model of this complex using the construction kit. Are there any possible non-superimposable isomers of this complex? Use differently coloured balls to represent ligands of different types. (*)

You should find no isomers of this complex. There is no way in which one can arrange 5 similar ligands and 1 odd ligand around a metal centre such that any distinguishable isomers are made.

<u>Frame 4</u>

Consider now a complex ion with 4 ligands of one type and 2 of a different type. A complex ion of this sort is the dichloro tetraammine cobalt (111) cation. Samples of this particular complex are given in model 6 and it exists in a green form and a violet form. Explain this in terms of isomerism, using your construction kit to assemble isomers of this complex ion, and draw their structures in your workbook. (*)



<u>Frame 5</u>

A green form and a violet form of this complex ion exist because there are two distinguishable isomers of the complex. These two non-superimposable forms of the complex are illustrated in the workbook by figures (a) and (b). Isomer (a) corresponds to the green form and isomer (b) to the violet form. If you did not manage to construct the two isomers correctly, stop /

stop the tape and make them now. (*)

Isomers (a) and (b) differ in the arrangement of the two chloro ligands and four ammine ligands around the cobalt. In isomer (a) the 2 chloro ligands are 180^{o} apart, that is the chloro, cobalt chloro bond angle is 180^{o}. Thus the chloro ligands are as far apart as possible in the complex ion. The chloro ligands are said to be trans in this case and isomer (a) is called the trans isomer of the dichloro tetraammine cobalt (111) cation.

Compare this with the situation in isomer (b). Here the 2 chloro ligands are next to each other and the chloro, cobalt, chloro bond angle is only 90^{o}. The chloro ligands are said to be cis in this case, and isomer (b) is called the cis isomer of the dichloro tetraammine cobalt (111) cation.

Note that these definitions of cis and trans isomers differ from the definitions met in organic chemistry. You should notice that in every octahedral complex, for each ligand site, there are 4 equivalent ligand sites which are cis to that site and one site which is trans.

Cis and trans isomers are not superimposable, nor are they mirror images, and so they are not enantiomers.

We call such isomers geometric isomers. Geometric isomers differ in the cis and trans arrangement of ligands around the metal ion centre.

Frame 6

An analogous situation exists when the two odd ligands are themselves of different types as in the bromo chloro tetraammine cobalt (111) cation. Again, 2 geometric isomers exist, one in which the bromo and chloro /

chloro ligands are trans in the complex, and the other where these 2 ligands are arranged cis. Use your construction kit to check if any other structures are possible. (*)

You should find no other isomers of this complex.

<u>Frame 7</u>

Consider now a complex where the central transition metal is surrounded by 3 ligands of type A, 2 of type B, and 1 of type C. A complex of this sort would be bromo dichloro triammine cobalt (111). Use the construction kit to decide how many geometric isomers of this complex are possible, and draw the structure of each isomer in your workbook. (*)

<u>Frame 8</u>

You should have found 3 distinct geometric isomers of the complex. These are illustrated in the workbook. Relate these diagrams to the isomers which you made to ensure you constructed them correctly. If you failed to make the 3 correct geometric isomers, construct them now using the diagrams in the workbook to help you. (*)

In isomer (a), the chloro ligands are <u>trans</u> to each other, and the bromo ligand is cis to both chloro ligands.

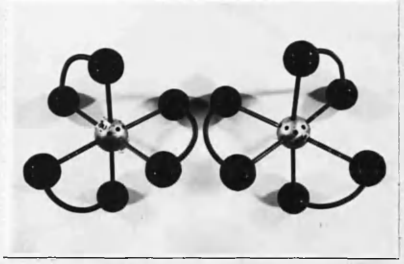
In isomer (b) the chloro ligands are <u>cis</u> to each other, and the bromo ligand is trans to one chloro ligand, and cis to the other. Isomer (c) again has the chloro ligands cis, as in isomer (b), but here the bromo ligand is <u>cis</u> to <u>both</u> chloro ligands.

Use your constructed models to check these cis and trans relationships. (*)

<u>Frame 9</u> /

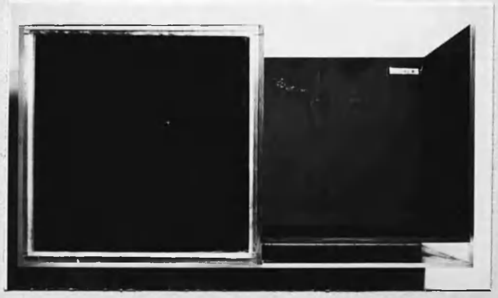
Frame 9

Chiral isomers, or in other words enantiomers, are also encountered in complexes of transition metals. In such isomers the structures do not differ in the arrangement of cis and trans ligands, but one isomer is a non superimposable mirror image of the other isomer. An example of this type of isomerism is illustrated when a transition metal ion is surrounded by 3 bidentate ligands, for example a cobalt^{3+} ion surrounded by 3 ethylene diamine ligands, or 1,2 diamino ethane ligands to give them a more systematic name. The resulting complex ion is the tris (ethylenediammine) cobalt (111) ion shown in the workbook. The 2 forms of this complex are illustrated by models 7a and 7b.



At first sight, these propeller shaped complexes may appear identical. However, try to superimpose 7a upon 7b. (*)

It is not possible to superimpose the two structures. Models 7a and 7b are mirror images. To demonstrate this for yourself, hold the models in front of you in the positions they are shown in the workbook, and imagine a mirror plane between them. You should find 7a is an exact reflection of 7b. (*)



Another way of illustrating enantiomerism is by using model 8. Having established that models 7a and 7b are distinguishable, that is they are not superimposable, we can show that they are mirror images by holding one model upright on the shelf with your right hand, and holding the other model in front of the mirror with your left hand, in such a position that its reflection in the mirror is identical to the model /

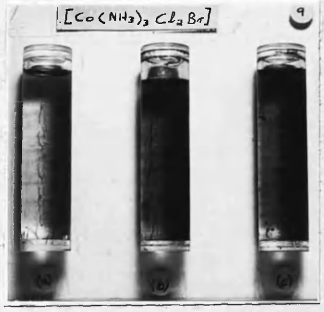
model on the shelf. This proves conclusively that 7a and 7b are mirror images. Perform this operation for yourself. (*)

These models which are non superimposable mirror images illustrate another type of isomerism found in octahedral transition metal complexes, namely chiral isomerism. Any two isomers which are mirror images, while at the same time being non-superimposable, are called enantiomers.

Frame 10

Transition metal complexes exist which display both geometric and chiral isomerism. For example, the dichloro bis (ethylenediamine) chromium (111) cation is known to exist in 3 forms, 2 of which are violet, and one of which is green. The 3 forms are to be seen in tubes (a), (b) and (c) in model 9.

Explain these 3 forms in terms of geometric and chiral isomerism, using your construction kit. Draw the structures of any isomers you find. (*)



Frame 11

The isomers of the complex in question are drawn in the workbook in diagrams (a), (b) and (c) corresponding to tubes (a), (b) and (c) in model 9. Isomer (a) which is the green isomer occurs when the chloro ligands are trans to each other in the complex. In both violet isomers (b) and (c), the chloro ligands are cis to each other. There are therefore two geometric isomers which differ in the cis and trans arrangement of chloro ligands. The green form is the trans isomer of the complex, and the violet form is the cis isomer.

However, there are two non superimposable mirror images /

images of the cis form as indicated by isomers (b) and (c) in the workbook. Thus there is a pair of cis enantiomers.

There are, therefore, three isomers altogether, two of which are enantiomers. Use your constructed models of the cis enantiomers to convince yourself that they are non-superimposable and also mirror images. Model 8 may help you to convince yourself that they are mirror images. (*)

Frame 12

To gain more practise in looking for isomerism, consider the complex ion shown in the workbook, namely the dichloro diammine ethylene diamine cobalt (111) ion. How many geometric isomers are possible with this complex ion, and how many of these geometric isomers have non-superimposable mirror images, that is, how many pairs of enantiomers are there? Use your construction kit, and draw the isomers in your workbook. (*)

Frame 13

There are 3 geometric isomers and 1 pair of enantiomers possible, making a total of 4 isomers altogether. These are drawn in the workbook. If you did not make all 4 correctly do so now. (*)

Isomer (1) has the ammine ligands trans to each other in the complex, and the chloro ligands cis to each other.

Isomer (2) has the chloro ligands trans to each other and the ammine ligands cis to each other.

Isomers 3a and 3b have the ammine ligands cis and also the chloro ligands cis.

Isomers (1), (2) and (3) are geometric isomers.

Isomers /

Isomers 3(a) and 3(b) form a pair of non-superimposable mirror images and hence form a pair of chiral isomers or enantiomers.

Remember that all geometric isomers, for example isomers 1, 2 and 3 in this case, differ in the cis and trans arrangement of ligands in a complex, while chiral isomers, for example isomers 3a and 3b have the same overall cis and trans arrangement of ligands, but are non-superimposable mirror images of each other.

Would you now please complete post-test 3 and place your answer card in the box provided.

END OF PROGRAM

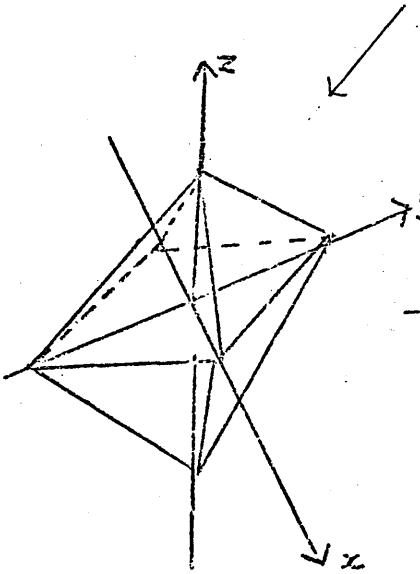
TRANSITION METAL CHEMISTRY
WORKBOOK 4

CRYSTAL FIELD THEORY

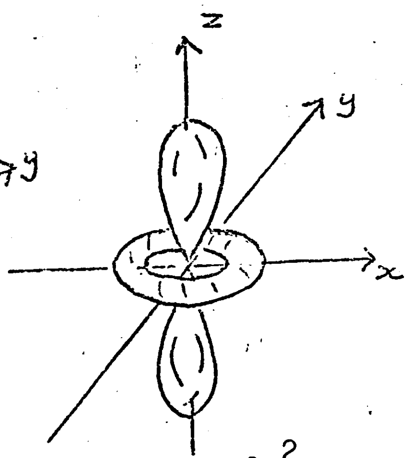
OBJECTIVES : As given in Chapter 4.3

Frame 1

Regular Octahedron

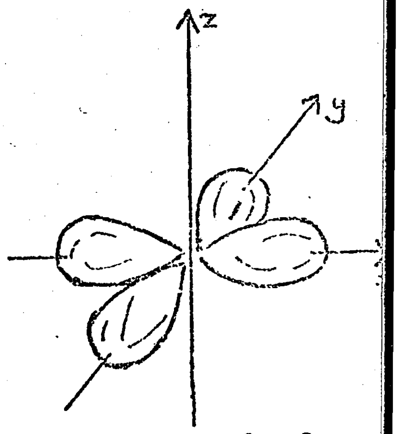


8 faces
6 corners
12 edges



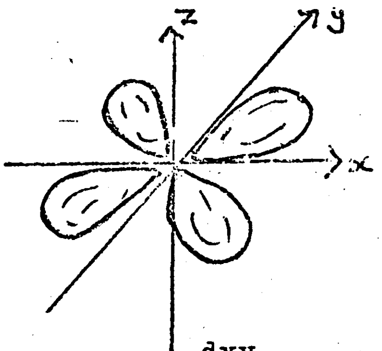
dz^2

(white)



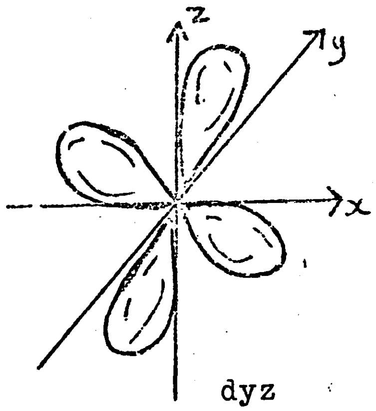
dx^2-y^2

(red)



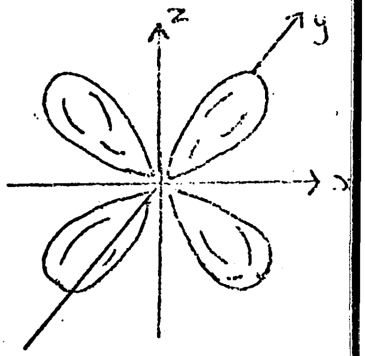
dxy

(orange)



dyz

(blue)

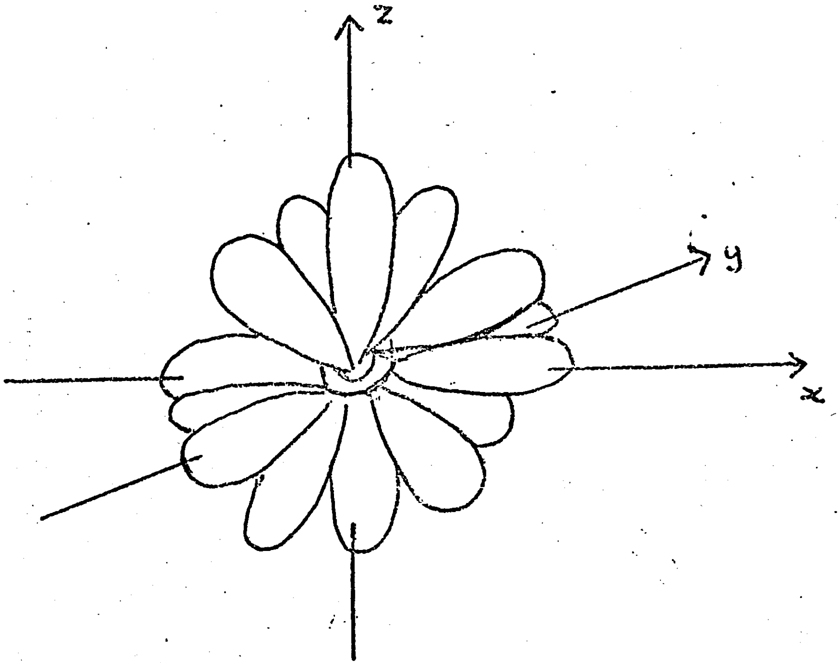


dxz

(green)

Frame 2

Combined d orbital picture



Note almost spherical arrangement of orbitals.

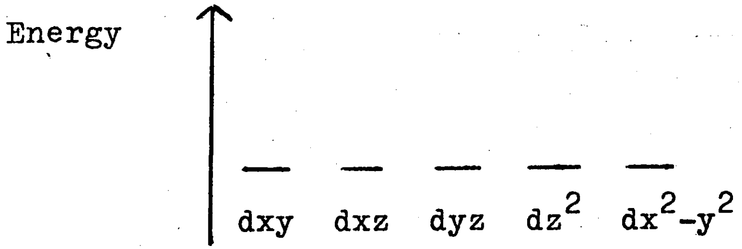
Question : Name the orbitals which have lobes pointing directly along the axes.

Answer :

Frame 3

Free transition metal ion M^{n+}

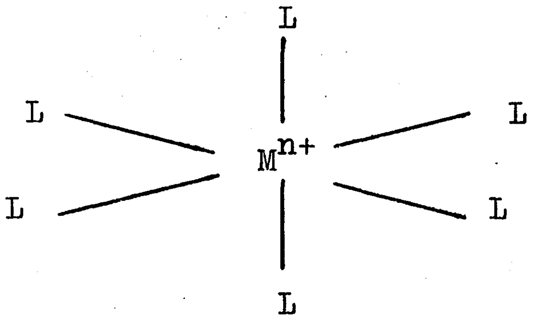
5 degenerate d orbitals



Frame 4 /

Frame 4

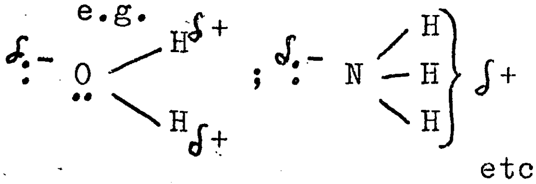
octahedral complex



where

L = negatively charged ligand, e.g. $Cl^{\ominus}$, $Br^{\ominus}$, $CN^{\ominus}$ etc., or negatively polarised ligand,

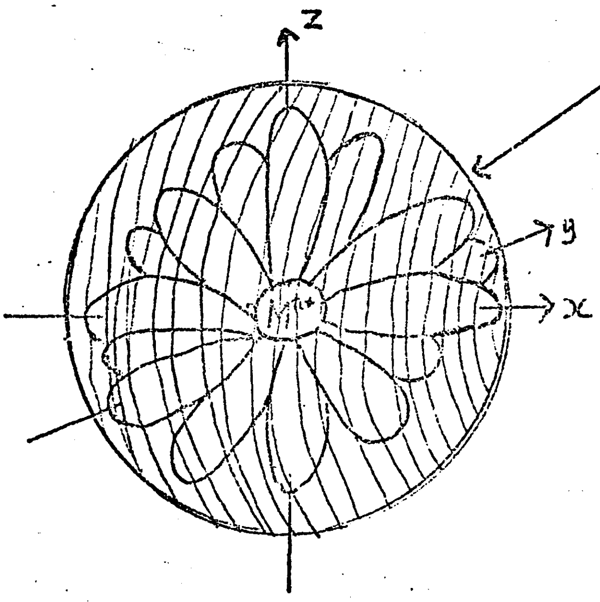
e.g.



etc.

Frame 5

Spherical Approximation



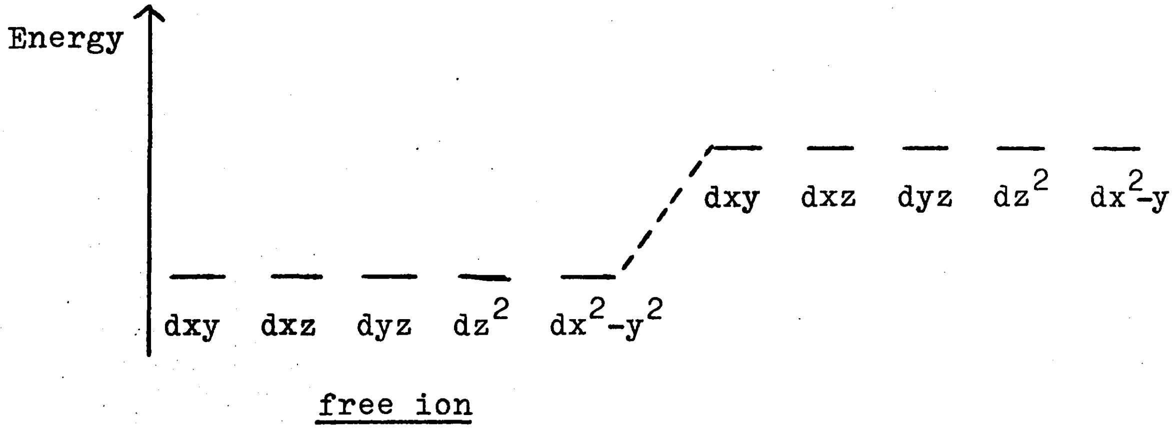
evenly distributed sphere of negative charge

Question : What effect will this sphere of negative charge have on the energy levels of the five d orbitals in comparison with the free ion situation?

Answer :

Frame 6

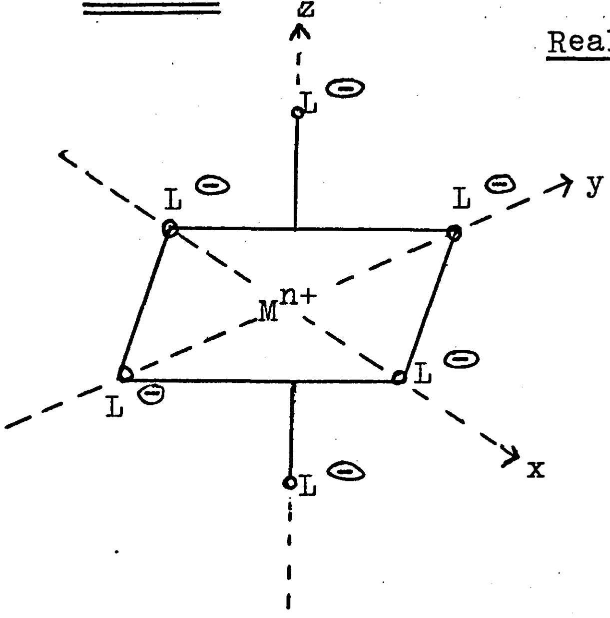
Energetics of spherical approximation



Spherical Approximation

(6 units of negative ligand charge spread evenly around the transition metal centre)

Frame 7



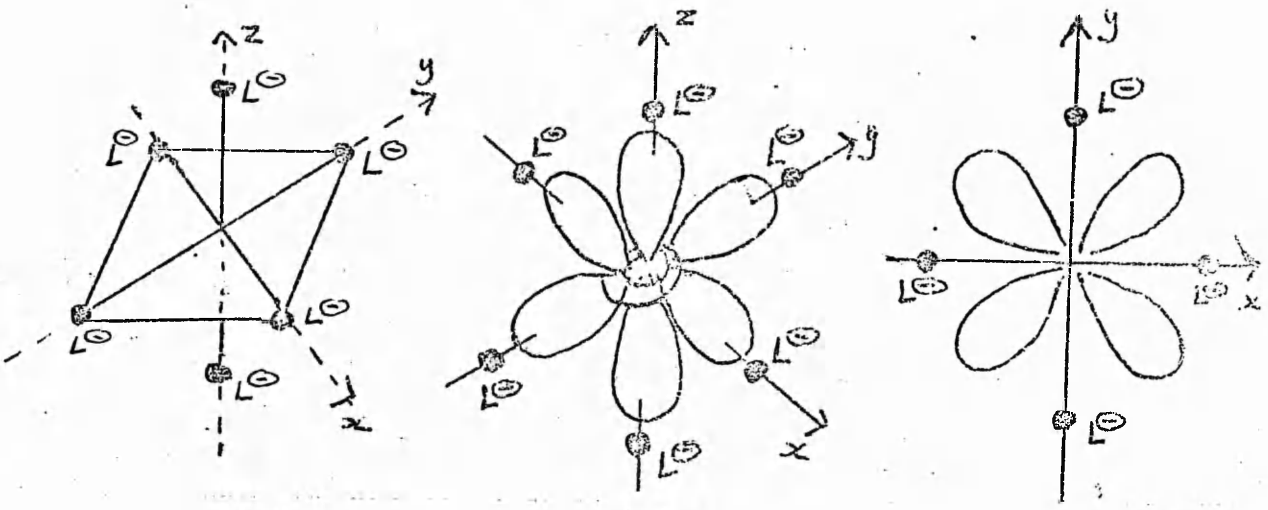
Real Situation

In real octahedral complexes ligand charges are localised at the 6 corners of a regular octahedron.

Frame 8 /

Frame 8

d orbital involvement in octahedral complexes



(a) (b) (c)

Lobes on dx^2-y^2 and dz^2 orbitals point directly along axes to ligands.

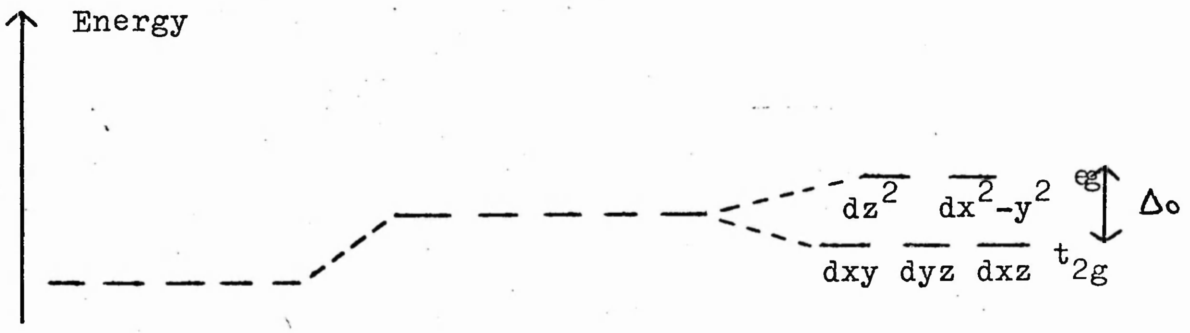
.'. These two orbitals interact most strongly with the ligands.

Lobes on the dxy, dyz and dxz orbitals lie between axes.

.'. These three orbitals interact weakly with the ligands.

Frame 9

d orbital energetics in octahedral complexes



free ion

(five degenerate orbitals)

spherical approximation

(five degenerate orbitals)

Ion in octahedral ligand field

- orbitals split

Δo = crystal field splitting energy for an octahedral complex

TRANSITION METAL CHEMISTRY
Taped Commentary for Program 4

CRYSTAL FIELD THEORY

For this program, in addition to this tape and Workbook 4, you require models 10 and 11 and the overlay book. During this program you will frequently be asked to examine a model, look at the overlay book, or write down the answer to a question in your workbook. To perform these tasks, switch off the tape after you hear this sound. (*)

Restart the tape only after you have completed the task to your satisfaction.

Work at your own pace through the program. You are free to stop the tape at any time in order to revise a point which you failed to understand.

Space is provided in the workbook if you wish to take notes from the program.

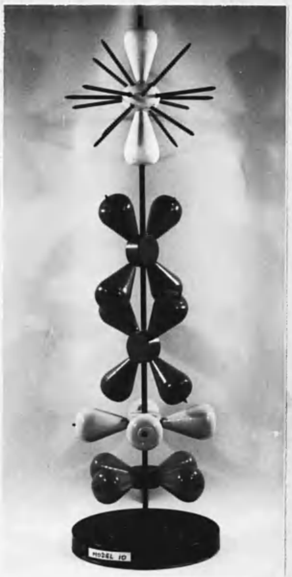
Objectives for Program 4 : As given in Chapter 4.3

Frame 1

1st, 2nd and 3rd row transition metals are characterised by filled, or more commonly, partially filled d subshells of electrons. There is a total of five d orbitals in each subshell, and each has a characteristic shape and orientation in space with respect to three mutually perpendicular x, y and z axes. The five d orbitals are represented in model 10. If the coloured orbitals are attached in the combined orbital position at the top of the model, detach the orange, red, blue and green lobes and place them on the appropriate spikes below, according to the coloured disc in the middle of each set of spikes. (*) The white /

The white orbital at the top represents the dz^2 orbital. The two lobes lie directly along the z axis, and therefore point to the top and bottom corners of the octahedron shown in the workbook.

The red orbital is the dx^2-y^2 orbital, which is shaped like a four-leafed clover, having four coplanar lobes at right angles to each other. These four lobes lie directly along the x and y axes and hence point to the remaining 4 corners of the octahedron shown in the workbook.



Together, therefore, the dz^2 and dx^2-y^2 orbitals point to all 6 corners of a regular octahedron.

The orange, green and blue coloured orbitals are the dxy, dyz and dxz orbitals respectively, and are all exactly similar in shape. These orbitals each have four coplanar lobes at right angles to each other, and they differ, however, in their orientation in space. The four lobes in each orbital bisect the angle between two axes. For example, each of the four lobes in the dxy orbital lie at 45° between the x and y axes.

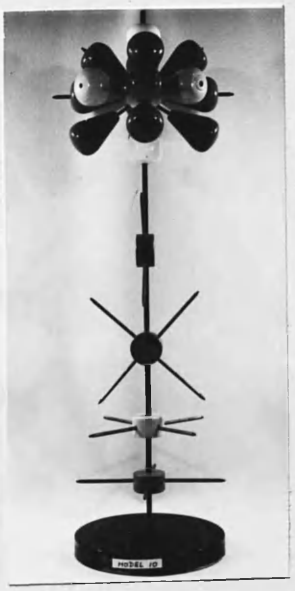
The dxy, dyz and dxz orbitals are mutually at right angles in space, and between them their total of twelve lobes point to the 12 edges of the regular octahedron drawn in the workbook.

The shape of these orbitals represents the regions of high probability of finding an electron in a particular d orbital, in other words the shape of a given d orbital represents the regions in space where an electron is most likely to be found in that orbital. Do not confuse the individual lobes in each orbital with /

with complete orbitals. In the dxy orbital for example, each lobe represents $\frac{1}{4}$ of the region in space where an electron in the dxy orbital is likely to be found. The complete dxy orbital consists of all four lobes.

Frame 2

It is rather artificial to separate the individual d orbitals as you have them in model 10 at present. Combine all five orbitals around the dz^2 orbital at the top of model 10, by detaching the red, orange, green and blue lobes of the bottom four orbitals and placing them on the correct spikes around the dz^2 orbital, paying particular attention to place the orbitals in their correct orientation in space. (*)



You can now see how the five individual d orbitals would appear when combined round a transition metal centre. Note the almost spherical overall arrangement of orbitals. In this combined orbital situation, how many of the orbitals have lobes pointing <u>directly</u> along the x, y or z axes? Write the name of those orbitals in your workbook. (*)

There are two d orbitals with lobes pointing directly along the axes. The dz^2 orbital has both its lobes directed along the z axis, while the 4 lobes of the dx^2-y^2 orbital point directly along the x and y axes. The lobes on the dxy, dyz and dxz orbitals all lie between the axes.

Frame 3

In a free transition metal ion, that is one without any ligands attached, all five d orbitals sit at the same energy level. Orbitals having the same energy level /

level are said to be degenerate. In the free ion situation therefore we have five degenerate d orbitals. This state of affairs is represented by the bottom overlay in the overlay book. (*)

As each of the orbitals sits at the same energy level, an electron has an equal chance of being accommodated in any of the five d orbitals.

Frame 4

Now consider the situation where the transition metal ion is not free, but in the centre of a complex ion. In an octahedral complex ion, the transition metal ion is bonded to 6 negatively charged ligands, or at least 6 ligands polarised in such a way that the positive metal ion bonds to the negative end of the dipoles. We can consider that we have bonds of an electrostatic nature between the positively charged metal ion, and the negatively charged ligands. Crystal field theory states that the presence of these six negatively charged or polarised ligands has a considerable effect on the d orbitals at the metal centre. We will now consider exactly how the presence of these ligands affects the five d orbitals.

Frame 5

Suppose we consider the negative charges on the six ligands in an octahedral complex, not as six charges at localised points, but smeared or spread over the surface of a sphere with the transition metal ion at the centre. Obviously this is an unreal situation, but it may help us to develop the ideas of crystal field theory. Model 11 demonstrates this concept.

Turn the black knob on the model as far anticlockwise as possible, and then plug the model in to switch it on. (*)

The whole sphere is coloured pale red to indicate six /

six units of negative charge spread evenly over a sphere round the metal centre. This situation is called the <u>spherical approximation</u>.

How easy do you think it would be to introduce an electron into a d orbital now when the metal ion is surrounded by a spherical negative charge? Would it be harder or easier than in the case of the free ion? If it is harder the energy level of the d orbitals will increase and if it is easier the energy level will fall. What charge, therefore, will occur in the energy level of the five degenerate d orbitals when the metal ion is enclosed in an evenly distributed sphere of negative charge as in the spherical approximation? (*)

<u>Frame 6</u>

The effect of the spherical approximation upon the five degenerate d orbitals would be to make all five orbitals sit at a higher energy level while still remaining degenerate, as shown in the workbook. Thus it would be <u>harder</u> than before to insert an electron into any of them.

This can be rationalised if we remember that the sphere of ligand charge surrounding the central transition metal is negatively charged as are the electrons contained in the d orbitals of the transition metal. Thus, due to repulsion between the spherical ligand charge and the d electrons of the ion, energy will have to be expended to get the spherical ligand charge into position. Thus the energy level of all five d orbitals will be increased due to this repulsion and will be increased by an equal amount as the spherical charge is <u>not</u> directional along any particular axis and hence electrons in each orbital will be repelled equally.

Thus, /

Thus, the net effect of a spherical field of ligand charge is to increase the energy level of all the d orbitals with respect to their energy level in the free ion. All five orbitals however, remain degenerate.

As the energy level of the d orbitals is increased, it is consequently more difficult for these d orbitals to accept an electron than in the case of the free ion.

If overlay 2 in the overlay book is superimposed upon overlay 1 the situation we have now reached is summarised. (*)

Frame 7

As has been stated, the spherical approximation is an artificial state of affairs. In practice in octahedral complexes, the six ligand charges are not spread evenly around the metal centre, but localised at the six corners of an octahedron.

Switch on model 11 again and turn the knob fully clockwise to illustrate the real situation. (*)

This situation is different from that encountered in the spherical approximation as the ligand charges are now localised at specific points in space, namely at the corners of a regular octahedron, or put in another way, placed at opposite ends of the x, y and z axes. You can demonstrate this by attaching the balls which go with model 10 onto the end of the spikes in the combined orbital model. (*)

Frame 8

We are now interested in the effect of these six ligand point charges upon the energy levels of the five /

five degenerate d orbitals in the spherical approximation which we now take as our base as that is the <u>average</u> energy level of five d orbitals surrounded by 6 units of negative ligand charge.

In the real situation we still have six units of negative charge around the metal centre, only now the charge is localised at the corners of an octahedron as shown in figure (a) in the workbook. These negative ligand charges will repel most strongly electrons which lie in orbitals having lobes pointing to the corners of the octahedron, that is pointing directly along the x, y or z axes.

From both model 10 and figure (b) in the workbook, we can see that most repulsion of electrons will occur with the dz^2 and dx^2-y^2 orbitals, and that electrons in these two orbitals will be repelled equally. This is because the lobes on these two orbitals lie directly along the axes, and hence interact most strongly with the ligand charges. Thus the dz^2 and dx^2-y^2 orbitals will have an energy level which is greater than the energy level of the five degenerate d orbitals in the spherical approximation as the negative ligand charge directly interacting with these two orbitals is more intense than in the spherical approximation.

Contrast this with the situation in the other three d orbitals. Remember that these three orbitals each have lobes which bisect the axes, and point to the twelve edges of an octahedron where the effect of the negative ligand charge is less. Figure (c) in the workbook illustrates the case of the dxy orbitals. The lobes of the dxy, dxz and dyz orbitals are as far away from the localised ligand point charges as possible, and so electrons in these orbitals are repelled <u>less</u> strongly than in the spherical approximation.

Thus, all three orbitals will sit at a lower energy level than in the spherical approximation.

<u>Frame 9</u> /

Frame 9

The overall energy level picture is shown in the workbook and also if overlay 3 is superimposed on the other two overlays. (*)

The energy level of the dz^2 and dx^2-y^2 orbitals is greater than that of the five degenerate d orbitals of the spherical approximation, while the dxy, dxz and dyz orbitals sit at a lower energy level than in the spherical approximation. Note however, that the energy level of these three orbitals is still greater than in the case of the free ion as some repulsion of electrons is experienced.

If we consider an electron in the system requiring accommodation in the d subshell, the three d orbitals having a lower energy level will be easier to enter than the two d orbitals at a higher energy level, and hence an electron will 'prefer' to go into a dxy, dxz or dyz orbital than into a dx^2-y^2 or dz^2 orbital when the transition metal ion is in an octahedral ligand field.

The five d orbitals are no longer degenerate and are now said to be split to give two eg orbitals at the same energy level and three t_{2g} orbitals at the same energy level. The names eg and t_{2g} arise from symmetry considerations, and the derivation of the letters need not concern us. We can just think of them as names for the two energy levels. The energy difference between the t_{2g} orbitals and the eg orbitals is called the crystal field splitting energy, or Δo, where the o stands for octahedral.

END OF PROGRAM

TRANSITION METAL CHEMISTRY
WORKBOOK 5

COLOUR AND MAGNETIC PROPERTIES IN TRANSITION METAL CHEMISTRY

OBJECTIVES : As given in Chapter 4.3

Frame 1

The Visible Spectrum

	Colour	Wavelength (Å)	Energy (k.J./mole)
combine to give white light	Red	7600 - 6200	170
	Orange	6200 - 5950	193
	Yellow	5950 - 5600	200
	Green	5600 - 5000	220
	Blue	5000 - 4600	250
	Indigo	4600 - 4300	265
	Violet	4300 - 3800	295

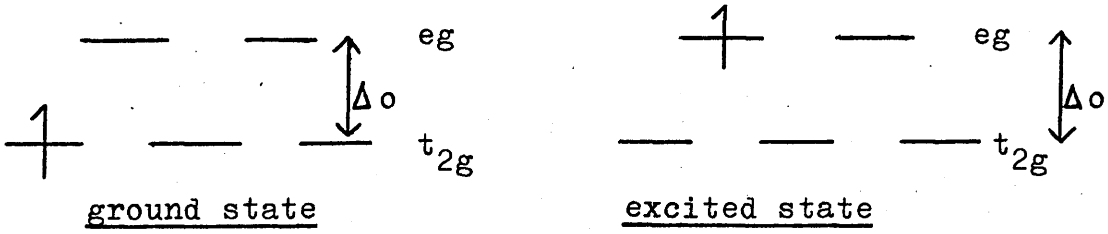
Colour = white light - (part of the visible spectrum)

Frame 2

$$Ti^{3+} + H_2O \longrightarrow [Ti(H_2O)_6]^{3+}$$

Ti^{3+} --- 1 d electron

$[Ar]\,3d^1$



ground state

excited state

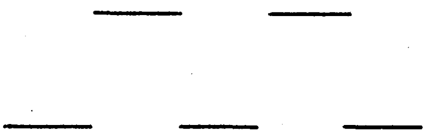
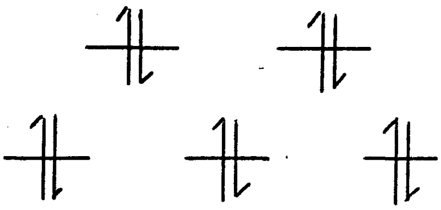
Δo /

Δo for $[Ti(H_2O)_6]^{3+}$ = ~220 k.J/mole

i.e. absorbs light from the green part of the spectrum (from Frame 1)

∴ red + violet = purple light transmitted

Frame 3

	Na^+ solution	Zn^{2+} solution
Number of d electrons	0	10
		
	colourless solution in water	colourless solution in water

Frame 4

Transition metal complexes can be many colours (model 13)

Question : Is the value of Δo constant for all complexes, or does it vary from complex to complex?

Answer :

Frame 5 /

Frame 5

Factors affecting size of Δo :- 1) oxidation state of metal,
2) ligands present.

1) Oxidation State

List (a)	Ion	Size of Δo for hexaaquo complex
	Ti(111)	244 k.J/mole
	V (111)	214 "
	Cr(111)	210 "
	Mn(111)	252 "
	Co(111)	218 "
List (b)	Co(11)	118 k.J/mole
	Ni(11)	101 "
	Fe(11)	125 "

Frame 6

2) Effect of ligands present upon size Δo in a complex

Ion	Δo for different ligands (k.J/mole)		
	6 H_2O	6 NH_3	6 $CN^{\ominus}$
Cr(111)	210	259	319
Co(111)	218	275	418
Ni(11)	101	130	
Fe(11)	125		406

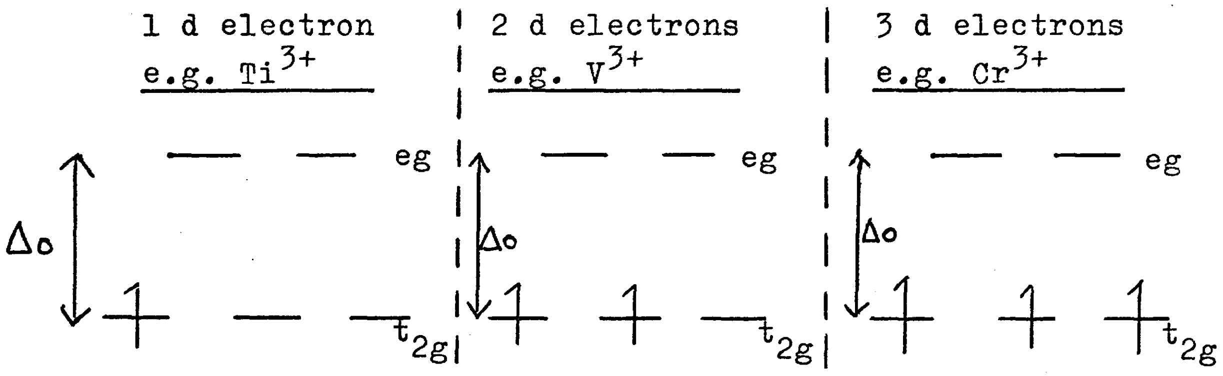
$\longrightarrow$

stronger
ligands
producing
larger Δo

Frame 7 /

Frame 7

Way in which split d orbitals fill up with electrons



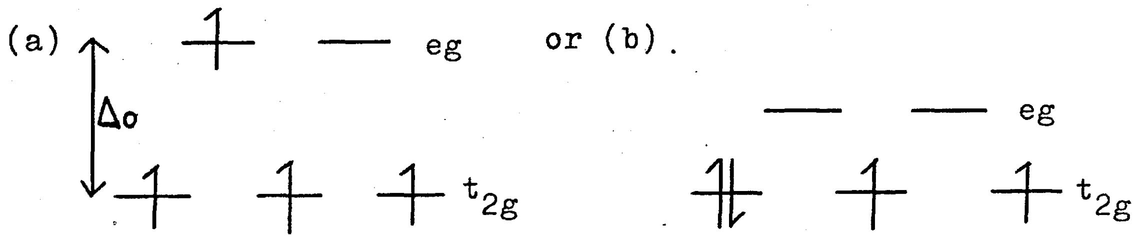
n.b. singly occupied orbitals (Hund's Rule)

Spin Pairing Energy

Frame 8

4 d electron situation e.g. Mn^{3+}, Cr^{2+} complexes

2 possibilities



Question : What two factors will have to be weighed up to decide whether situation (a) or situation (b) above prevails?

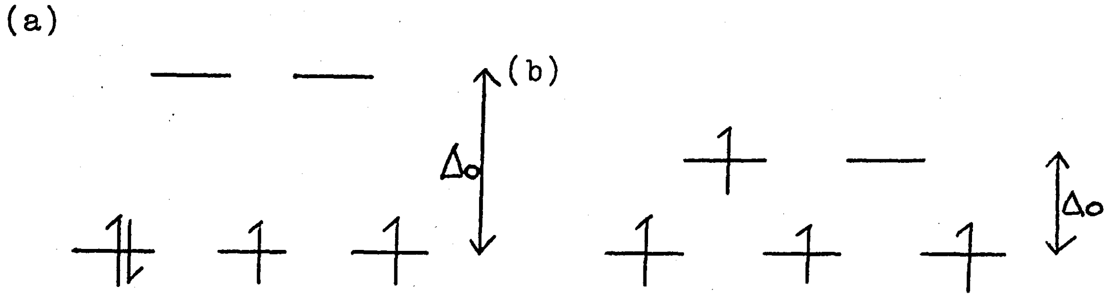
Answer :

Frame 9 /

Frame 9

Factors 1) Size of Δo
2) Energy required to pair electrons in the same orbital

d^4 system --- 2 possibilities

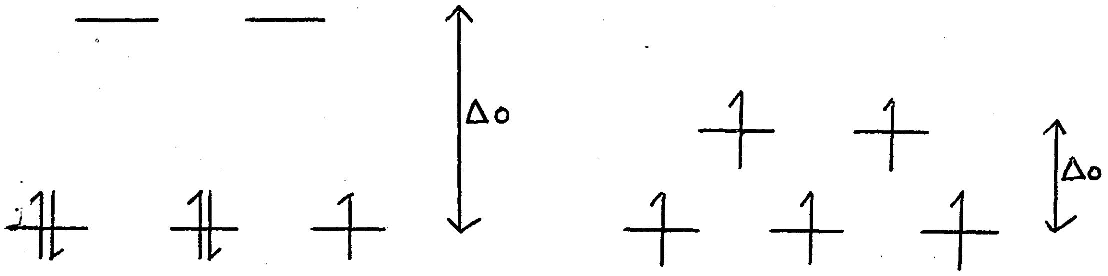


Large Δo	Small Δo
∴ Δo greater than pairing energy	∴ Pairing energy greater than Δo
→ Low spin system	→ High spin system

Frame 10

5 d electron situation e.g. Fe(111) complexes

$[Fe(NH_3)_6]^{3+}$	$[FeF_6]^{3-}$
hexaammine iron (111) ion	hexafluoro ferrate (111) ion



strong NH_3 ligands produce large Δo	weak F^- ligands produce small Δo
∴ Low spin system	∴ High spin system

Frame 11 /

Frame 11

Paramagnetism - involves unpaired electrons. Paramagnetic substances are attracted into a magnetic field, but retain no permanent magnetism when withdrawn.

Diagmagnetism - involves NO unpaired electrons. Diagmagnetic substances tend to be repelled by a magnetic field.

Ferromagnetism - Ferromagnetic substances are strongly attracted into a magnetic field, and retain a permanent magnetism when removed. This is exclusively a property of the solid state (e.g. iron).

Frame 12

Paramagnetism can be used to count the number of unpaired electrons in a complex.

Number of Unpaired Electrons	Magnetic moment (in Bohr magnetons)
0	0 (Diagmagnetic)
1	approx. 2
2	" 3
3	" 4
4	" 5
5	" 6

Question : What would be the expected magnetic moments (in Bohr magnetons) for a transition metal complex ion containing six d electrons, for both high spin and low spin situations?

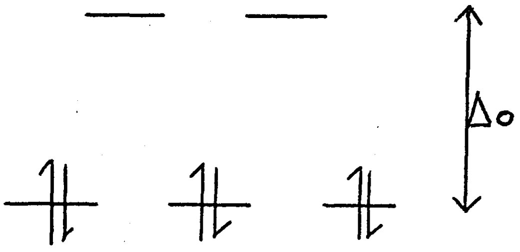
Answer :

Frame 13

Six d electron situation e.g. Co(111) complexes

$[Co(NH_3)_6]^{3+}$ hexaammine cobalt (111) ion

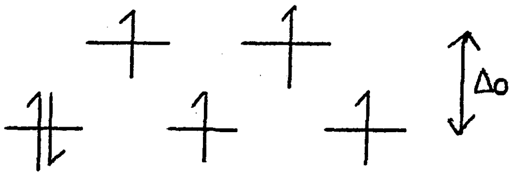
$[CoF_6]^{3-}$ hexafluoro cobaltate (111) ion



low spin

No unpaired electrons

∴ Magnetic moment = 0 B.M.



high spin

4 unpaired electrons

∴ Magnetic moment = ∼5 B.M.

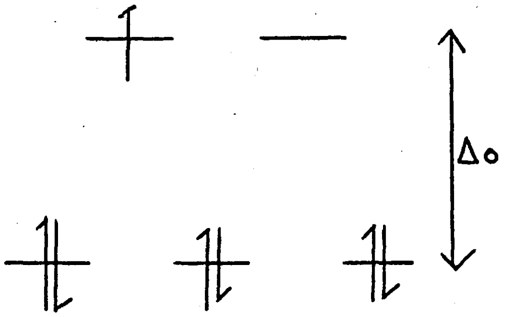
Question : What is the maximum number of d electrons which can lead to both low spin and high spin complexes?

What is the expected magnetic moment for both cases?

Answer :

Frame 14

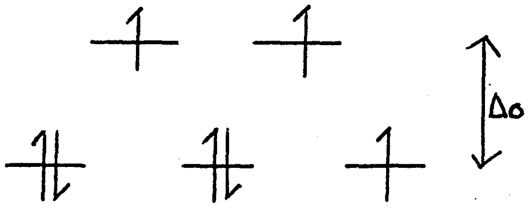
Seven d electrons (as in Co(11) complexes for example) is the maximum number possible to illustrate both high spin and low spin complexes.



Large Δo --- Low spin

1 unpaired electron

∴ Magnetic moment = ∼2 B.M.



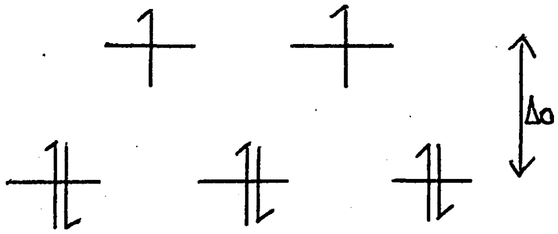
Small Δo --- High spin

3 unpaired electrons

∴ Magnetic moment = ∼4 B.M.

For eight, nine or ten d electrons, there is only one way in which the split d orbitals can be filled.

e.g. eight d electrons (as in Ni(11) complexes)



Two unpaired electrons

∴ Magnetic moment = ∼3 B.M.

TRANSITION METAL CHEMISTRY
Taped Commentary for Program 5

COLOUR AND MAGNETIC PROPERTIES IN TRANSITION METAL CHEMISTRY

For this program, you require models 12 and 13, in addition to this tape and Workbook 5. During the course of the program, you will be asked to answer several questions. After you hear this sound (*), stop the tape, and write the answer to each question in the space provided in your workbook. Restart the tape only when you are ready.

You may also stop the tape at any time if you wish to revise any part of the program.

Space is provided in the workbook if you wish to take notes from the program.

Objectives for program 5 : As given in Chapter 4.3

Frame 1

Crystal Field Splitting Theory can be used to "explain" why certain transition metal complexes are coloured while other metal ion compounds are colourless. Model 12 contains solutions of (a) sodium ions, (b) titanium^{3+} ions and (c) zinc^{2+} ions.

White light is made up of several coloured components which are shown in the workbook. Each coloured part of the spectrum corresponds to light of a different wavelength and energy.

Solutions (a) and (c) are colourless because all of the white light passing through the solution is transmitted /

transmitted again and none absorbed.

Solution (b) is highly coloured because certain parts of the visible spectrum are being absorbed, and the rest of the spectrum is transmitted. Hence the solution appears coloured, as colour can be defined as white light minus part of the visible spectrum.

We will have to answer the question why most solutions of normal ions, for instance sodium, are colourless, while most solutions of transition metal ions, for example titanium, are coloured, that is, they absorb part of the visible spectrum. Note however, that not all transition metal ion solutions are coloured as zinc is a transition metal, and solution (c) is colourless.

Frame 2

First we will consider why solutions of titanium ions are coloured. When dissolved in water, titanium ions form an octahedral complex with water to give the complex $Ti(H_2O)_6^{3+}$.

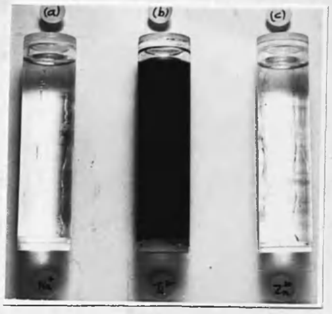
The five d orbitals split as shown in the workbook, and as the titanium $^{3+}$ ion has only one d electron, this single electron will go into one of the three orbitals of lower energy. This is the ground state of the complex. If sufficient energy is supplied, the electron is promoted into one of the two orbitals of higher energy, and the complex would then be in an excited state.

It so happens that radiation of the energy required to promote this electron jump is found in the green part of the visible spectrum. Thus the complex absorbs green light and transmits red and violet light to give the solution a purple colour.

The same /

The same theory can be extended to explain why other transition metal complexes are coloured, for example, copper ion solutions in water are blue and nickel ion solutions in water are green or blue.

Frame 3

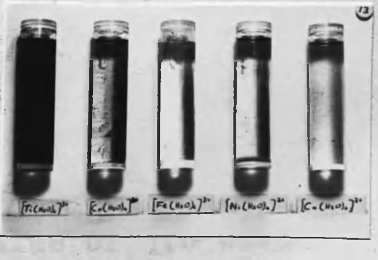


We can see from model 12(a) that solutions of sodium ions in water are colourless. In the ground state, there are no d electrons in a sodium ion hence no promotion of d electrons can occur. However, at higher energies, electron promotion can occur from s orbitals to d orbitals, but this occurs in the high energy ultra violet region of the spectrum, and so the visible region of the spectrum is not affected and the solution appears colourless.

Zinc ion solutions are also colourless because in this case there are ten d electrons and there are, therefore, no vacant higher energy d orbitals to which electrons in the three lower energy d orbitals can be promoted, so no absorbtion of any part of the visible spectrum occurs, and the solution is therefore colourless.

Frame 4

Colours of transition metal complexes can be many and varied as demonstrated by model 13 which contains solutions of five different transition metal complexes. The transition metals involved are copper, nickel, cobalt, iron and titanium. Each solution is a different colour and therefore each complex is absorbing light in different parts of the visible spectrum. From this, do you conclude the value of Δo - the crystal /



the crystal field splitting energy - is the same for all transition metal complexes, or does it vary from complex to complex? (*)

The value of Δo varies from complex to complex. Because different complexes are different colours, the energy being absorbed by these complexes must vary, or in other words, radiation of different energy is absorbed by individual complexes, because the size of Δo varies from complex to complex.

In octahedral transition metal complexes, this energy is used to promote a d electron from an orbital of lower energy to one of higher energy. The difference in energy between these two sets of orbitals is Δo, and in order to cause the electron jump, energy equal to the size of Δo must be absorbed by the complex. As the energy of absorbed light varies from complex to complex, therefore, the size of Δo must also vary from complex to complex.

Frame 5

The actual size of Δo depends mainly upon the oxidation state of the transition metal ion and also the particular ligands present in the complex. First we will look at the effect of oxidation state upon the size of Δo.

List (a) in the workbook shows a series of transition metal ions in the +3 oxidation state. The value of Δo for complex ions in which the transition metal ion is surrounded by six aquo ligands is also given. Although the values of Δo are not exactly the same, they are approximately the same for the same ligand.

List (b) shows a series of transition metal ions in the +2 oxidation state. Here the value of Δo for a complex with six aquo ligands is again approximately the same, but much different from the value of Δo when the metal /

the metal ion was in the +3 oxidation state as in List (a).

Thus, a change of oxidation state in a complex markedly changes the value of Δo.

Frame 6

The table in the workbook illustrates the fact that Δo is also dependent upon the particular ligands present in the complex. The wide variety of possible ligands in transition metal complexes, in addition to the wide variety of oxidation states, explains the many possible colours of transition metal complexes.

A stronger ligand is by definition one which produces a greater crystal field splitting than a weaker one, and will displace a weaker ligand from a complex.

Ligands are essentially nucleophiles, so we have the situation of a stronger nucleophile displacing a weaker one.

Frame 7

Let us now consider the way in which d orbitals that have been split in an octahedral crystal field fill up with electrons in the ground state. Obviously, transition metal ions with one d electron, for example the Ti^{3+} ion, can have the single electron going into any one of the three t_{2g} orbitals at the lower energy level. A molecule with two d electrons, for example V^{3+}, will have any two of the t_{2g} orbitals singly occupied.

A complex containing a transition metal ion with three d electrons, for example Cr^{3+}, will have all three t_{2g} orbitals singly occupied. Note that no doubly occupied orbitals are possible for either V^{3+} or Cr^{3+}. This situation obeys Hund's Rule which states that when degenerate /

degenerate orbitals are present electrons will go into an unoccupied orbital rather than pair up with another electron. This is because energy is required to put two electrons of opposite spin into the same orbital. The energy which is required is called the spin pairing energy. The situation can be likened to filling a double decker bus. The lower deck fills up first as people prefer not to climb the stairs to the top deck. In the lower deck, all the double seats are singly filled first as most people prefer to sit by themselves on a bus when there are spare seats available.

However, the situation becomes more complicated when all the seats in the lower deck are singly occupied. A person has to decide between climbing upstairs to get a seat by himself, or staying downstairs, hence expending less energy, but having to sit beside someone else. Thus, the person has to weigh up two opposing factors.

Frame 8

A situation analagous to the bus example exists when we have four d electrons to fill five d orbitals which are split in an octahedral ligand field, as in the case of Mn^{3+} or Cr^{2+} complexes. If we put three of the electrons into separate t_{2g} orbitals, there are two possible things we can do with the remaining electron. (a) We can put it into an eg orbital giving a total of four singly occupied d orbitals; or (b) we can put the electron into a t_{2g} orbital which is already occupied by one electron, that is we can pair electrons.

What two factors will influence the system in deciding whether situation (a) or situation (b) prevails? (*)

Frame 9

The two factors involved are the size of Δo, the crystal /

crystal field splitting energy, or in other words, the extra energy required to put an electron into an eg orbital compared to a t_{2g} orbital, and secondly the energy required to pair electrons in the same orbital. Both these processes involve the input of energy, and whether the electron goes into an eg orbital or pairs up with another electron in a t_{2g} orbital depends on the relative amount of energy required. If Δo is relatively large as in figure (a) in the workbook, the energy required to put an electron into an eg orbital is greater than the energy required to pair electrons. Thus a t_{2g} orbital becomes doubly occupied. Such a system as (a) is called a low spin system, because there is the minimum number of unpaired electrons.

Figure (b) illustrates the case when Δo is relatively small and more energy is required to pair electrons in a t_{2g} orbital than to promote the odd electron to an eg orbital. Thus we get four singly occupied d orbitals.

This situation is called a high spin system, because there is the maximum number of unpaired electrons.

Frame 10

A similar situation arises when five d electrons are present in a transition metal ion in an octahedral complex. As has been stated, the size of Δo depends on the type of ligands present in the complex. Ammine ligands are stronger ligands than fluoro ligands, so it follows that Δo is greater for hexaammine complexes than for hexafluoro complexes. It is, therefore, easy to explain why the hexaammine iron (111) ion is a low spin system, while the hexafluoro ferrate (111) ion is a high spin system.

Frame 11

High and low spin complexes can be identified by magnetic /

magnetic measurements which can 'count' the number of unpaired electrons in a complex.

A system containing unpaired electrons is said to be paramagnetic. The more unpaired electrons in the system, the more paramagnetic it is, and conversely from the amount of paramagnetism in a system we can deduce the number of unpaired electrons present. Paramagnetic substances are pulled into a magnetic field, but retain no permanent magnetism.

A diamagnetic system is one in which no unpaired electrons are present, and tends to be repelled by a magnetic field.

A ferromagnetic substance is one such as iron which is strongly attracted into a magnetic field and shows permanent magnetism when removed from such a field. Ferromagnetism is exclusively a property of the solid state, unlike paramagnetism and diamagnetism which apply equally well to the liquid and gas phases.

Frame 12

Paramagnetic systems involve unpaired electrons. The number of unpaired electrons in a system can be obtained from measurements of magnetic moments. As has been stated paramagnetic compounds are pulled into a magnetic field. The force with which they are pulled into the field is related to the number of unpaired electrons present. Thus the value of the magnetic moment, which is measured in units of Bohr magnetons, leads to an estimate of the number of unpaired electrons in the substance. The approximate value of the magnetic moments in Bohr magnetons for systems containing different numbers of unpaired electrons is shown in the workbook.

A transition /

A transition metal with one unpaired electron would have a magnetic moment of about two Bohr magnetons, while one with five unpaired electrons would have a magnetic moment of around six Bohr magnetons.

A diamagnetic system would not have a magnetic moment since no unpaired electrons are present.

Thus measurement of magnetic moments in transition metal complexes is a simple way of distinguishing high and low spin systems.

What would be the expected magnetic moments for a transition metal ion in a complex ion containing six d electrons for both high and low spin situations? (*)

Frame 13

An ion containing six d electrons is the Co^{3+} ion. The hexaammine cobalt (111) ion is a low spin system due to the large Δo produced by the six strong ammine ligands. Thus all six d electrons are paired and are situated in the three t_{2g} orbitals. There are no unpaired electrons on a low spin d^6 system and therefore no magnetic moment. This is a diamagnetic complex.

The hexafluoro cobaltate(111) ion is a high spin complex as the fluoro ligands are weak and Δ o is therefore small. You will see from the workbook that four unpaired electrons are present, and the complex is therefore paramagnetic and has a magnetic moment of around five Bohr magnetons.

What is the maximum possible number of d electrons which can lead to both high and low spin systems, and write down the expected magnetic moment for both cases. (*)

Frame 14 /

Frame 14

The maximum number of d electrons which leads to both high and low spin systems in octahedral transition metal complexes is seven. You will see from the workbook that low spin d^7 complexes have only one unpaired electron, and a corresponding magnetic moment of about two Bohr magnetons, while high spin d^7 complexes have three unpaired electrons, and hence have a magnetic moment of about four Bohr magnetons.

With eight, nine, or ten d electrons, there is only one way in which the split d orbitals can be filled. The situation for eight d electrons is drawn in the workbook. In d^8 systems, all octahedral transition metal complexes have two unpaired electrons, and therefore a magnetic moment of around three Bohr magnetons.

You should now be in a position to fulfil all the objectives listed at the start of the program. If you are still unsure about any of the topics covered in any of the five programs on transition metal chemistry, go over them again, and if you remain puzzled, consult the Floor 9 Chemistry Tutor in the Self-teach Laboratory.

Would you now please complete the post-test 4, and place your answer card in the box provided.

END OF PROGRAM

TEST 1 (PROGRAM 1)

Question 1 Which one of the electronic configurations shown below does not belong to a transition element?

A. [Ar] $4s^2$ $3d^2$
B. [Ar] $4s^2$ $3d^{10}$ $4p^6$ $5s^2$
C. [Xe] $6s^2$ $4f^7$
D. [Ar] $4s^2$ $3d^{10}$
E. Don't know

Question 2 The electronic configuration of nickel is [Ar] $4s^2$ $3d^8$. What is the electronic configuration of the Ni^{2+} ion?

A. [Ar] $4s^2$ $3d^6$
B. [Ar] $4s^1$ $3d^7$
C. [Ar] $4s^0$ $3d^8$
D. [Ar] $4s^2$ $3d^{10}$
E. Don't know

Question 3 What is the oxidation state of chromium in the $[Cr_2O_7]^{2-}$ ion ?

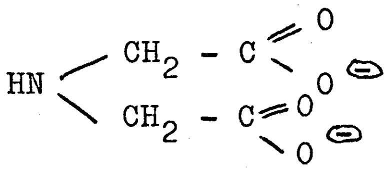
A. -1
B. +5
C. +6
D. +8
E. Don't know

Question 4 In the complex $[FeCl_3(H_2O)_3]^x$ what is the value of the charge x on the complex when Fe(111) is present?

A. x = -1
B. x = 0
C. x = +1
D. x = +3
E. Don't know

Question 5 /

Question 5



The ligand shown above is

A. Monodentate
B. Bidentate
C. Tridentate
D. Pentadentate
E. Don't know

Question 6 For the coordination compound $[Pt(NH_3)_3Cl_3]Cl$, the inner coordination sphere of platinum consists of -

A. 3 NH_3 molecules
B. 4 $Cl^{\ominus}$ ions
C. 3 NH_3 molecules and 4 $Cl^{\ominus}$ ions
D. 3 NH_3 molecules and 3 $Cl^{\ominus}$ ions
E. Don't know

Question 7 A coordination compound has the empirical formula $Pt\ Cl_4(NH_3)_3$. Titration against $AgNO_3$ indicates that there is only one mole of free chloride ions per mole of coordination compound. What is the formula of the coordination compound?

A. $[Pt(NH_3)_3Cl_3]Cl$
B. $[Pt(NH_3)_3Cl]Cl_3$
C. $[Pt(NH_3)_3Cl_2]Cl_2$
D. $[PtCl_4](NH_3)_3$
E. Don't know

Question 8 What is the coordination number of cobalt in the coordination compound $[Co(en)_2Cl_2]Cl$ where en = ethylene diamine (NH_2-CH_2-CH_2-NH_2) ?

A. 4
B. 5
C. 6
D. 7
E. Don't know

TEST 2 (PROGRAM 2)

Question 1 A complex ion contains three types of ligand, aquo, cyano and bromo. In which order should these ligands be arranged when naming in a complex ion ?

A. aquo cyano bromo
B. aquo bromo cyano
C. bromo cyano aquo
D. cyano bromo aquo
E. Don't know

Question 2 What is the correct systematic name for the complex ion $[Co(NH_3)_6]^{3+}$?

A. Hexaammine cobalt (111) ion
B. Hexanitro cobalt (111) ion
C. Hexaammonia cobalt (111) ion
D. Hexaamine cobalt (111) ion
E. Don't know

Question 3 What is the correct name for the complex ion $[Co(en)_2F_2]^+$?

A. difluoro di(ethylene diamine) cobalt (111) ion
B. difluoro bis(ethylene diamine) cobalt (111) ion
C. bisfluoro bis(ethylene diamine) cobalt (111) ion
D. bis (ethylene diamine) bisfluoro cobalt (111) ion
E. Don't know

Question 4 What is the name of the coordination compound $K_2[PtCl_6]$?

A. Potassium hexachloro platinum (1V)
B. Potassium hexachloro platinate (11)
C. Potassium hexachloro platinum (11)
D. Potassium hexachloro platinate (1V)
E. Don't know

Question 5 /

Question 5 What is the correct molecular formula for the coordination compound chloropentaaquo chromium (111) chloride?

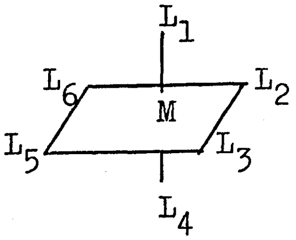
A. $[Cr(H_2O)_5Cl]Cl$
B. $[Cr(H_2O)_5Cl]Cl_2$
C. $[Cr(H_2O)_5Cl]Cl_3$
D. $[Cr(H_2O)_5Cl]_2Cl$
E. Don't know

TEST 3 (PROGRAM 3)

Question 1 A transition metal ion M^{n+} is bonded to six ligands L in the transition metal complex $[ML_6]^{n+}$. What is the shape of this complex ion?

A. Tetragonal
B. Cubic
C. Hexagonal
D. Octahedral
E. Don't know

Question 2 The transition metal complex below has six ligands surrounding the central metal ion. Which of the following assignments of the relative cis and trans arrangement of the given ligands is correct?



	L_1 and L_5	L_2 and L_4	L_3 and L_6
A.	cis	cis	cis
B.	cis	trans	cis
C.	trans	trans	trans
D.	cis	cis	trans
E.	Don't know		

Question 3 How many geometric isomers are there of the transition metal complex $[M X_5 Y]^{n+}$ where X and Y are different types of ligand and M is a transition metal?

You may draw
here if you
wish

A. /

A. 1
B. 2
C. 4
D. 6
E. Don't know

<u>Question 4</u> How many geometric isomers are there of the complex ion $[M\ X_3\ Y_2\ Z]^{n+}$ where X, Y and Z are different types of ligand and M is a transition metal?

You may draw
here if you
wish

A. 1
B. 3
C. 4
D. 6
E. Don't know

Questions 5, 6, 7 and 8 all concern the complex ion $[Co(en)(NH_3)_2Cl_2]$, where 'en' is the bidentate ligand ethylene diamine. In each question you will be shown two representations of this complex, and you are required to answer which of the following statements is correct for each case.

A. Figures (1) and (2) are identical
B. Figures (1) and (2) represent enantiomers, but not geometric isomers
C. Figures (1) and (2) represent geometric isomers, but not enantiomers
D. Figures (1) and (2) represent both enantiomers <u>and</u> geometric isomers
E. Don't know

<u>Question 5</u> Which of the above statements is correct for

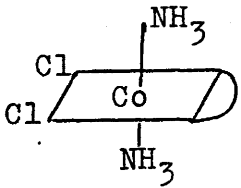


Figure (1)

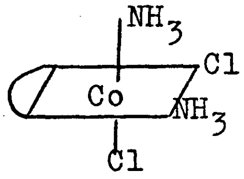


Figure (2)

Question 6 Which of the above statements is correct for

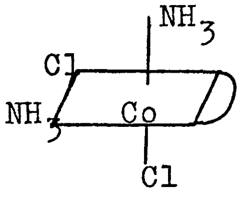


Figure (1)

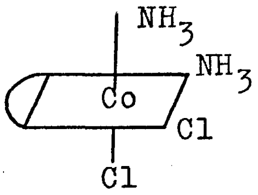


Figure (2)

Question 7 Which of the above statements is correct for

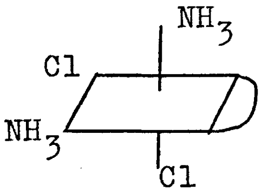


Figure (1)

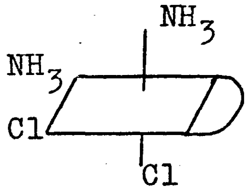


Figure (2)

Question 8 Which of the above statements is correct for

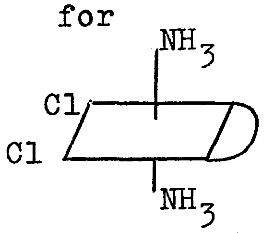


Figure (1)

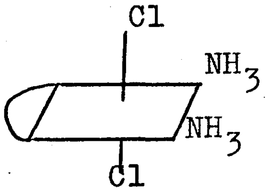
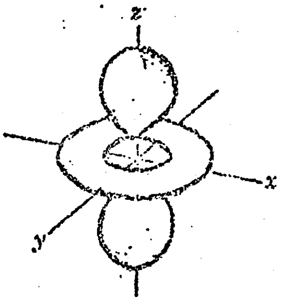


Figure (2)

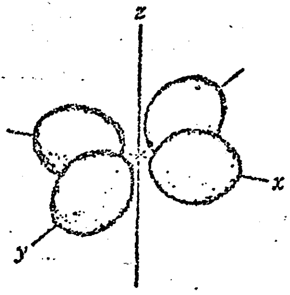
TEST 4 (PROGRAMS 4 AND 5)

Question 1 There are five d orbitals altogether. Which of the following represents the dxy orbital?

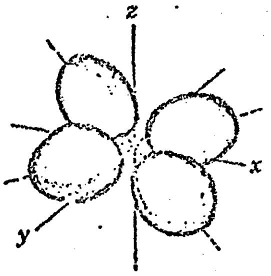
A.



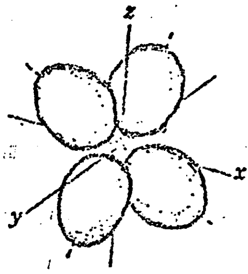
B.



C.

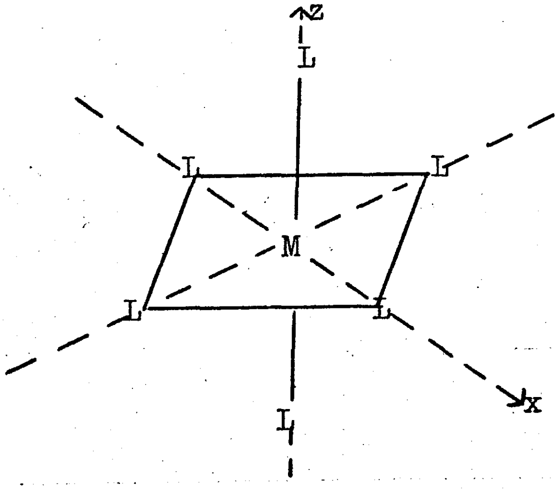


D.



E. Don't know

Question 2 In the transition metal complex shown below, which of the five d orbitals point directly along the axes to the ligands L ?



A. $dx^2 - y^2$ and dz^2
B. dz^2 and dxy
C. dxy, dyz and dxz
D. $dx^2 - y^2$ and dxz
E. Don't know

Question 3 When the d orbitals of a transition metal are split in an octahedral crystal field, which of the following statements is correct?

A. There are three eg orbitals which are of higher energy than two t_{2g} orbitals.
B. There are two eg orbitals which are of higher energy than three t_{2g} orbitals.
C. There are three t_{2g} orbitals which are of higher energy than two eg orbitals.
D. There are two t_{2g} orbitals which are of higher energy than three eg orbitals.
E. Don't know

Question 4 The difference in energy between the t_{2g} and eg energy levels is Δo – the crystal field splitting energy. For two complex ions $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{3+}$, what would you predict about the relative sizes of Δo in these complexes?

A. Δo for $[Co(H_2O)_6]^{2+}$ is the same as Δo for $[Co(H_2O)_6]^{3+}$.
B. Δo for $[Co(H_2O)_6]^{2+}$ will be greater than Δo for $[Co(H_2O)_6]^{3+}$.
C. Δo for $[Co(H_2O)_6]^{2+}$ will be less than Δo for $[Co(H_2O)_6]^{3+}$.
D. It is impossible to say anything about the relative sizes of Δo from the information available.
E. Don't know

Question 5 Which of the following statements is true for the complex ions $[Co(H_2O)_6]^{3+}$ and $[Co(NH_3)_6]^{3+}$?

A. Δo for $[Co(H_2O)_6]^{3+}$ will be the same as Δo for $[Co(NH_3)_6]^{3+}$.
B. Δo for $[Co(H_2O)_6]^{3+}$ will be greater than Δo for $[Co(NH_3)_6]^{3+}$.
C. /

C. Δo for $[Co(H_2O)_6]^{3+}$ will be less than Δo for $[Co(NH_3)_6]^{3+}$.

D. It is impossible to say anything about the relative sizes of Δo from the information available.

E. Don't know

Question 6 Which of the following statements is true for high spin d^6 system in a transition metal complex?

A. The complex is diamagnetic

B. The complex is ferromagnetic

C. The complex is paramagnetic with a magnetic moment of about 3 Bohr magnetons

D. The complex is paramagnetic with a magnetic moment of about 5 Bohr magnetons

E. Don't know

Question 7 Which of the following statements is true for a low spin d^6 system in a transition metal complex?

A. The complex is diamagnetic

B. The complex is ferromagnetic

C. The complex is paramagnetic with a magnetic moment of about 3 Bohr magnetons

D. The complex is paramagnetic with a magnetic moment of about 5 Bohr magnetons

E. Don't know

Question on Transition Metal Chemistry included in first year degree examination in chemistry (Glasgow University - June, 1975)

Question 7 An aqueous solution of a chromium (111) complex $Cr Cl_3 . 6H_2O$, contains three species of cation having overall charges of +1, +2 and +3 respectively.

(a) Draw the geometrical structures of each of these species of cation and name any one of them. (5)

(b) These three species can be separated. After separation a millimole of one of them (cation A), on suitable treatment, released its Cl^- ligands and these, when treated with excess $AgNO_3$ solution, yielded 0.285 g of dry precipitate. Which of the three species was cation A ? (5)

[10]

CHAPTER 5

'PROTEINS AS HUMAN FOOD'

- A COMMUNICATION EXERCISE

CHAPTER 5

'PROTEINS AS HUMAN FOOD' - A COMMUNICATION EXERCISE

5.1 The Need for a Communication Exercise

It was argued in Chapter 2 that, of the traditional instructional methods, the group tutorial situation was the only one which was capable of developing in students skills in communication, although often the opportunity was lost due to the adoption of a 'mini-lecture' approach.

Due to the large numbers (over 550) studying first year chemistry at Glasgow University, no formal group tutorials are given because of difficulties in organisation. The main tutoring service provided involves the availability of members of staff whom students can approach at any time with individual problems. As a result, first year chemistry undergraduates have little opportunity to develop skills in communication during their course, as lectures and laboratories are ill-suited to this end.

It was to help bridge this gap in the course that it was decided to devise an exercise in which the main aims involved the development of communication and inter-personal skills using chemistry and related subjects as the vehicle. In conjunction with the development of these skills, it was also intended that decision making skills should be incorporated, in addition to some cognitive attainment and possibly some attitudinal changes.

5.2 Previous Styles of Communication Exercises

One problem commonly encountered in group tutorials, even when a skilful tutor is involved and a 'mini- /

'mini-lecture' is avoided, is that some students, possibly through lack of confidence, fail to become involved in the discussion which is often dominated by the tutor and one or two group members. One of the major problems in designing a communication exercise, therefore, is to involve everybody in the group to an approximately equal extent.

Previously devised communication exercises have taken the form of 'information games' in which the emphasis is laid on communication skills involving delivering and receiving scientific information, in association with problem solving skills. Rae(103) has described examples of such games in which each group member (player) is given one piece of written information on a card which, when considered along with other players' information, leaves the group in a position to solve a given problem. Smith and Jepson (104) have used this approach with students of biochemistry. Seven students in a group each received a specific piece of biochemical information which they had to communicate verbally to the rest of the group before applying the pooled information to solve a problem. The information may be given in written, graphical or tabular form.

5.3 Design of the Exercise

To ensure the participation of all students in the "discussion", it was decided to adopt a format in which students in a group were given individual information sheets on a common topic so that each student had a part to play in communicating relevant information into a central information 'pool' upon which other students could draw when considering different aspects of the topic. By using this approach it was hoped that less confident students would feel less inhibited, since they would be in sole possession of information without which parts of the exercise could not /

not be attempted successfully. Considerably more information was given to each student than in previous 'information games' reported.

The topic

The broad topic of "proteins and the world food shortage" was taken as the basis for the exercise for several reasons. Firstly, the topic involved many disciplines, not only chemistry, and hopefully students could draw on knowledge outside the content of the exercise to add to the discussion of certain points. Secondly, it was felt that such a subject was likely to be sufficiently emotive and relevant that student interest would be high. It was hoped that students would appreciate that chemistry has significance far beyond the text book, and that chemical considerations often fade in importance when compared to geographical, economic, ethical, social or political factors.

The objectives of the communication exercise on "Proteins as Human Food" consequently included the following:-

Objectives of "Proteins as Human Food"

At the end of the exercise, the student will be expected to be able to:-

1. write down the general formula for an α-amino acid;
2. appreciate the importance of proteins in living systems;
3. state why certain amino acids are called essential;
4. describe a peptide link and its importance in protein chemistry;
5. identify factors contributing to the world protein problem;
6. extract general trends and relevant information from tabulated data.

In addition, the exercise intends to develop in the student the ability to:-

7. /

7. communioate information fluently and grammatically;
8. argue logically and precisely;
9. teach others in public;
10. apply a scientific approach to general problems;
11. appreciate the value of group discussion for co-operation in discovery;
12. identify problems and devise means of solving them;
13. look for best compromises in matters of conflicting interest;
14. realise the existence of interconnections across subject barriers;
15. be aware of the limitations of science in solving some problems.

Objectives 1 to 6 deal with cognitive outcomes, while objectives 7 to 15 are concerned with the broader outcomes of science courses including communication, interpersonal, problem solving and decision making skills, allied to desirable attitudinal traits.

<u>The strategy</u>

It was decided to involve groups of six students in a structured discussion of the topic in question. Each group of six students consisted of one group leader plus five group members. The exercise was designed so that it could be run with the minimum of staff participation.

The group participants received the following sheets:-

Group member	——	List of Objectives List of Amino Acids and their structures Group Member's Guide An Information Sheet
Group Leader	——	List of Objectives List of Amino Acids and their structures Group Leader's Guide

The /

The List of Amino Acids and their Structures, referred to as 'Table 1' in the exercise, is appended on p. 209.

The Group Member's Guide introduced the nature of the study to the students and described how group members were expected to participate. The guide can be found on p. 211.

An individual Information Sheet was issued to each group member, and the students given twenty minutes before the exercise to read and digest its content. Each of the five sheets contained information on a different aspect of the topic, which resulted in the group possessing five 'subject specialists' each with a different area of expertise.

The titles of each information sheet are given in Table 5-1.

Information Sheet	Title	Appendix
1	Chemistry of Proteins and Amino Acids	p. 213
2	Essential Amino Acids and Protein Usability	p. 218
3	Conventional Sources of Protein and their Content	p. 224
4	Human Protein Requirements and some Novel Ways of Meeting Protein Demand	p. 232
5	Ecological and Economic Factors in Protein Production	p. 239

Table 5-1 Protein Information Sheets

The /

The Group Leader's Guide explained the leader's function in the exercise and contained a brief summary of the contents of each of the five information sheets. The group leader, who did not receive an information sheet, had to act as chairman of the group. The guide contained a series of questions which formed the basis of the structured discussion. The leader was not necessarily required to adhere rigidly to the order or content of each question and could ask supplementary questions at his/her discretion. The questions listed in the leader's guide also indicated the information sheet(s) in which relevant information was contained. The guide is appended on p. 245.

The first series of questions in the exercise were purely factual and required an answer from one student at a time in order to build up a pool of information from the five topic areas. As time progressed the questions often required co-operation from several students for an adequate answer, and students were encouraged to draw on information outside their scripts if necessary. Towards the end of the exercise, the questions posed dealt with ethical matters in which moral considerations had to be balanced against scientific, political, economic, geograhical, ecological and social factors. The result was that students were forced into the position of making value judgements. At the completion of the exercise each student received a complete set of information sheets to take away.

It was hoped that students who participated in the exercise gained not only in factual knowledge, but in discussion skills and confidence, in critical thinking, in co-operating with others in trying to solve common problems, and in addition it was hoped that the chemistry was seen to have a part in other disciplines, with purely chemical decisions being affected by many other considerations.

Organisational points

The exercise, although originally designed for first year undergraduates, is also suitable for use with sixth year school pupils. Including the time allowed for reading and digesting information sheets, the exercise takes between 1½ and 2 hours to complete. If the information sheets and other materials are issued previously, the exercise could easily fit into a tutorial slot, one hour long. The leader of the group of six students may be a volunteer or democratically chosen by the other group members. Alternatively he/she may be selected by a tutor.

5.4 Assessment of the Material

Early trials

Before any formal assessment was attempted, the exercise underwent trials with two groups of first year undergraduates to check for ambiguities and organisational difficulties. As a result of these trials, additional material was added to information sheets 1, 2 and 3 in order to obtain a better balance in group discussions. Other amendments of a minor nature were made to each sheet. Allied to the alterations in the information sheets corresponding changes were made to the group leader's guide, including additional questions. The amended version is given in the appendix. The original version contained no information on fertilizers or fish farming. Following later trials using the amended version, it was considered that no other major amendments were necessary.

Assessment procedures used

The objectives of the exercise (p. 185-186) are concerned with a variety of outcomes including cognitive, communication, /

communication, problem solving and interpersonal skills, of which cognitive attainment is probably easiest to assess. The attainment of the other broader skills is less easy to measure and it is very doubtful if a single exercise of this nature can do little more than increase the confidence of participants in skills such as communication, discussion and in working with other students. Almost certainly, other exercises of this nature would be required to capitalise on any increased confidence gained during the protein exercise. Two general assessment procedures were used.

(a) A written assessment involving pre- and post-tests was completed by students involved in the exercise. Four basic techniques were involved, namely:-

(i) Multiple choice objective items based on the cognitive objectives of the exercise, (see p. 251).

(ii) Likert-type statements based on the broader objectives. Students were asked to signify their degree of agreement to each statement on a five-point scale. Statements based on communication skills were concerned with the students' confidence in using such skills, (see p. 252).

(iii) A rating grid on which students indicated how successful or otherwise the exercise had been in achieving each of the fifteen objectives listed on p. 185-186. This acted as a check on the assessment methods using objective testing and Likert techniques, and also provided some indication on the attainment of certain objectives which were difficult to test directly, (see p. 253).

(iv) Questions based on the semantic differential technique in which students who had completed the exercise rated it in terms of value, interest and enjoyment, (see p. 255).

Procedures /

Procedures (i) and (ii) were used in the pre-test to the exercise, while all four procedures were involved in the post-test. In addition, space was provided in the post-test for students to comment on the exercise. In order to encourage honest responses to all questions, students were not required to put their names on the question sheets, but they were asked instead to put some identifying mark on each sheet, so that pre- and post-tests could be matched up.

(b) An analysis of tape recordings of the discussions of several of the groups who participated in the exercise was done in addition to the self-reporting and objective testing techniques. It was attempted to identify communication patterns and patterns of student involvement during the course of the exercise. It was hoped to gain an insight into the value and operation of the exercise which was independent of student opinion.

Details of sample population

Major difficulties with introducing supplementary material into an undergraduate timetable include the fact that free time is exceedingly difficult to find, and also that students are unwilling to surrender what little free time they possess to attempt material which is not part of the prescribed course. Consequently numbers who have attempted the exercise are low, and students from institutions other than Glasgow University have also been included in the assessment. These students included sixth formers from a large Scottish comprehensive school, and students from Liverpool University studying for a Post Graduate Certificate of Education (P.G.C.E.). The Liverpool students were used in the assessment despite being older than the original target population.

Glasgow University	3 groups	(17 students)
Liverpool University	2 groups	(11 students)
School Sixth formers	2 groups	(11 students)
Total	7 groups	(39 students)

This list /

This list does not include the groups who participated in the early trials of the material. Three of the groups consisted of only five students. In such cases, the author participated in the group, either as group leader or group member.

One disadvantage of being forced to rely on volunteers is that such students may not be representative of the target population, and may in fact represent the most motivated students. This possibility must be borne in mind in considering assessment results.

Results of Assessment

(a) Written assessment

The results of the seven groups to whom the written assessment was given are considered collectively below as consideration of students from individual institutions is not practical due to small numbers.

(i) Objective items

Three multiple choice objective items (p. 251) were designed to measure specific cognitive attainment from the exercise. The item by item analysis is given in Table 5-2, while a pre/post test response comparison is given in Table 5-3.

Item / Option	1(a)	1(b)	1(c)
A	2 (1)	(0) (1)	8 (1)
B	*21 (29)	3 (2)	1 (0)
C	5 (5)	*25 (35)	(0) (0)
D	3 (4)	5 (1)	*25 (38)
E	8 (0)	6 (0)	5 (0)
Facility (Pre) value (Post)	.54 (.74)	.64 (.90)	.64 (.97)
Difference in facility values	Not Sig.	Sig. 1%	Sig. 1%

<u>Table 5-2</u> <u>Item by Item Analysis of Objective Items</u>
(Post-test figures are given in brackets below pre-test figures)

* Indicates the correct response for each item (the key)

The test of significance used is given on p. 68.

	Item (a)	Item (b)	Item (c)
Right → Right	21	24	25
Wrong → Right	5	7	8
Don't know → Right	3	4	5
Right → Wrong	0	1	0
Wrong → Wrong	5	1	1
Don't know → Wrong	5	2	0
Facility Value (Pre)	.54	.64	.64
Facility Value (Post)	.74	.90	.97

<u>Table 5-3</u> <u>Pre/Post test Response Comparison</u>

Even /

Even with the numbers available significant differences between pre- and post-tests are evident in items (b) and (c), with the difference in item (a) being almost significant at the 5% level.

It would appear that cognitive objectives 1, 3 and 4 on p. 185 are being at least partially achieved by means of the discussion exercise. How much more (or less) efficiently they could be achieved by other, perhaps more traditional, teaching methods is open to question.

(ii) <u>Likert-type questions</u>

Ten statements with which the student had to indicate his agreement or otherwise on a five point scale were included in both pre- and post-test (see p.252). Total responses to each statement are given in Table 5-4 and a further breakdown of the responses to indicate changes in the degrees of agreement/disagreement for statements in pre- and post-tests is given in Table 5-5.

N.B. Statements marked * were phrased in such a way that trends towards greater <u>disagreement</u> indicated the degree of achievement of the objective in question.

		Strongly Agree	Agree	Don't know/ Undecided	Disagree	Strongly Disagree
Factual gains	Statement (a) (Objective 5)	0 (14)	15 (25)	12 (0)	10 (0)	2 (0)
Data handling	Statement (b) (Objective 6)	7 (9)	18 (23)	11 (6)	3 (1)	0 (0)
confidence in communication skills	Statement (c) (Objective 7)	11 (13)	15 (20)	6 (4)	7 (2)	0 (0)
	Statement (d) (Objective8,9)	4 (5)	15 (22)	10 (8)	8 (2)	2 (2)
*	Statement (e) (Objective 9)	5 (0)	8 (6)	4 (8)	20 (17)	2 (8)
Value of teamwork	Statement (f) (Objective 11)	18 (22)	19 (16)	2 (1)	0 (0)	0 (0)
Willingness to compromise	Statement (g) (Objective 13)	5 (6)	18 (26)	12 (5)	3 (2)	1 (0)
Interconnections across subject barriers *	Statement (h) (Objective 14)	0 (0)	0 (0)	2 (0)	13 (9)	24 (30)
*	Statement (i) (Objective 14)	1 (0)	5 (0)	9 (0)	18 (18)	6 (21)
Limitations of science *	Statement (j) (Objective 15)	0 (0)	3 (1)	10 (9)	17 (11)	9 (18)

<u>Table 5-4</u> <u>Responses to Likert-type Statements</u>

(Post-test figures are given in brackets below pre-test figures)

N.B. Statements marked * were phrased in such a way that trends towards greater <u>disagreement</u> indicated the degree of achievement of the objective in question.

	Unchanged responses	More Agreement			Less Agreement		
		By 1 point on scale	By 2 points on scale	By 3 points on scale	By 1 point on scale	By 2 points on scale	By 3 points on scale
Statement (a) (Objective 5)	6	16	15	2			
Statement (b) (Objective 6)	29	9	1				
Statement (c) (Objective 7)	22	11	3		3		
Statement (d) (Objective 8,9)	22	11		1	4	1	
* Statement (e) (Objective 9)	20	1	1		12	5	
Statement (f) (Objective 11)	30	7			2		
Statement (g) (Objective 13)	26	12			1		
* Statement (h) (Objective 14)	32				7		
* Statement (i) (Objective 14)	15				17	6	1
* Statement (j) (Objective 15)	20	4			14	1	

Table 5-5 <u>Agreement/Disagreement Trends between Pre- and Post-Test for Likert-type Statements</u>

Table 5-4 reveals a general movement of opinions in the directions consistent with the objectives of the exercise, for each statement under consideration. Although only 39 students participated in the formal assessment, χ^2 tests indicated significantly more agreement between pre- and post-test at the 0.1% level for statement (a) (familiarity with factors contributing to the world protein shortage), and at the 5% level for statement (g) (willingness to compromise). Significantly less agreement was found at the 0.1% level for statement (i) (interconnections between science and non-science subjects) and at the 5% level for statement (e) (confidence in giving a talk to other students on an aspect of science).

Much larger sample sizes would be necessary, however, before statistical analysis would become really meaningful and could show up significant changes for other statements.

Table 5-5 clearly shows the agreement/disagreement changes for each statement. All the statements show some degree of overall change in opinion in the desired direction. It is interesting that statements (c), (d), (e) and (f), which were designed to measure changes in confidence in communication skills, indicate a minority of students whose confidence appears to have decreased as a result of the exercise. This reversal may be a direct result of the exercise having the opposite of its desired effect, but another explanation may be that the student's first estimation of his confidence was too high, and the exercise has involved some self-appraisal of the student's communication ability. Obviously more students would be required if this line of enquiry were to be pursued.

On the basis of the Likert-type assessment it would seem that the objectives involved were all partly achieved by the exercise with varying degrees of success. No objective appears to have been in general negatively achieved.

(iii) Objective rating grid

As a further check on the attainment of all fifteen objectives, an objective rating grid was included in the post-test (see p. 253). Students were asked to rate on a five point scale, how successful the exercise had been for each objective. The results are given in Table 5-6.

	Very successful	Fairly successful	Average	Not very successful	Dismal failure
Objective 1	13	12	6	6	2
Objective 2	10	12	11	6	0
Objective 3	19	15	1	3	1
Objective 4	6	7	12	13	1
Objective 5	26	13	0	0	0
Objective 6	9	15	12	3	0
Objective 7	9	19	10	1	0
Objective 8	9	18	8	4	0
Objective 9	8	14	12	4	1
Objective 10	6	19	11	3	0
Objective 11	22	12	4	0	1
Objective 12	6	18	14	1	0
Objective 13	6	17	12	2	2
Objective 14	22	13	3	1	0
Objective 15	16	16	5	1	1

Table 5-6 Objective Rating Grid Responses

On the basis of the students' opinions it would appear that objective 5 was achieved best of all. This objective was a cognitive, but not necessarily chemical one. The objective perceived by students to be least well achieved was objective 4 on the peptide link and its importance in protein chemistry. Objective test item (b) indicated a significant improvement in the number of students who could recognise a peptide bond after the exercise, but the importance of the bond and its relation to the overall context of the exercise was probably underemphasised, hence the objective's low /

low rating..

The objectives concerned with the development of communication skills (i.e. objectives 7, 8, 9, 11) appear to have been achieved moderately well in the students' opinion. That these objectives were not marked higher was to be expected, as it is likely that skills in communication and discussion, and the ability to talk in public are not assimilated in one session, but would require several such sessions.

Objective 14, on the realisation of interconnections across subject barriers, appears to have been particularly well attained, and this is confirmed by the responses to statements (h) and (i) in the Likert-type scale (Tables 5-4 and 5-5). The remaining objectives would seem to have been successfully attained to varying extents with no objective (apart perhaps from objective 4) being seen by the students to be entirely outwith the scope of the exercise. It must be remembered that this method of assessment is crude and gives only an indication of the success of each objective.

(iv) Semantic differential type questions

Four questions of this type were employed to obtain an impression of how students viewed the exercise in general terms such as value, interest and enjoyment (see p. 255). The responses to the questions, which were included in the post-test, are given in Table 5-7.

Question / Option	(a)	(b)	(c)	(d)
A	21	17	23	17
B	16	17	15	18
C	2	5	1	1
D	0	0	0	3
E	0	0	0	0

Table 5-7 Student opinion of the exercise

From /

From Table 5-7 it would appear that most students found the exercise valuable and enjoyable, and there was a general feeling that the discussion exercise benefitted the students' general education in chemistry. Responses to question (b) would seem to indicate some attitudinal change towards the problem of world protein shortage, although little weight should be attached to the responses to this single question. More sophisticated testing would be necessary to assess the extent (if any) of any general attitudinal changes towards the subject matter.

Conclusions The preceding results from the various assessment procedures would appear encouraging. However, it must be remembered that only 39 students were available, all of whom were volunteers, so that statistical analysis of the results is precarious, quite apart from the fact that the sample is probably biased towards the more enthusiastic and co-operative students.

However, within this small, biased sample the gains which were made in the cognitive and attitudinal aspects of the topic, allied with the general increase in confidence in communication skills would appear to be some justification for further trials of exercises such as 'Proteins as Human Food', although it is probable that the beneficial effects of a series of similar communication exercises over a session would probably be greater and more permanent than the effects of such exercises in isolation.

(b) Analysis of tape recordings

Tape recordings were made of the procedings in five of the groups who participated. The groups involved were two groups of sixth year school pupils (groups (a) and (b)), two groups of students from Liverpool University (groups (c) and (d)) and one group of Glasgow University students (group (e)). A summary of the analysis of the recordings from groups (a) /

(a) to (e) are to be found on pages 203 to 207.

The summary gives information on the total time each individual spent communicating and the number of contributions from each student in each ten minute interval in the exercise. Hence the percentage time spent in communicating and the average length of each contribution can be calculated for each interval.

General features of the five analyses include:-

(i) The total percentage time spent communicating in the exercise as a whole never fell below 10% for any individual. It would appear that the exercise has been successful in its aim of encouraging more reticent students to become involved in the exercise.

(ii) The average length of the communications in each exercise varies greatly, e.g. from an average of 6.8 secs. in group (a) to 15.0 secs. in group (b). The length of communications would therefore appear to be controlled more by the individual group members than by the exercise format.

(iii) A pattern of communication within each group usually takes the form of the discussion being dominated at first by the group leader and those students possessing information sheets 1 and 2. As the exercise proceeds group members 3, 4 and 5 are brought into the discussion to add their specialised information. In the last twenty minutes or so of each exercise, a more general discussion of broader issues involves all students, although the discussion may be dominated by certain students independently of the information sheets possessed.

(iv) The group leader appears to integrate well into the exercise despite being without an information sheet. The group leader also appears to maintain a high level of involvement throughout the exercise /

the exercise. However, in all five analyses, the group leader was selected by a tutor or teacher who had prior knowledge of the students' personalities. How well the exercise would proceed with a randomly selected leader is unknown.

It should be emphasised that the above subjective generalisations would need to be confirmed by further analyses of this sort. It may be of interest to study the group interactions in more detail during the course of the exercise. Adoption of a method of interaction process analysis such as is described by Bales(91) would be required.

GROUP(a) - SIXTH YEAR SCHOOL PUPILS

Interval (mins) / ROLE	1-10		11-20		21-30		31-40		41-50		51 - 60		61 - 70		71 - 80		81 - 88		TOTAL	
GROUP LEADER	130	13	143	19	55	7	94	9	101	15	45	7	80	10	26	5	100	18	774	103
	21.7	10	23.8	7.5	9.2	7.9	15.7	10.4	16.8	6.7	7.5	6.4	13.3	8	4.3	5.2	20.8	5.5	14.7	7.5
SHEET 1	81	3	82	7	98	11	53	6	54	12	125	26	124	34	130	27	137	28	884	154
	13.5	27	13.7	11.7	16.3	8.9	8.8	8.8	9	4.5	20.8	4.8	20.7	3.6	21.7	4.8	28.5	4.9	16.7	5.7
SHEET 2	114	7	32	4	87	12	76	8	83	12	58	10	105	19	118	21	36	9	709	102
	19	16.3	5.3	8	14.5	7.2	12.7	9.5	13.8	6.9	9.7	5.8	17.5	5.5	19.7	5.6	7.5	4	13.4	6.9
SHEET 3	39	3	145	9	105	10	71	8	56	9	97	17	91	19	95	20	34	8	733	103
	6.5	13	24.2	16.1	17.5	10.5	11.8	8.9	9.3	6.2	16.2	5.7	15.2	4.8	15.8	4.7	7.1	4.2	13.9	7.1
SHEET 4	82	8	121	13	134	11	98	10	71	12	92	16	83	16	72	14	79	18	832	118
	13.7	10.2	20.2	9.3	22.3	11.2	16.3	9.8	11.8	5.9	15.3	5.7	13.8	5.2	12	5.1	16.4	4.4	15.8	7.1
SHEET 5	154	14	77	11	121	12	208	19	235	27	183	26	117	27	159	31	94	24	1348	191
	25.7	11	12.8	7	20.2	10.1	34.7	10.9	39.2	8.7	30.5	7	19.5	4.3	26.5	5.1	19.6	3.9	25.5	7.1

KEY

Time spent communicating (secs)	No. of contributions
% of time spent communicating	Av. length of contributions (secs)

OVERALL TOTAL

5280	771
100	6.8

GROUP(b) - SIXTH YEAR SCHOOL PUPILS

Interval (mins) / ROLE	1-10		11-20		21-30		31-40		41-50		51 - 60		61 - 70		71 - 80				TOTAL	
GROUP LEADER	220	15	217	21	154	16	141	13	94	11	141	15	222	15	212	15			1401	121
	36·7	14·7	36·2	10·3	25·7	9·6	23·5	10·8	15·7	8·5	23·5	9·4	37·0	14·8	35·3	14·1			29·2	11·6
SHEET 1	209	9	9	2	18	2	41	3	53	4	102	7	74	5	66	5			572	37
	34·8	23·2	1·5	4·5	3	9	3·8	13·7	8·8	13·2	17	14·6	12·3	14·8	11	13·2			11·9	15·5
SHEET 2	156	5	88	9	0	0	66	3	18	2	30	3	64	6	64	4			486	32
	26	31·2	14·7	9·8	0	—	11	22	3	9	5	10	10·7	10·7	10·7	16			10·1	15·2
SHEET 3	10	2	286	12	194	11	90	5	92	7	72	5	109	11	35	2			888	55
	1·7	5	47·7	23·8	32·3	17·6	15	18	15·3	13·1	12	14·4	18·2	9·9	5·8	17·5			18·5	16·1
SHEET 4	5	1	0	0	133	5	239	10	234	11	56	5	62	4	161	7			890	43
	0·8	5	0	—	22·2	26·6	39·8	23·9	39	21·3	9·3	11·2	10·3	15·5	26·8	23			18·5	20·7
SHEET 5	0	0	0	0	101	5	23	2	109	7	199	9	69	5	62	4			563	32
	0	—	0	—	16·8	20·2	3·8	11·5	18·2	15·6	33·2	22·1	11·5	13·8	10·3	15·5			11·7	17·6

KEY

Time spent communicating (secs) → top left

← No. of contributions → top right

% of time spent communicating → bottom left

← Av. length of contributions (secs) → bottom right

OVERALL TOTAL		
	4800	320
	100	15·0

GROUP(c) - LIVERPOOL UNIVERSITY P.G.C.E. STUDENTS

ROLE \ Interval (mins)	1-10		11-20		21-30		31-40		41-50		51-60		61-64						TOTAL	
GROUP LEADER	113	21	102	16	55	7	98	6	105	7	67	4	16	2					556	63
	18.8	5.4	17	6.4	9.2	7.9	16.3	16.3	17.5	15	11.2	16.7	6.7	8					14.5	8.8
SHEET 1	220	10	108	6	0	0	15	2	43	4	57	6	11	1					456	29
	37	22.2	18	18	0	—	2.5	7.5	7.2	10.7	9.5	9.5	4.6	11					11.9	15.7
SHEET 2	183	10	133	9	13	2	13	2	39	4	83	14	67	10					531	51
	30.5	18.3	22.2	19.3	2.2	6.5	2.2	6.5	6.5	9.7	13.8	5.9	27.9	6.7					13.8	10.4
SHEET 3	64	4	126	7	201	11	169	14	152	14	217	20	63	9					992	79
	10.7	16	21	18	33.5	18.3	28.2	12.1	25.3	10.8	36.2	10.8	26.2	7					25.8	12.6
SHEET 4	8	2	101	7	256	10	129	6	80	6	155	9	73	5					802	45
	1.3	4	16.8	14.4	42.7	25.6	21.5	21.5	13.3	13.3	25.8	17.2	30.4	14.6					20.9	17.8
SHEET 5	10	2	30	3	75	5	176	7	181	9	21	3	10	2					503	31
	1.7	5	5	10	12.5	15	29.3	25.1	30.2	20.1	3.5	7	4.2	5					13.1	16.2

KEY

Time spent communicating (secs) →		← No. of contributions
% of time spent communicating →		← Av. length of contributions (secs)

OVERALL TOTAL

3480	298
100	12.9

GROUP(d) LIVERPOOL UNIVERSITY P.G.C.E. STUDENTS

Interval (mins) / ROLE	1-10		11-20		21-30		31-40		41-50		51 – 60		61 – 67						TOTAL	
GROUP LEADER	161	17	150	19	91	11	63	12	90	11	106	13	59	7					720	90
	26·8	9·5	25	7·9	15·2	8·3	10·5	5·2	15	8·2	17·7	8·2	14	8·4					17·9	8
SHEET 1	275	12	129	8	45	5	131	9	77	5	76	6	74	6					807	51
	45·8	22·9	21·5	16·1	7·5	9	21·8	14·5	12·8	15·4	12·7	12·7	17·6	12·7					20·1	15·8
SHEET 2	131	7	171	10	12	2	30	5	105	8	67	5	43	3					559	40
	21·8	18·7	28·5	17·1	2	6	5	6	17·5	13·1	11·2	13·4	10·2	14·3					13·9	14
SHEET 3	7	1	92	5	120	5	66	4	80	6	92	10	56	6					513	37
	1·2	7	15·3	18·4	20	24	11	16·5	13·3	13·3	15·3	9·2	13·3	9·3					12·8	13·9
SHEET 4	0	0	18	2	154	9	91	4	123	6	61	3	39	2					486	26
	0	—	3	9	25·7	17·1	15·2	22·7	20·5	20·5	10·2	20·3	9·3	19·5					12·1	18·7
SHEET 5	26	3	40	7	178	11	219	14	125	7	198	9	149	8					935	59
	4·3	8·7	6·7	5·7	29·7	16·2	36·5	15·6	20·8	17·8	33	22	35·5	18·6					23·3	15·8

OVERALL TOTAL	
4020	303
100	13·3

KEY

Time spent communicating (secs)	No. of contributions
% of time spent communicating	Av. length of contributions (secs)

GROUP(e) FIRST YEAR GLASGOW UNIVERSITY STUDENTS

interval (mins) / ROLE	1-10		11-20		21-30		31-40		41-50		51-58								TOTAL	
GROUP LEADER	203	27	91	14	77	11	59	6	105	11	37	5							572	74
	33.8	7.5	15.2	6.5	12.8	7	9.8	9.8	17.5	9.5	7.7	7.4							16.4	7.7
SHEET 1	138	9	108	9	42	6	80	11	131	17	116	14							615	66
	23	15.3	18	12	7	7	13.3	7.3	21.8	7.7	24.2	8.3							17.7	9.3
SHEET 2	149	8	114	7	78	11	25	7	42	9	30	6							438	48
	24.8	18.6	19	16.3	13	7.1	4.2	3.6	7	4.7	6.2	5							12.6	9.1
SHEET 3	65	5	101	8	135	13	73	11	77	8	96	9							547	54
	10.8	13	16.8	12.6	22.5	10.4	12.2	6.6	12.8	9.6	20	10.7							15.7	10.1
SHEET 4	9	2	78	9	131	9	90	8	65	5	117	10							490	43
	1.5	4.5	13	8.7	21.8	14.6	15	11.2	10.8	13	24.4	11.7							14.1	11.4
SHEET 5	36	8	108	12	137	14	273	23	180	11	84	8							818	76
	6	4.5	18	9	22.8	9.8	45.5	11.9	30	16.4	17.5	10.5							23.5	10.8

OVERALL TOTAL

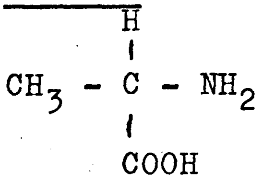
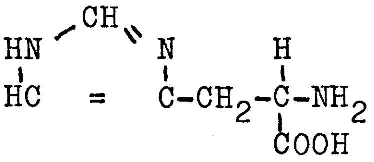
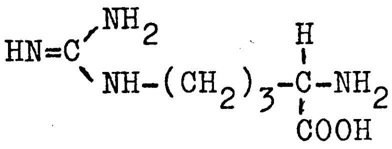
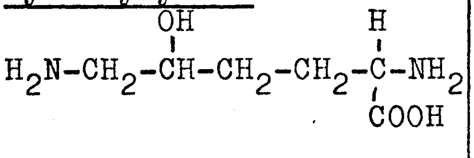
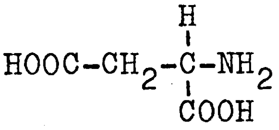
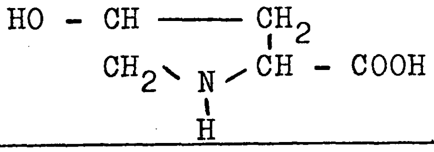
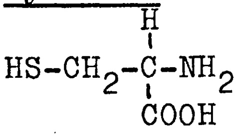
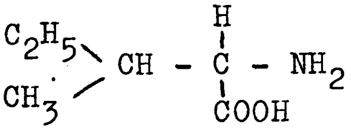
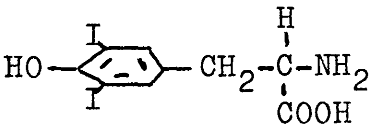
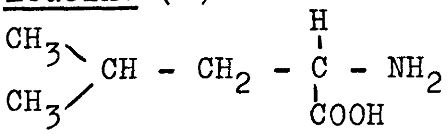
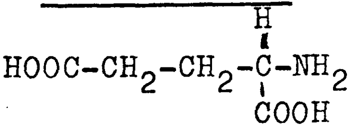
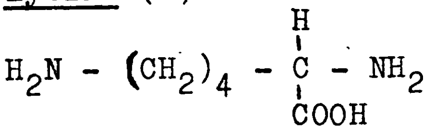
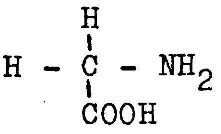
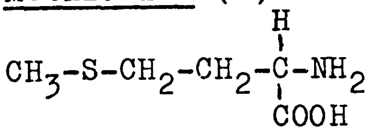
3480	361
100	9.6

KEY

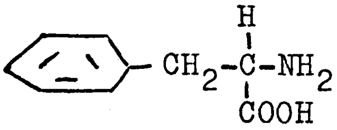
Time spent communicating (secs) →	← No. of contributions
% of time spent communicating →	← Av. length of contributions (secs)

APPENDIX TO CHAPTER 5

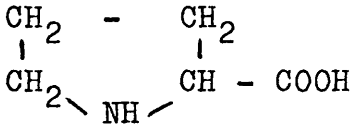
Table 1 Amino Acids and their Structures
(*) denotes essential amino acid for humans

1) **Alanine**  $\mathrm{CH_3-\overset{H}{\overset{\vert}{\underset{COOH}{\underset{\vert}{C}}}}-NH_2}$	8) **Histidine** 
2) **Argenine** 	9) **Hydroxylysine**  $\mathrm{H_2N-CH_2-\overset{OH}{\overset{\vert}{C}}H-CH_2-CH_2-\overset{H}{\overset{\vert}{\underset{COOH}{\underset{\vert}{C}}}}-NH_2}$
3) **Aspartic Acid**  $\mathrm{HOOC-CH_2-\overset{H}{\overset{\vert}{\underset{COOH}{\underset{\vert}{C}}}}-NH_2}$	10) **Hydroxyproline** 
4) **Cysteine**  $\mathrm{HS-CH_2-\overset{H}{\overset{\vert}{\underset{COOH}{\underset{\vert}{C}}}}-NH_2}$	11) **Isoleucine** (*) 
5) **Diiodotyrosine** 	12) **Leucine** (*) 
6) **Glutamic Acid**  $\mathrm{HOOC-CH_2-CH_2-\overset{H}{\overset{\vert}{\underset{COOH}{\underset{\vert}{C}}}}-NH_2}$	13) **Lysine** (*)  $\mathrm{H_2N-(CH_2)_4-\overset{H}{\overset{\vert}{\underset{COOH}{\underset{\vert}{C}}}}-NH_2}$
7) **Glycine**  $\mathrm{H-\overset{H}{\overset{\vert}{\underset{COOH}{\underset{\vert}{C}}}}-NH_2}$	14) **Methionine** (*)  $\mathrm{CH_3-S-CH_2-CH_2-\overset{H}{\overset{\vert}{\underset{COOH}{\underset{\vert}{C}}}}-NH_2}$

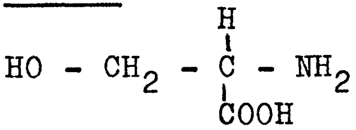
15) Phenylalanine (*)



16) Proline

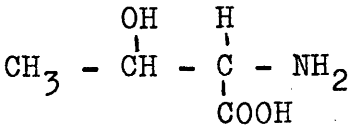


17) Serine



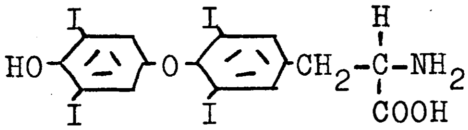
$HO - CH_2 - \overset{H}{\underset{COOH}{C}} - NH_2$

18) Threonine (*)

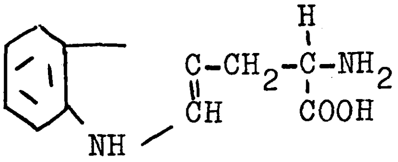


$CH_3 - \overset{OH}{CH} - \overset{H}{\underset{COOH}{C}} - NH_2$

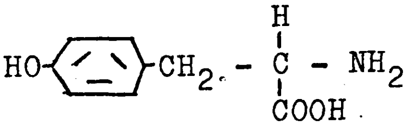
19) Thyroxine



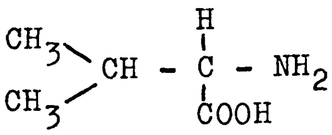
20) Tryptophan (*)



21) Tyrosine



22) Valine (*)



PROTEINS AS HUMAN FOOD (Group Members' Guide)

Proteins are fundamental molecules of living matter constituting the cell. They are the basic building bricks of life and are common to all living creatures from the whale to the smallest micro-organism.

Without proteins life would come to a stop. In man and the higher animals they are necessary for the growth, repair and replacement of body tissues. They are the main constituent of enzymes, without which the body would cease to function, and are also contained in certain hormones.

However, at present the world cannot feed its population of nearly 4,000 millions adequately, the major problem being a deficit of proteins. This can result in a reduction of both physical and mental development, and the problem is not confined to the underdeveloped countries. Under these circumstances, the population explosion offers cold comfort for the future.

You have received information on one aspect of the subject of "Proteins as Human Food", and other members of the group have received information on other aspects of this topic. Collectively, the group possesses enough information to obtain a reasonably balanced picture of what proteins are, where the protein deficiency problem arises, and possible ways of combating this problem.

The exercise involves communication of your information to the rest of your group, and understanding and assimilating their information. You are encouraged to ask for clarification of any points not made clear enough, and also to express any opinions you may /

may feel on the subject after being given all the information. You may take notes if you wish.

The group leader should act as chairman and peace-keeper in the group, but he need not be the dominant figure in the group. The group leader does not have access to any information, and the exercise will begin with the group leader asking specific questions about the subject which one (at least) of the group should be in a position to answer. This will continue until each group member has a general acquaintance with the subject. A more general discussion of broader aspects of the topic can then be undertaken by the group as a whole. In both the question session and the discussion, you should state any relevant information you possess - either from your information sheet, or from prior knowledge.

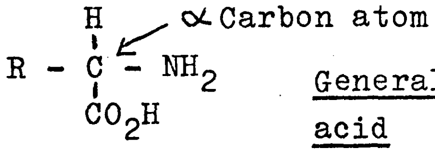
The nature of the exercise is basically informal, and you should not feel inhibited about asking questions and stating opinions. In topics such as this one, there are few, if any, conclusions which are satsifactory for everybody - most decisions are a compromise of conflicting interest.

The entire exercise will take about 1½ to 2 hours and you will be given 15-20 minutes at the start to read your particular information sheet at least a couple of times, so that you will become an 'expert' in your particular field, capable of contributing to discussion in the group.

CHEMISTRY OF PROTEINS AND AMINO ACIDS (Information Sheet 1)

Protein is the most abundant organic constituent of our bodies; some 54% of the total organic mass. Proteins hold our bodies together, and they run it. They are found in all living cells, and are the principal material of the skin, muscle, tendons, hair, nerves and blood, as well as enzymes, antibodies and many hormones.

Chemically, proteins are high polymers. The units from which they are built contain both a basic amino group ($-NH_2$), and a carboxylic acid group ($-CO_2H$). These units are called <u>alpha amino acids</u> (α-amino acids), meaning that the $-NH_2$ group is attached to the α carbon atom - the one next to the $-CO_2H$ group. The general formula for an α- amino acid is shown below.



$$R - \overset{\displaystyle H}{\underset{\displaystyle CO_2H}{C}} - NH_2$$

General Formula of an α - amino acid

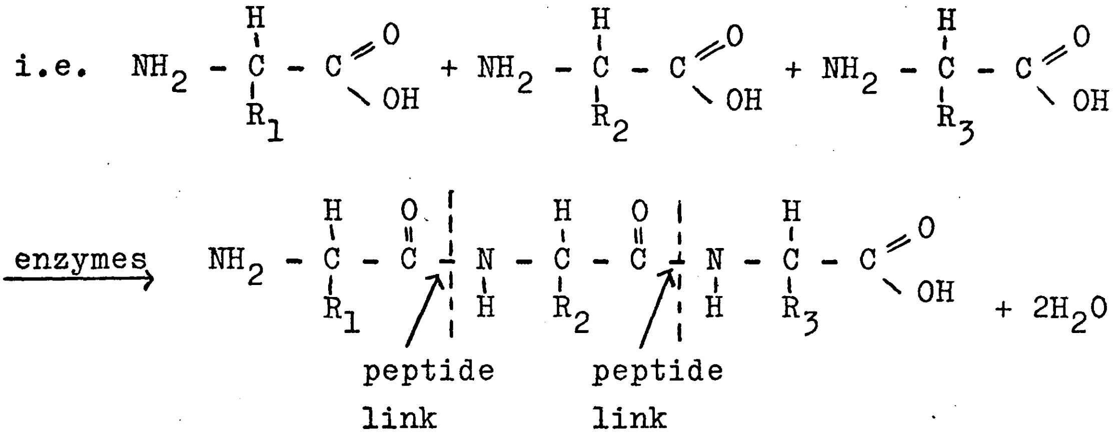
The R group may be one of over twenty different atomic groupings. A list of amino acids involved in the synthesis of animal protein is given in Table 1.

A <u>single</u> protein molecule contains hundreds, or more probably, thousands of amino acid units linked up. The number of different combinations of these amino acids to produce a protein molecule is almost infinite. It is likely that tens of thousands of different proteins are required to make up and run the human body - and this set of proteins is not identical with the set required by an animal of a different species. Further, the set of proteins required are not randomly constructed from any amino acids, but follow a definite pattern, dictated by the body's machinery.

When /

When appropriate proportions of the desired amino acids are present in the body, protein synthesis can occur by joining up the amino acid units in a predetermined fashion, with the exclusion of a water molecule for each linkage.

i.e.



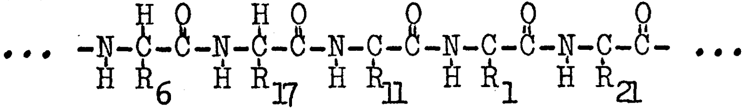
$$NH_2-\overset{H}{\underset{R_1}{C}}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}+NH_2-\overset{H}{\underset{R_2}{C}}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}+NH_2-\overset{H}{\underset{R_3}{C}}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}$$

$$\xrightarrow{\text{enzymes}} NH_2-\overset{H}{\underset{R_1}{C}}-\overset{O}{\overset{\|}{C}}\,\vdots\,\underset{H}{N}-\overset{H}{\underset{R_2}{C}}-\overset{O}{\overset{\|}{C}}\,\vdots\,\underset{H}{N}-\overset{H}{\underset{R_3}{C}}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}+2H_2O$$

peptide link

peptide link

Proteins are made up of <u>peptide chains</u>, that is, of amino acid residues joined by amide linkages, called peptide links. A fully synthesized protein molecule may be of the form -



$$\ldots\ -\underset{H}{N}-\overset{H}{\underset{R_6}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\overset{H}{\underset{R_{17}}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{R_{11}}{C}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{R_1}{C}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{R_{21}}{C}-\overset{O}{\overset{\|}{C}}-\ \ldots$$

A reaction which is the reverse of protein synthesis occurs when an animal eats and digests protein as food. In this case, enzymes in the body break down the protein to its constituent amino acids, then rebuild these amino acid units again to form new protein of a kind which is of use to the particular animal concerned. Hence, for example, protein from plants can be reformed into animal protein.

i.e. $$\text{Plants synthesise amino acids}\xrightarrow{\text{plant enzymes}}\text{Plant proteins}\ -\ \xrightarrow{\text{animal enzymes}}$$

$$\text{Amino acids}\xrightarrow{\text{animal enzymes}}\text{Animal protein}$$

The human body can synthesize for itself all but eight /

eight of the amino acids it requires for protein synthesis. These eight amino acids, therefore, need to be obtained from protein foods containing these amino acid units in reasonable proportions. The importance of these amino acids cannot be over-emphasized and they are called the essential amino acids and are denoted by (*) in Table 1.

FERTILIZER MANUFACTURE AND COSTS

Manufacture

The most important nitrogen-containing fertiliser is ammonium nitrate (NH_4NO_3) because of:-

(a) its high nitrogen content (about 35%),
(b) its relative cheapness and simplicity to manufacture.

The overall reaction involves the direct combination of ammonia and nitric acid.

$$NH_3\ (g) + HNO_3\ (aq) \rightarrow NH_4\text{-}NO_3\ (aq) \quad \Delta H = -20.6\ \text{K cal.}$$

The most important industrial use of nitric acid is, in fact, in the manufacture of fertilisers.

The ammonia is produced by the combination of hydrogen and nitrogen via the Haber process.

$$3\ H_2\ (g) + N_2\ (g) \xrightarrow[\substack{1000\ \text{atm.} \\ 500^\circ\ \text{C.}}]{\text{iron oxides}} 2\ NH_3\ (g)$$

Large quantities of hydrogen are produced industrially by catalytically reacting hydrocarbons, from petroleum, with steam to yield hydrogen and carbon oxides. The most commonly used raw material is methane, although other natural and oil refinery hydrocarbons including naptha cuts may be used.

Care must be taken when handling solid ammonium nitrate, for as well as being a fertiliser, it is also an explosive. The equation for the explosive reaction is/

is .

$$NH_4NO_3\ (s) \rightarrow N_2\ (g) + 2H_2O\ (g) + \tfrac{1}{2}\ O_2\ (g) \quad \Delta H = \text{large} \\ -ve$$

This exothermic reaction will take place only at fairly high temperatures. In the Texas City disaster some years ago, a ship loaded with ammonium nitrate caught fire and exploded, killing almost 600 people and destroying over 33 million dollars worth of property.

About 90% of ammonium nitrate produced is used as fertiliser, the rest being used as an explosive.

Cost factors in fertiliser manufacture

Following the recent world increases in the price of oil from the Middle East, the cost of fertiliser to the consumer has quadrupled from £20 per tonne to £80 per tonne.

Table 2 contains information from I.C.I.'s cost sheets for the production of ammonium nitrate during March 1974 and September 1974 - a space of only five months.

The increases in oil prices have affected not only the power costs in the final process, but also the cost of production of all the raw materials, in particular ammonia as the hydrogen involved in the synthesis of ammonia is produced from petroleum products. The cost of power and steam are grouped together in Table 2 as both costs directly involve the burning of oil or oil products.

The total cost of power per tonne of ammonium nitrate produced is given at the bottom of the table, and it is obvious that the figure has risen quite dramatically since even March 1974. The March 1974 power figure is some 8% of the total production cost per tonne; the September 1974 figure is 19% of the total production cost per tonne.

Table 2 Breakdown of industrial Costs involved in the Production of ammonium nitrate for March and September, 1974

	MARCH 1974			SEPTEMBER 1974		
	Usage tonnes	Cost per unit	Value	Usage tonnes	Cost per unit	Value
Materials						
Ammonia	347.2	£32-00	£11,110	610	£35-00	£21,350
Weak Nitric Acid	1258.6	£17-80	£22,356	2080.5	£19-17	£39,884
*Armeen	2.06	£403-60	£833	3.9	£654-00	£2,551
Wages			£9,873			£13,466
Services						
Air (x 10^3 m^3)	72	£2-48	£179	67.7	£3-45	£234
Water (x 10^3 gallons)	480	£0-15	£74	1088	£0-16	£172
Power (M.W.H.)	95	£9-90	£942	111.7	£19-43	£2,165
Steam (Tonnes)	2147	£1-70	£3,667	4597	£3-80	£17,312
Other Overheads			£8,002			£6,792
Total			£57,036			£103,926

Total Tonnage produced = 1,437.9 tonnes = 2,391.5 tonnes
Total Power cost = £4,609 = £19,477
∴ Unit cost of power per tonne = £3.2053 = £7.726
Production cost of fertiliser per tonne = £39.66 = £43.46

* "Armeen" is the trademark for a series of high molecular weight aliphatic amines used as chemical intermediates or catalysts in many industrial processes.

ESSENTIAL AMINO ACIDS AND PROTEIN USABILITY

(Information Sheet 2)

Essential amino acids are those which cannot be synthesized by the body, and hence have to be obtained directly in the diet, from food containing a protein which is constituted of reasonably large proportions of the desired essential amino acids. There are eight essential amino acids for humans, and these are designated (*) in Table 1. All the other amino acids can be synthesized by the human body. (Note that those amino acids essential for one species may not be essential for another. Thus in listing essential amino acids, it is necessary to name the species involved.)

It is important to recognise that there are degrees of essentiality. The quantity of any one amino acid which must be included in the diet of a given species is often different from the required amount of another amino acid. Thus proper proportions of each of the eight essential amino acids must be available simultaneously for protein synthesis to occur. Hence, the type of protein eaten will determine how useful it is to the body. The quality of a protein is dependent, therefore, upon how usuable its component amino acids are for the human body, i.e. how closely its amino acid pattern matches the unique pattern which the body can best use. The percentage usability of protein from food sources is indicated in Table 2.

Table 2

Food	% of protein which can be used by the body
Human milk	100%
Eggs	90%
Cows' milk	82%
Meats	70-75%
Plants	40-70%

In /

In general, proteins derived from plants are deficient in certain essential amino acid. Also plant proteins tend to vary more than do proteins of animal origin from the unique amino acid pattern which the body can fully use.

If we take theprotein from human milk, which is specially designed by the body to specifically match the protein requirements of babies, as our standard, or "perfect" protein source, we can calculate the amounts of essential amino acids in some staple plant proteins as a percentage of the content of a similar quantity of protein from human milk. This is done in Table 3.

The limiting factor in the usability of any individual plant protein is the essential amino acid which is the least abundant. Hence for example, protein from wheat is only 44% usable by the body even although wheat protein is quite rich in most of the essential amino acids. The limiting factor is the low content of <u>lysine</u> (see Table 3). Thus, any human using wheat as his sole source of lysine would need to consume more than twice as much wheat protein for his body than he would human milk protein to obtain the same amount of "usable" protein. If we could, however, bolster up the lysine content of wheat with a protein which was rich in lysine - soya protein for example, which has 103% as much lysine in its protein as human milk - we could "plug" this deficiency. A mixture of equal parts of wheat protein and soya protein, for example, would have a lysine content of about 74% that of human milk protein. (44 + 103 ÷ 2). The limiting factor now would be the methionine content which would be (61 + 77 ÷ 2) → 69% that of human milk protein. Hence the protein usability is 69% which is approximately on a par with protein from steak.

The point is that, by skilful blending of cereal and /

and pulse proteins, plus certain nut and loaf proteins, it is possible to obtain mixtures of two or three plant proteins with protein usabilities of not less than 75% - i.e. at least as usable as protein from meat.

Essential Amino Acids in some plant proteins

The quantities of individual essential amino acids in a particular plant protein are expressed as a percentage of the amount of that amino acid in an equal amount of protein from human milk.

Table 3 /

Table 3

(* - figures not available)

Source of protein	Iso-leucine	Leucine	Lysine	Meth-ionine	Phenyl-alanine	Threo-nine	Trypto-phan	Valine
Leaf Proteins								
Brussel sprouts	74	46	69	46	*	75	60	69
Cabbage	51	44	59	46	*	61	50	54
Pea pods	89	73	85	46	*	89	60	74
Spinach	71	68	82	85	*	89	110	82
Broccoli	69	56	87	85	*	75	80	67
Turnip tops	57	66	56	115	*	93	90	82
Pulse Proteins								
Soya	94	81	103	61	84	89	90	75
Groundnuts	74	66	56	46	*	64	70	79
Nut Proteins								
Almond	69	70	41	61	86	61	40	79
Brazil	66	73	41	246	*	57	70	77
Cashew	100	75	59	77	74	75	140	118
Coconut	80	76	56	85	74	68	130	90
Filbert	103	66	59	46	*	64	90	100
Walnut	77	73	41	85	*	75	60	87
Cereal Proteins								
Barley	69	73	54	69	81	82	90	79
Maize	71	127	49	100	71	93	50	90
Oats	83	75	59	69	78	75	80	87
Rice	86	87	67	100	67	86	90	100
Wheat	69	68	44	77	75	64	80	69

FERTILISERS

Why ammonium nitrate is an important fertiliser

The most important, and almost ideal, nitrogen-containing fertiliser is ammonium nitrate (NH_4NO_3) partly because of its very high nitrogen content (35%).

Ammonium nitrate has an added advantage as a fertiliser because its nitrogen is present in two forms, i.e. NH_4^+ ions and NO_3^- ions. The nitrate nitrogen is generally more quickly taken up by a crop, while the nitrogen from the ammonium ion, which has first to be oxidised by bacteria to the nitrate, takes longer before it becomes available to be assimilated by the crop. The supply of nitrogen is thus prolonged - it is given first rapidly and then more slowly - and this has obvious advantages for the growth of crops.

The world shortage of fertiliser

Due to Arab increases in oil prices, the cost of fertiliser has quadrupled from £20 per ton to £80 per ton. This huge increase in cost, allied to the fact that there is currently a world shortage of fertiliser (due to mismanagement and miscalculation in the producing countries), has resulted in a critical shortage of fertiliser in the poorer countries of the world.

Increased prices affect these countries even more than in the more affluent countries and the situation has not been helped by the fact that due to the shortage some countries (especially in the Communist block) have been defaulting on promises of fertiliser to the needy countries so that they have enough for themselves. (e.g. In 1974, Russia gave India less than half of the fertiliser promised.)

Partially as a result of not receiving enough fertiliser, India is heading for its worst-ever famine.

A case /

A case has been made for a more efficient use of what fertiliser is available. For example, one ton of fertiliser in the Punjab produces twice as much grain as in the United States, while over 15% of all fertiliser used in the United States goes on golf courses, avenues, public gardens, etc.

CONVENTIONAL SOURCES OF PROTEIN AND THEIR CONTENT

(Information Sheet 3)

Broadly speaking, there are two sources of protein available for consumption by human beings, namely plants and animals. Table 4 gives some examples of foods in each of these categories.

Table 4

Plant Proteins	Animal Proteins
Cereals e.g. wheat	Meat e.g. beef
rye	pork
barley	mutton
oats	bacon
maize	chicken etc.
rice etc.	Fish e.g. haddock
Pulses e.g. lentils	cod
peas	salmon
soya beans	prawns
groundnuts etc.	shellfish
Vegetables	trout etc.
e.g. spinach	Milk products
broccoli	e.g. cows' milk
brussels sprouts	human milk
cabbage	cheeses
spring greens etc.	powdered milk
Nuts e.g. almond	cream etc.
brazil	Eggs
peanut	
cashew	
coconut	
walnut etc.	
Starchy roots	
e.g. sweet potatoes	
yams etc.	

Information /

Information on the percentage of crude protein in some common natural foods (by weight) is given in Table 5. This shows that, when prepared for consumption, nuts and pulses compare favourably with cheese, and exceed meat and fish, and especially eggs and milk in their crude protein content. Allowance has been made in Table 5 for inedible materials, e.g. hide, skin, and bones in meat, and peel and seeds in fruit.

Note that although the protein present in milk for example, is of a high quality for use by the body, only 3½% of the mass of milk is actually protein. The actual make-up of milk from an Ayrshire cow is -

Water	87.0%
Protein	3.4%
Fat	3.9%
Lactose	5.0%
Ash	0.7%

Note that most of milk is water, hence the increase in protein content of dried milk.

Another type of food is peanuts. These are 30% protein, the remainder being made up of -

Water	12%
Ash	8%
Crude Fibre	12%
Crude Lipide	8%
Nitrogen-free extract	30%

Table 5

Average % of Crude Protein (by weight) in foods as ready for consumption

	Food	Percentage Protein
*	soya flour	40%
	dried skim milk	37%
	parmesan cheese	36%
*	peanuts	30%
	cheddar cheese	26%

* /

Table 5 (cont'd)

	Food	Percentage Protein
*	lentils	26½
*	dried peas	24½
*	pistachio nuts	24½
	pork	24%
	beef	23%
*	almonds	20%
*	haricot beans	20%
	sardines	20%
*	butterbeans	18%
	salmon	18%
	cod	15%
	haddock	15%
	herring	15%
	chicken	14%
	bacon	13%
*	Brazil nuts	13%
	eels	13%
	mutton	13%
*	cashew nuts	10%
	eggs	10%
*	walnuts	9%
*	brown bread	8%
*	white bread	7%
*	English flour	7%
*	rice	7%
*	broccoli	5%
	cows' milk	3½%
	human milk	3%
*	potatoes	2%

(* - plant proteins)

Increasing conventional protein supplies

The most obvious way of increasing the world protein supply is to grow more of those familiar foods which are rich in protein. Table 6 shows the sources of protein for the well-fed countries of the world (Europe, North /

North America, Oceania and the River Plate countries) and for the ill-fed countries (the Far East, the Middle East, Africa and most of South America). The striking difference is the use of animal proteins in the well-fed countries. It also highlights the importance of the contribution of pulses, e.g. soya, peas, lentils, in the ill-fed countries.

Table 6

Grams of protein available per head per day

	Protein Source	Countries	
		Well-fed	Ill-fed
Plant	Cereals	21.0 g	28.4 g
	Nuts and Pulses	23.4 g	12.0 g
	Vegetables	4.1 g	2.7 g
	Roots	3.9 g	2.5 g
Animal	Meat	18.7 g	5.8 g
	Eggs	2.2 g	0.9 g
	Fish	2.6 g	2.3 g
	Milk Products	14.2 g	3.5 g
	Total	90.1 g	58.1 g

No one protein source is likely to solve the world food problem partly because people prefer a mixed diet, and partly because climatic and geographical conditions vary considerably throughout the world, and dictate the type of food which may be produced.

For example, near the shore of an unexploited lake or sea, fish deserve most attention. Indeed, fish farming is one of the most promising ways of increasing protein available from animal sources. Because fish are cold-blooded and can move fairly effortlessly in their environment, they consequently do not burn up much energy keeping warm or rushing about. Thus, they are very efficient converters of food. For instance, trout can grow to be one pound in weight after consuming only one and a half pounds of dry /

dry feed, while vegetarians like carp are able to survive on waterweed and other pond growth, so that the food conversion ratio can be reduced to a neat one to one.

Thus, fish are really the answer to a prayer in factory farming, where the emphasis is on maximum output for minimum input. The advantages of fish are obvious when one considers that, despite much scientific assistance, the average bullock consumes three tons of feedstuff to reach a bodyweight of ten cwts. - a food conversion ratio of six to one, and that even with the broiler chicken, technology has failed to reduce the food conversion ratio to below two and a half to one. With feed prices rising and profit margins tighter, such figures are increasingly important, and there is little doubt that in factory farming the name of the game is 'food conversion'. Another important cost factor is that some fish can thrive on foods such as chicken giblets, waste corn and other farm rubbish for which there is no market and can be obtained extremely cheaply.

Big business such as Shell, Unilever, I.C.I., Rank Hovis and British Oxygen are now realising the potential of fish farming and investing quite heavily in it; particularly in Scotland where inland lochs prove ideal sites.

At present the average world citizen consumes some twenty-six pounds of fish per year; and recent estimates by the International Food and Agriculture Organisation (F.A.O.) suggest that this will increase to thirty pounds per head by 1980, and thirty-six pounds by the turn of the century. Taken in conjunction with the expected world population increase, this means that global demand for fish could increase from the present seventy million tons per year to one hundred and twenty-eight million tons by the year 2000.

F.A.O, estimates indicate that the present total world output of farmed fish amounts to 4.5 million tons, with half of these home-grown fish being reared in mainland China (2.24 million tons) followed at some distance by India (0.5 million tons) and Russia (0.2 million tons). At present Britain does not feature prominently in the world fish farm league - the present total being little more than the total catch of a single large modern trawler after a sixty day voyage - but, with some of the best grounds being fished out or made unavailable, the upsurge of fish farming is increasing at a considerable rate, with the emphasis in this country being put on trout, salmon and carp. Modern technology is constantly increasing efficiency (British Oxygen now reckon to be able to produce eight pounds of trout per cubic foot of production space), although it is in America that technology is accelerating fastest. Fish farmers predict that they should be able to produce fish more cheaply than the fishing industry despite the fact that unexpected disease, pollution and/or climatic upsets can spell disaster (as a rule of thumb, trout farmers brace themselves to lose one harvest in five through natural disaster).

The production of factory fish, therefore, now appears inevitable and a necessary source of relatively cheap protein rich food. By the year 2000, the U.S. Department of Commerce estimates global fish farm output could increase from the present 4.5 million tons to top the 40 million ton mark, (25% of the predicted world demand).

Plant protein production also is dependent upon climatic conditions. For instance, in regions where there is adequate spring rain, followed by a hot summer, no source of protein is likely to outyield soya and the other pulses, e.g. peas, lentils, etc.

However, in conditions where it rains almost every day (about one fifth of the world's population live /

live in such conditions) the pulses are more likely to rot than ripen, and here coconuts and green vegetables should be the preeminent protein sources, as these give a greater yield of protein than any other crop extensively grown in those parts. The main problem with coconuts and green leaves is that the protein is accompanied with so much fibre that people cannot eat much. However, rapid progress has been made in developing enzymic and mechanical methods for separating protein from the fibrous mass, and these extraction procedures are simple enough to be feasible as a village industry in such tropical areas. The protein-deficiency problem in the tropics could be partly alleviated if the people realised the importance of growing these protein-rich crops, rather than crops such as tomatoes, for instance. Some knowledge of modern protein separation procedures would also increase the benefit. In short, a massive public information campaign could be mounted in such areas.

At present, cereals supply, and will probably continue to supply, between half and a third of the world's protein. The protein content of maize and other cereals has been increased due to the scientific development of new strains, e.g. a tetraploid oat contains 23-30% protein, and some sorghums contain 18-26% protein. Even if the promise of these discoveries is fulfilled, and protein-enhanced cereals are bred to grow in all parts of the world where cereal growing is traditional, other protein sources will still be needed. For instance, in the wet tropics, cereals, like pulses, do not ripen. Also it is hazardous to become wholly dependent on a single crop, for diseases have a disquietening ability to change their virulence, and people, quite wisely, want variety.

Science has a major role to play now that the protein shortage is known to be the world's most acute nutritional /

nutritional problem not least in increasing the yield and efficiency of protein production from conventional sources. A re-appraisal of world plant-breeding policies is probably overdue, and while advances are now being made in increasing the protein content of cereals, similar research could be started in developing new strains of soya, coconuts, leaf-crops, etc. in which the protein content is both abundant and more easily extracted.

HUMAN PROTEIN REQUIREMENTS AND SOME NOVEL WAYS OF MEETING PROTEIN DEMAND (Information Sheet 4)

At present, our numbers are increasing at a rate which would double the population of the world in thirty years. This rate of increase is unlikely to continue indefinitely, but no confident prediction can be made about the time world population will level off.

With regard to the protein needs of each individual in the world, purely biochemical and physiological considerations should specify how much protein each person needs. Some of the poorer countries in the world contain communities in which protein consumption is only 40 g of usable protein per person per day, whereas in other communities the average is over 100 g. The question arises, "Would the first community fare better on more protein, or the second on less?" Obviously, someone whose body is not getting enough protein to maintain his physical stature will be depleted until such a time when an equilibrium is established at which metabolism is depressed so much that it matches protein intake. If is unfounded, therefore, to assume that if the balance is struck at, say, 40 g of usable protein per day, nutrition is adequate. It has been estimated that, in order to maintain an equilibrium a person requires 0.38 g of usable protein per lb. of body weight. Thus, a 12 stone man requires about 65 g of usable protein per day to maintain his physique, while an 8 stone man requires about 42 g of usable protein per day.

The World Health Organisation has defined health as, "the state of complete physical, mental and social well-being, and not merely the absence of disease or infirmity". The ideal has been stated that "a person is /

is not getting enough protein when well-being is increased by eating more protein". This statement is open to controversy, however, with several sets of conflicting evidence being available.

In the well-fed countries we tend to believe that bigger is better, but we are not necessarily right, although many people, especially Americans, believe that the amount of protein consumed per day should be 100 g (U.S. astronauts get 120 g of usable protein per day). To feed greater numbers of the world's population anything approaching 100 g of protein per day would put tremendous pressures on world resources, and man's ingenuity, as the world protein deficit is already over 20 million tons per year, using the ungenerous estimate that individual needs range from 40 - 52 g of usable protein per day. A further 200 million tons per year would be needed by the end of the century to meet this demand. Thus if we wish to raise the nutritional standard of the world by even a small amount, we not only need to increase our protein potential from conventional sources, which at present is increasing at less than 2% per year, but also we must look for novel ways of increasing the world protein supply.

Novel approaches and their Acceptance by the population

A rough classification of the merits and demerits of some novel protein sources is attempted in Table 7. This table could have been constructed twenty-five years ago, as it was obvious then that there was a protein shortage, and it was likely to worsen. Only now, in fact, is research starting on a serious scale.

It should be recognised that various potential sources of protein are seen as complements rather than alternatives to our traditional protein sources. No single novel source of protein is likely to satisfy the impending need, partly because people like a mixed diet /

diet, and also because people are often slow to accept change.

Of the possible sources of protein listed in Table 7, source (e), protein from the cultivation of micro-organisms is probably the most promising for the future. Such single-cell micro-organisms in the form of yeasts, bacteria, fungi or algae can be cultivated on the products, in part, of past photosynthesis, e.g. fossil fuels and agricultural by-products.

B.P. have been one of the prime movers in this field, and already have plants in France and Grangemouth producing a high protein yeast grown on oil fractions. In its basic state, the yeast is a cream coloured powder consisting of dead cells, and is odourless and tasteless. The powder has a crude protein content of 70%, and a protein usability of 55%. The protein usability is low because the yeast is deficient in an essential amino acid called methionine, but if extra methionine is added, the protein usability rises to 90% which is similar in value to milk and eggs.

Table 7

The ways in which some novel protein sources differ

Novel Source of protein	Especial Merits	Main Limitation
(a) Fish: fresh, and protein made from mixed marine fauna.	Familiarity in principle but the type of fish used and the end product may be novel.	Ultimate probable yield 5% of total requirements. General consumption depends on efficient transport.
(b) Leaves: for direct consumption, or as sources of extracted protein.	Most productive use of arable land in wet tropics. Little need for transport.	The colour is unfamiliar, e.g. slimy green.

(c) /

Table 7 (cont'd)

Novel Source of protein	Especial Merits	Main Limitation
(c) Pulse residues: (e.g. soya, groundnuts, etc.)	The source material already exists, and production could be easily expanded. These form the basis of synthetic high protein "meats".	None, in suitable climates.
(d) Wild animals	By feeding on shoots and leaves as well as grazing they make fuller use of land than domestic animals, and are more resistant to many diseases.	Collection difficult and hygiene uncertain. Ultimate probable yield 5% of total requirement. May have ecological and conservational drawbacks.
(e) Yeasts and other micro-organisms	Use made of under-used agricultural by-products and fossil fuels.	Sophisticated technique required, this limits the centres of production.

Micro-organisms can thrive on many carbon sources; for example, bacteria will assimilate methane, while n-alkanes in the range C_{12} - C_{20} and upwards (gas oil) are readily assimilated by some yeasts. For some reason not yet understood, alkanes in the range C_2 - C_{10} are not readily acceptable by either bacteria or yeasts.

The yeast produced by B.P., which is the first food of this type to be produced industrially, grows and /

and reproduces in an aqueous medium, breathing oxygen from the air, and consuming n-alkanes contained in oil, which supply it with carbon and energy. The yeast is not chemically synthesized but is biosynthesized, i.e. produced by life.

Although such microbial proteins are classified as unconventional or new, it is not really the yeasts or bacteria themselves which are unconventional, but the way in which they are produced. In fact, the growth of micro-organisms has been known since very early times, e.g. yeasts have long been produced in bulk for brewing and baking. Micro-organisms are, therefore, a naturally occurring source of protein, and the production of micro-organisms as food can be considered as micro-farming. The major advantages of micro-organisms as food are:-

1. They are a rich source of protein.
2. The "harvest" can occur all year round, and is not affected by climatic or other natural hazards.
3. The production potential is very high. The present world production of petroleum is sufficient to permit the potential production of 20 million tons per year of petroleum fermentation proteins. In addition, the potential becomes almost limitless if techniques are developed to use limestone, methane or agricultural by-products as the source of carbon, and much research is being done in this area.
4. Micro-organisms have very short growth periods. A freely growing single cell yeast, for example, under optimum conditions, divides at approximately twenty minute intervals, each cell then speedily growing to the size and weight of the parent cell. This advantage is illustrated in the astonishing figures below which indicate the differences in protein yield between a developing young bullock and freely growing yeast.

Yield /

	Yield of new protein per day
Bullock (weighing 10 cwts.)	1 lb.
Yeast (10 cwts.)	50 tons (112,000 lbs.)

5. The production of yeast from oil fractions serves a dual industrial purpose. As well as being a valuable source of protein, the yeast consumes the n-alkanes from an oil fraction which are undesirable in certain petroleum products as they effect the flow of these products. This process is difficult by other means and is called "dewaxing" the oil.

At present, the major disadvantages of microbial proteins are:-

(a) Yeasts and the other micro-organisms can only be produced in industrial centres at present, because of the sophisticated techniques involved in cultivating the micro-organisms, and removing fuel residues from them. The most important area of microbial protein as far as the developing world is concerned is better use of molasses and other existing agricultural by-products on which micro-organisms can be grown. However, the products produced at present do not suffer in transportation and could be carried to more distant parts, although this would involve increased costs.

(b) As this is a very recent field of development, safety tests have only just been successfully completed on the initial products. The products are being solely used as supplements to animal feed at present, hence reducing the benefit to man, although the use of micro-organisms as livestock feed frees other food for human consumption.

Acceptance of new foods by the public

Acceptance by the public could be a major problem in the /

in the production of protein from new sources. Fish and flesh of unfamiliar animals fit easily into accepted culinary patterns, and are likely to prove acceptable if propaganda for them is managed skilfully so that they are given prestige, and not presented as substituents for which there is a regretted necessity.

Acceptability by humans is the reason why industrially produced yeasts are being fed to animals at present and not humans, who are very conservative in their eating habits. There are many cases of people dying of malnutrition because they refused to accept food to which they were unaccustomed. It takes time, technology, education and competent market research to discover what people will accept in the many different areas of the world, and to process and distribute a product to meet their requirements. The yeast produced by B.P. will have to be textured, flavoured, and coloured in many different ways to suit people in different parts of the world, and this calls for much skill, technology, and time. This is the main reason why such foods are used only as livestock feed at present, as these techniques have not yet been fully developed and marketed.

It is by no means easy to texture and flavour products so that they resemble well known and traditional foods, as the texture, aroma, and taste of most natural products result from a very complex mixture of organic compounds. For instance, the aroma of coffee is due to at least 160 different compounds. The major problem with B.P.'s yeast product is texture, as, although flavour and appearance can be made reasonably enticing, the chewy, fibrous nature of meat or chicken has not been reproduced completely successfully.

The oft-quoted official line that, "people will never change their habits" is open to argument when one considers the change in eating habits in Britain over the past century, but the change is a gradual process, and populations have to be encouraged to sample new products.

ECOLOGICAL AND ECONOMIC FACTORS IN PROTEIN PRODUCTION

(Information Sheet 5)

Nutritional experts agree that shortage of protein in human diets is the most important part of the world food problem. Table 8 summarises the world food protein position for both Group 1, the poorer developing countries containing 2,900 million people, and Group 2, the richer countries containing 1,100 million people. Group 1 involves such areas as the Far East (including mainland China), the Near and Middle East, Africa and Latin America), while Group 2 countries include areas such as Europe (including U.S.S.R.), North America and Oceania.

Table 8

World Protein Consumption (as estimated for 1975)

Protein Source	Group 1 countries (poor) (2,900 ml people)	Group 2 countries (rich) (1,100 ml people)	Entire World (4,000 ml people)
Animal			
Meat	10%	20.7%	14.5%
Fish	4%	2.9%	3.5%
Eggs	1.5%	2.4%	2.0%
Milk and Cheese	6%	15.8%	9.8%
Total Animal Protein	21.5%	41.8%	29.8%
Plant			
Fruit and vegetables	4.6%	4.6%	4.6%
Nuts and Pulses (soya, etc.)	20.6%	26.0%	22.3%
Cereals	49.0%	23.3%	39.0%
Starchy foods	4.3%	4.3%	4.3%
Total Plant Protein	78.5%	58.2%	70.2%

Table 8 (cont'd)

Protein Source	Group 1 countries (poor) (2,900 ml people)	Group 2 countries (rich) (1,100 ml people)	Entire World (4,000 ml people)
$\frac{\text{Plant Protein}}{\text{Animal Protein}}$ ratio	3.5	1.4	2.3
Average daily intake per head of protein	58 g	90 g	66.8 g

The average daily intake per head of population in Group 1 and Group 2 countries is 58 g and 90 g respectively. The percentages given in the table are the percentages of specific types of protein consumed in the total diet of people in each group. For instance, an average person in a Group 1 country gets 10% of his 58 grams of protein per day from meat, while an average person in a Group 2 country gets 20.7% of 90 grams of his protein from meat. Thus the average daily protein consumed per head from all animal sources in Group 1 countries is about 12 grams, 58 x (21.5 ÷ 100) , compared to 38 grams in the Group 2 countries.

The Plant Protein/Animal Protein ratio (the P/A ratio) affords a convenient method of comparing the relative contributions of plants and animals to human nutrition. It is seen from Table 8 that, for the whole population, the P/A ratio will be about 2.3 in 1975. Note also that the ratio is much higher for the developing countries than for the richer countries. For individual countries this ratio ranges from 0.39 in North America to 8 in China.

The American meat-centred diet is, in fact, an oddity in the world - a result of agricultural, economic and political factors unique to that country. However, it often appears that the North American strongly meat dependent diet is the target which many other countries /

countries seek to attain. The U.S.A. could, in fact, reduce livestock production by 25% and still provide every American with over 200 g of meat and poultry per day - almost enough in itself to provide each individual's total protein needs without any help at all from other food.

A meat-centred diet is the most resource-expensive of all diets. An American steer consumes over 20 Kg of plant protein to produce only 1 Kg of protein in steak for the plate. Thus to supply each person in the world with a meat diet of North American standard for one year would require the equivalent of one ton of grain per person for livestock feed. To raise this amount of grain requires nearly three times as much agricultural land as is available for the world at present. Thus, in view of the increasing world population, which at the present rate of increase will nearly double in the next thirty years, and increasing living standards, especially in the developing countries, a serious ecological problem is raised.

Table 9 below indicates the weight of plant protein (in Kg.) fed to livestock to produce one Kg of animal protein for human consumption.

Table 9

Type of animal protein	Amount of plant protein fed to livestock to produce 1 Kg of animal protein
Beef steak	21.4 Kg
Pork	8.3 Kg
Chicken	5.5 Kg
Cows' milk	4.4 Kg
Eggs	4.3 Kg

Overall, the average amount of plant protein fed to livestock to produce 1 Kg of animal protein is about 10 Kg. It has been estimated that the rich countries import /

import a net gain of one million tons of plant protein from poorer countries - largely to be used as livestock feed. This situation cannot continue as developing countries begin to demand a more equitable share of economic and political power, and we in the richer countries are now realising how much cattle compete with us for grain.

In North America, 86% of all corn, barley and oats, and over 90% of the non-exported soya crop is fed to livestock. 42% of all wheat as well as large quantities of wheat germ, bran, fishmeal, and milk products are also used as livestock feed. This is done so that the livestock fatten quicker, and hence become profitable. Overall, about half the crops grown in the entire U.S.A. are fed to livestock.

These foods which we are feeding to livestock contain proteins of as high or higher quality than the animals themselves can produce, while only a small fraction are returned to us as edible meat. Accordingly, in a single year, eighteen million tons of protein are lost to human consumption in the U.S.A. alone - an amount which approaches the world protein deficit - the difference between the totalprotein consumed by world population, and that which would be needed to meet minimum requirements for good health.

Another point which deserves mention is the fact that water is becoming an ever-increasing scarcity. Plant foods are less demanding on water supplies than animal foods. It has been estimated that to obtain 1 Kg of meat requires 25 times as much water as 1 Kg of vegetables. A diet in which much of the protein comes from meat could require more than eight times as much water as a diet from which most of the protein comes from plants.

Costs of Animal and Plant Proteins

The greater demands on land, labour, water, fertiliser, /

fertilizer, etc. made by animal foods, are reflected in the higher cost of protein they provide. This is shown in data for the U.K., U.S.A. and India, summarised in Table 10, which shows not the cost of each food but the cost of the <u>protein</u> in the food.

The cheapest protein in the U.S.A. comes from defatted soya, and costs the equivalent of 16 p per pound of protein, (cottonseed and groundnut cake are not eaten in the U.S.A.).

For political, ecological and economic reasons it is unreasonable to assume that one group of countries will make itself permanently responsible for supplying protein to another. This means that the most useful contribution a prosperous country, with an efficient research organisation, can make is to devise means whereby an ill-fed one can produce its own protein. A few countries may be able to exist, as we do in Britain, by importing protein and other foodstuffs, but it is not easy to see what most of the ill-fed parts of the world could expect to pay for their imports with.

<u>Table 10</u> /

Table 10

Cost of proteins eaten in food

(in pence per lb. of crude protein in the food)

FOOD	COST	
	U.S.A. and India (wholesale)	U.K. (retail)
* Cottonseed	13p	
* Groundnut cake	15p	
* Defatted soya	16p	
* Chick peas	25p	
* Wheat flour	28p	68p
* Beans	31p	72p
Skimmed milk powder	33p	
* Dried pulses		89p
Dried fish	34p	90p
* White bread		105p
* Multipurpose food	36p	69p
Herrings		124p
* Oatmeal		124p
Cheese		162p
* Nuts		162p
* Potatoes		162p
Milk		223p
White fish		223p
Pork		232p
Eggs	188p	243p
Beef	138p	296p
Chicken	138p	296p
Mutton		334p
Bacon		334p
Smoked salmon		445p

(* - plant protein)

PROTEINS AS HUMAN FOOD (Group Leader's Guide)

In this exercise it is your task to act as chairman and peace-keeper in the group. In your group of six students, the other five each possess different pieces of information related to different aspects of the subject "Proteins as Human Food" such as protein chemistry, protein requirements of humans, and factors related to the world protein shortage. It is your job to stimulate discussion and to encourage other students to communicate relevant pieces of information so that a complete balanced picture of the combined information is available.

The other students in your group possess sheets containing information on one of the following areas:-

Sheet 1 "Chemistry of Proteins and Amino Acids"

This sheet contains information on what a protein is in chemical terms, and how one is assembled from amino acid units. Information is also given on the manufacturing process and costs involved inproducing a fertiliser (ammonium nitrate) on an industrial scale.

Sheet 2 "Essential Amino Acids and Protein Usability"

Information is contained on the amount of protein in plants which can be effectively used by the human body, and why different proteins are less useful than others because they are deficient in some of the so called "essential" amino acids. Also given is some data on why ammonium nitrate is an important fertiliser, and the current world shortage of fertiliser - possible consequences and partial solutions.

Sheet 3 "Conventional Sources of Protein and their Content"

Some of the common protein-rich food sources are listed. /

listed. The percentage composition of some common types of food is given to indicate what substances are present other than protein. A list of the percentage protein in some common foods is also given, and some ways of increasing supplies from conventional protein sources are suggested.

Sheet 4 "Human Protein Requirements and Some Novel Ways of meeting Protein Demand"

The amount of protein consumed per head per day is considered. Variation occurs in different parts of the world, and the idea of one's metabolism rate being in equilibrium with the amount of protein consumed is discussed. The topic of novel approaches to increasing protein supplies is discussed and examples are given of new techniques of protein production which are being developed, in particular microbial protein. Merits and demerits of these novel approaches are mentioned, as are the problems of making a new product or foodstuff acceptable to a population.

Sheet 5 "Ecological and Economic Factors in Protein Production"

This sheet contains information on how much plant and animal protein is consumed in different parts of the world. The richer countries consume far more meat than the poorer countries, and the consequences and expense of this in terms of land, foodstuffs, and other resources are discussed. (e.g. Over 20 Kg of plant protein is required as feed to produce 1 Kg of steak from an American steer.) Finally, the cost of protein from several different sources is tabulated.

The sheets consist mainly of facts and current opinion with occasionally some suggestions. Neither the opinions nor suggestions need be accepted by the group and are open to criticism and discussion.

Before /

Before you can tackle the problems raised in the subject as a whole, the information contained in each sheet must be made known to the group so that a complete picture of the subject is available. Thus, each member of the group must communicate his or her information to the rest of the group at appropriate points in the discussion.

To assist you to extract relevant pieces of information from the group members, the following questions are a guide to those which you might like to ask, but you are not obliged to use all or indeed any of the questions or statements.

When you feel a balanced, and fairly complete review of the subject has been given, you should discuss general problems and possible solutions arising from them.

Any member of the group may write or draw during the exercise.

Here are some possible questions which you may find useful to encourage group members to communicate their individual information. The numbers in brackets following each question indicate the sheet containing relevant information, although anyone may offer an answer, including yourself. Instruct the group to indicate anything they do not understand during the discussion.

(a) What is the general formula for the units which go to form a protein, and how do these units link up? (1)

(b) How does the body transform protein from food into human protein? (1)

(c) Why are some amino acids regarded as "essential" to humans? (2)

(d) Why are some protein containing foods of less use to the body than others? (2)

(e) Explain how plant foods can complement each other to produce protein of higher quality than either of the individual proteins (2)

(f) Discuss the popular belief that meat is pure protein, or at least contains the highest amount of quality protein of any food. (2) (3)

(g) What are some of the major conventional sources of protein in the world? (3)

(h) What other substances are present in some foods besides crude protein? (3)

(i) How much protein does a person require each day? Discuss this in terms of equilibrium between food intake and body weight. (4)

(j) What is the P/A ratio, and discuss it in terms of the rich and poor countries in the world? (5)

(k) Explain the industrial processes involved in the manufacture of ammonium nitrate fertiliser. Why is care needed when handling this product? (1)

(l) Why is ammonium nitrate such an important fertiliser? (2)

(m) What has been the major factor involved in the increase in the price of ammonium nitrate fertiliser? How seriously and in what ways does this affect the cost of the product? (1)

(n) How will increased price of fertiliser affect the poorer countries in the world, considering the other difficulties involving the amount of fertiliser available? Is there any way in which the fertiliser shortage could be eased in the short term? (2)

(o) How could we increase the world supply of protein from conventional sources? (3)

(p) Discuss the main factors involved in trying to increase protein production from conventional sources (e.g. climate, conditions, etc.) (3)

(q) What novel sources of protein are being developed? (4)

(r) What might be some of the difficulties is getting these new foods accepted by the public, and how might they be overcome? (4)

(s) Discuss the resource-expensiveness of the meat-centred diet, and the problems this raises for the future. (5)

(t) /

(t) How expensive, in terms of cash, are proteins from plant and animal sources? Account for any differences. (5)

(u) Can the rest of the world hope to achieve the United States' standard of protein intake, or is this an unattainable standard of living? (5)

You may ask supplementary questions if you feel some aspect of the topic is unclear. When you feel that your group has a satisfactory idea of the subject as a whole, you should discuss some of the moral and practical problems involved. A few examples of areas you may wish to discuss are given below, but if you want to discuss other topics you are free to do so. Try to involve all the group in the discussion.

(i) With the current economic crises in the West, should we continue to help the underdeveloped countries, or concentrate on helping ourselves? Does it benefit Britain (either directly or indirectly) to hand out foreign aid to the poorer countries? Would you expect the rich oil producing countries in the Middle East to contribute more to the cause of the under-privileged?

(ii) Why not leave things as they are in the poor countries? If people are kept alive in these countries, the populations of these countries will grow and cause an even greater world food shortage.

(iii) Should we spend less on feeding the underdeveloped countries, and more in educating them in contraception?

(iv) As scientists, what do you think would be the most profitable way to spend available money on research into increasing the world's protein supply in view of increasing world population?

The form /

The form of the discussion is in no way rigid, and you are free to follow up and discuss points or arguments which either you, or another member of the group, has raised.

The entire exercise should take about $1\frac{1}{2}$ - 2 hours to complete. Allow the group about twenty minutes at the start to become thoroughly familiar with their information, so that they become experts in their designated area of the topic. It is your job to pace the exercise so that it is completed neither too early or too late.

PROTEIN EXERCISE ASSESSMENT

The questions below are designed to help us assess the value of discussion exercises in Science Education. There is no need to put your name on this sheet and your answers to these questions will not be held against you.

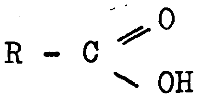
Tick the appropriate box for each question, and tick only one box per question.

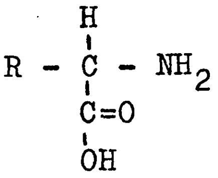
Please answer the questions as correctly and/or HONESTLY as you can.

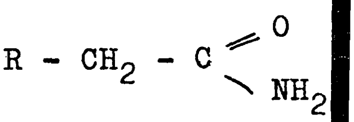
(i) Objective items (used in pre- and post-test)

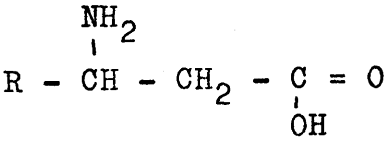
Question 1

(a) What is the correct general formula for an α-amino acid?

(A)

$\mathrm{R-C(=O)-OH}$

(B)

$\mathrm{R-\overset{\displaystyle H}{\underset{\displaystyle C(=O)OH}{C}}-NH_2}$

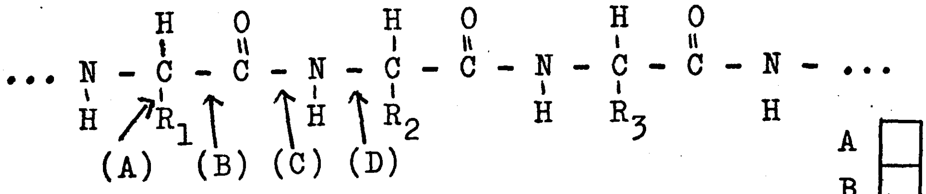
(C)

$\mathrm{R-CH_2-C(=O)-NH_2}$

(D)

$\mathrm{R-\overset{NH_2}{CH}-CH_2-\underset{OH}{C}=O}$

(E) Don't know

A ☐
B ☐
C ☐
D ☐
E ☐

(b) In the portion of the protein molecule shown below, which bond is the peptide link?



(E) Don't know

A ☐
B ☐
C ☐
D ☐
E ☐

(c) /

(c) Why are some amino acids called "essential"?

(A) Because they are the only amino acids which can be used to form protein
(B) Because they occur much less commonly than other amino acids
(C) Because they are a necessary addition to plant fertilisers
(D) Because the human body cannot synthesize them, and, therefore, they have to be supplied directly in the diet
(E) Don't know

A	
B	
C	
D	
E	

(ii) <u>Likert-type statements</u> (used in pre- and post-test)

<u>Question 2</u>

For each of the following statements, indicate in the box provided the response which most accurately represents your own personal position or opinion. (Be honest!)

	Strongly agree	Agree	Don't know/Undecided	Disagree	Strongly disagree
(a) I am familiar with most of the reasons contributing to the worldwide shortage of protein at the present time.					
(b) Given a set of figures in tabulated form, I could recognise general trends as well as extract specific information from the figures.					
(c) If I knew a piece of information which was of relevance to a class discussion, I would be eager and willing to communicate verbally the information to the rest of the class.					

(d) /

	Strongly agree	Agree	Don't know/Undecided	Disagree	Strongly disagree
(d) I have confidence in my ability to argue a point in a logical and scientific fashion during a general class discussion.					
(e) The thought of giving a short talk on an aspect of science to other students makes me feel very uncomfortable.					
(f) Good teamwork can be of great value in scientific discovery.					
(g) In matters of conflicting interest, I usually arrive at a suitable compromise.					
(h) Science subjects such as physics, chemistry, biology, astronomy are almost complete units within themselves and have very few interconnections.					
(i) Science subjects have little or no connection with non-science subjects such as economics, politics, geography, moral philosophy, etc.					
(j) There is no problem in the world today that cannot be solved by science.					

(iii) <u>Objective rating grid</u> (used in post-test only)

<u>Question 3</u>

At the start of this exercise you were given a list of fifteen objectives. Would you please indicate

(by /

(by means of a tick in the appropriate box) how successful or otherwise, in your opinion, the exercise has been in achieving each objective.

	Dismal Failure	Not very successful	Average	Fairly successful	Very successful
Objective 1					
Objective 2					
Objective 3					
Objective 4					
Objective 5					
Objective 6					
Objective 7					
Objective 8					
Objective 9					
Objective 10					
Objective 11					
Objective 12					
Objective 13					
Objective 14					
Objective 15					

(iv) /

(iv) Semantic differential-type questions (used in post-test only)

Question 4

(a) In view of the objectives of the exercise, do you think that the time spent on "Proteins as Human Food" has been -

- (A) Extremely valuable ☐
- (B) Fairly valuable ☐
- (C) Undecided ☐
- (D) Not valuable ☐
- (E) A complete waste of time ☐

(b) As a result of the "Protein" exercise has your awareness and interest in the problem of world protein shortage -

- (A) Increased dramatically ☐
- (B) Increased slightly ☐
- (C) Neither increased nor decreased ☐
- (D) Decreased slightly ☐
- (E) Decreased dramatically ☐

(c) How enjoyable did you find the exercise?

- (A) Very enjoyable ☐
- (B) Quite enjoyable ☐
- (C) Average ☐
- (D) Unenjoyable ☐
- (E) Very unenjoyable ☐

(d) Do you think that the exercise benefitted your overall education in chemistry?

- (A) Yes, definitely ☐
- (B) Yes ☐
- (C) Don't know ☐
- (D) No ☐
- (E) No, definitely ☐

Do you have any other comments, critical or otherwise, of your experience of the "Proteins" exercise?

CHAPTER 6

'POLYWATER' - A CASE HISTORY

CHAPTER 6

'POLYWATER' - A CASE HISTORY

6.1 The Need for a Library/Discussion Exercise

Little is done in many tertiary chemistry courses to develop library skills as defined on p. 41. Certainly most students are given little practice in library use in the first two years of an undergraduate chemistry course, while use of library facilities in the third and fourth years is often confined to reading review articles to complement lecture notes, and to consultations of standard references such as Beilstein. Skills in reading and precising scientific papers, in discussing the relative merits of conflicting evidence from various sources, and in discriminating between hard facts and mere speculation or opinion are often not consciously taught in many courses. Such skills may be instrumental in developing in students a healthy scepticism towards the written word instead of the blind acceptance of much of the scientific literature on the grounds that it has been published in a reputable journal or written by an eminent scientist.

In an attempt to develop these skills and attitudes it was decided to mount an exercise in which the main objectives concerned the development of library and discussion skills through the medium of the chemical literature. It was also hoped that the exercise would enable students to follow the development of an actual piece of chemical research.

6.2 Previous Styles of Library Exercises

Exercises or courses in library skills have recently been reported in several forms.

Some courses, such as that produced by Southampton University,(105) rely on a tape/slide presentation to train /

train students in the use of Chemical Abstracts. de Winter Hebron(106) has also used audio visual techniques to teach students skills in precising literature extracts. Broader courses in skills in handling chemical literature have been described by Jones(107) and Steedman.(108) Jones, whose work was done at Keele, recognised the need for developing library skills in undergraduates and organised a course involving seminars and literature searches, while Steedman, at Heriot Watt University, combined lectures in the structure of chemical literature with library searches, essays and projects. Both authors stated a major disadvantage of the courses was that they were very time consuming to construct and administer. Parker(109) noted a similar complaint in devising a course to give students increased exposure to chemical literature. Crombie,(110) however, in a course on the chemical literature at Huddersfield Polytechnic claims to have avoided the problem by using a combination of lectures, seminars and handouts in conjunction with small retrieval projects based on organic problems. Bartsch(111) has described a comprehensive course on chemical literature using lectures, seminars and prescribed texts to teach the history of chemical literature, to review some of the modern sources of chemical information, to introduce Chemical Abstracts, Science Citation Indices, and Beilstein, and to trace the steps involved in publishing a paper. The course is concluded by an individual library assignment.

Youmans(62) has used less formal methods to develop literature and communication skills. The method involves students reading an assigned paper from a journal, presenting a critical account in a small group seminar and writing a 500-word summary of the paper. The lecturer is present only as an adviser and arbiter. It is claimed that students gain in factual knowledge, critical thinking and communication skills, although no assessment is given.

Epstein /

Epstein(63) has described a similar method in which research papers were issued to students who were then encouraged to question the research and to suggest possible further stages in the enquiry, i.e. they were put in the role of the researcher. The lecturer could use the material to point out parts of the research where standard course work was relevant. The aim of the course was to illustrate to students ways in which scientists think and how some research projects have proceeded. Harben(112) has also used an historical approach at school level to illustrate the work of famous chemists, the development of important chemicals and the development of well-known concepts.

6.3 Design of the Exercise

It was not the aim of the exercise to train students in the formal structure of the chemical library, but it was hoped to develop the broader library skills similar to those described by Youmans.(62)

A case history format was adopted so that students could follow through research on a single topic in order to gain insight into the direction and pitfalls of an actual research programme as well as observing the 'scientific method' at work.

It was decided that the exercise should not be used to teach cognitive content, but that students would have to draw on previously gained cognitive skills to interpret spectra and analyse data.

The topic

The phenomenon of 'polywater' which aroused much interest from the mid-sixties to the early seventies was taken as the subject matter of the exercise. Reasons for this choice of topic included:-

(a) Many scientific papers (over 550) were written on the subject so that moderately large numbers could participate simultaneously in the exercise.

(b) /

(b) The papers were written in many different styles which were categorised as -

  (i) informal science articles and letters;
  (ii) experimental research;
  (iii) theoretical research.

(c) The subject matter would be new to most students, and concerned the possibility of making a polymeric form of water - the most important substance on earth. Hence it was hoped that student interest and motivation would be high.

(d) The papers on the topic were published in journals of chemistry (all branches), physics, biochemistry, geology and astronomy as well as in general science journals, and it was hoped that students would appreciate the existence of interconnections across science subject barriers, as a result of the exercise.

(e) Many aspects of the research were controversial and could form the basis of discussion.

(f) Some of the research work was of dubious quality, and claims were sometimes made on the basis of inadequate evidence or inaccurate work. It was hoped this feature of the research would develop a degree of scepticism towards scientific literature.

The library/discussion exercise on 'Polywater' included the following objectives:-

<u>'Polywater' objectives</u>

On completion of the case history, the student should be able:-

1) to locate a given reference in the library;
2) to read a scientific paper efficiently and discerningly;
3) to summarise a scientific paper efficiently in written and verbal form;
4) to discriminate between fact and opinion;
5) /

5) to realise that the scientific literature can sometimes be misleading;
6) to spot key facts among less relevant data;
7) to see flaws in arguments and hypotheses;
8) to communicate fluently and grammatically;
9) to teach others in public;
10) to argue logically;
11) to co-operate in discovery;
12) to realise the need for precision in analytical work;
13) to realise the hazards of lack of thoroughness (or honesty) in scientific research;
14) to apply a precise, scientific approach to problems;
15) to appreciate how the 'scientific method' can solve a chemical problem;
16) to realise the existence of interconnections across subjects barriers;
17) to appreciate the value of historical lessons in science.

The nature of the subject was so advanced that the exercise was directed at senior (i.e. third and fourth year) undergraduate level. Less advanced students would not have possessed the cognitive skills to deal with many of the papers involved in the exercise. In addition, organisational difficulties would have arisen if large numbers were involved in the exercise.

The strategy

It was decided to involve groups of six to eight students working together on the problem. At the start of the exercise each of the students was issued with a list of objectives, a sheet entitled, "Introduction to the 'Polywater' Case History" (appended on p.280) and a list of journals referred to in the study together with their location(s) in the University (appended on p. 284). The introductory sheet gave information on both the topic and the nature of the exercise. Individual students were then given the references /

references to one or two papers (depending on the papers' length) and sent to the library to find these, precis them, and when the group re-assembled 30 to 40 minutes later each student presented his/her findings orally to the group. Following the presentation of papers, a group discussion ensued to discuss the research findings, including ambiguities, and to suggest further lines of enquiry. The first set of papers came from the early years of the research (1966-1969) and showed the idea of 'polywater' on the ascendancy.

Another set of references was then given to the students and the search resumed, and the reporting and discussion repeated. Papers from the year 1970 were chosen, some of which threw doubt on the phenomenon.

A final set of references from the period 1971-1973 enabled students to discredit the 'polywater' theory for themselves.

The librarian co-operated in the exercise to help students who experienced difficulty with the library system.

The tutor's role in the exercise was that of chairman, timekeeper and arbiter. The tutor was issued with an abstracted version of every paper used in the exercise so that he could ensure that students did not digress too far from the point of each paper. The "Tutors' Guide to the 'Polywater' Exercise" is appended on p. 286 .

Organisation of the exercise

The strategy given above would require about 4½ hours to complete, as each 'cycle' of searching, reading, precising, reporting and discussion takes at least 1½ hours. The organisation is dependent on the time available, the number of students involved, and the availability of certain journals. The organisation is best /

best explained by referral to "Notes for the Organisation of the 'Polywater' exercise" which is in the appendix on p. 289.

A list containing 115 of the references which could be used in the study is also given in the appendix, on p. 298.

Towards the end of the organisational notes, a possible set of references is given for a single group of eight students when only three hours, and hence two cycles are possible. Tutors' abstracts of each of the papers involved are given in the appendix, starting on p. 309.

6.4 Assessment of the Material

It will be seen from the list of objectives (p. 260-261) that the desired outcomes of the exercise were not of a simple cognitive nature but involved various skills in library use, skills in oral presentation and discussion, and the development of attitudes including a healthy scepticism towards the written word. The exercise was also intended to illustrate to students the manner in which an actual research enquiry unfurled chronologically.

Early trials of the material with a group of senior undergraduates indicated that the exercise could be organised and run in a satisfactory manner. The trial session lasted three hours, and it became clear that strict timetabling was necessary to complete the exercise in that time.

As with the protein exercise, it was recognised that a single library/discussion exercise could not fully achieve all the objectives of the study, so the assessment procedures used often attempted to identify increased confidence in the skills involved, rather than total attainment.

A similar /

A similar assessment style to the protein exercise was adopted for the 'Polywater' exercise in that two general procedures were used.

(a) A written assessment involving the following four techniques:-

- (i) A situational technique was used which involved giving students an extract from a paper and asking them to summarise it, to pick out important points and reject less relevant data, and to give an opinion as to the merits and importance of the content. (See p. 339)
- (ii) Likert-type statements were used to assess changes in confidence and attitudes as a result of the exercise. A five point scale was used, and the statements were closely related to the objectives of the study. (See p. 340)
- (iii) A semantic differential technique was used to measure student opinions on the scientific literature and the 'Polywater' case history. (See p. 341)
- (iv) An objective rating grid allowed students to indicate the degree of success achieved by the case history in achieving certain objectives of the exercise. (See p. 342)

Space was provided on the assessment sheets to enable students to make critical comments.

(b) An analysis of tape recordings of the proceedings in two of the groups who participated was done. The procedure was similar to that used in the analysis of the protein exercise.

Details of the sample

A group of six third year undergraduates and four groups of fourth year undergraduates (two groups of seven students and two groups of eight students) from Glasgow University participated in further trials of the material.

As free /

As free time is at a premium for senior undergraduates, the third year group was made up of volunteers, but the fourth year groups involved used a three-hour slot made available in the course of their timetable, and hence constituted a more representative sample than obtained in a group of volunteers.

Due to the small class sizes involved it was impossible to assess changes by comparison with an identical control group. Responses of the fourth year class to the situational and Likert-type assessment techniques were compared to responses of the third year class who did not receive the exercise. The comparison is by no means ideal or indeed particularly meaningful but was done in the absence of other alternatives. Although the third year responses to the assessment questions are given, it is not intended to use them in a direct comparison with fourth year responses.

The group of six third year students who participated in the exercise did not attempt the situational problem, but completed the Likert-type assessment in both pre- and post-test form.

A summary of the number of students who completed various parts of the assessment is given in Table 6-1.

	'Polywater'			No 'Polywater'
	3rd Year (n=6)		4th Year (n=30)	3rd Year (n=38)
	Pre	Post	One Test Only	One Test Only
(i) Situational technique (Q.1)	-	-	15	18
(ii) Likert-type statements (Q.2)	6	6	21	34
(iii) Semantic (Q.3)	-	-	21	34
differential technique (Q.4)	-	6	21	-
(iv) Objective Rating (Q.5)	-	6	21	-

Table 6-1 Numbers of students completing individual parts of the assessment

It will be seen that some students failed to return various parts of the assessment procedure, in particular the situational problem. Retrieval of all assessment sheets was made particularly difficult due to the proximity of university holidays.

Results of assessment

(a) Written assessment

(i) Situational technique (p. 339) The method was used in the assessment more to gain insight into its potential as an assessment tool in simulation exercises than to throw much light on the effectiveness of the study, as lack of sufficient numbers and adequate control groups made this impossible.

The questions posed at the end of the extract were scored as follows:-

Part (a) The three essential points were -

(i) a trend towards greater complexity;
(ii) the new emphasis of Linnett;
(iii) the successes of his approach.

\- 1 mark was awarded for each identified point.

Part (b) Linnett's approach lays much emphasis on an electron's "preference" not to pair
\- 1 mark.

Part (c) More information is required
\- 1 mark.

Part (d) was not marked but was included for interest.

The average scores for Parts (a), (b) and (c) are given in Table 6-2.

	'Polywater' Students	Non 'Polywater' Students
Section	4th Year (n = 15)	3rd Year (n = 18)
Part (a) (out of 3)	2.13	1.77
Part (b) (out of 1)	0.67	0.67
Part (c) (out of 1)	0.53	0.33

Table 6-2 Average scores in Parts (a), (b) and (c) of situational problem for fourth year 'Polywater' students and third year non 'Polywater' students.

From the above results, little can be said about the effectiveness of the 'Polywater' exercise due to the unmatched 'control' group. However, in answering Part (c) several students who had completed the 'Polywater' exercise seemed sceptical of Linnett's theory on the grounds that he had been wrong about 'polywater'. It could be that the exercise made some students over-sceptical of the scientific literature.

The situational technique would appear to be an effective assessment tool for simulation exercises only when large enough numbers enable fair control groups to be possible. A problem with the method appears to be that students seem less willing to complete situational assessment problems compared to other types of assessment techniques (see Table 6-1). This may be due to their time-consuming nature.

(ii) Likert-type statements (p. 340) Objectives 1, 5, 9, 10, 12, 16 and 17 were assessed by means of Likert-type statements which were designed to measure students' confidence in their communication and library skills and their attitude towards certain aspects of chemistry such as the value of analytical work, the interconnections between science subjects, and the use of /

of historical experience in scientific research.

The six third year students who completed the exercise responded to the statements before and after the exercise, while the fourth year students responded only after completion of the exercise.

The pre-/post-test responses for the third year students are given in Table 6-3, with post-test figures given in brackets below pre-test figures.

		Strongly Agree	Agree	Don't Know/ Undecided	Disagree	Strongly Disagree
Library skills	Statement (a) (objective 1)	2 (4)	2 (2)	2 (0)	0 (0)	0 (0)
	Statement (b) (objective 5)	0 (0)	2 (0)	1 (0)	2 (4)	1 (2)
Confidence in communication skills	Statement (c) (objective 9)	2 (0)	1 (2)	1 (1)	1 (3)	1 (0)
	Statement (d) (objective 10)	1 (0)	3 (3)	1 (2)	0 (1)	0 (0)
Value of accuracy	Statement (e) (objective 12)	4 (6)	2 (0)	0 (0)	0 (0)	0 (0)
Subject Interconnections	Statement (f) (objective 16)	0 (0)	1 (1)	0 (0)	2 (0)	3 (5)
Use of historical lessons	Statement (g) (objective 17)	4 (5)	1 (1)	1 (o)	0 (o)	0 (o)

Table 6-3 Responses to Likert-type Statements for third year group (n = 6)

The changes in degrees of agreement/disagreement between pre- and post-test are summarized in Table 6-4 for each statement.

		Unchanged	More agreement		More disagreement	
			By one point on scale	By two points on scale	By one point on scale	By two points on scale
Library skills	Statement (a) (objective 1)	3	2	1	-	-
	Statement (b) (objective 5)	3	-	-	-	3
Confidence in communication skills	Statement (c) (objective 9)	2	1	-	2	1
	Statement (d) (objective 10)	3	-	1	1	1
Value of accuracy	Statement (e) (objective 12)	4	2	-	-	-
Subject interconnections	Statement (f) (objective 16)	4	-	-	2	-
Use of historical lessons	Statement (g) (objective 17)	4	2	-	-	-

Table 6-4 Agreement/Disagreement Trends for Likert-type Statements

With only six students completing pre- and post-tests no firm conclusions can be drawn from Tables 6-3 and 6-4, although it is interesting that some individuals appear less confident in their communication and discussion ability after completing the exercise, (statements (c) and (d)), although the effect may be due to the student appreciating his/her limitations through the exercise.

The responses to the Likert-type statements for the fourth year students (n = 21) and the third year 'control' group (n = 34) are given in Table 6-5. (Third year figures are given in brackets below fourth year figures.)

		Strongly Agree	Agree	Don't Know/ Undecided	Disagree	Strongly Disagree
Library skills	Statement (a) (objective 1)	14 (7)	7 (18)	0 (8)	0 (1)	0 (0)
	Statement (b) (objective 5)	0 (3)	3 (9)	1 (7)	11 (14)	6 (1)
Confidence in communication skills	Statement (c) (objective 9)	3 (8)	3 (14)	3 (4)	10 (7)	2 (1)
	Statement (d) (objective 10)	1 (4)	10 (12)	7 (9)	3 (5)	0 (4)
Value of accuracy	Statement (e) (objective 12)	16 (18)	5 (14)	0 (1)	0 (1)	0 (0)
Subject interconnections	Statement (f) (objective 16)	0 (0)	0 (1)	0 (0)	3 (7)	18 (26)
Use of historical lessons	Statement (g) (objective 17)	15 (19)	5 (8)	0 (5)	1 (2)	0 (0)

<u>Table 6-5</u> <u>Response to Likert-type Statements for fourth year 'Polywater' Students (n=21) and third year Non 'Polywater' Students (n=34)</u>

Previous arguments about unmatched samples prevent any direct comparison, although it does appear that attitudes and confidence in communication and library skills differ between the third and fourth year students. How much the increased confidence and different /

different attitudes of the fourth year students is due to the 'Polywater' exercise, which they had just completed, is unknown, although information on this point could be obtained by issuing the assessment sheet to the third year 'control' group one year later.

(iii) Semantic differential techniques (p. 341) Two types of assessment using this technique were used to measure (a) attitudes to the scientific literature (Question 3), and (b) attitudes to the 'Polywater' exercise (Question 4).

Table 6-6 summarizes the responses to Question 3 for the fourth year group of 'Polywater' students and the third year group who did not attempt the exercise. (Figures for third year students (n=34) are given in brackets below the figures for fourth year students (n=21).

Straightforward	0 (0)	7 (7)	11 (23)	3 (4)	0 (0)	Misleading
Easy to understand	0 (0)	4 (13)	13 (26)	4 (3)	0 (2)	Difficult to understand
Dull	3 (4)	4 (6)	6 (3)	8 (21)	0 (0)	Interesting
Clear	0 (0)	7 (13)	9 (10)	4 (7)	1 (4)	Confusing
Inaccurate	0 (0)	0 (0)	13 (10)	8 (18)	0 (6)	Accurate
Not able to correct previous error	1 (2)	2 (7)	6 (4)	10 (18)	2 (3)	Able to correct previous error

Table 6-6 Attitudes of students to the Scientific Literature

Again little weight can be laid on these results due to the differences in the two samples. If this method were to be used when more matchable samples are available, it is recommended that the 'neutral' option be removed by the adoption of either a four or six point scale.

Students' /

Students' attitudes to the 'Polywater' exercise as measured by Question 4 are summarized in Table 6-7, with third year figures (n=6) given in brackets below fourth year figures (n=21).

Valuable	2 (1)	10 (5)	8 (0)	1 (0)	0 (0)	A waste of time
Boring	0 (0)	2 (0)	4 (1)	8 (2)	7 (3)	Interesting
Relevant to my education in chemistry	4 (4)	9 (1)	6 (1)	1 (0)	1 (0)	Irrelevant to my education in chemistry
Enjoyable	2 (3)	8 (3)	5 (0)	5 (0)	1 (0)	Dull
Taught me new skills	2 (3)	7 (2)	6 (1)	4 (0)	2 (0)	Failed to teach me new skills

Table 6-7 Students' attitudes to the 'Polywater' Exercise for fourth year Students (n=21) and third year Students (n=6)

It would appear that the general opinion of the exercise was favourable. The third year students reacted more favourably than the fourth year students. This can possibly be traced to the fact that the third year group volunteered to participate in the exercise. If the assessment were to be repeated a four or six point scale again might prove superior.

(iv) Objective Rating (p. 342) Some of the objectives of the exercise not directly assessed by other methods were rated by the students on their degree of achievement.

The results are summarized in Table 6-8 with third year figures (n=6) given in brackets below fourth year figures (n=21).

	Very successful	Fairly successful	Average	Not very successful	Dismal Failure
(a) Objective 8	1 (0)	8 (4)	6 (2)	5 (0)	1 (0)
(b) Objective 13	14 (6)	4 (0)	2 (0)	1 (0)	0 (0)
(c) Objective 4	5 (3)	12 (2)	2 (0)	2 (1)	0 (0)
(d) Objective 6	5 (2)	9 (4)	4 (0)	3 (0)	0 (0)
(e) Objective 7	3 (2)	10 (2)	4 (1)	3 (1)	1 (0)
(f) Objective 3	5 (3)	10 (2)	5 (1)	1 (0)	0 (0)

Table 6-8 Objective Rating Grid Responses for fourth year students (n=21) and third year students (n=6)

Objective 13 (to realise the hazards of lack of thoroughness in scientific research) appears to have been exceptionally well achieved by the exercise, while the objective seen to be least well achieved of the six is objective 8 on communication ability. The remaining objectives were considered by the students to be achieved moderately well.

Student comments

Those /

Those students who commented on the assessment sheets (about half of the students) made constructive comments on differing points. The biggest single complaint was that students were too rushed during the three-hour session and that more time should be allocated to the exercise - some suggested it should be run over an entire day. (This was also the opinion of the group tutors who participated in the exercise.)

Several students commented on the value of the exercise and indicated that the method was preferable to the lecture/laboratory situation for achieving the objectives in question.

Conclusion

Lack of numbers in senior honours classes, and lack of adequate control groups make valid assessment of exercises such as 'Polywater' even more difficult than usual. The assessment procedures and results mentioned above are, therefore, far from perfect, but do indicate that the 'Polywater' exercise may be achieving, if only partially, many of its objectives, although further and more controlled testing is required. Trials of the exercise have shown that the exercise is popular with students and workable with several groups of undergraduates working simultaneously.

(b) Analysis of Tape Recordings

The proceedings in two of the groups (a third year group of six students (Group A) and a fourth year group of eight students (Group B)) were recorded on tape so that the patterns of communication during the reporting and discussion stages of the 'Polywater' exercise could be analysed.

The procedure was similar to that used in analysing the recordings of 'Proteins as Human Food'. ("Communication" included not only verbal communication, but also included time spent drawing on the blackboard.)

The analysis /

The analysis for Group A and Group B are given in Tables 6-9 and 6-10 respectively. The general pattern of communication within the group appears to be different from the protein discussion exercise. The analyses indicate the pattern of individual students giving summarized accounts of the paper(s) they had read, and at the end of each session, the general discussion involving the students and the tutor is evident. Little discussion, however, took place during the summarized accounts apart from tutor intervention.

The sessions were largely student dominated, with the tutor contributing no more to the overall exercise than the average individual student. As with the 'protein' exercise, the 'Polywater' exercise, through its design, involved each student in making a positive and significant contribution to the exercise, as is confirmed by the overall percentage times for which each student was actively involved in communicating information or discussion.

TABLE 6-9

Analysis of Communication in 'Polywater' Exercise

Group A (6 students)

	FIRST SESSION														SECOND SESSION										OVERALL TOTAL	
	1 – 10		11 – 20		21 – 30		31 – 40		41 – 50		51 – 58		Total		1 – 10		11 – 20		21 – 30		31 – 40		Total			
Tutor	105	17.5	69	11.5	98	16.3	122	20.3	57	9.5	143	29.8	594	17.1	56	9.3	73	12.2	49	8.2	120	20	298	12.4	892	15.2
Student(a)	306	51	3	0.5	16	2.7	0	0	43	7.2	49	10.2	417	12	0	0	11	1.8	268	44.7	138	23	417	17.4	834	14.2
Student(b)	165	27.5	452	75.3	2	0.3	0	0	7	1.2	65	13.5	691	19.9	1	0.2	133	22.2	227	37.8	45	7.5	406	16.9	1097	18.7
Student(c)	4	0.7	70	11.7	256	42.7	0	0	4	0.7	78	16.3	412	11.8	5	0.8	330	55	31	5.2	98	16.3	464	19.3	876	14.9
Student(d)	12	2	3	0.5	224	37.3	47	7.8	7	1.2	65	13.5	358	10.3	192	32	33	5.5	0	0	43	7.2	268	11.2	626	10.6
Student(e)	4	0.7	3	0.5	2	0.3	391	65.2	4	0.7	27	5.6	431	12.4	180	30	11	1.8	25	4.2	62	10.3	278	11.6	709	12.1
Student(f)	4	0.7	0	0	2	0.3	40	6.7	478	79.7	53	11	577	16.6	166	27.7	9	1.5	0	0	94	15.7	269	11.2	846	14.4

KEY

Time spent Communicating (secs) → ☐☐ ← % time spent Communicating

TABLE 6·10

Analysis of Communication in 'Polywater' Exercise

Group B (8 students)

	FIRST SESSION												SECOND SESSION												OVERALL TOTAL	
	1 – 10		11 – 20		21 – 30		31 – 40		41 – 49		Total		1 – 10		11 – 20		21 – 30		31 – 40		41 – 44		Total			
Tutor	84	14	52	8·7	17	2·8	45	7·5	108	20	306	10·4	32	5·3	21	3·5	22	3·7	107	17·8	52	21·7	234	8·9	540	9·7
Student(a)	342	57	12	2	6	1	0	0	66	12·2	426	14·5	246	41	10	1·7	8	1·3	16	2·7	47	19·6	327	12·4	753	13·5
Student(b)	174	29	131	21·8	30	5	0	0	38	7	373	12·7	265	44·2	0	0	2	0·3	38	6·3	28	11·7	333	12·6	706	12·7
Student(c)	0	0	298	47·7	6	1	0	0	12	2·2	316	10·7	43	7·2	207	34·5	0	0	3	0·5	17	7·1	270	10·2	586	10·5
Student(d)	0	0	90	15	162	27	7	1·2	45	8·3	304	10·3	0	0	270	45	0	0	18	3	4	1·7	292	11·1	596	10·7
Student(e)	0	0	0	0	307	51·2	3	0·5	81	15	391	13·3	0	0	92	15·3	118	19·7	26	4·3	15	6·3	251	9·5	642	11·5
Student(f)	0	0	7	1·2	54	9	221	36·8	12	2·2	294	10	10	1·7	0	0	236	39·3	24	4	6	2·5	276	10·5	570	10·2
Student(g)	0	0	0	0	14	2·3	229	38·2	52	9·6	295	10	0	0	0	0	211	35·2	70	11·7	42	17·5	323	12·2	618	11·1
Student(h)	0	0	10	1·7	4	0·7	95	15·8	126	23	238	8	4	0·7	0	0	3	0·5	298	49·7	29	12·1	334	12·7	569	10·2

KEY

Time spent Communicating (secs) → ☐☐ ← % time spent Communicating

APPENDIX TO CHAPTER 6

STUDENTS' INTRODUCTION TO THE 'POLYWATER' CASE HISTORY

> '"Now suppose", chortled Dr. Breed, enjoying himself, "that there were many possible ways in which water could freeze. Suppose that the sort of ice we skate upon and put into highballs - what we call ice-1 - is only one of several types of ice .... And suppose, that there was one form, which we will call ice-9 - a crystal as hard as this desk - with a melting point of, let us say one hundred degrees Fahrenheit, or better still, a melting point of one hundred and thirty degrees"'
>
> From "Cat's Cradle" by Kurt Vonnegut

A substance even stranger than that mentioned in Vonnegut's 1963 science fiction novel has, until quite recently, been the subject of a serious and important international research effort.

The research was initially started in Russia in 1961, but the phenomenon did not come to the notice of Western scientists until 1966 following a series of papers by a Russian chemist named Boris V. Deryagin (elsewhere spelled Derjuaguin or Deryaguin) which described extraordinary and totally unexpected properties of water which had been condensed in pyrex or quartz capillaries.

This previously unidentified form of water attracted several names in the scientific literature including anomalous water, orthowater, polywater, water II, superwater, cyclimetric water, water $\underline{X}$, polymeric water and superdense water, and soon became extensively studied by scientists throughout the world. The main reason for the interest was the extreme importance to mankind should a new allotrope of water, the world's most abundant and /

and most vigorously studied compound, exist. The extremely simple and inexpensive apparatus involved in the production of polywater was also responsible, to some extent, for the scale of interest.

Design of the Case History

Between the years 1966 and 1973, over five hundred scientific papers were published on the polywater phenomenon. This case history involves a roughly chronological study of some of these papers which are available in this University, with the aim that it should be possible to trace some of the avenues which the original research followed.

The research into polywater represented a sharp contrast with most physical science problems, as the largest share of published material was outside the scientific journals. It is probable that this fact alone caused great uneasiness amongst scientists, and headlines in the national press such as "Scientists growing wet, creepy water" and "Polywater threatening life on earth" unquestionably coloured some scientists' attitudes towards the polywater problem. However, the polywater phenomenon concerned the single substance (water) which is of most concern to every person on earth, and therefore there can be little surprise at the extensive press coverage in the public and popular science media.

The above reason also explains the range of scientific journals which published papers on polywater. As well as all types of chemistry journals and general science journals, papers on the subject appeared in physics journals, geology journals, biology journals, biochemistry journals, astronomy journals, and science education journals. This highlights the importance of the phenomenon over the whole range of science subjects.

For the purposes of this study, only papers or articles /

articles from scientific journals have been selected, and these have been divided into three general categories.

Type (a) articles are a selection of informal reports and letters from general science magazines such as New Scientist, Scientific American etc., and reflect opinions and summaries of recent research rather than reporting directly on original work.
Type (b) articles consist of original papers reporting on experimental work on polywater.
Type (c) papers represent some of theoretical research published on possible structures and stability of polywater.

A total of one hundred and fifteen references have been compiled and are listed under the headings (a), (b) or (c) and the relevant year of publication.

The case study was produced to help develop some of the skills which are expected of a chemistry graduate, although little is done to teach these skills in a conventional lecture/laboratory situation.

It is hoped that the exercise will enhance (a) communication skills, (b) skill in handling the scientific literature, (c) discussion skills, (d) library skills, and (e) skill in co-operation. A more detailed list of objectives is attached to this guide.

For the purposes of this exercise, the class will be divided into groups of eight students. Each member of the group will be issued initially with an individual reference or set of references, as well as information on where to find them. Each student will then find his reference(s), read it, summarise it and report back to the group on the important points in the paper(s). Each student will be expected to talk to the rest of the group for about five minutes on his designated paper(s), emphasizing their value to polywater research as a whole. Theoretical and technical details are less important than results, conclusions and postulated explanations. Care should be taken too, however, to

emphasize /

emphasize whether or not conclusions or hypotheses are based on hard facts or merely opinions. Any member of the group possessing relevant supplementary or conflicting evidence on another member's research paper(s) is encouraged to take part in the discussion. During the discussion period you should be evaluating the evidence available and thinking what work should have been done next if you were a researcher at the time, and how it could best be done.

Following discussion of the entire group's set of papers, each student will receive a reference to another and more recent paper, or set of papers, which he will study and summarise as before, after which the group will again reassemble to discuss each paper, with a five minute summary from each student again being required.

Finally the group will discuss their impressions of the overall research effort, and any lessons or features of it which were particularly apparent. As some students in the class may require to see identical papers, or papers from the same volume of a journal, Xeroxed copies of some papers have been made, but each student will have to search for at least one article in the library during the exercise.. A tutor will advise you whether a particular reference which you have been given is to be found in the main library, chemistry branch library, or if a Xeroxed copy is to be used.

LIST OF JOURNALS REFERRED TO IN THIS STUDY

Journal	Abbreviation	Location
Chemical Physics Letters	Chem.Phys.Lett.	Chemistry Library
Chemistry and Industry	Chem. Ind.	Chemistry Library
Clays and Clay Minerals	Clays Clay Min.	Library Fl. 2 (Geology)
Discussions of the Faraday Society	Disc.Far.Soc.	Chemistry Library Library Fl. 2 (Chemistry)
Icarus	Icarus	Library Fl. 2 (Astronomy)
Journal of the American Chemical Society	J.A.C.S.	Chemistry Library Library Fl. 2 (Chemistry)
Journal of Chemical Education	J.Chem.Ed.	Chemistry Library
Journal of Chemical Physics	J.Chem.Phys.	Chemistry Library
Journal of the Chemical Society (D) Chemical Communications	J.C.S.Chem.Comm.	Chemistry Library Library Fl. 2 (Chemistry)
Journal of Colloid and Interfacial Science	J.Coll.I.Sci.	Chemistry Library
Journal of Physical Chemistry	J.Phys.Chem.	Chemistry Library
Nature	Nature	Chemistry Library Library Fl. 1 (General)
Nature Physical Science	Nat.Phys.Sci.	Library Fl. 1 (General)
New Scientist	New Scientist	Library Fl. 1 (General)
Philosophical Magazine	Phil.Mag.	Library Fl. 1 (General)
Philosophical /		

Journal	Abbreviations	Location
Philosophical Transactions of the Royal Society	Phil.Trans. Roy.Soc.	Library Fl. 1 (General)
Physics Today	Physics Today	Library Fl. 1 (Physics)
Russian Journal of Physical Chemistry	Russ.J.Phys.Chem.	Chemistry Library
School Science Review	Sch.Sci.Rev.	Library Fl. 1 (General)
Science	Science	Library Fl. 1 (General)
Scientific American	Sci. Am.	Library Fl. 1 (General)
Theoretica Chemica Acta	Theor.Chem.Acta	Chemistry Library
Zeitschrift Anorganische Chemie	Z.Anorg.Chem.	Chemistry Library (Store)

TUTORS' GUIDE TO THE 'POLYWATER' EXERCISE

A general outline of the 'polywater' case history and a list of objectives for the exercise are contained in the "Introduction Sheet".

The class will be divided into groups of six to eight, and each group will operate as an individual unit with its own staff tutor.

The organiser of the exercise should issue you with several sets of cards containing references to papers on polywater research, as well as instructions on how to timetable the exercise.

At the start of the exercise, after a brief introduction to the nature of the exercise, issue each student with an individual card containing the reference to an early paper on polywater. (Some cards may contain more than one reference - in these cases, the papers involved are relatively short.) The students should then go to find their references in the library, read them, summarize them and return after a time indicated by the organiser. Some students may be asked to read a Xeroxed copy of a paper rather than the original. The organiser of the exercise should inform you where this is necessary, and provide you with the necessary copies.

On returning from the library, each member of the group will then be expected to talk to the group for five to ten minutes (or a time suggested by the organiser) on the contents of his paper(s).

Abstracts of each paper used in the study will be available for consultation by the tutor during the summary sessions, so that a student can be advised if he is tending to stray off the point.

The students should be asked to give their mini-lecture in such an order that a roughly chronological order /

order of presentation of papers is given. Before starting the summary of each paper, the student should inform the rest of the group of the author(s), the year of publication, the country of origin and the journal in which the paper appeared. Ensure that each talk is kept relevant to the topic, and that results, conclusions, opinions, suggested structures etc. are given more attention than the lesser important experimental details and background theory. Each student should appreciate whether the conclusions reached in his paper(s) are based on facts, educated opinion, speculation or otherwise.

When all the students have discussed the contents of their papers a short general discussion should follow which should involve any criticism of the experimental work, rationalisation of any conflicting evidence, and suggestions for what experiments could be done to clarify any outstanding anomalies. The class should also be encouraged to form an opinion on the possibility of the existence of polywater, based on the evidence known to date.

Following the general discussion, each student will be given another reference or set of references (which will again have been pre-determined by the organiser) to a more recent research paper - and the acts of reading, summarising, talking and discussing should be repeated as before.

The process should continue for the number of times indicated by the organiser in the timetable of the exercise, so that the students should see the research unravelling in such a fashion that polywater is initially seen on the ascendancy, then some doubt is cast upon its existence, and finally enough evidence is amassed for one to be able to say, with a fair degree of certainty, that a stable polymer of water does not exist and that the phenomenon is due to impurities of different sorts in ordinary water. In the concluding discussion /

discussion, students should be encouraged to express critical opinions on the research as a whole and point out which lessons are apparent from the overall research effort.

The tutor's role throughout the exercise is <u>not</u> to lead or dominate the discussion, but merely to chair it, and where necessary, to stimulate thought and clarify factual points in research papers (the abstracts should help in this respect). It is important to keep closely to the timetable suggested by the organiser, otherwise the exercise may not reach a satisfactory conclusion through lack of time. Students should, therefore, be advised exactly when to return from the library and the exact time their summary talks should last.

If you experience any difficulties in the organisation of the exercise, report these to the organiser so that alterations can be made for future runs.

NOTES FOR THE ORGANISATION OF THE 'POLYWATER' EXERCISE

Introduction

The general aims of the 'polywater' case history are to help develop in the student:- (a) skills in communication, (b) skills in handling and reading the scientific literature, and (c) a healthy scepticism of the literature through the ability to recognise shoddy or inadequate research work and skill in assessing whether conclusions or speculations are entitled to be drawn from the facts available.

A more detailed list of objectives is given in the "Introduction to the 'Polywater' case history".

The exercise takes as its theme the controversy over the existence or otherwise of 'Polywater' which raged in the scientific literature from 1966 to 1973.

The general strategy involves issuing a card containing a reference to a paper on the 'polywater' phenomenon to each student in a group. Each student then departs to the library to find, read and summarise his paper(s) before returning to report the contents of his paper(s) to the other group members. After each student has summarised his paper, a general discussion follows on the standard of research, conflicting evidence, what should be done next, etc.

Following the discussion, each student is given a reference to a later paper on the topic and the process is repeated until the available time has been exhausted.

Thus, as the exercise follows the chronological appearance of papers in the literature, the students should see the general pattern of the 'polywater' theory at first on the ascendancy, then some doubt being cast upon its existence, until finally the case against its existence is overwhelming and even 'polywater's' strongest advocates admit they were wrong.

Organisation

The organisation of the 'polywater' exercise cannot be simply explained as it is dependent on several variables, including (a) the number of students and staff participating, (b) the total time available, (c) the availability and proximity of journals, and (d) the allocation of papers for each group.

It is obvious therefore that no hard and fast rules can be given - it is up to the organiser to devise a timetable and select references to suit the conditions. However, there are several constraints in the above variable factors which will affect the organisation.

(a) The number of students participating should be no less than six and no more than forty-eight.

Groups should consist of six, seven or eight students - enough to get a general picture of 'polywater' research without the group becoming too large. Obviously the numbers in individual groups will depend on the total number of students (and staff) available. Each group should be under the control of a group tutor. When the organisation of the exercise has been decided, each tutor should be given the list of references to be used by his group and explicit details of the timetabled arrangements of the exercise.

(b) The organisation of the exercise is dependent upon the time available. The minimum time recommended for the exercise is three hours.

The basic unit of the exercise consists of issuing a reference to each student who then goes to read it before returning to discuss his paper(s) and the general research effort to date. This unit takes one and a half hours (at least) to complete, so that the total time for the exercise is dependent on the number of units which the organiser wishes to include. Obviously the more /

more units used in the exercise, the more clearly can the student see the research unfurling with time.

(c) Before selecting the references to be used in the exercise, first check whether any of the journals used in the study are not available in the library (or libraries) which will be used. If some are not available this will obviously affect the choice of references to some degree. The proximity of the library to the discussion room used in the exercise will also affect the logistics of the exercise.

(d) The final selection of papers to be used, apart from relying on the availability of journals, also depends on (i) the relative importance of certain papers both with respect to the research effort and also the objectives of the exercise and (ii) the fact that several of the journal volumes used in the exercise contain two or more papers on polywater, hence restricting the availability of some papers, unless Xeroxing facilities are used.

It is obvious, therefore, that no one correct method exists for selecting references, but it is up to the organiser to select references to suit the prevailing conditions.

As an aid to the selection of references, a chronological list of those papers used in the exercise is attached at the back of these sheets, giving information on the availability and relative importance of papers. The papers are coded in the same way as in the "List of Scientific Papers used in the Polywater Case History" available elsewhere.

On the sheets at the back the square bracketed numbers to the left of some reference codes indicate that that reference occurs in the same journal volume as other references used in the study. For example, reference 1969 (b) 1 occurs in the same journal as reference 1969 (b) 2 as both have [2] to the left of the code /

the code, hence both appear in the same volume of a journal.

The letters to the right of the reference code numbers, under the heading "Importance" indicate the relative importance of each paper to the 'Polywater' research effort. A. indicates a very important paper; B. indicates a quite important paper; C. indicates a useful paper; D. indicates a paper which is not particularly illuminating. It must be emphasised that this is just a guide.

The situation may arise in which the organiser wishes to give the same reference to members of two or more groups. If this is the case, the Xeroxing of that particular paper may be the only solution, unless another copy of the journal is available elsewhere. If however, any student receives a Xeroxed copy of a paper as his reference, the organisation of the exercise should be such that that student has to go to the library to find at least one original reference at some other point in the exercise.

In deciding which papers to use, it will be of great use to consult the tutor's summary of each paper listed, in order that a well-balanced set of papers is selected to illustrate the major points and lessons from the research.

Care should be taken to give each student reading material which will keep the students occupied for approximately equal lengths of time. This will probably involve giving <u>some</u> students more than one paper to read at each library session. If this is the case, remember that several minutes extra will be involved for the student who has to locate a second (or third) paper. The reference(s) for each student at each stage should be written down for the student on a card. On returning from the library each student will be /

will be expected to give a short summary of his paper(s) to the rest of the group. It is important at this "summary" stage that the papers should be reported chronologically as far as possible, as later papers often make reference to earlier papers, either confirming or criticising earlier work.

Example of a typical timetable

The organisational variables involved in this study mean that the final timetable can take a number of forms, but it is important that once a suitable timetable has been devised it is strictly adhered to, otherwise the exercise may be forced to finish without a satisfactory conclusion to the 'polywater' saga, and some of the lessons therein may be lost.

The reasons for close adherence to the timetable are illustrated in the following simple example of a typical timetable for one group of eight students attempting the exercise for the minimum of three hours.

Typical timetable when time available = 3 hours

Time (cumulative)	Group activity
0 mins.	Group assembles to receive instructions and first set of references.
5 mins.	Group in library studying papers published from 1966 to 1970 (inclusive).
50 mins.	Group reconvenes to summarise and discuss papers read. Each student must give a five minute summary of his paper(s).
1 hr. 30 mins.	Group in library for second session studying papers published from 1971 to 1973 (inclusive).
2 hrs. 15 mins.	Group reconvenes to summarise and discuss papers read as well as implications and lessons from the research.
3 hrs.	End of Exercise.

It is obvious from the above timetable that when only three hours are available, the exercise must be tightly structured. If, however, more time is available the structuring need not be as rigid, and more library sessions may be accommodated as well as the facility for following up lines of discussion which would of necessity have been dealt with less thoroughly in the short version. In addition, a longer version including additional library sessions, more accurately illustrates the chronological path of the overall research effort.

However, keeping to the example above of a three hour timetable, one of the many possible examples of the references given to individuals in a group of eight students is given below.

Example of possible set of references given to Group during a three-hour exercise

Library Session 1 1966 - 1970

Student	1	2	3	4	5	6	7	8
References (coded)	1967(b)1 1967(b)2	1969(b)1 1969(b)3	1969(b)5	1969(a)3abcd 1970(b)1 Xerox	1969(c)1 1969(c)2	1970(c)1	1970(c)9 1970(c)13	1970(b)16 1970(b)18

Library Session 2 1971 - 1973

Student	1	2	3	4	5	6	7	8
References (coded)	1971(b)1 1971(b)26	1971(a)2 1971(b)2	1971(b)23 1971(b)24	1971(c)3	1971(b)6 1972(a)2	1972(b)3 1972(b)4 1972(b)5	1971(c)7 1973(b)1 1973(b)2	1973(a)1 1973(a)2

It may appear at first sight that the organisation is time consuming. This may be so, but once a suitable scheme has been thought out and proved satisfactory, the organisational work in future years should be minimal.

Importance and Availability of Papers

		Importance
	1966(b)1	A
	1967(b)1	A
	2	A
	1968(b)1	C
	2	C
	1969(a)1	C
	2	B
[1]	3a,b,c,d	B
	4	C
[2]	1969(b)1	B
[2]	2	C
	3	B
[1]	4	B
	5	A
	1969(c)1	B
[3]	2	B
[3]	3	B
	4	B
	1970(a)1	B
	2	C
	3	C
	4	B
[4]	5	D
[5]	6	C
[6]	1970(b)1	B
[6]	2	B
[6]	3	B
[6]	4	B
[6]	5	C
[6]	6	B
[4]	7	D
[5]	8	A
[5]	9	D
[7]	10	C

		Importance
[7]	1970(b)11	B
[8]	12	B
	13	C
[5]	14	C
	15	D
[9]	16	B
	17	C
	18	C
	19	B
	20	B
[6]	1970(c)1	A
[7]	2	B
	3	C
	4	D
	5	B
[10]	6	D
[6]	7	C
[4]	8	B
[4]	9	B
[9]	10	C
	11	C
[10]	12	D
	13	B
[7]	14(a)	C
[8]	14(b)	C
	1971(a)1	C
	2	B
[11]	3	C
[12]	1971(b)1	A
[13]	2	A
[13]	3	B
[14]	4	B
[14]	5	B
[11]	6	B
[15]	7	C
	8	B
	9	B

		Importance
[16]	1971(b)10	B
[16]	11	B
[16]	12	B
[16]	13	B
[16]	14	C
[16]	15	C
[16]	16	C
[16]	17	C
[16]	18	C
[16]	19	C
[16]	20	D
[16]	21	C
[16]	22	C
	23	B
[17]	24	B
[17]	25	D
[12]	26	B
[11]	1971(c)1	C
[15]	2	C
[16]	3	B
[16]	4	C
[16]	5	C
[16]	6	D
	7	A
	8	C
	1972(a)1	D
	2	B
	1972(b)1	C
[18]	2	B
[19]	3	B
[19]	4	B
	5	B
	6	B
	7	C
[18]	8	B

	Importance
1973(a)1	C
2	C
1973(b)1	A
2	A
3	B

A LIST OF SCIENTIFIC PAPERS USED IN THE 'POLYWATER' CASE HISTORY

The 115 references listed fall into three general categories:-

(a) informal scientific reports and letters;
(b) experimental papers;
(c) theoretical papers.

The following table indicates how many of each category are represented for the years between 1966 and 1973.

	(a)	(b)	(c)
1966		1	
1967		2	
1968		2	
1969	7	5	4
1970	6	20	15
1971	3	26	8
1972	2	8	
1973	2	3	

(a) General Science Papers

1969(a)

1. Anon. Scientific American. 1969 221 (3) (Sept.) p. 90
"Polywater"

2. Anon. Physics Today. 1969 22 (Sept.) p. 61-62
"Spectra suggest Anomalous water is a stable polymer of H_2O"

3a. F.J. Donahoe Nature 1969 224 198
"Anomalous Water"

3b. J.D. Bernal et al. Nature 1969 224 393
"Anomalous Water"

3c. D.H. Everett et al. Nature 1969 224 394
"Anomalous Water"

3d. N.G. Anderson Nature 1969 224 626
"Anomalous Water"

4. /

4. Anon. , New Scientist 1969 42 456 (May 29)
"The Cell's water may be anomalous"

1970(a)

1. Anon. New Scientist 1970 45 599 (March 26)
"After Anomalous Water and Polywater - cyclimetric water"

2. Anon. New Scientist 1970 47 121 (July 16)
"Throwing Cold Water on Polywater"

3. J.H. Hilderbrand Science 1970 168 1397
"Polywater Hard to Swallow"

4. D.L. Rousseau Physics Today 1970 23 (October) p. 17
"'Anomalous Water' : polywater or impurities"

5. R.A. Horne Science 1970 168 151
"Water : nomenclature"

6. L.C. Allen Science 1970 169 718
"Polywater : Ideal Research Topic"

1971(a)

1. Anon. New Scientist 1971 49 (Jan. 28) p. 171
"Another Anomaly for Anomalous Water"

2. Anon. New Scientist 1971 50 (June 17) p. 670
"Polywater Takes on Universal Appeal"

3. Anon. Nature 1971 230 11
"Polywater Drains Away"

1972(a)

1. E. Deeson School Science Review 1972 53 (no. 185) p. 727-734
"What is polywater"

2. H. Freizer J. Chem. Ed. 1972 49 445
"What is polywater"

1973(a)

1. L.C. Allen New Scientist 1973 59 (Aug. 16) p. 376-380
"The Rise and Fall of Polywater"

2. /

2. J. Finney New Scientist 1973 59 (Sept. 6) p. 582
"Polywater"

(b) Experimental Papers

1966(b)

1. B.V. Deryagin Disc. Far. Soc. 1966 42 109-119
"Effect of lyophile surfaces on the properties of boundary liquid film"

1967(b)

1. B.V. Deryagin, N.N. Fedyakin J. Coll. I. Sci. 1967 24 132-3
"Concerning the modified state and structural polymerism of liquids condensed from their unsaturated vapours in quartz capillaries"

2. V.I. Anisimova, B.V. Deryagin et al Russ. J. Phys. Chem. 1967 41 1282-4
"Preparation of structurally modified water in quartz capillaries"

1968(b)

1. A.D. Bangham, D.H. Bangham Nature 1968 219 1151-2
"Very long-range structuring of liquids, including water, at solid surfaces"

2. V.V. Karasev, Yu M. Luzhov Russ. J. Phys. Chem. 1968 42 1255-6
"Apparatus for studying formation of the structurally modified state of liquids"

1969(b)

1. L.J. Bellamy, E.R. Lippincott et al Chem. Ind. 1969 p. 686-8
"Studies of the molecular structure and spectra of anomalous water"

2. D.H. Peel, F.S. Martin Chem. Ind. 1969 p. 1046
"The preparation of anomalous water"

3. /

3. E. Willis et al Nature 1969 222 159-161
"Anomalous water"

4. A. Cherkin Nature 1969 224 1293
"Anomalous water : A silica dispersion?"

5. E.R. Lippincott et al Science 1969 164 1482-1487
"Polywater"

1970(b)

1. T.F. Page, R.S. Jakobsen, E.R. Lippincott Science 1970 167 51
"Polywater : Proton Nuclear Magnetic Resonance Spectrum"

2. G.A. Petsko Science 1970 167 171
"Proton Magnetic Resonance Spectrum of Polywater"

3. G.A. Castellion et al Science 1970 167 865-8
"Polywater : Methods for Identifying Polywater Columns and Evidence for ordered growth"

4. D.L. Rousseau, S.P.S. Porto Science 1970 167 1715-9
"Polywater : polymer or artifact"

5. J.W. Linnett Science 1970 167 1719-1720
"Structure of Polywater"

6. S.L. Kurtin et al Science 1970 167 1720-2
"Polywater : A Hydrosol?"

7. A.G. Leiga et al Science 1970 168 114-5
"Polywater : An attempt at Synthesis in a gas discharge"

8. S.W. Rabideau, A.E. Florin Science 1970 169 48-52
"Anomalous water : Characterization by Physical Methods"

9. M.T. Shaw Science 1970 169 705
"Polywater discovered 30 years ago?"

10. J. Middlehurst, L.R. Fisher Nature 1970 227 57
"A new Polywater"

11. /

11. V.V. Morariu et al Nature 1970 227 373-4
"Equivalence of Anomalous water and Silicic acid Solutions"

12. W.D. Bascom et al Nature 1970 228 1280-4
"Evidence that Polywater is a colloidal silicate solution"

13. P.F. Low, J.L. White Clays and Clay Minerals 1970 18 63-66
"Hydrogen bonding and polywater in clay-water systems"

14. R.H.Wentorf Science 1970 169 175-6
"Anomalous Water : Attempts at High-Pressure Synthesis"

15. A.C. Hall J. Phys. Chem. 1970 74 2742-6
"Optical Studies of Thin Films on Surfaces of fused quartz"

16. D.H. Everett et al Nature 1970 226 1033-7
"Colligative Properties of Anomalous water"

17. B.V. Deryagin Scientific American 1970 223 (5) 52-72
"Super Dense Water"

18. D.A.I. Goring et al J. Coll. I. Sci. 1970 33 486
"Polywater and Silicone Grease"

19. M. De Paz et al Chem. Phys. Litt. 1970 7 23-4
"Mass spectrometric evidence against 'Polywater'"

20. F.J. Donahoe Icarus 1970 12 424-430
"Is Venus a Polywater Planet?"

1971(b)

1. P.A. Christian, L.H. Breka J.C.S. Chem. Comm 1971 p. 487-8
"Anomalous columns produced from non-hydrogen bonded liquids"

2. R.E. Davis, D.L. Rousseau, R.B. Board Science 1971 171 167-170
"Polywater : Evidence from electron spectroscopy for chemical analysis (E.S.C.A.) of a complex salt mixture"

3. D.L. Rousseau Science 1971 171 170-2
"Polywater and sweat : Similarities between the infra red spectra"

4. B.A. Pethica et al Nature Physical Science 1971 229 21
"Anomalous water, not 'Polywater'"
(See (ref. 1971(b)9))

5. P. Hoekstra et al Nature Physical Science 1971 229 92-4
"Microwave Dielectric measurements on Anomalous water"

6. P. Barnes et al Nature 1971 230 31-3
"Polywater and polypollutants"

7. W.M. Madigosky Science 1971 172 264-5
"Polywater or sodium acetate"

8. S.B. Brummer et al J.Phys. Chem. 1971 75 2976-2980
"A High Yield method for the preparation of anomalous water"

9. B.V. Deryagin, N.V. Churaev Nature Physical Science 1971 232 131
"Anomalous water"
(Reply to (ref. 1971(b)4))

* Polywater Conference Report J. Coll. I. Sci. 1971 36 415-566

10. B.V. Deryagin, N.V. Churaev J. Coll. I. Sci. 1971 36 515-426
"Investigation of the properties of water II"

11. T.F. Page, R.J. Jakobsen Ibid p. 427-433
"Some evidence for the existence of water II"

12. D.L. Rousseau Ibid p. 434-442
"An alternative explanation for Polywater"

13. E.R. Lippincott et al Ibid p. 443-460
"Polywater - a search for alternative explanations"

14. /

14. D.H. Everett et al Ibid p. 483-8
"The Thermodynamics of anomalous water solutions. 1. Vapour pressure and enthalpy of evaporation."

15. S.B. Brummer et al Ibid p. 489-502
"Anomalous water - factors affecting its yield"

16. G.A. Petsko Ibid p. 503-7
"Proton magnetic resonance studies of polywater-water mixtures"

17. G.A. Petsko, W.R. Massey Ibid p. 508-512
"X-ray diffraction investigations of anomalous water"

18. F.M. Fowkes et al Ibid p. 522-8
"Anomalous water experiments with silica powders"

19. D.H. Everett, R.J. McElroy Ibid p. 529-531
"The enthalpy of evaporation of anomalous water"
(see (ref. 1972(b)1))

20. G. Graf et al Ibid p. 532-5
"Some chemical and physical properties of anomalous water"

21. E.H. Taylor Ibid p. 543-6
"A Kinetic argument against the existence of anomalous water"

22. M.R. Lauver et al Ibid p. 552-3
"Polywater preparation and silicone grease"

23. W.A. Adams et al Nature Physical Science 1971 230 39-40
"Anomalous water, porous glass and silicic acid"

24. B.F. Howell J. Chem. Ed. 1971 48 663-7
"Anomalous water : Fact or Figment"

25. P.A. Christian, L.H. Berka J. Chem. Ed. 1971 48 667-8
"Polywater : A lesson and opportunity in Science"

26. B.F. Howell, J. Lancaster J.C.S. Chem. Comm. 1971 p. 693-4
"Polywater : Is it a silica sol.?"

1972(b)

1. B.V. Deryagin et al J. Coll. I. Sci. 1972 40 481-2
"Reply to Article by Everett"
(Ref. 1971(b)19)

2. M.P. Gingold Nature Physical Science 1972 235 75-78
"Origin of anomalous water"

3. W.D. Bascom J. Phys. Chem. 1972 76 456-7
"Polywater"
(Letter concerning (ref. 1971(b)8))

4. S.B. Brummer et al J. Phys. Chem. 1972 76 457-8
"Polywater : an organic contaminant"
(Reply to above)

5. B.F. Howell, G. Chappue J.C.S. Chem. Comm. 1972 p. 20-22
"Thermal expansion behaviour of SiO_2/H_2O and $SiO_2/H_2O/NaOH$ mixtures"

6. B. Buoy et al Chem. Phys. Lett. 1972 13 328-330
"Mass spectrometric study of a pseudo-'polywater'"

7. V.D. Perevertaev, M.S. Metsik Russ. J. Phys. Chem. 1972 46 1322-4
"Thermal expansion of water films of mica crystals near 0°C."

8. J. Glass et al Nature Physical Science 1972 235 14-15
"Directional correlation study of capillary grown anomalous water"

1973(b) /

<u>1973</u>(b)

1. B.V. Deryagin, N.V. Churaev Nature 1973 <u>244</u> 430-1
   "Nature of 'anomalous water'"

2. J.J. Bikerman Nature 1973 <u>245</u> 343
   "Anomalous water"

3. B.V. Deryagin Recent Advances in Adhesion 1973 p. 23-31 (Xerox only)
   "The state-of-the-arts in liquids' modification by condensation"

(c) <u>Theoretical Papers</u>

<u>1969</u>(c)

1. R.W. Bolander et al Nature 1969 <u>221</u> 1233-1234
   "Cluster Structure of the Anomalous liquid water"

2. L. Pederson Chem. Phys. Lett. 1969 <u>4</u> 280-2
   "Possible contributing Structures of Polywater"

3. K. Morakuma Chem. Phys. Lett. 1969 <u>4</u> 358-360
   "Symmetric versus Asymmetric Hydrogen bonds in Polymeric Water"

4. J. Donohue Science 1969 <u>166</u> 1000-2
   "Structure of Polywater"

<u>1970</u>(c)

1. L.C. Allen, P.A. Killman Science 1970 <u>167</u> 1443-1453
   "A Theory of Anomalous Water"

2. L.C. Allen Nature 1970 <u>227</u> 372-3
   "A Bonding Model for Anomalous Water"

3. L.C. Allen, P.A. Kollman J.A.C.S. 1970 <u>92</u> 4108-4110
   "Cylic Systems containing Divalent Hydrogen Symmetrically placed between SP^2 hydridised Electron-Rich Atoms. A New Form of Chemical Bond?"

4. /

4. S.R. Sabin, P.A. Kollman, L.C. Allen Theor. Chim. Acta 1970 18 235-8
"Ab Initio MO-SCF calculations on a model of Anomalous Water"

5. A. Azman et al Chem. Phys. Lett. 1970 5 157-8
"A C.N.D.O. Calculation of Ring Models of Polywater"

6. J.B. Bates, E.R. Lippincott et al J. Chem. Phys. 1970 52 3731-9
"Dynamics of some Lattice Models of Polywater"

7. J.W. Linnett Science 1970 167 1719-1720
"Structures of Polywater"

8. R.P. Messmer Science 1970 168 479-480
"Polywater : Possibility of p-electron Delocalisation"

9. C.T. O'Konski Science 1970 168 1089-1091
"Covalent Polymers of Water"

10. A.P. Minton Nature 1970 226 151-2
"Can Water Polymerize? An inquiry into the possible existence of strong bonds between water molecules"

11. A. Goel et al J.C.S. Chem. Comm. 1970 423-4
"Molecular orbital calculations on the Structure of Polywater"

12. J. Del Bene, J.A. Pople J. Chem. Phys. 1970 52 4858-4866
"Theory of Molecular Interactions
1. Molecular orbital Studies of water polymers using a minimal Slater-type basis."

13. M. Ageno Theor. Chim. Acta 1970 17 334-8
"An alternative model for anomalous water"

14a. K.S. Chua Nature 1970 227 834-6
"Structure of Anomalous Water and its Mechanism"

14b. I. Cherry, P. Barnes, J. Fullman Nature 1970 228 590
"Anomalous Water"
(Comment on (ref. 1970(c)14a) replied to in (ref. 1971(c)1))

1971(c)

1. K.S. Chua Nature 1971 230 379
"Reply to Cherry, Barnes, Fullman"
(Ref. 1970(c)14a)

2. B. Kamb Science 1971 172 231-242
"Hydrogen-Bond Stereochemistry and 'Anomalous Water'"

3. L.C. Allen, P.A. Kollman J. Coll. I. Sci. 1971 56 461-8
"A comparison of Theoretical Models for Anomalous Water"

4. L.C. Allen, P.A. Kollman Ibid p. 469-482
"What can theory say about the existence and properties of Anomalous Water?"

5. H.S. Aldrich et al Ibid p. 536-542
"The Structure of Water II"

6. C.T. O'Konski, S. Levine Ibid p. 547-551
"Instability of Water Polymers"

7. L.C. Allen, P.A. Killman Nature 1971 233 550-1
"Theoretical Evidence Against the existence of polywater"

8. L.C. Allen, J. Donohue Science 1971 173 1252
"Polywater"
(2 small notes in reply to Kamb (ref. 1971(c)2))

SELECTION OF ABSTRACTS MADE AVAILABLE TO TUTORS

(a) General Science Papers

[Ref 1969 (a) 3a]

F.J. Donahoe Nature 1969 224 198
"Anomalous Water"

This letter, from an eminent chemist, is a "prophet of doom" correspondence.

As it has been reported that polywater chains are some 250 - 440 K.Joules/mole of monomer more tightly bound than normal water, Donahoe suggests that the Earth's water could all be transformed into polywater, and Earth could become like Venus.

Once nuclei of polywater had formed, it is suggested that polymerisation could be rapid, i.e. that the "metastable" phase of water may be normal water, and not polywater.

Donahoe is convinced that polywater exists, and suggests that it could be the most dangerous material on earth, and warns about the dangers of its disposal 'as if it was a deadly virus'.

[Refs 1969 (a) 3b,3c,3d]

J.D. Bernal et al Nature 1969 224 393 "Anomalous Water" [Ref 3b]

(Letter in reply to Ref 3a)

This letter criticises Donahoe as "alarmist" and "misleading" especially as the press has caught on and printed some "alarming reports".

It continues that Donahoe's "facts" are still not certain, and that Lippincott's structure and binding energy figures are still speculative (as other evidence contradicts them).

In the lab. there is no evidence that polywater grows /

grows at the expense of normal water, and indeed evidence exists of its breakdown. Donahoe is severely criticised for "science fiction worries" and for alarming everybody.

D.H. Everett et al "Anomalous Water" Ibid. p. 394
[Ref 3c]
(Letter in reply to Ref 3a)

Another letter in same vain but not so cutting. Donahoe's figures are "unproven" and no evidence exists which shows that polywater is more stable than ordinary water. As there is some evidence of polywater in natural materials, polywater must have been here for all geological time, without any serious effects.

Donahoe's doubts are respected but the evidence does not warrant his pessimistic conclusions.

N.G. Anderson "Anomalous Water Ibid. p. 626 [Ref 3d]
(Letter in reply to Ref 3a)

Donahoe's explanation about nucleating seems unfounded due to the vast range of surfaces and conditions found on earth.

It is suggested that certain enzymes could depolymerise polywater and it is further hypothesized that polywater is the natural state of water in the absence of organic evolution. It is therefore proposed that all contaminates of biological origin are removed to see if this is correct.

[Ref 1971 (a) 2]
Anon New Scientist 1971 <u>50</u> (June 17) 670
"<u>Polywater takes on universal appeal</u>"

Reports are noted of work done showing anomalous forms of water and other polar liquids (e.g. methanol, acetone, acetic acid, etc.) which indicate the established rationalisations are no longer tenable. Polymeric species or inorganic impurities are two possible explanations.

Now, /

Now, work done by Christian and Berka [Ref 1971 (b) 1] suggests that new anomalous non-polar liquids have been found (e.g. benzene, toluene, carbon tetrachloride).

Anomalous forms of these liquids have been formed after a vigorous cleaning preparation, to prevent impurities, and these liquids are even more stable than polywater.

With these liquids there is no chance of either polymerisation or inorganic impurities, and if the impurities are organic in nature, the problem arises of their origin.

The author suggests that work should be done on non-polar, non-hydrogen bonded liquids to arrive at the true nature of anomalous liquids.

[Ref 1972 (a) 2]
H. Freizer J. Chem. Ed. 1972 49 445
"Polywater and analytical chemistry - A lesson for the future"
(Letter)

Freizer expresses concern about the polywater saga, and especially about the reliability of the observations which are the foundations of science. He states:- "Chemistry is only as strong as its experimental foundation and as the reliability of measurements."

It is suggested that the elaborately inflated structure of water came about because of poor analytical work. The solution to the problem was finally obtained by proper analysis, although these techniques were available long before the answer was found.

An argument is put forward for more analytical work in universities at a time when it is being phased out. Analytical chemistry deserves an important place in the training of both graduate and undergraduate chemists, and without this training chemists will begin to lose credibility.

[Ref 1973 (a) 1]

L.C. Allen New Scientist 1973 59 (August 16)
p. 376-380

"The Rise and Fall of Polywater"

A very good summary of the history of polywater dating from Russian research in 1961 to the eventual disproof of the polywater theory.

The preparation apparatus is well described and some of the early evidence for the existence of polywater is given, including the spectral evidence of Lippincott, the distillation experiments of Deryagin, and the early theoretical work of Allen and Kollman.

The attempts at disproof are well summarized and recent experiments are described which indicate that the phenomenon is associated with the heat treatment when drawing capillaries, and interaction with small numbers of silicon atoms and some high stability, simple organic compounds. Recent theoretical studies also indicate that a polymeric form of water is unlikely.

Allen criticises the attitude of some scientists who could not accept polywater, partly because of the public coverage given to the topic by the press, and suggests that scientists instinctively question the ability of public media to give a true view of scientific matters.

Although polywater has been disproved, Allen cites similar cases which have resulted in success rather than failure despite widespread criticisms by scientists at first (e.g. noble gas compounds, and the double helical structure of D.N.A.). A less Victorian approach by scientists and a greater willingness to co-operate in "unpopular" research without fear of being scorned by one's contemporaries is called for.

In view of the short time the polywater question took to be resolved, Allen is of the opinion that the overall research program is a fine example of the scientific method.

[Ref 1973 (a) 2]

J. Finney New Scientists 1973 <u>59</u> (September 6)
p. 582

This letter by one of the British workers on polywater is in response to Allen's article [Ref 1973 (a) 1] on the "Rise and Fall of Polywater".

Finney feels that Allen was too complimentary about the standard of work done on polywater and criticises some workers for, "unexpected and depressing secrecy, a reluctance to share data, and premature publication of results and speculations". The "<u>bandwagon effect</u>" is also mentioned.

Impurity problems have turned out to be much greater than normal in samples of about 1 m.g., but this should have been investigated and recognised <u>before</u> the phenomenon broke into epidemic proportions. That this was not done implies a restricted scientific specialism and/or deficient communications within science.

Although it is conceded that there have been valuable "spin-offs" from the saga, Finney disagrees with Allen who describes the history of polywater as an object lesson in how to perform a scientific enquiry. The use of micro-analysis techniques (which were available at the time and were ultimately used to solve the problem) and more co-operation between workers involved would have resulted in the problem being resolved far quicker, and also prevented "scare" stories in the press.

The author concludes that if less than half a dozen laboratories out of over four hundred scientists were effective in sorting out the problem it is not really a classical application of the "scientific method", and does not say much for the efficiency of science. It could and should have been better!

(b) Experimental Papers

[Ref 1967 (b) 1]

B.V. Deryagin, N.N. Fedyakin J. Coll. I. Sci. 1967
24 132-3

"Concerning the modified state and structural polymorphism of liquids condensed from their unsaturated vapours in quartz capillaries"

Although recent Russian research appears to indicate the presence of polymorphism in the liquid state, the authors point out that the direct influence of the capillary walls and "leaching" of impurities from them cannot yet be completely eliminated as possible explanations of the phenomenon.

The substance of Deryagin's paper [Ref 1966 (b) 1] is repeated, with particular attention being paid to a description of the preparation method (diagram given) and factors affecting it.

One of the properties of the anomalous liquid formed in the capillaries is that its vapour pressure is less than that for real water, and as the magnitude of this vapour pressure is independent of capillary radius (capillaries of radius 1 to 30 microns were used) it is concluded that the columns possess the properties of a bulk liquid phase, which is different from the normal phase, implying that the anomalous liquid has a different, more compact and ordered molecular structure.

A mechanism involving water molecules interacting with the silicate surface and other molecules to form a network of hydrogen bonds of unusual structure is suggested, and evidence for the epitaxial nature of this mechanism is that anomalous columns never grow in capillaries which have been wetted with normal water, but only when dry.

Evidence that the structure of anomalous water is denser, and more compact than normal water, is that its viscosity /

viscosity is fifteen times greater than for normal water (calculated from the velocity of movement of the columns of liquid under the action of a small pressure drop).

[Ref 1967 (b) 2]

V.I. Anisimova, B.V. Deryagin et al   Russ. J. Phys. Chem. 1967 41 p. 1282-4

"Preparation of structurally modified water in quartz capillaries"

A method of producing anomalous water quicker and in larger quantities (by using more capillaries) is described (with a diagram). The conditions of production are described and capillaries with diameters between 5 and 30 μ.m. are used. After five to seven days, columns of anomalous water were observed in 5 to 20% of the columns.

The unusual thermal expansion curves of the anomalous liquid is described (with diagram) and it is obvious that the behaviour differs markedly from both ordinary water and from saturated electrolyte solutions. The two phase behaviour of anomalous water at low temperatures is also mentioned.

The authors state that the wide variety of methods found for the preparation of anomalous water columns shows that it is a reproducible phenomenon and not associated with any pecularities of the apparatus used.

It is concluded that the thermal expansion information confirms that the anomalous properties of the condensate cannot be explained by contamination of the capillaries with the solution used in the preparation or by leaching from the capillary walls.

[Ref 1969 (b) 1]

L.J. Bellamy, E.R. Lippincott et al Chem. Ind. 1969
p. 686-8

"Studies of the molecular structure and spectra of anomalous water"

Deryagin's Russian work is summarised and some of the properties of anomalous water are listed including:- (1) low vapour pressure, (2) cooling behaviour (no maximum density at 4°C), (3) the ability to remain liquid at low temperatures (down to -100°C), (4) a density of about 1.4 g/cm^2, (5) high viscosity and, (6) it remains unchanged after being subjected to temperatures up to 400°C.

The authors have repeated the preparation in quartz and "Pyrex" capillaries and confirm Deryagin's findings. The possibility of contaminants is recognised, but it is thought to be very unlikely for three reasons:-

(a) water condensed into the same tubes under a reversed temperature gradient shows normal properties;
(b) the anomalous properties are retained after distillation;
(c) no residue can be observed microscopically on the walls of the tube after distillation.

It is suggested that anomalous water consists of "pure" anomalous water plus normal water and it can be concentrated by distillation into a larger tube.

Spectroscopic studies on the condensate were carried out by running (a) the near infra red spectrum and (b) the high frequency Raman spectrum. Diagrams of both are given.

In (a) a considerable reduction in the intensities of both normal water bands at 6900 cm^{-1} and 5150 cm^{-1} was noted, although no new bands could be noted with any certainty.

In (b) the anomalous component is characterised by a shift of the 3,400 cm^{-1} Raman band in normal water to a /

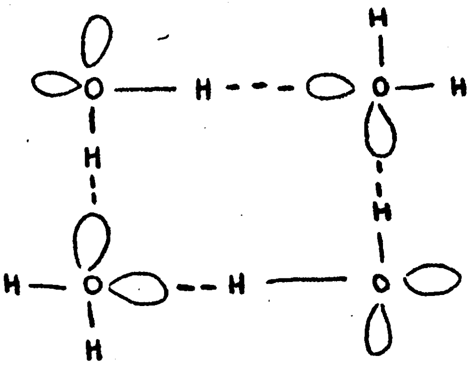
to a higher frequency of 3,440 cm^{-1}. These changes in Raman spectra are very similar to those produced by dissolved salts, but the authors claim that as the samples were distilled, it is clear that the changes are not due to this cause.

It is confidently stated that the spectra indicate some new form of water and are not the result of casual contamination.

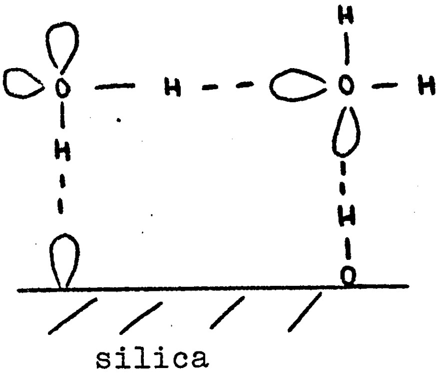
A suggested structure for anomalous water is made in view of the evidence which implies that anomalous water is a stable and closely packed form of water. The analogy of diamond and graphite is made and it is clear a fairly large entropy term must be involved in its formation.

Although they have no evidence, the authors speculate on a tetramer structure which seems consistent with the facts. A mechanism for formation, which involves using the silica surface, is also postulated.

Structure



Mechanism



This tetramer structure involves 90° angles in water, but the authors say this is possible in view of the wide range of angles commonly occurring in crystals.

It is concluded that anomalous water consists of tetramers, or higher weight polymers orientated to reduce lone pair/lone pair repulsion.

[Ref 1969 (b) 3]

E. Willis et al   Nature 1969 222 159-161

"Anomalous Water"

Anomalous water was produced using Deryagin's method [Ref 1966 (b) 1] . The properties of the anomalous liquid produced confirmed Deryagin's findings, namely (a) lower vapour pressure than normal, (b) up to fifteen times higher viscosity, (c) greater density (ρ = 1.2 to 1.3 g/cm^2), (d) unusual thermal expansion behaviour (diagram given), (e) phase separation at low temperatures (photographs given).

In addition, the anomalous water was investigated using, (a) mass spectrometry, (b) infra red spectrometry and (c) proton n.m.r. spectrometry.

All three methods showed no observable difference from normal water.

The workers conclude that the existence of anomalous water as a stable and distinct molecular entity will only be established when it becomes available in amounts for unequivocal characterisation.

It is further concluded that anomalous water consists chiefly of normal water, and that some of its properties are consistent with those of a gel.

The possibility that the gel is formed by leaching of silica from the capillary walls is mentioned, but it is stated that it is unlikely as bulk water in similar capillaries retains its normal properties indefinitely and also Deryagin has produced anomalous water in pure quartz capillaries from which such leaching is most unlikely.

[Ref 1969 (b) 5]

E.R. Lippincott et al Science 1969 164 1482-7

"Polywater - Vibrational spectra indicate unique stable polymeric structure"

This paper first coins the name of "polywater" for the anomalous liquid which condenses in fine capillaries.

The early work of Deryagin is summarised, and the known properties of polywater are listed.

The spectral work done by Willis et al [Ref 1969 (b) 3] and Bellamy et al [Ref 1969 (b) 1] is also briefly summarised, and it is emphasised that a severe limitation of this previous spectral work was the minute quantities of anomalous water prepared. This has also been the major limitation in the analyses for possible contaminants.

This paper reports on recent work on (a) the infra red spectrum, (b) the Raman spectrum, and (c) chemical analyses of polywater.

The results are interpreted that the substance is a true polymer of H_2O.

(a) The infra-red spectrum of polywater was run both inside and outside the tubes of formation. The near infra red spectrum (between 5000 cm^{-1} and 10,000 cm^{-1}) was run with the polywater inside the capillaries. The normal water combination bands at 6950 cm^{-1} and 5100 cm^{-1} were either partially or completely removed, depending on the amount of normal water in the sample. After the polywater was heated to a high temperature, overtone bands for normal water re-appeared.

The mid infra red spectrum (between 4000 cm^{-1} and 400 cm^{-1}) was run on diamond platelets. The spectrum appears to be unique and is not the spectrum of any known substance. The unusual features include the complete /

the complete absence of O-H absorption between 2500 cm^{-1} and 4000 cm^{-1}, the presence of a strong band near 1595 cm^{-1}, and an intense doublet in the 1400 cm^{-1} region. There is also no absorption from 1951 cm^{-1} to 2500 cm^{-1}.

There are no features in the spectrum to indicate the presence of contaminants, e.g. hydrogen peroxide, silica gel, silicic acids or silicates.

(b) The laser-excited Raman Spectrum of polywater is strikingly different from normal water. The most prominent feature is a very strong band at 620 cm^{-1} with a shoulder at 640 cm^{-1}. Other bands appear which are much weaker. A band at 3420 cm^{-1} (very weak) can be attributed to residual traces of water.

Reproductions of both the I.R. and Raman Spectra are given.

(c) Three methods of chemical analysis were used:-
1. Spectrochemical analyses by laser probe excitation indicated only trace quantities of cation contaminants (limits of detection 10^{-11}g); 2. A copper spark method detected no impurities (limit of detection 10^{-9}g); 3. Microprobe analysis showed the presence of silicon in trace quantities and of sodium ($<$ 0.5%). No halogens or other elements were detected.

The refractive index for polywater was calculated to be 1.48, exactly the same as reported by Deryagin, and the calculated density was 1.39 g/cm^3.

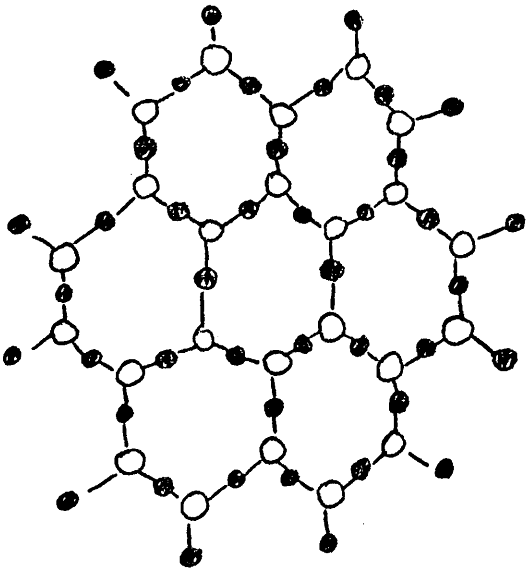
The interpretation of the results is that new and previously unreported strong, symmetric O-H-O bonds are formed, isoelectronic with $FHF^{\ominus}$. These bonds are regarded as responsible for the remarkable properties of polywater, and have considerable covalent character. They are so strong that they cannot be considered as normal O —— H hydrogen bonds.

It is proposed that extensive electron delocalisation could /

could occur in structures which involve oxygen atoms in <u>three</u> equivalent bonds, where each O-H unit has a bond order of $\frac{2}{3}$. The bond energy per O-H-O unit is given as approximately 125 to 210 K.J/mole, and there is increase in stability in the range of 250 to 420 KJ per H_2O structural unit above normal water, i.e. it is implied that polywater is <u>more stable</u> than normal water.

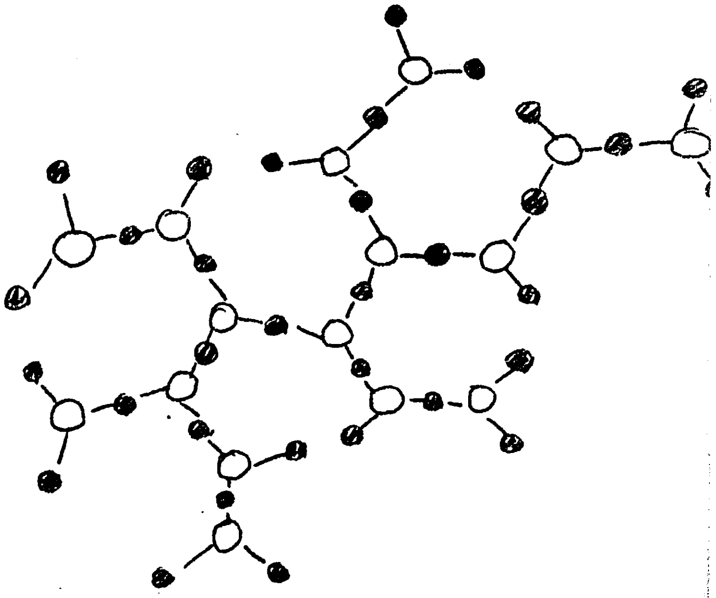
As previously postulated structures do not explain the spectra, two possible types of structure are proposed, embodying the structural principles previously mentioned.

(a) Hexagonal units in which the layers are stacked to form a 3-dimensional framework



Several resonance forms of this structure are given

(b) Highly branched polymer chains



O – oxygen
● – hydrogen

It is further noted that polywater appears to be soluble in normal water, and that purity is of primary importance in distinguishing its properties from ordinary water.

The mechanism of formation of polywater is unknown, but appears to be affected by the conditions of the "catalyst" surface.

[Ref 1970 (b) 1]

T.F. Page, R.J. Jakobsen, E.R. Lippincott Science
1970 167 51

"Polywater : Proton nuclear magnetic resonance spectrum"

The proton n.m.r. of polywater was run (spectrum given). The polywater protons give a broad peak about 300 Hz (5 ppm) downfield from normal water. This is in agreement with the expected chemical shift for a proton strongly hydrogen-bonded or bridged between two oxygen atoms, as in the structures suggested by Lippincott et al [Ref 1969 (b) 5]. The shift is downfield, because the hydrogen is deshielded by two electronegative oxygens.

The breadth of the polywater peak (about 100 Hz) is also consistent with the above-cited structures, due to restricted internal molecular motion in polymers.

An infra red spectrum was also run (between 400 cm^{-1} and 4000 cm^{-1}) which confirms the I.R. run by Lippincott et al [Ref 1969 (b) 5]. A little residual 'normal' water is indicated by the broad peak at 3450 cm^{-1}. A band occurs at 1100 cm^{-1} which could be due to impurities, but a note added at the end states that polywater has since been prepared in which this band is missing.

A copy of the infra red spectrum is printed.

[Ref 1970 (b) 16]

D.H. Everett, J.M. Haynes, P.J. McElroy Nature
1970 226 1033-7

"Colligative Properties of Anomalous Water"

The authors accept the premise that "anomalous" water consists of an "anomalous" part in ordinary water.

An investigation is made into the phase behaviour on freezing and subsequent melting, and also the vapour pressure of anomalous water. These investigations indicate /

indicate that anomalous water is a solution containing a fixed amount of relatively involatile material in normal water. There seems to be no need to postulate the existence of a new polymer of water in such solutions. If only water and silica are present, the properties are consistent with those of a silicic acid gel (although it is not proved that silica is present).

The spectral work of Lippincott [Ref 1969 (b) 5] is criticised for lack of thoroughness and it is suggested that the spectra could be explained in terms of silica/water systems. Lippincott is also criticised for saying that no impurities are present.

At the end of the paper, several questions are posed:-

(a) By what mechanism is the anomalous component formed?
(b) Is the solubility of the anomalous component consistent with the known properties of silica sols?
(c) Is the hypothesis about silica sols consistent with the fact that it is claimed that anomalous water can be distilled?
(d) Are the analytical data of Lippincott reliable?
(e) Are other physical properties of anomalous water, e.g. high viscosity, compatible with known properties of silica sols?
(f) Is an explanation avoiding polymerisation equally acceptable in the cases of "anomalous" properties of <u>other</u> liquids?
(g) Is there any reason to doubt that similar anomalies are to be expected in the presence of other solids (apart from silica)?

The authors add that theoretical calculations about the possible structure of polywater are largely irrelevant until the need for them is called for.

The evidence for "polywater" is not conclusive and the other explanations should be looked for first.

[Ref 1970 (b) 18]

D.A.I. Goring et al J. Coll. I. Sci. 1970 33 486-7

"Polywater - Silicone Grease"

It is pointed out that several workers have stated polywater could be explained in terms of some type of siliceous gel.

Silicone grease is universally used in glassware with ground joints, thus it is possible that polywater contains a component of silicone grease which migrates into the capillaries from the surface of the glassware used. Although the authors do not prove this hypothesis, they warn polywater growers of the possible dangers.

[Ref 1971 (b) 1]

P.A. Christian, L.H. Breka J.C.S. Chem. Comm. 1971 p. 487-8

"Anomalous columns produced from non-hydrogen bonded liquids"

Residual columns of an extremely involatile nature were produced by concentrating liquid columns condensed from the saturated vapours of the non-hydrogen bonded liquids carbon tetrachloride, benzene, and toluene in microscopic capillaries by a procedure successfully used to produce polywater and residues of other hydrogen bonded liquids.

It is obvious that neither hydrogen-bonding nor any of the previously suggested polymeric structures hold for non-hydrogen bonded liquids, and the suggested impurities (e.g. Si and Na) seem unlikely in organic liquids.

It is concluded that this behaviour appears to be a general phenomenon of liquids, and if impurities are to blame, there must be a wide variety of substances involved, and not just one. Thus, it is suggested that an overall understanding of the anomalous liquid phenomenon can only be obtained by investigating the nature of a wide range of anomalous liquids.
(An article on this paper occurs in [Ref 1971 (a) 2].)

[Ref 1971 (b) 2]

R.E. Davis, D.L. Rousseau, R.D. Board Science 1971
171 167-170

"'Polywater' : Evidence from electron spectroscopy for chemical analysis (E.S.C.A.) of a complex salt mixture"

E.S.C.A. involves the high resolution measurement of electrons ejected from a substance during X-ray excitation. The observation of X-ray - produced photoelectrons from each element in characteristic regions, as well as the measurement of the chemical shift - makes possible the identification of the oxidation state of the element, and therefore the chemical environment of as little as 10^{-8}g of material.

Samples from two labs were studied and rich E.S.C.A. spectra were obtained for every sample of the viscous non-volatile material prepared in capillaries. In each case the I.R. spectrum and the physical properties were similar to those claimed for "polywater".

The presence of high concentrations of ionic impurities (e.g. sodium, potassium sulphate, chloride, nitrate, borates, silicates and trace amounts of other impurities) were found along with carbon-oxygen compounds which the authors rate as especially significant because salts of simple carboxylic acids quite accurately reproduce the I.R. spectrum of polywater, and large signals consistent with such salts were found in each sample. Thus, it is very likely that this type of grouping is responsible for much of the reported I.R. spectrum of polywater. Very little water was found in the samples.

It is concluded that the consistent evidence that polywater samples are highly contaminated makes it unlikely that the unique properties result from polymerized H_2O units, and the phenomenon very probably results from a complex mixture of salts.

[Ref 1971 (b) 6]

P. Barnes et al Nature 1971 230 31-33

"Polywater and Polypollutants"

Deryagin's most recent paper [Ref 1970 (b) 17] is summarised and its implications discussed.

A fairly good summary of recent "polywater" literature is given, and the pre-polywater research is criticised as "at first impressive, but closer examination shows it to be careless, inconclusive and often misleading if not wildly conjectural".

After studying the recent research it is concluded that -

1) the properties of anomalous water are the results of gross impurities or impurity effects enhanced by surface activity;
2) if sufficient precautions are taken to exclude contaminants, no polywater is produced in the capillaries;
3) different types of anomalous water mirror the different levels of impurities;
4) "polywater" is highly unlikely to exist.

[Ref 1971 (b) 23]

W.A. Adams et al Nature Physical Science 1971
230 39-40

"Anomalous Water, Porous Glass and Silicic Acid"

Anomalous water was prepared and concentrated. The apparatus is described in detail. After concentration, "solid bodies" as were detected by Morariu [Ref 1970 (b) 11] were noticed, and analysed by electron microprobe. The findings revealed 10 - 30% silicon and about 5% sodium by weight in the solid bodies.

It is concluded that anomalous water is probably a silicic acid solution.

[Ref 1971 (b) 24]

B.F. Howell J. Chem. Ed. 1971 48 663-667

"Anomalous Water : Fact or Figment"

This article summarises the literature on polywater from 1961 until the time of writing.

It is stated that some of the early Russian research findings can be explained with hindsight. For example, it is known that freshly drawn silica capillaries often contain fine silica particles which can serve as nucleii for the formation of droplets of liquid water, and lead to the production of silica sols. Also, as soon as capillaries are pulled, they become partially coated with whatsoever substances are present in the surrounding air, so it is possible for these materials to go into solution.

Deryagin's distillation evidence is refuted as it is known that silica sols or borate solutions can also be distilled at temperatures of up to 400°C without loosing their character.

The early "bandwagon" research effort is described and several of the postulated "polywater" structures are drawn. The experimental findings and interpretations of Lippincott are described.

Recent evidence which casts doubt on the existence of "polywater" is reviewed and a large volume of literature which points to its non-existence is cited.

The "obituary to polywater" published in Nature [Ref 1971 (a) 3] is mentioned as is the ever-increasing volume of evidence that polywater owes its properties to impurities.

[Ref 1971 (b) 26]

B.F. Howell, J. Lancaster J.C.S. Chem. Comm. 1971 693-4

"Polywater, is it a silica sol?"

Anomalous water samples were prepared using a standard /

standard method, and particular care was taken to ensure cleanliness.

Electron microprobe analysis revealed the presence of Ni, Mg, Si, Na, Cl, S, K, P, Ca as well as trace amounts of Mn and Fe.

Features of "polywater" spectra are assigned to impurities, and it is concluded that anomalous water is <u>not</u> an allotrope of normal water, and that all its reported anomalies are exhibited by mixtures of ordinary water, silica and sodium oxide.

[Ref 1972 (b) 3]

W.D. Bascom J. Phys. Chem. 1972 <u>76</u> 456-7

"<u>Polywater</u>"

Brummer et al's paper on "A high yield method for the preparation of anomalous water" [Ref 1971 (b) 8] is discussed, in particular the findings that yields of "anomalous water" are greater in strained regions of the glass or quartz capillary. Bascom says there is now much evidence for surface corrosion of the capillary, which would result in an alkali silicate sol or gel.

The author goes on to discuss the infra red spectral evidence of several workers and possible causes of the typical 1600 cm^{-1} and 1400 cm^{-1} "polywater" bands. It is noted that the bicarbonate-silicate infra red spectrum is very similar to the polywater spectrum.

It is suggested that "polywater" could easily result from the surface corrosion of the capillaries to form an alkaline product that absorbs CO_2 from the air. This could account for Rousseau's reported presence of carboxylic acid groups, and the high carbon content in polywater, reported by some workers.

[Ref 1972 (b) 4]

S.B. Brummer et al J. Phys. Chem. 1972 <u>76</u> 457-8

"<u>Polywater, an organic contaminant</u>"

Brummer examines the two major claims made in

Bascom's /

Bascom's paper [Ref 1972 (b) 3] namely:- (a) that anomalous water is not polymeric water, and (b) that it is a silicate-bicarbonate residue.

The relevant evidence for both claims is reviewed.

(a) The only remaining evidence supporting a polymeric structure for anomalous water is that of Deryagin, and the authors are not in a position to confirm this work. They agree with Bascom on the point that anomalous water is not a polymeric form of water.

(b) The authors disagree with the argument that the phenomenon is due to an inorganic contaminant (in particular silicate and bicarbonate) as there is much evidence which indicates that there is very little silicon present in anomalous water samples.

It is also claimed that Bascom's infra red spectra are not typical "polywater" spectra, as they contain some peaks never obtained in other workers' spectra.

Brummer et al conclude that the contaminant is organic in nature, but cannot name it. This organic contaminant probably comes from the glass.

American "polywater" research is urged to link more closely to the Russian research, so that the case can finally be concluded.

[Ref 1972 (b) 5]

B.F. Howell, G. Chappue J.C.S. Chem. Comm. 1972 p. 20-22

"Thermal Expansion Behaviour of SiO_2 - H_2O and SiO_2 - H_2O - NaOH mixtures"

The thermal expansion behaviour of water solutions containing various percentages of SiO_2 or SiO_2 and NaOH was studied. The behaviour of the $H_2O/NaOH/SiO_2$ mixtures closely resembled that reported for anomalous water. The results support the contention that silica/sodium hydroxide/water mixtures exhibit all the properties /

properties of anomalous water, and agree with the electron microprobe analysis of samples produced in the standard way, in which equal amounts of Na and Si were found.

It is concluded that it is not necessary to postulate a new allotrope of water to explain the anomalous properties.

[Ref 1973 (b) 1]

B.V. Deryagin, N.V. Churaev Nature 1973 244 430-1
"Nature of Anomalous Water"

A one page letter in which the originator and champion of polywater eventually admits defeat.

Deryagin performed neutron activation analysis on his samples and detected fairly large amounts of sodium and silicon in anomalous water. The electron probe method was also used on all samples. It was established that there were no condensates both free of impurity and exhibiting anomalous properties and the properties of anomalous water are now attributed to these impurities. The anomalous component is probably a mixture of silicic acid colloidal particles, and dissolved compounds of Na, Si, O, C, K, Cl and S, causing increased viscosity, density and refractive index.

The reason why no anomalous features were noted for capillaries containing ordinary water is probably because of the higher dissolving power of freshly condensed water. The O, Na and Si probably originate from the surface of the freshly drawn capillaries.

Attempts to produce anomalous water in "sterile" conditions have failed.

Thus the Russian workers finally reject the theory of polymerised water and state the reason for all the anomalous properties is a reaction taking place between the vapour and the solid surfaces during the process of condensation.

[Ref 1973 (b) 2]

J.J. Bikerman Nature 1973 245 343-4

"Anomalous Water"

This short letter on Deryagin's eventual rejection of "polywater" theory states that Deryagin's reasons for rejection are unconvincing, and adds that many of Deryagin's observations cannot be accounted for by minute amounts of impurities.

The density, viscosity and thermal conductivity of anomalous water deviate so much from normal water that no trace amounts of impurities (e.g. silica) can explain the deviations.

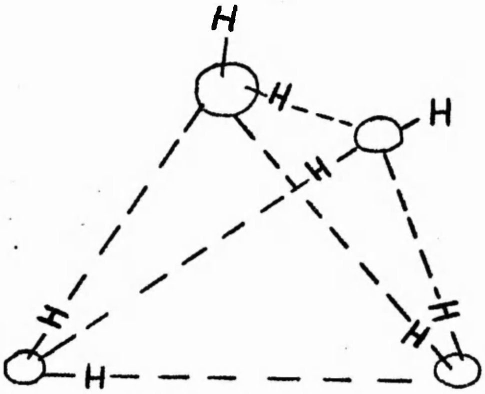
(c) Theoretical Papers

[Ref 1969 (c) 1]

R.W. Bolander et al   Nature   1969 221 1233-4

"Cluster Structure of Anomalous Water"

A brief summary of polywater research to date is given, and a stable, tetrahedrally bonded cluster structure for anomalous water is proposed $(H_2O)_4$.



It is suggested that this structure can exist in both liquid and vapour phases, and may only form with the aid of a quartz surface.

A mechanism for the formation of these clusters is proposed, involving the arrangement of oxygen atoms on the faces of silica tetrahedra. These oxygen atoms have a triangular configuration which matches the proposed cluster configuration.

The known properties of anomalous water are explained in terms of this model, although no theoretical basis is given for the proposed structure, and it is conceded that further work is needed to test the model.

[Ref 1969 (c) 2]

L. Pederson   Chem. Phys. Lett.   1969 4 280-2

"Possible contributing structures of Polywater"

An attempt was made to evaluate quantum mechanical properties for some of the possible structures of polywater.

The INDO (Intermediate Neglect of Overlap) molecular orbital /

orbital technique was used. This technique is approximate and does not treat absolute energies properly, and therefore it is not used as a criterion for stability. The object of the work was to demonstrate that some proposed polymeric species of water lead to enhanced bond orders.

Several possible "polywater" structures were chosen for investigation, but the list was not exhaustive, and the author points out that there are many other possible structures which may also contribute to the ultimate structure of polywater. Some of the possible cyclic and non-cyclic structures were investigated.

It was found that the total bond order of many of the polymeric structures is apparently greater than that expected from normal hydrogen bonding.

Although the author concedes that it is possible that cumulative inaccuracies in the method may account for the results, in the absence of accurate calculations the conclusion is drawn that forms other than "normal" water are possible, and that the extra bond energy may be as much as three times that of ordinary water.

This extra stability is a result of a compromise between oxygen-oxygen repulsion and the symmetrical "inner" oxygen-hydrogen attraction.

This stability in no way arises from a "resonance" effect as in conjugated hydrocarbons (all six π orbitals, including the three antibonding orbitals are filled) but instead from maximising the sigma oxygen-hydrogen interaction.

[Ref 1970 (c) 1]

L.C. Allen, P.A. Kollman Science 1970 167 1443-1453

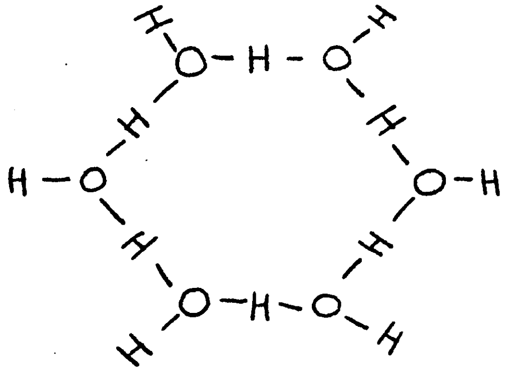
"A Theory of Anomalous Water"

Arguments are presented, supported by quantitative quantum mechanical calculations, which are believed to establish /

establish the existence of polywater and characterize its properties.

The development of suitable computational methods involved critical analysis of existing semi-empirical schemes and use of ab initio wave functions as a reference.

The structure proposed consists of a lattice structure of formula $(H_2O)n$ whose planar layers are composed of hexagonally arranged, four coordinate oxygen atoms, with hydrogen atoms placed symmetrically between them, i.e.



Several layer separation distances and stacking patterns are possible, and each gives rise to a density greater than that of normal water.

Several other possible structures were considered but none fit the experimental data as well as the above model.

An important conclusion of the calculations is that the internal energy of anomalous water is comparable to that of the normal liquid. Failure to observe anomalous water more widely in nature is an immediate consequence.

The high kinetic barrier computed for ring opening explains the apparent stability at high temperatures.

The infra red and n.m.r. spectroscopic properties of anomalous water are all consistent with the model, and collaborated by computed electronic wave functions.

It is suggested that this new type of bonding may occur equally well in other species such as alcohols and acids.

The new /

The new structure is termed "cyclimetric water" and a mechanism of formation is proposed involving hydrogen bonded hydroxyl pairs present at capillary surfaces.

[Ref 1970 (c) 9]

C.T. O'Konski Science 1970 168 1089-1091

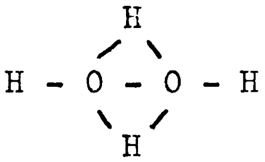
"Covalent polymers of Water"

A new covalent structural scheme for water polymers is proposed.

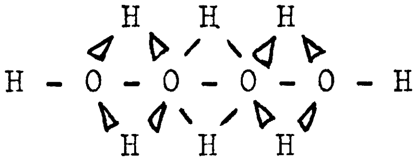
After briefly outlining polywater research to date and some of the structures proposed, O'Konski criticises the models containing symmetrical O-H-O bonds, because the unsymmetrical bond is much more stable. Most previously proposed structures are criticised and a new type of structure suggested using directed valence and molecular orbital concepts.

These structures contain a linear array of oxygen-oxygen σ-bonds, with pairs of hydrogen atoms in symmetrical bridges, each pair being involved with two oxygen atoms in π-type bonds.

e.g.



dimer



tetramer

It is claimed these structures agree with the infra red spectrum and many other properties of poly-water including n.m.r. spectrum, dielectric constant, sharp X-ray diffraction rings etc. It is postulated that all the observed properties of "polywater" are related to the structure of the suggested homologous series of molecules.

Mechanisms for formation of these structures are suggested.

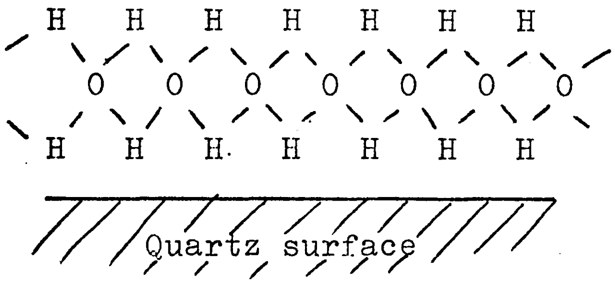
[Ref 1970 (c) 13]

M. Ageno Theor. Chim. Acta 1970 <u>17</u> 334-8

"<u>An Alternative Model for Anomalous Water</u>"

An alternative and completely original structure for anomalous water is proposed, in which all hydrogen atoms are involved in hydrogen bonds.

The idea is that water molecules line up on the quartz surface to form linear polymers of the type shown below.



Two such linear polymers can close their free ends to form a closed chain structure. The author claims that when the closed chain is sufficiently large it is energetically stable.

No proof theoretical or otherwise is given for this hypothesis, but it is claimed that such a model agrees well with the main experimental properties of polywater and also with the known infra red and Raman spectroscopic evidence of Lippincott et al [Ref 1969 (b) 5] .

[Ref 1971 (c) 3]

L.C. Allen, P.A. Kollman J. Coll. I. Sci. 1971 <u>36</u> 461-8

"<u>A Comparison of Theoretical Models for Anomalous Water</u>"

This paper is primarily concerned with a comparison of published quantum mechanical results. Practically all of the work done has been directed towards the relative stability and geometry of $(H_2O)_n$.

The three /

The three different levels of approximate quantum mechanical theory used in studying anomalous water structures are:- (1) non-empirical (ab initio) molecular orbital methods, (2) all-valence electron semi-empirical (CNDO or INDO) methods which neglect differential overlap and include only two-centre electron repulsion terms, and (3) one-electron schemes (e.g. extended Huckel theory) which omit all consideration of electron repulsion. In all three methods, one-electron molecular orbitals for the system are determined as linear combinations of the atomic orbitals.

The three methods are examined in the light of their successes and failures in quantitatively describing typical covalent and conventional hydrogen bonds. Criteria found from this analysis are employed in a comparison of proposed theoretical models for anomalous water as $(H_2O)_n$.

New computational results are presented for some theoretical models which have previously only been suggested qualitatively.

Two of the models which have been proposed are modifications of qualitative normal liquid theories, and in these cases, spectroscopic evidence must be employed for their evaluation.

The paper concludes that only ab initio calculations can provide quantitative insight into the bonding in anomalous water.

The article shows that the most satisfactory theoretical geometry of all those proposed is the cyclic, symmetric array. It is also shown that cyclic symmetric hydrogen bonding is considerably less stable than the conventional asymmetric form, and this therefore constitutes very strong evidence against the existence of polywater.

This paper represents a change of mind by Allen and Kollman from their first paper on "polywater" [Ref 1970 (c) 1] .

[Ref 1971 (c) 7]

L.C. Allen, P.A. Kollman Nature 1971 233 550-1

"Theoretical Evidence Against the Existence of Polywater"

New results are presented which disprove the authors' previous graphite-like model for polywater [Ref 1970 (c) 1]. This conclusion is derived from semi-empirical calculations, and correlation of the model with experimental observations including the molecular weight of 180 measured by Deryagin, which is far too low for this model.

Thus, Allen and Kollman are in the situation of first proposing the model, and then disproving it.

Disproof of this model casts serious doubt on the existence of a new water allotrope.

'POLYWATER' ASSESSMENT

(i) Situational technique

Question 1

Read the following extract carefully, and answer the questions that follow on the paper provided.

"The trend toward increasing complexity in theories of the chemical bond, which has been dominant for the past generation, may be losing its momentum. In 1963, R.J. Gillespie, in his electron repulsion pair theory of molecular structure, demonstrated that the concept of hybrid orbitals is unnecessary; and, Professor Bent remarked that quantum chemistry has so far failed to become a workable, everyday theory of chemical structure.

However, the strongest challenge to the dominant trend is that of Professor J.W. Linnett in his book, 'The Electronic Structure of Molecules'. His approach has a simplicity and an elegance all of its own. His theory can be stated as follows:-

> 'Consistent with the requirement of minimum energy as determined by the positive charge of the nucleus, the valency electrons in an atom arrange themselves around the nucleus according to the following postulates:-
>
> (1) All electrons have electrostatic repulsion for one another;
> (2) Because of their magnetic interaction, at a given separation, two electrons of opposite spin have less repulsion for each other than two electrons of the same spin have for each other;
> (3) The electrons in the valency shell tend to minimise their mutual repulsion.'

While /

While postulates (1) and (3) are familiar enough, postulate (2) is a different form of the familiar Pauli Principle; however, it lays much more emphasis on an electron's "preference" not to pair.

In describing species like Ne, F^- and O^{2-}, the electron arrangement obtained for valence electrons does not involve any electron pairing. Three of Linnett's most impressive successes are his formulae for oxygen, ozone and benzene - in all of which known structural details arise logically by applying the principles of the theory."

(J.C.E. 1967 44 (4) 206 adapted)

(a) Summarise the essential points expressed in the extract in three short sentences.
(b) In what one key way does the new theory of Linnett differ from previous approaches?
(c) Should current theories be thrown out or modified as a result of the Linnett approach?
(d) Over eight years have elapsed since Linnett published his ideas, yet little notice has been paid to his argument; suggest why this is so.

(ii) Likert-type statements

Question 2

For each of the following statements, indicate which of the possible responses most accurately fits your own personal opinion or reaction:-

	Strongly agree	Agree	Don't know/Undecided	Disagree	Strongly disagree
(a) Given the reference of a paper in a scientific journal, I would quickly be able to locate the article in the library.					
(b) Having read a scientific paper by an eminent chemist, I would accept the conclusions without hesitation.					
(c) The thought of giving a small lecture or talk on an aspect of chemistry to other students makes me feel very uncomfortable.					
(d) I have confidence in my ability to argue a point in a logical fashion.					
(e) Extremely accurate and precise work is very important in analytical work in chemistry.					
(f) Science subjects such as physics, chemistry, biology, astronomy etc. are complete units within themselves, and have very few inter-connections.					
(g) Lessons learned from past experience in scientific research can prove of use in future research.					

(iii) <u>Semantic differential technique</u>

<u>Question 3</u>

If you were asked your opinion about "chemistry" as a subject for study, you could indicate your opinion by ticking in one box:-

Interesting ☐ ☐ ☐ ☐ ☐ Boring

A tick /

A tick in the first box would indicate that you found the subject very interesting; the second box, that you found it interesting; the third that you found the subject neither interesting nor boring; and so on.

Use the same method of ticking to express your opinion about scientific literature (journals); remember, use only <u>one</u> tick per line, and don't leave any line unanswered.

I find scientific literature -

Straightforward						Misleading
Easy to understand						Difficult to understand
Dull						Interesting
Clear						Confusing
Inaccurate						Accurate
Not able to correct previous error						Able to correct previous error

<u>Question 4</u>

In the same way as for Question 3, indicate, by means of a tick in the appropriate box, your opinions of the "Polywater" case history.

I found the "polywater" exercise -

Valuable						A waste of time
Boring						Interesting
Relevant to my education in chemistry						Irrelevant to my education in chemistry
Enjoyable						Dull
Taught me new skills						Failed to teach me new skills

(iv) <u>Objective rating grid</u>

<u>Question 5</u>

Indicate, by means of a tick in the appropriate box, how successful or otherwise in your opinion, the case /

case history, has been in achieving the following objectives:-

	Very successful	Fairly successful	Average	Not very successful	Dismal Failure
(a) To communicate fluently;					
(b) To realise the lack of thoroughness in scientific research;					
(c) To discriminate between fact and opinion;					
(d) To spot key facts among less relevant data;					
(e) To see flaws in arguments and hypotheses;					
(f) To summarise a scientific paper.					

Please add here any other comments you may have about the "Polywater" study, including critical comments:-

CHAPTER 7

'WHAT HAPPENS WHEN THE GAS RUNS OUT .... ?' - A PROBLEM CASE STUDY

CHAPTER 7

'WHAT HAPPENS WHEN THE GAS RUNS OUT .... ?' - A PROBLEM CASE STUDY

7.1 The Need for the Case Study

Chemistry students at Glasgow University have for some years been exposed to an industrial case study in the first year. The simulation is a decision making exercise based on the production of sodium carbonate from a hypothetical field of salt which has been located in Dumfriesshire. Students have to decide, amongst other things, how to exploit the deposit in chemical terms, what chemical processes are necessary, what size of plant is required, what effect on the economics of the processes will the selling of by-products have, how long will it take before the plant breaks even, and what ecological problems will the factory cause. The exercise takes three hours to complete.

It was felt that exercises capable of promoting decision making, problem solving and interpersonal skills should be included at more advanced levels of the chemistry course, with the aim that students would learn to approach all problems in a scientific manner. In addition, in order to build on previous exercises, it was felt necessary to design more open-ended exercises so that students would learn to make assumptions, control variables and make decisions often on the basis of incomplete evidence as is often the case in the real world.

7.2 Design of the Exercise

The topic

It was decided that the exercise should concern Britain's supplies of North Sea gas and various possibilities open /

open to the gas industry in the future. Reasons for the choice of topic included:-

(a) the subject was very topical and hence it was hoped that student interest would be high;
(b) many of the problems and decisions discussed in the exercise might well become reality within the lifetime of the students;
(c) the exercise involved discussion of a real situation using actual up-to-date data so that students could appreciate its relevance;
(d) the eventual solutions to many parts of the exercise are not yet known but the exercise was made deliberately open-ended so that students could discuss the relative merits of various solutions and perhaps arrive at reasonable estimates in certain parts of the exercise by making assumptions which were felt to be valid or reasonable;
(e) the topic involved disciplines other than chemistry, such as economics. It was hoped that students would draw on knowledge other than that information given in the structure of the exercise to add to the discussion of certain points.

The objectives of the decision making exercise, which was entitled, 'What happens when the Gas runs out .... ?' included the following:-

Objectives of Gas case study

At the end of the exercise, the student should be able to:-

1) Recognise the chemistry relevant to the system under consideration.
2) Extrapolate trends from tables and graphs.
3) Make chemical and industrial decisions on the basis of chemical and economic considerations.
4) Assess the relative importance of a number of variables in a given situation.
5) /

5) Spot key facts among less relevant data.

In addition, the student should develop:-

6) An increased sensitivity to the contribution of chemistry to the economic and social welfare of the community.
7) A commitment to the application of a scientific approach to general problems.
8) An awareness that many decisions are a compromise of conflicting interest.
9) A growth of confidence leading to a willingness to take decisions on information available.
10) An appreciation of the existence of interconnections across subject barriers;
11) An appreciation of the value of working and discussing in groups.

The material

It was decided to involve groups of four to six students working together in a co-operative effort on all parts of the exercise. The students' text is contained in the appendix on p. 357. The exercise was split into five parts which the students tackled sequentially. Successive parts were not handed out to the students until the previous part had been completed to the tutor's satisfaction. The tutor's guide to the exercise is included in the appendix on p. 367. (It is recommended that the students' text and the tutor's guide be read together for each part of the case study in order to gain greater insight into the structure and nature of the exercise.) The tutors did not need to be in attendance continually and were free to leave the group on their own for a period of time to consider certain parts of the exercise. Four graphs were included in the exercise and these are contained in the appendix on p. 382.

The organisation of the case study is summarized at the start of the tutor's guide. The exercise was designed /

designed to fit into a laboratory period three hours long and for students in the second or third year of their chemistry course. Although the actual chemistry content of the exercise is not particularly difficult, it was felt that the open-ended nature of the exercise was more suitable for students who had completed at least one year at university.

The case study was compiled with the aid of the most recent information and figures available to British Gas and the Department of Energy. Broadly, the areas covered by the study were as follows:-

Part 1 This section introduced the students to the study and surveyed some of the recent developments in the gas industry in Britain. Students then studied different properties of town gas and natural gas (e.g. calorific value and air requirements) before discussing how these and other properties (e.g. flame burning velocity) would affect the conversion of gas appliances to burn natural gas.

Part 2 Students investigated the possible lifetime of North Sea gas on the British energy scene. Possible reserves were studied as were recent consumption patterns before an estimate was attempted. The estimate was dependent on the assumptions which the students made as a group. A reasonable set of assumptions might lead to the conclusion that North Sea gas supplies would become in increasingly short supply soon after the year 2000, well within the students' lifetime.

Part 3 Faced with depletion of gas supplies in the relatively near future, students were asked to consider, in general terms, options which might help solve the problem and the advantages and disadvantages of these options.

Part 4 This part considered the chemical and technical problems attached to one possible solution, i.e. making a synthetic substitute for natural gas from (a) oil (naphtha) fractions and (b) coal. Students discussed /

discussed, in general terms, the conditions required from thermodynamic and kinetic considerations.

Part 5 This part dealt with the economic facets of each process and discovered that even at today's prices, synthetic natural gas would be many times more expensive than North Sea gas. After discussing the major cost factors involved for each process, and considering how these may vary in years to come, students were asked to suggest a policy which the British Gas industry could follow over the next thirty years.

7.3 Assessment of the Material

Before the case study was attempted by students, the exercise, in draft form, was read by four university lecturers for critical comment. Three of the lecturers were chemists while one lectured on industrial science. All four had previous experience of the construction and organisation of simulation exercises. Following discussions with each lecturer, alterations and additions were made in parts of the exercise where errors of confusion existed. The re-written exercise was again issued for approval before being given to students for trials.

Volunteers from a class of third year chemistry undergraduates have participated in initial trials of the case study. A combination of proximity of examinations and time-tabling arrangements allowed only seven students to volunteer for the exercise, hence generalisations from the assessment of the exercise are impossible. However, the responses of the seven students will be given for interest. The students worked in two groups, one of three and the other of four individuals.

The broad skills which the exercise attempted to develop were decision making skills, problem solving skills, and inter-personal skills. In addition the exercise attempted to emphasise the social and economic implications /

implications of chemistry. The success of the exercise in achieving these aims was assessed by two basic self-reporting techniques.

(a) Likert-type statements were used to assess changes in attitudes and confidence as a result of the case study. A four point scale was used to avoid the option of a neutral response. Students completed this part of the assessment in both pre- and post-test form (see p. 386).

(b) On completion of the exercise, students were asked to rate the degree of success the case study had in achieving each of the listed objectives of the exercise. A four point scale was again used. (See p. 387)

In addition to the above techniques, the students were also asked to attempt a situational problem on completion of the exercise. The question was designed to see how students coped with a multi-variate situation similar to situations met in the case study in order to test if transfer of learning had occurred. Due to small numbers of an unrepresentative volunteer sample, the question was not given to a 'control' group. However, the question was included in the assessment sheet to test its potential for future assessments. Unlike the situational problem in the 'Polywater' exercise, all students attempted the problem. The problem which is given on p. 388 , appears useful if adequate experimental and control groups were available, but will not be discussed further with respect to the trial group of students.

Results of assessment

(a) Likert-type statements (p. 386) The statements attempted to identify changes in student attitudes to various aspects of chemistry and industry including the social and economic implications. The question also attempted to gain information on the effect of the study on /

on decision making, confidence and interpersonal skills.

The pre/post-test responses for the seven third year volunteers is given in Table 7-1 with post-test figures given in brackets below pre-test figures.

	Strongly agree	Agree	Disagree	Strongly disagree
(a) Industrial chemical decisions cannot be taken without considering the economic implications.	3 (5)	3 (2)	0 (0)	1 (0)
(b) Problems in the economic and political areas of life should be tackled in a scientific manner.	1 (3)	5 (4)	1 (0)	0 (0)
(c) Working in a group does not assist in making well-considered decisions.	0 (0)	1 (2)	6 (4)	0 (1)
(d) Chemists should confine their attention to chemistry, leaving economics to economists.	0 (0)	1 (0)	5 (2)	1 (5)
(e) The division of knowledge into separate divisions hinders effective decision making.	0 (1)	4 (2)	2 (2)	1 (2)
(f) It is the duty of chemists to warn of future trends in natural resources (e.g. shortage).	3 (4)	3 (3)	1 (0)	0 (0)
(g) Decisions on the use and exploitation of natural resources are based on clear-cut evidence.	0 (0)	2 (0)	5 (6)	0 (1)
(h) I feel reasonably confident that, given the basic information, I could take a decision.	0 (0)	5 (6)	2 (1)	0 (0)

(i) /

	Strongly agree	Agree	Disagree	Strongly disagree
(i) I enjoy working in a group.	1 (1)	4 (5)	2 (1)	0 (0)
(j) I feel that, as a chemist, I need not worry too much about the social and economic implications of chemistry.	0 (0)	1 (0)	4 (3)	2 (4)
(k) I benefit more from reading a text book than from participating in a case study.	0 (0)	1 (1)	5 (5)	1 (1)
(l) I prefer pure academic chemistry to social and applied chemistry.	1 (0)	1 (2)	4 (3)	1 (2)

Table 7-1 Responses to Likert-type statements

The changes in degrees of agreement/disagreement between pre- and post-test are summarized in Table 7-2 for each statement.

	Unchanged	More agreement			More disagreement	
		By one point on scale	By two points on scale	By three points on scale	By one point on scale	By two points on scale
Statement (a)	5	1		1		
Statement (b)	4	3				
Statement (c)	5	1			1	
Statement (d)	2				5	
Statement (e)	5	1				1
Statement (f)	5	2				
Statement (g)	4				3	
Statement (h)	4	2			1	
Statement (i)	6	1				
Statement (j)	4				3	
Statement (k)	7					
Statement (l)	3	1			3	

Table 7-2 Agreement/Disagreement Trends for Likert-type Statements

Changes and trends although by no means statistically significant are generally in the direction suggested by the aims and objectives of the exercise. Statement (d) (Chemists should confine their attention to chemistry, leaving economics to economists) prompted the largest change of opinion with five out of seven students disagreeing more strongly after the study, while one of the students whose attitude remained unchanged 'strongly disagreed' with the statement in the pre-test.

(b) <u>Objective rating</u> (p. 387) The results are summarized in Table 7-3.

	Very successful	Moderately successful	Slightly successful	Unsuccessful
(1) Recognise the chemistry relevant to the system under consideration.	0	7	0	0
(2) Extrapolate trends from tables and graphs.	0	5	2	0
(3) Make chemical and industrial decisions on the basis of chemical and economic considerations.	0	7	0	0
(4) Assess the relative importance of a number of variables in a given situation.	1	5	1	0
(5) Spot key facts among less relevant data.	0	5	2	0
(6) Increased sensitivity to the contribution of chemistry to the economic and social welfare of the community.	3	3	1	0
(7) A commitment of the application of a scientific approach to a general problem.	2	3	2	0
(8) An awareness that many decisions are a compromise of conflicting interest.	2	5	0	0

(9) /

	Very successful	Moderately successful	Slightly successful	Unsuccessful
(9) A growth of confidence leading to a willingness to take decisions on information available.	1	1	5	0
(10) An appreciation of the existence of interconnections accross subject barriers.	0	5	1	1
(11) An appreciation of the value of working and discussing in groups.	1	4	2	0

Table 7-3 Objective Rating Responses

Once more, no firm conclusions can be made, but it is interesting that Objective 6 (An increased sensitivity to the contribution of chemistry to the social and economic welfare of the community) has been scored quite highly. This would appear to tie in with the responses to Statement (d) in the Likert-type assessment. Objective 9 (A growth of confidence leading to a willingness to take decisions on information given) does not appear to have been well achieved, which is disturbing in view of the fact that the exercise was primarily designed as a decision making exercise. However, students regarded Objective 3 (To make chemical and industrial decisions on the basis of chemical and economic decisions) to have been achieved moderately well. Further testing would be required to confirm these observations.

Conclusion

Lack of numbers and a biased sample make the drawing of firm conclusions impossible, but the responses are encouraging enough (apart from the point made above on Objective 9) to advocate perseverence with exercises of this nature in undergraduate chemistry courses.

APPENDIX TO CHAPTER 7

WHAT HAPPENS WHEN THE GAS RUNS OUT .... ?

Students' Text

Part 1

Introduction

In the last ten years or so, the British gas industry has undergone an astonishing transformation. In 1960, about 90% of the total gas manufactured in the country was derived from coal, using a process which had been established for about 150 years. However, research in gas-making technology resulted in new processes in which gas could be made more cheaply from oil, and full scale plants were soon built to replace the old-fashioned coal gas plants. By the mid-sixties the proportion of total gas still being made from coal had already been halved.

It was at this point that the first strike of natural gas was made under the North Sea; and by 1966 it was clear that enough had already been found to sustain a British gas industry based entirely on natural gas. By 1974 about 95% of the total gas supplied in the U.K. was derived from natural gas. However, can this new found source of cheap energy meet all the country's energy needs indefinitely, and what would happen if reserves of natural gas became depleted?

In this exercise, you will estimate how long North Sea gas can supply Britain's gas needs and investigate some of the alternatives available in the event of supplies of natural gas becoming exhausted.

The figures in the study are genuine. It is up to you to interpret them in a realistic manner. The problem raised by some of the statistics will become reality in the future and will affect your life whether you continue to study chemistry or not.

Natural /

Natural Gas and Town Gas

Typical analyses of traditional town gas from coal, of modern town gas from oil and of natural gas from the North Sea are given below showing composition in percent by volume.

Constituent	Town Gas from coal	Town Gas from oil	Natural Gas (North Sea)
Hydrogen	51.0	55.9	-
Carbon Monoxide	14.6	5.5	-
Methane	20.8	17.9	94.4
Other hydrocarbons (mainly C_2H_6)	3.5	7.4	4.1
Nitrogen	6.1	-	1.4
Carbon dioxide	3.6	13.3	0.1
Oxygen	0.4	-	-

(i) Calculate the calorific values (in kJm^{-3}) for -
(a) town gas from oil, and
(b) North Sea natural gas
given the following enthalpies of combustion:-

Substance	Enthalpy of combustion (kJ/mole)
Hydrogen	285.8
Carbon monoxide	283
Methane	882
Ethane	1542

(Assume the molar volume of each gas is 22.4 litres)

(ii) What volume of air will be required to burn 1 m^3 of oil-based town gas compared to 1 m^3 of North Sea Gas? (You may assume that the percentage of oxygen in air is 21%.)

(iii) How will these factors affect the conversion of gas appliances from town gas to natural gas, and what other property of town gas and natural gas should be taken into account when converting gas appliances?

Part 2

How long can North Sea gas last?

In this section you will investigate the possible life-time of natural gas from the North Sea on the British energy scene.

Table 1 shows the estimated British North Sea gas reserves (1975 figures). "Proven" reserves are virtually certain to be technically and economically producible while "probable" and "possible" reserves have a greater than 50% and less than 50% chance respectively of being viable propositions.

Table 1

Total Natural Gas Reserves (x 10^9 m^3)

	Proven	Probable	Possible	Total
Field presently being produced or under contract to British Gas	597.1	39.6	42.5	679.2
Other discoveries believed to be commercial but not yet under contract to British Gas	164.1	229.2	183.9	577.2
TOTAL	761.2	268.8	226.4	1,256.4

However, the total estimated reserves from all categories has been increasing since the discovery of gas in the North Sea, as illustrated by Table 2.

Table 2

Estimated Total Possible reserves of North Sea Gas (x $10^9 m^3$)

1967 - 707.5
1968 - 764.1
1969 - 820.7
1970 - 849.0
1971 - 905.6
1972 - 990.5
1973 - 1033.0
1974 - 1174.5
1975 - 1256.4

(a) From Tables 1 and 2, estimate a possible range of the total reserves of natural gas in the North Sea. How much of this total is likely to be economically and technically viable?

To relate the gas reserve figures to the expected lifetime of North Sea Gas in Britain, it is necessary to estimate likely consumption trends for gas over the coming years. Table 3 shows the consumption trends of the important primary fuels in the U.K. over a recent ten year period.

Table 3

Inland consumption of Primary Fuels in U.K. (x 10^6 tonnes of coal or coal equivalent)

	Coal	Petroleum	Natural Gas	Nuclear elect.	Hydro-elect.	TOTAL
1965	184.6	102.8	1.3	6.0	2.3	297.0
1966	174.7	111.7	1.2	7.8	2.4	297.8
1967	163.8	119.3	2.1	8.9	2.7	296.8
1968	164.5	125.9	4.7	10.1	2.2	307.4
1969	161.1	135.7	9.2	10.5	2.0	318.5
1970	154.4	145.6	17.6	9.4	2.6	329.6
1971	138.7	147.3	28.4	9.7	1.8	325.9
1972	120.9	157.6	40.3	10.5	2.0	331.3
1973	131.3	159.4	43.5	9.9	2.0	346.1
1974	115.9	149.0	52.1	11.9	2.1	331.4

(b) The natural gas consumption figure is given rather than the total gas consumption figure. Why?

Table 4 shows the relative amounts of town gas and natural gas sold to consumers in recent years.

Table 4 /

Table 4

Gas sold to consumers (x 10^6 tonnes of coal equivalent)

	Natural Gas	Town Gas	TOTAL
1965	1.3	12.4	14.7
1966	1.2	14.6	15.8
1967	2.1	15.5	17.6
1968	4.7	14.7	19.4
1969	9.2	12.5	21.7
1970	17.6	7.6	25.2
1971	28.4	3.8	32.2
1972	40.3	2.2	42.5
1973	43.5	3.0	46.5
1974	52.1	1.7	53.8

(c) Using Tables 3 and 4, suggest possible consumption levels over the next decade or so.

(d) How long can gas from the North Sea cope with the likely demand?

(Note: 1 tonne of coal equivalent = 708 m^3 natural gas)

Part 3

What possibilities are available?

From Part 2, it should be clear that if consumption of natural gas from the North Sea maintains its present course, supplies will be depleted well within your lifetime. In this section you should consider ways in which the problem of replacement could be approached. Discuss with your group what possibilities you think are available to the country faced with a declining North Sea gas industry.

What advantages, problems and drawbacks are associated with each possibility?

Part 4

Synthetic Natural Gas (SNG) - Chemical considerations

Suppose it has been decided to investigate the possibility of manufacturing a synthetic substitute for natural gas.

Two of the major contenders for gasification to produce SNG are -

(i) oil fractions (especially naphtha which is a mixture of hydrocarbons), and

(ii) coal.

Below is a brief summary of the gasification process for each feedstock.

(i) Gasification of naphtha

The overall reaction is

(1) $4(-CH_2-)_{(g)} + 2\,H_2O_{(g)} \longrightarrow 3\,CH_{4(g)} + CO_{2(g)}$

$\Delta H = -ve$

The CO_2 produced can be removed from the mixture of product gases to leave a gas containing a high proportion of methane. The reaction is irreversible and is exothermic for naphtha and other hydrocarbon feedstocks, but the situation is oversimplified because in practice the reaction occurs over a catalyst and other equilibria are established, namely:-

(2) $CH_{4(g)} + H_2O \rightleftharpoons CO_{(g)} + 3H_{2(g)}$

(3) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

Another point to note is that excess steam must be used so as to prevent the methane or carbon monoxide produced being decomposed to deposit carbon by the following reactions:-

(4) $CH_4 \rightleftharpoons C + 2H_2$

(5) $2CO \rightleftharpoons C + CO_2$

Thus /

Thus the products of the overall reaction include, in addition to the CH_4 and CO_2 also CO, H_2 and H_2O which obviously reduces the efficiency of reaction (1).

From equilibria (2), (3), (4) and (5), what generalisations can you make about levels of pressure and excess steam required to maximise the amount of CH_4 produced and minimise the volume of by-products?

(ii) Coal Gasification

This is much more difficult than for oil fractions and other feedstocks of lower $C/_H$ ratio. Here the feedstocks cannot be purified or vapourised and so direct catalytic hydrogenation is out of the question. There are two possible routes to methane from coal: (a) hydrogenation, and (b) synthesis.

(a) Hydrogenation Route

Gasification $C+2H_2O \xrightarrow{+O_2} 2H_2+CO_2$ $\Delta H = +90kJ$

Hydrogenation $C+2H \longrightarrow CH_4$ $\Delta H = -75kJ$

$2C+2H_2O \longrightarrow CH_4+CO_2$ $\Delta H = +15kJ$

(b) Synthesis Route

Gasification $2C+3H_2O \xrightarrow{+O_2} CO+3H_2+CO_2$ $\Delta H = +22kJ$

Synthesis $CO+3H_2 \longrightarrow CH_4 + H_2O$ $\Delta H = -206kJ$

$2C+2H_2O \longrightarrow CH_4 + CO_2$ $\Delta H = +15kJ$

Which of the above two alternative routes do you think would be the most efficient and inexpensive on an industrial scale?

Part 5

Synthetic Natural Gas - Economic Facets

In the previous section you discovered that it should be technically feasible to produce S.N.G. from an oil fraction (naphtha) and from coal. In this section you will investigate whether or not either process could be economically feasible.

From Graph 2 (Part 4) you should be able to estimate the amounts of (a) naphtha and (b) coal required to produce $10^6 n^3$/day of SNG. Graph 4 shows the estimated capital costs for building SNG plants using feedstocks of varying $^{C}/H$ ratio. Why do you think the capital costs vary with $^{C}/H$ ratio in the manner shown?

Assuming plants capable of producing $3 \times 10^6 m^3$/day of SNG, calculate the cost (in pence per 10^6kJ) of producing SNG using (a) naphtha and (b) coal as feedstock. Assume depreciation losses of 10% of capital cost per annum, and use Graph 2 to help you estimate the feedstock costs. You may further assume that other costs such as labour, operation and distribution costs are negligible compared to feedstock and depreciation costs, although in practice this is an oversimplification. (The cost of oil sold to industry is £39 per tonne while coal costs industry £19.50 per tonne - prices in October, 1975.) Gas at present is sold at an average 39 pence per 10^6kJ (10^6kJ $\equiv 26m^3$ of natural gas).

Discuss your findings with the group and tutor. What place do you think SNG will have in the country's energy plans? In what way could future developments or price variations affect the costs of the two processes?

How many SNG plants capable of producing $3 \times 10^6 m^3$/day would be required to meet the total gas demand postulated /

postulated in Part 2 around the year 2000?

Finally, drawing on information from all parts of this exercise, discuss the future of the gas industry in Britain and suggest a policy which the industry could follow over the next thirty years.

WHAT HAPPENS WHEN THE GAS RUNS OUT .... ?

Tutor's Guide

Course Organisation

The exercise will involve groups of students working in a co-operative venture. Where calculations are required ensure that the work is shared by the students to create greater efficiency. The group should complete each part of the exercise before receiving the next part.

The case study is self-explanatory and requires no greater introduction than a short briefing on the nature of the exercise and what is expected of the students. You should stress that in certain parts of the exercise, questions are posed to which there is no one correct answer. The exercise is based on a real situation and this should be emphasized.

A suggested time-tabling of the three-hour period is:-

		cumulative
Part 1	40 minutes	0.40
Part 2	40 minutes	1.20
Part 3	35 minutes	1.55
Part 4	20 minutes	2.15
Part 5	45 minutes	3.00

Part 1

(i) The calorific values for town gas and natural gas can be calculated as follows:-

(a) Town gas (oil based)

Constituent	Heat given out/m^3 of town gas (kJ)
H_2	$285.5 \times \frac{1000}{22.4} \times \frac{55.9}{100} = 7{,}132$ kJ
CO	$283 \times \frac{1000}{22.4} \times \frac{5.5}{100} = 695$ kJ
CH_4	$882 \times \frac{1000}{22.4} \times \frac{17.9}{100} = 7{,}048$ kJ

C_2H_6 /

C_2H_6 . $1542 \times \frac{1000}{22.4} \times \frac{7.4}{100} = \underline{5,094 \text{ kJ}}$

$\therefore$ Calorific value of town gas (oil) = $\underline{19,969 \text{ kJm}^{-3}}$

(The calorific value of coal based town gas is almost identical.)

(b) North Sea Natural Gas

Constituent	Heat given out/m^3 of natural gas (kJ)
CH_4	$882 \times \frac{1000}{22.4} \times \frac{94.4}{100} = 37,170 \text{ kJ}$
C_2H_6	$1542 \times \frac{1000}{22.4} \times \frac{4.1}{100} = \underline{2,822 \text{ kJ}}$

$\therefore$ Calorific value of natural gas = $\underline{39,992 \text{ kJm}^{-3}}$

Thus, 1 m^3 of natural gas gives out about twice as much heat as the same volume of town gas, when burned.

(ii) The volumes of air required to burn 1 m^3 of North Sea gas and town gas from oil are given below:-

North Sea Gas	Oxygen required
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$2 \times \frac{94.4}{100} \text{ m}^3 = 1.888 \text{ m}^3$
$C_2H_6 + \frac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O$	$\frac{7}{2} \times \frac{4.1}{100} \text{ m}^3 = \underline{0.144 \text{ m}^3}$
	$\underline{2.032 \text{ m}^3}$

2.032 m^3 of O_2 are contained in $2.032 \times \frac{100}{21}$ m^3 of air

= $\underline{9.68}$ m^3 of air

Town Gas (oil)	Oxygen required
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$\frac{1}{2} \times \frac{55.9}{100} \text{ m}^3 = 0.2795 \text{ m}^3$
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$\frac{1}{2} \times \frac{5.5}{100} \text{ m}^3 = 0.0275 \text{ m}^3$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$2 \times \frac{17.9}{100} \text{ m}^3 = 0.3580 \text{ m}^3$
$C_2H_6 + \frac{7}{2} O_2 \rightarrow 2 CO_2 + 3H_2O$	$\frac{7}{2} \times \frac{7.4}{100} \text{ m}^3 = \underline{0.2590 \text{ m}^3}$
	$\underline{0.924 \text{ m}^3}$

0.924 m^3 O_2 are contained in 4.40 m^3 of air.

Thus /

Thus 1 m^3 of natural gas requires 9.68 m^3 of air for complete combustion, while 1 m^3 of town gas requires only 4.40 m^3 of air.

(iii) Conversion of Appliances to Natural Gas

A major factor concerned in the conversion of appliances is that the calorific value of natural gas is about double that of town gas, therefore $\frac{1}{2}$ m^3 of natural gas gives the same amount of heat as 1 m^3 of town gas.

Thus to give the same amount of heat (say, 19,969 kJ) an appliance burning town gas requires (1 + 4.4) = 5.40 m^3 of gas/air mixture while an appliance burning natural gas requires $(\frac{1}{2} + (\frac{1}{2} \times 9.68)) = 5.45$ m^3 of gas/air mixture. Thus some modification in the appliance is required to admit more air. Another factor in conversion is the burning velocity of gas. Town gas (because it contains a large percentage of hydrogen) burns with a flame speed which is about 3 times faster than for natural gas, so appliances must be adjusted to compensate for this also, otherwise the natural gas/air mixture will burn with a flame at a point well away from the burner outlet, since the gas/air mixture has spread out to become more diffuse and also slow moving. One way of surmounting this problem is to increase the area of flame in the appliance so that the velocity of the gas/air mixture coming from them will be reduced so that the flame is stabilised at the burner jet.

Part 2

In this section it should be emphasised that the correct answer to the questions posed is unknown. The students have to make an estimate using current trends and reasonable assumptions.

Thus the answers given below are merely suggestions, and by no means unique. Each problem can be approached in /

in a number of different ways, and each possible solution depends on which assumptions are made. Students should be encouraged to make their own assumptions, although the tutor should ensure they are reasonable ones.

(a) Table 2 shows that the estimated total gas reserves in the North Sea has been increasing steadily over the past few years. It may be expected that this increase may continue for the next decade or so but eventually most of the recoverable reserves of North Sea gas will have been discovered.

On average, over the past nine years estimated supplies of gas have increased by an average of about 70×10^9 m^3 each year, although since 1970 the increase has been over 80×10^9 m^3 per year. On this basis we could expect total supplies to be between about $2{,}000 \times 10^9$ m^3 and $2{,}150$ 10^9 m^3 by 1985. It would be over optimistic, at present to assume that overall total supplies of gas are greater than $2{,}250 \times 10^9$ m^3.

Table 1 indicates that, at present, about 18% of total gas reserves are classified as "possible" (less than 50% chance of being a viable proposition) while a further 21% is classified as "probable" (greater than 50% chance of being viable). Thus if we assume eventual total reserves to be about $2{,}150 \times 10^9$ m^3 it may be that only about $1{,}700 \times 10^9$ m^3 could turn out to be technically and economically viable.

(b) In Table 3 the natural gas consumption figure is given because the table is concerned only with primary fuels consumed in the U.K., and town gas is a secondary fuel manufactured from primary fuels such as coal and oil.

(c) Tables 3 and 4 show the remarkable increase in gas usage in the U.K. In 1965 all gas (town and natural) accounted for only 5% of total U.K. energy supplies, while /

while in 1974 gas (town and natural) supplied over 16% of the country's energy requirements. It can be seen from the table that this upsurge is mainly due to the introduction of natural gas which has now almost totally replaced town gas.

The rate of increase in total gas sold, given in Table 4 (which has been an average 16% per annum over the ten years shown) cannot go on indefinitely, and a reasonable assumption might be that the gas consumption will eventually level off at about 20% of the total U.K. energy market within a very few years.

Table 3 shows that total energy consumption in Britain was rising steadily (about 2% per year on average) until 1973 when a combination of increased prices, strikes and lack of economic growth reduced both supply and demand.

It might be expected that total energy consumption might maintain its present level for the following year or two before increasing at roughly the previous level when the economic climate improves, because, although the population of Britain is expected to remain relatively constant, a country's energy consumption is also related to its gross national product.

A possible pattern of gas consumption related to total energy consumption may be as follows:-

($x\ 10^6$ tonnes of coal or coal equivalent)

	Total Energy Consumption	% Gas of total	Total Gas	Volume of Natural Gas
1975	330.0	18%	59.4	$42.05 \times 10^9\ m^3$
1976	330.0	19%	62.7	44.39
1977	336.6	20%	67.3	47.65
1978	343.3	20%	68.7	48.64
1979	350.2	20%	70.0	49.56
1980	357.2	20%	71.4	50.55
1981	364.3	20%	72.9	51.61
1982	371.6	20%	74.3	52.60
1983	379.0	20%	75.8	53.67
1984	386.0	20%	77.3	54.73
1985	394.3	20%	78.9	55.86

1 tonne of coal equivalent ≡ 708 m^3 / natural gas

(d) Using the figures above, by 1985, Britain will have used over $550 \times 10^9\ m^3$ of her natural gas reserves. If consumption continues to follow the trend shown above, supplies of natural gas from the North Sea could be almost depleted by the year 2000 assuming total viable reserves of $1700 \times 10^9\ m^3$ as suggested in part (a).

Part 3

You should try to get the students to think of the options open to the country faced with depletion of natural gas.

A large amount of tutor participation may be necessary in this section, but wait to see what is suggested before becoming deeply involved in the discussion. Some suggestions which may arise are:-

(a) Import liquified natural gas (LNG) from other countries.

This is done at present on a small scale and is used /

used mainly to augment supplies at times of high demand. To import LNG on a larger scale would be extremely expensive although perhaps imports could be increased to some extent in order to complement Britain's own reserves and help postpone the problem of total depletion.

Graph 1 shows the relative cumulative cost of importing LNG compared to the cost of North Sea Natural gas. Storing up to about six days supply per year of LNG is quite cheap, but when much more than that is stored, storage costs soar rapidly so that only storing relatively small quantities is economically viable.

An additional problem is that since most LNG comes from North Africa, it may be politically unwise to become over-dependent on imported gas.

(b) Revert back to production of town gas from oil and coal.

Town gas is not interchangeable with natural gas and so gas appliances in areas where town gas was to be used would need to be re-converted to burn town gas. It is estimated that the recent conversion of appliances to burn natural gas cost the gas industry £530 millions. Another point is safety, as town gas is very toxic due to its carbon monoxide content. In fact, due to increased use of natural gas in the 1960's deaths from carbon monoxide poisoning in England and Wales dropped from 1,327 deaths in 1963 to 320 deaths in 1970. However, one point in favour of the proposal is that some plants for producing town gas still exist and the technology of the process is well established.

(c) The country could allow gas supplies to become depleted and use another fuel.

This would be possible if there was an alternative fuel, but new energy technology (e.g. solar and tidal power) is not expected to have advanced sufficiently until sometime after the year 2000. Coal production could /

could be increased, but probably not by the required amount.

In addition, if the gas industry is allowed to die the capital investment involved in the distribution technology (e.g. national grid) and consumer appliances will be completely wasted.

(d) The possibility of manufacturing synthetic natural gas (SNG) could be investigated. It is this possibility which will be examined in the remainder of the study.

Before going on to Parts 4 and 5 which will investigate some chemical and economic aspects of producing SNG, you should discuss two points with your group.

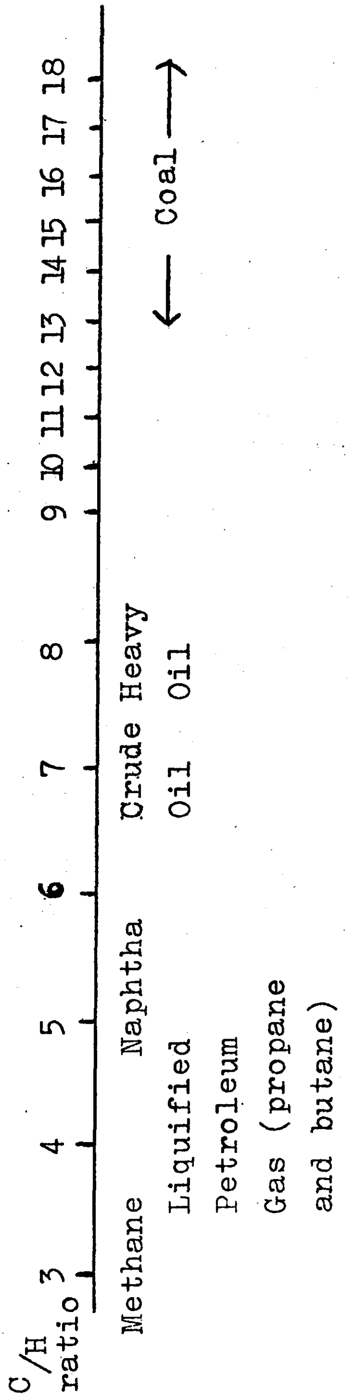
(i) What would be the chemical composition and burning properties ideally required by SNG?

A synthetic substitute for natural gas should be completely interchangeable with North Sea Gas so that the two can be mixed easily and no conversion of appliances is necessary. Thus SNG should possess the same calorific value (about 39,992 kJm^{-3}), burning velocity and density as North Sea Gas. Obviously - as North Sea gas consists mainly of methane - SNG could fulfil all the above criteria if its main constituent was also methane.

(ii) What possible raw materials could be used in the production of SNG, and how could the conversion be accomplished?
(Students may need to be lead through this part, but avoid the temptation to "lecture".)

It is required to produce CH_4 which has a $\frac{\text{Carbon}}{\text{Hydrogen}}$ weight ratio of 3, i.e. $\frac{12}{4}$ which is the smallest $^{C}/_{H}$ ratio for any hydrocarbon. It would be possible to use as a starting material any carbon source, e.g. hydrocarbons /

hydrocarbons (oil) or coal. Hydrocarbons and coal have a $^{C}/H$ ratio greater than 3 as shown below.



To convert any hydrocarbon into CH_4 it is therefore necessary to remove carbon, add hydrogen, or both.

Water in the form of steam can, given certain conditions, accomplish both tasks.

Hydrogen is released by decomposing steam in a reaction with coal or hydrocarbons. Carbon is removed as carbon dioxide.

The /

The overall equations for the reactions are:-

Coal $2C + 2H_2O \rightarrow CH_4 + CO_2$

Oil $4(-CH_2-) + 2H_2O \rightarrow 3VH_4 + CO_2$

In practice, however, these reactions involve a series of steps.

Clearly, as the $^C/H$ ratio of the feedstock increases, the weight of steam required and the weight of CO_2 produced increases.

This is illustrated on Graph 2 which you should hand out to each student at this stage.

Note that the steam and carbon dioxide weights are nearly trebled for coal compared to naphtha as feedstock. With coal the weights of steam decomposed and CO_2 released are both greater than the weight of coal used for gasification. Thus, for coal, water is as much a feedstock as coal and the removal of CO_2 from the mixture of product gases is a substantial task. Partly for these reasons coal gasification is a far more complex and expensive operation than oil gasification.

Part 4

(i) In order to maximise the volume of CH_4 from reaction (1), reactions (2) and (3) are required to be suppressed. As reaction (3) relies on reaction (2) for production of CO, we need only suppress reaction (2). This reaction involves 2 volumes of gas being transferred to 4 volumes. Thus high pressure would push the equilibrium in favour of the reactants.

Steam in excess of the stoichiometric amount has to be present to prevent decomposition of methane and any CO produced. However, excess steam also benefits reactions (2) and (3) and hence should be kept to the absolute minimum which will still prevent reactions (4) and /

and (5) occurring. Also a large excess of steam will result in unreacted steam being present in the product gases, reducing the percentage of methane present, and increasing the scale of the drying operation.

Thus, ideal reaction conditions include (a) high pressure and (b) the minimum excess steam/feedstock ratio.

In addition to these conditions, other thermodynamic calculations on the five possible reactions in the system indicate that methane formation is favoured at low temperatures. However, the reaction occurs over a catalyst, and a temperature of around 350°C is necessary before the catalyst becomes active. Thus there is a kinetic constraint to counterbalance the thermodynamic consideration. (There is scope for research in this area to find a catalyst which is active at temperatures lower than 350°C.)

Graph 3 which you should hand out to each student at this stage shows the effect of increasing temperature and varying steam feedstock ratio on the composition of the product gas. Note the decrease in methane content with increasing temperature and steam/feedstock ratio.

Note that by varying temperature, pressure and steam ratio we could tailor-make a combustible gas to specific requirements of calorific value, burning velocity, and density.

(ii) In the two processes, although the overall sum of the heats of reaction is the same in both cases, the hydrogenation route has the advantage that the actual heat demand and heat evolved are much lower than in the synthesis route. Consequently the duties of heat exchangers are less exacting, i.e. less effort is required to prevent heat loss and there is less dependence on heat recovery. This in turn leads to greater efficiency /

efficiency and to economies in capital costs.

However, the true situation is more complex as all coal gasification processes involve both routes in varying degrees. On balance, the process depending least on the synthesis route is likely to be the most efficient and economical on an industrial scale.

Part 5

Graph 4 shows increasing capital costs for SNG plants with increasing $^{C}/H$ ratio of the feedstock used. The higher $^{C}/H$ ratio of the feedstock the more effort and plant is required to reduce the ratio to 3 (CH_4). In addition, the higher the $^{C}/H$ ratio the more difficult it is to vapourise the feedstock which in turn involves a more complex process and higher capital cost.

Cost of Production of SNG

(a) From Naphtha

Depreciation Costs

From Graph 4, capital cost for building SNG plant using Naphtha as feedstock ($^{C}/H$ ratio = 5 to 6) is about £5 per m^3/day of gas produced.

∴ For a 3×10^6 m^3/day plant, capital cost is £15.0 millions.

∴ Depreciation costs = £1.5 millions per year.

Feedstock Costs

From Graph 2, about 790 tonnes of naphtha are required to produce 10^6 m^3 SNG.

But plant will produce 3×10^6 m^3/day.

$\equiv 1095 \times 10^6$ m^3/year ($\equiv 42.1 \times 10^{12}$ kJ/year)

∴ Require 790 x 1095 tonnes of naphtha/year

= 865,050 tonnes of naphtha/year.

But naphtha costs £39 per tonne.

∴ /

$\therefore$ cost of feedstock per year = £33.7 millions.

$\therefore$ Total cost (excluding labour, operation, and distribution costs) = £35.2 millions.

It was shown that 1095×10^6 m^3/year natural gas $\equiv 42.1 \times 10^{12}$ kJ/year,

$$\therefore \quad \text{cost}/10^6\text{kJ} = \frac{35.2 \times 10^6}{42.1 \times 10^6} \times 100 \text{ pence}$$

$$= 83.6 \text{ pence}/10^6\text{kJ}$$

Cost of Production of SNG

(b) From Coal

Depreciation Costs

From Graph 4, capital cost for building SNG plant using coal as a feedstock ($^C/H$ ratio = 14 to 18) is about £28 per m^3/day of gas produced.

$\therefore$ For x 3×10^6 m^3/day plant, capital cost is £84 millions.

$\therefore$ Depreciation costs = £8.4 millions per year.

Feedstock Costs

From Graph 2, about 880 tonnes of coal are required to produce 10^6 m^3 SNG.

But plant will produce 2×10^6 m^3/day
$\equiv 1095 \times 10^6$ m^3/year ($\equiv 42.1 \times 10^{12}$kJ/year)

$\therefore$ Require 880 x 1095 tonnes of coal/year
= 963,600 tonnes of coal/year.

But coal costs £19.5/tonne

$\therefore$ Cost of feedstock per year = £18.8 millions

$\therefore$ Total cost (excluding labour, operation and distribution costs) = £27.2 millions.

$$\therefore \quad \text{Cost}/10^6\text{kJ} = \frac{27.2 \times 10^6}{42.1 \times 10^6} \times 100 \text{ pence}$$

$$= 64.6 \text{ pence}/10^6\text{kJ}$$

Discuss /

Discuss with your group the relationship between depreciation and feedstock costs for each process.

The route from naphtha is far more dependent upon feedstock costs and the plant can be built relatively cheaply. With the coal process, however, increases in the prices of construction or of coal would both seriously affect the financial advantage of the process.

It must also be remembered that in the near future, oil from the North Sea could lead to cheaper naphtha, and the price differential between the two processes may disappear or may even be reversed, especially if coal prices continue to rise.

Another factor to be considered is that the much greater capital costs involved in the coal route (over 5 times greater than the naphtha route) mean that it could be a very long time before the plant made an overall profit.

However, the costed prices of the two processes do not compare favourably with the present selling price of gas which is about 39 pence per 10^6kJ (Oct. 1975). The prices calculated for each process are only the cost of producing SNG and do not include any profit, labour and distribution costs, which account for most of the cost of North Sea Gas.

Would the consumer be willing to pay treble or even quadruple the price for gas?

However, it must be remembered that North Sea gas is virtually free for taking at present and the only problems are of a technical nature involving location and distribution.

From Part 2 (c) it might be expected, given present trends, that demand for gas may reach at least 75 x 10^9 m^3/year by the year 2000.

To cope /

To cope with the demand totally by SNG plants capable of producing 3 x 10^6 m^3/day would require around 68 plants.

$$75 \times 10^9 \ m^3/year \equiv 75/365 \times 10^9 \ m^3/day$$
$$\equiv 0.205 \times 10^9 \ m^3/day$$

.'. Number of plants required to meet <u>total</u> demand

$$= \frac{0.205 \times 10^9}{3 \times 10^6}$$

$$= 68$$

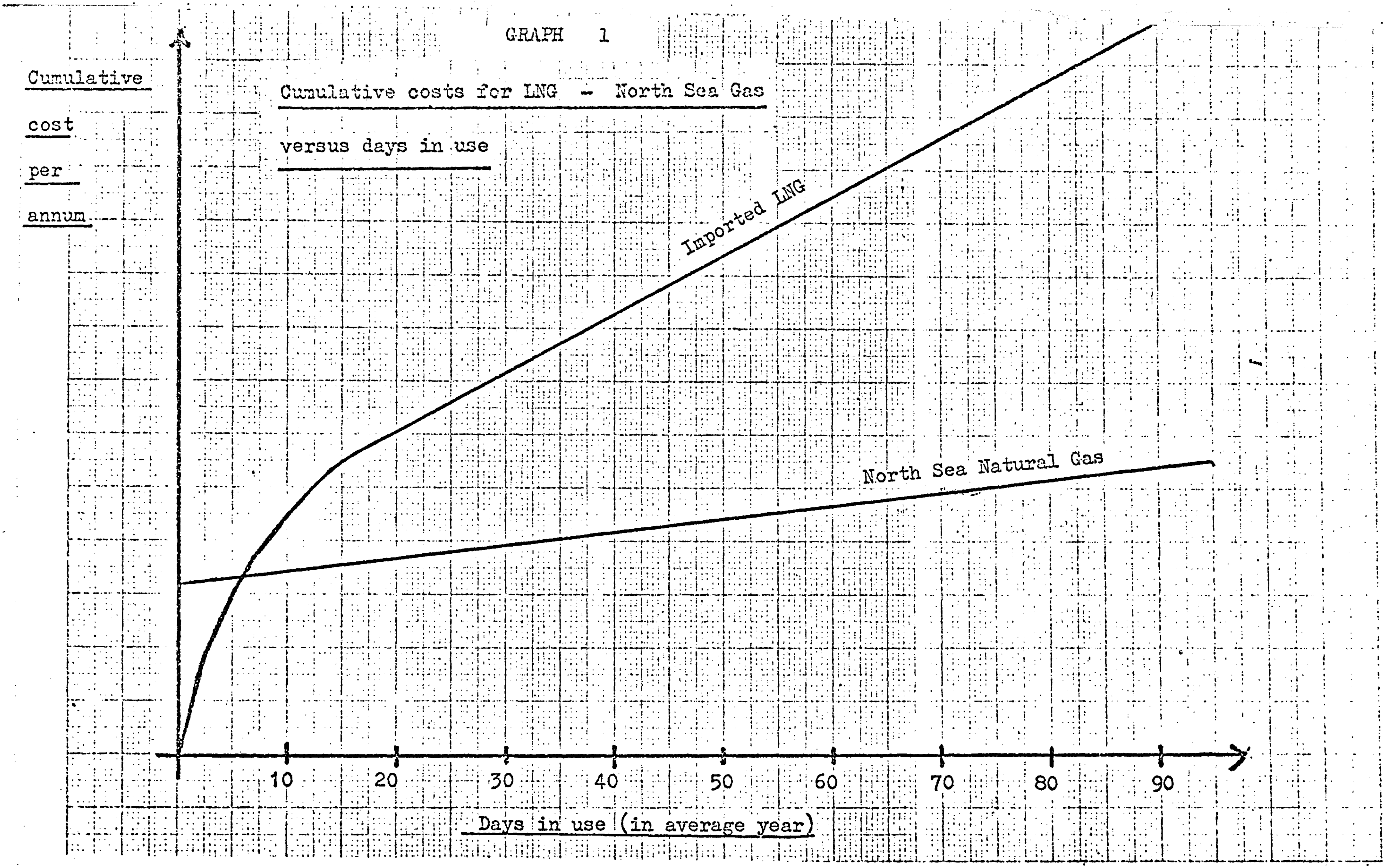
Each of these plants would be extremely large.

One way of introducing the consumer to the increased cost of SNG over North Sea Gas would be to start construction of such plants very soon so that the price of the gas increases gradually as more and more SNG is delivered into the system. This would also have the effect of conserving North Sea Gas supplies so that the increased price could be spread over a period of say fifty years, by which time the country could be capable of producing enough SNG to meet the total demand.

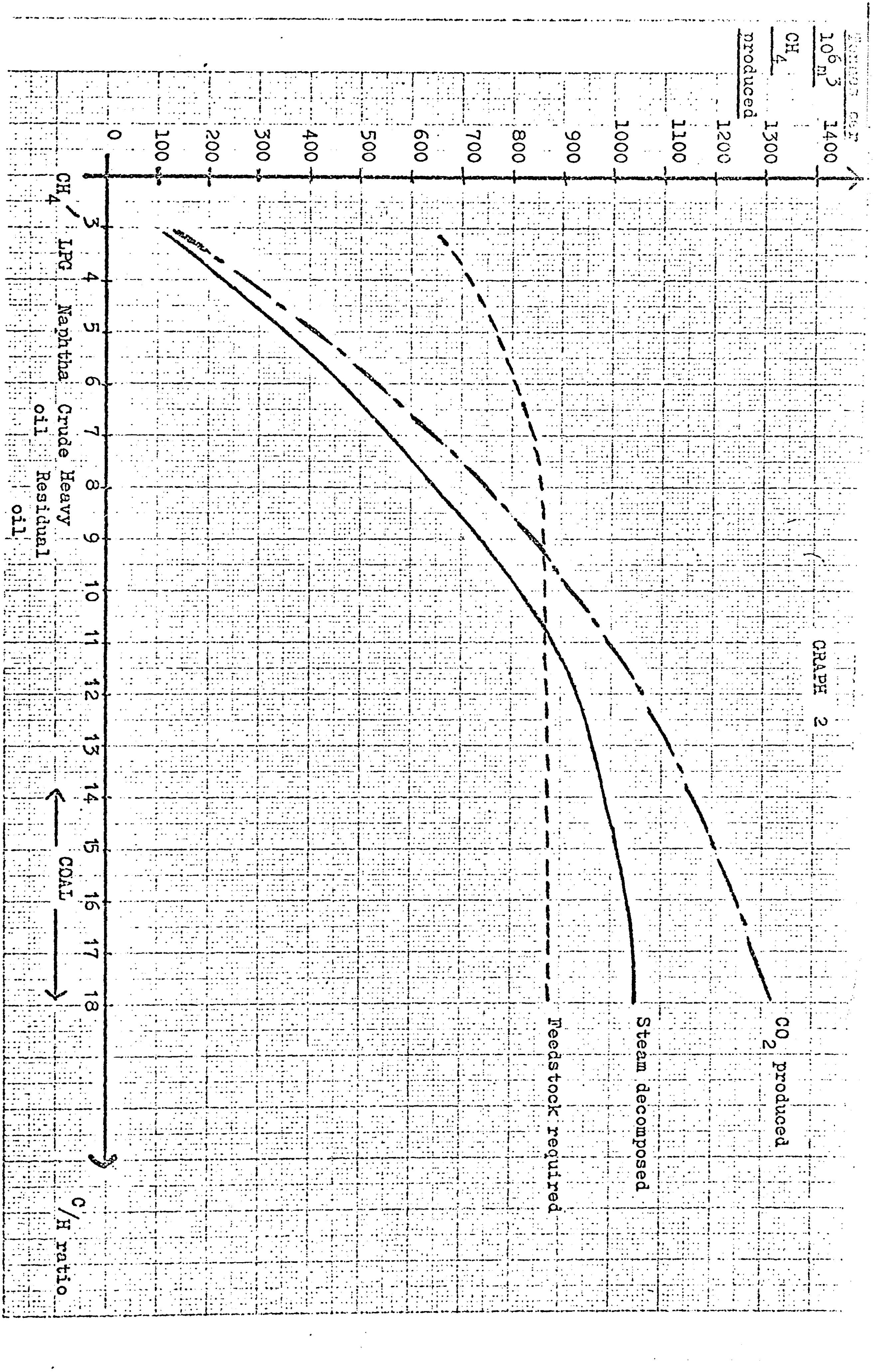
However, do not suggest this possibility to the students until they have discussed, themselves, the future of the British gas industry.

Finally, at the conclusion of the exercise underline the point that even before we have felt the full benefit of North Sea Gas in Britain, it is not too early to start planning ahead for the time that it will be finished.

GRAPH 1



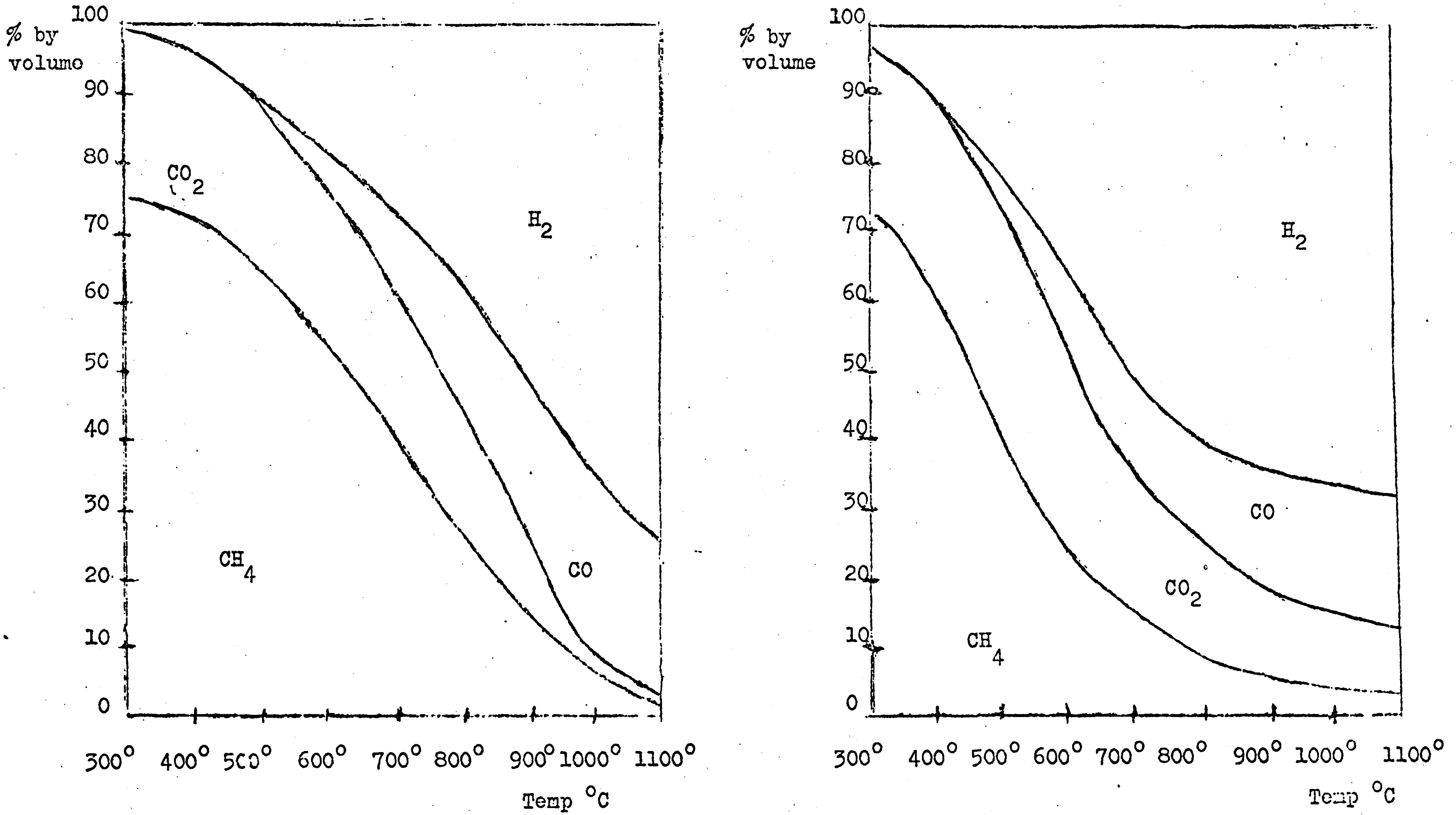
Cumulative costs for LNG - North Sea Gas versus days in use


GRAPH 2

$10^6 m^3$
CH_4 produced
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
CH_4
LPG
Naphtha
Crude oil
Heavy Residual oil
COAL
C/H ratio
CO_2 produced
Steam decomposed
Feedstock required

GRAPH 3

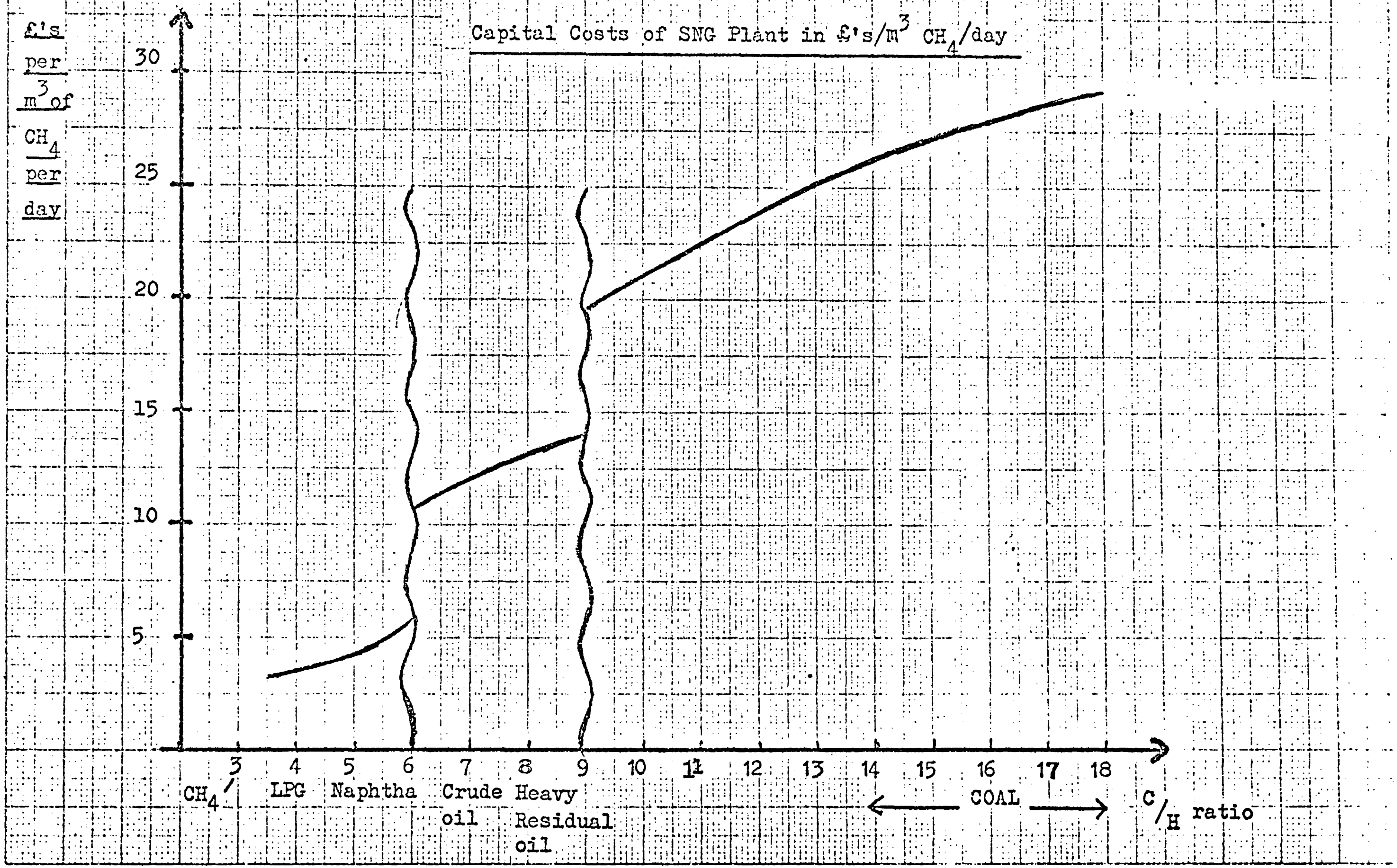
EQUILIBRIUM GAS COMPOSITIONS (DRY) FOR GASIFICATION OF NAPHTHA. at 25 atm.



Steam/feedstock ratio = 1.6 kg/kg

Steam/feedstock ratio = 4.0 kg/kg

GRAPH 4



Capital Costs of SNG Plant in £'s/m^3 CH$_4$/day

GAS CASE STUDY - ASSESSMENT

(i) <u>Likert-type Statements</u> (used in pre- and post-test)

<u>Question 1</u>

Read each of the following statements carefully, and tick the box which most closely represents your own honest opinion.

	Strongly agree	Agree	Disagree	Strongly disagree
(a) Industrial chemical decisions cannot be taken without considering the economic implications.				
(b) Problems in the economic and political areas of life should be tackled in a scientific manner.				
(c) Working in a group does not assist in making well-considered decisions.				
(d) Chemists should confine their attention to chemistry, leaving economics to economists.				
(e) The division of knowledge into separate divisions hinders effective decision making.				
(f) It is the duty of chemists to warn of future trends in natural resources (e.g. shortages).				
(g) Decisions on the use and exploitation of natural resources are based on clear-cut evidence.				
(h) I feel reasonably confident that, given the basic information, I could take a decision.				
(i) I enjoy working in a group.				
(j) I feel that, as a chemist, I need not worry too much about the social and economic implications of chemistry.				

(k) /

	Strongly agree	Agree	Disagree	Strongly disagree
(k) I benefit more from reading a textbook than participating in a case study.				
(l) I prefer pure academic chemistry to social and applied chemistry.				

(ii) <u>Objective Rating</u> (post-test only)

<u>Question 2</u>

The exercise has been designed to help you achieve the following objectives. In the boxes opposite each objective, place the letter which corresponds to your opinion on the achievement of the objective.

"A" - very successful
"B" - moderately successful
"C" - slightly successful
"D" - unsuccessful

At the end of the exercise, the student should be able to:-

(1) Recognise the chemistry relevant to the system under consideration. ☐
(2) Extrapolate trends from tables and graphs. ☐
(3) Make chemical and industrial decisions on the basis of chemical and economic considerations. ☐
(4) Assess the relative importance of a number of variables in a given situation. ☐
(5) Spot key facts among less relevant data. ☐

In addition, the student should develop:-

(6) An increased sensitivity to the contribution of chemistry to the social and economic welfare of the community. ☐
(7) A commitment to the application of a scientific approach to general problems. ☐
(8) /

(8) An awareness that many decisions are a compromise of conflicting interest. ☐

(9) A growth of confidence leading to a willingness to take decisions on information given. ☐

(10) An appreciation of the existence of interconnections across subject barriers. ☐

(11) An appreciation of the value of working and discussing in groups. ☐

(iii) Situational technique

Question 3

A chemical "Z" can be synthesised in the gaseous phase by the reaction

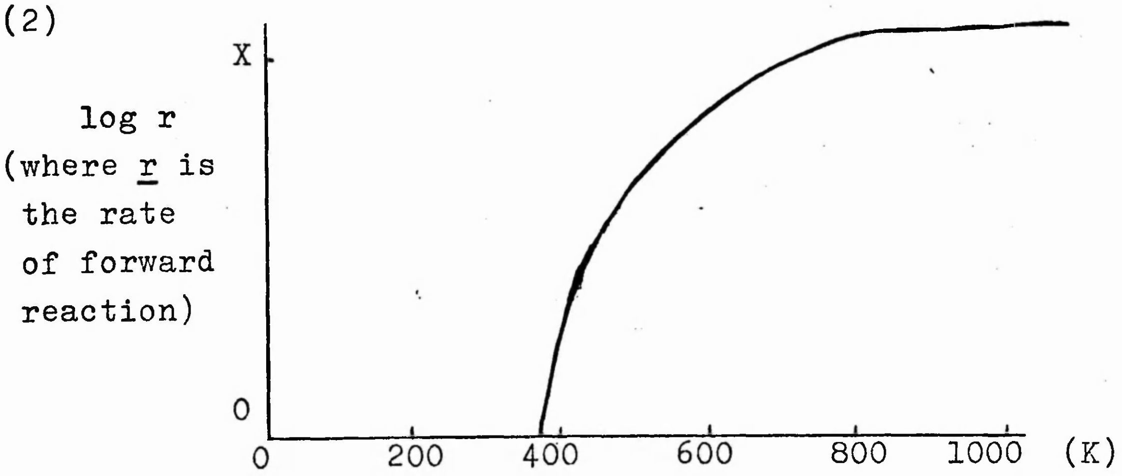
$$A(g) + B(g) = "Z"(g)$$

Some information has been gathered from many pilot studies:-

(1) % "Z" formed at equilibrium

Pressure (atmospheres)	200°	400°	600°	800° (°C)
1	5	2	0.5	0
50	30	6	1	0.5
100	70	25	8	1.5
200	88	36	13	3
1000	97	80	51	7

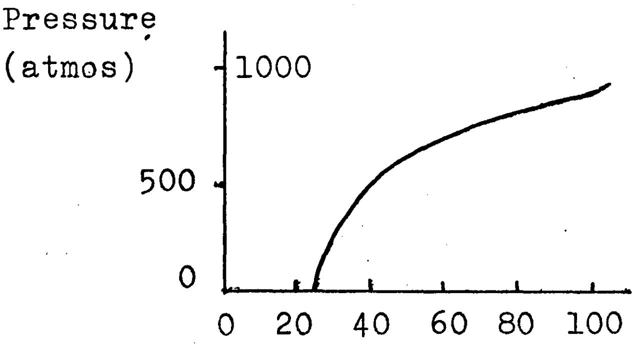
(2)



(X - represents the minimum reaction rate required for continuous flow industrial reaction conditions)

(3) /

(3)



Notes: Current selling price of "Z" - £100 per tonne.

YOUR TASK

Decide the best conditions of temperature (to nearest 50^0), and pressure (to nearest 50 atmospheres) in order to make the most profit out of the venture.

Your answer: Pressure -

Temperature -

CHAPTER 8

DISCUSSION

CHAPTER 8

DISCUSSION

8.1 Summary of This Work

Part of the research constituting this work has been into the literature of objectives in science teaching and the methods available to achieve effectively these objectives, with particular reference to the subject of chemistry. It has been found that much has been written, not only on the types of cognitive and manipulative skills a graduate in chemistry should possess, but also much emphasis has been laid on non-cognitive outcomes, such as modes of thinking and approaching problems, desirable attitudes, and broader skills such as communication and decision making skills, which would prove of value to a graduate whether he is employed as a chemist or not. Broadly speaking, this work has been concerned with devising teaching materials to complement traditional tertiary teaching methods in an effort to achieve a range of objectives of science teaching of both a cognitive and non-cognitive variety.

To complement the lecture in teaching a course on transition metal chemistry to first year undergraduates a series of self-instructional programs was produced. The course involved many concepts such as isomerism and crystal field theory which required a grasp of three-dimensional concepts. Consequently programs involving a combination of individual workbooks, tapes, models, construction kits and overlays were produced to give students a chance to master three-dimensional and other concepts in their own time. Diagnostic tests revealed no major ambiguities in the programs and that short-term mastery of the areas of the topic tested in each program was achieved to a large degree. A further study of subsequent performance in a degree examination in chemistry indicated that students /

students who completed relevant programs performed relatively better than expected in a question on transition metal chemistry. However, the comparison is complicated by the fact that it could be concluded from other questions in the paper that students who attempted the self-instructional programs had a generally higher chemical ability than those who did not - a fact which in itself is disturbing.

The remainder of this thesis was concerned with developing materials to achieve the broader outcomes of a science education discussed in Chapters 1 and 2. It has been argued that traditional teaching methods are ill-suited to achieve such outcomes, but that discussion methods, such as simulations, in which the student is active may be suitable for developing skills in communication, problem solving, decision making, library use and in dealing with and understanding other people. Claims have also been made that simulation methods may be effective in developing 'desirable' attitudes in students. A study of the literature revealed many varied, and possibly extravagant, claims for the benefits of simulations, most of which have yet to be verified by controlled experiments. In fairness, however, the experience gained in preparing this thesis has exphasised the often near-insuperable difficulties in expressing objectively the benefits of individual simulations. A combination of small and often unrepresentative sample sizes, due to a reliance on volunteers for testing, has had a detrimental effect on the generalising power of conclusions. The reliance on volunteers has also made impossible comparisons with matched control groups who did not attempt a particular simulation. This difficulty has had the effect of reducing the information gained from situational techniques in assessments to a negligible level. This was unfortunate as situational problems have possibly the greatest validity of all the assessment techniques used, as they attempt to measure transfer of learning to different situations, without which the use of most simulations /

simulations has little justification. The bulk of assessment of the simulations produced was done by self-reporting methods such as Likert, Semantic Differential and objective rating techniques. In addition, exercises in which the development of communication skills was a major aim, basic analyses of tape recordings was done. A battery of assessment procedures were used in an attempt to reduce any limitations of validity and reliability in any one technique.

Due to the reservations expressed above on the generalising power of the assessment results, very little can be said with absolute conviction or statistical significance about the changes produced in students by the simulations described. However, very few of the assessment results were in a direction opposite from that desired, and the short-term general trends apparent in the groups of students who participated in trials of the exercises were very encouraging, in most cases. A further quality of the simulation exercises produced was the observation, by all involved in overseeing the studies, of the enthusiasm, motivation and involvement amongst students. Although this is a subjective measure it is an important outcome of the use of simulation studies, but may be coloured by Hawthorne effects. Analyses of tape recordings indicated that the two exercises structured to promote communication skills each had the effect of involving <u>every</u> student in the groups concerned to a greater extent than might have been expected using more traditional discussion methods.

It is not suggested that the exercises which were produced are ideal, or that the technique of simulation is the panacea for all that ails education, but the exercises which were written, along with similar studies may prove an important weapon in a teacher's or lecturer's armoury in his attempt to produce intelligent, articulate, considerate and open-minded scientists as the products of tertiary education. The interest in the materials /

the materials from other universities, colleges and schools all over Britain has been extremely encouraging, with some of the materials already being included in the courses of some of these establishments. It is to be hoped that the seeds planted elsewhere flourish, so that the full potential of the range of simulation types can be fully realised and exploited.

8.2 Suggestions for Further Work

It is recommended that university chemistry departments take a hard, critical look at the courses which they provide and try to reconcile their courses with the type of graduate which they hope to produce to take his or her place in society. On the cognitive side, many topics would surely benefit from an approach other than the lecture in isolation. Topics involving three-dimensional principles such as crystal structure and organic stereochemistry immediately spring to mind as areas which would benefit from the production of tape/model programs similar to those on transition metal chemistry described in Chapter 4 of this thesis. University teachers should consider whether the lecture is necessarily the best method to suit their individual purposes and circumstances.

On the non-cognitive side, to appreciate the value of producing materials in an attempt to achieve the 'broader' aims of a university education, the question must be posed: "What is the purpose of an education in Science?" Obviously, in the case of chemistry, one of the aims is to produce competent chemists who can find employment using their chemical skills. Important as this group of graduates is, the majority of students studying chemistry at university do not become professional chemists. Even the professional chemist cannot hope to remember all the chemistry 'crammed' for the final examinations, and even if he could, he is unlikely to progress in a complex and changing society on the /

on the strength of his chemical knowledge alone. If education is, as it has sometimes been defined, 'what is left when the facts have been forgotten' the cognitive content of chemistry courses fades in importance, and what is left may possibly be ways of thinking and tackling problems, certain attitudes, and some of the 'broader skills' previously described.

Simulations may have an increasingly important role to play in 'educating for life' if it can be shown that they can be beneficial in this respect. This thesis has attempted only to look at the immediate short-term changes produced by specific simulations. It would be far more instructive to investigate if exposure to a planned series of simulation studies over a period of, say, one year produced long term changes in students, and if a series of simulations has a cumulative effect on students' broader skills and attitudes. The difficulties experienced in measuring short-term changes should serve as a warning as to the complexity of the task, but given a sympathetic department and the scope to introduce material to students on a general and not volunteer basis, the problems are not insuperable.

However, before a program on this scale is necessarily undertaken several other questions connected with simulation techniques require attention. Firstly it is not yet known how much any changes detected in students are due to a novelty or Hawthorne effect. Secondly, assessment procedures need to be carefully scrutinised for both reliability and validity. Improvements of assessment techniques may be necessary if a research effort to measure any cumulative effect of simulations was attempted, although in such a research effort situational techniques would surely play an important role. However, a great deal of work remains to be done in refining assessment techniques, although the use of several different techniques applied to one particular aspect of a skill or attitude is recommended /

recommended so that, by comparison, the limitations of each, if they exist, can be revealed. Refinement of the procedure of analysing recordings of discussion sessions may be one fruitful area. By using more sophisticated methods, such as forms of interaction analysis, it may be possible to obtain more information about the structure and content of discussions, and comparative analyses over a period of time may indicate cumulative changes in students' communication skills.

Although it has been suggested that more simulation studies be included in undergraduate courses, using chemistry and related subjects as the vehicle for achieving the broader aims of education, it is not suggested that the inclusion of simulations need necessarily be done at the expense of cognitive content. The potential of simulations, if not as yet necessarily proved by controlled experiments, is surely encouraging enough to find some time for their inclusion in any undergraduate chemistry course. Further, if the claims for the technique and the particular benefits of its different styles are unambiguously demonstrated, chemistry courses at tertiary level could take on new educational dimensions.

To summarize the suggestions for further work, it is considered that fruitful lines of enquiry could include that:-

(a) tertiary science teachers carefully scrutinize their cognitive and non-cognitive aims and objectives and match these with appropriate methods;

(b) the possible development of new assessment techniques for measuring the outcomes of simulation methods is investigated in conjunction with the refinement or validation of existing techniques;

(c) an evaluation of the extent of novelty or Hawthorne effects on simulation outcomes is attempted for various simulation styles;

(d) work is carried out to determine whether the beneficial effects of simulations are cumulative over a period of exposure to simulated materials, and whether any such changes are of a short or longer term (perhaps permanent) duration.

REFERENCES

1. Noll, V.H. : Teachers' College Record; 1933 35 1-9

2. Science Masters' Association : The Teaching of General Science, part II; Murray, 1938

3. Frutchley, F.P. and Tyler, R.W. : The Construction and Use of Achievement Examinations; Harrap, 1937

4. Kessler, O : Science Education 1945 29 273-278

5. Heil, L.M., Kambly, P.E., Mainardi, M. and Weisman, L. : The Forty-fifth Yearbook of the National Society for the Study of Education (Chapter 5); University of Chicago Press, 1946

6. Burmester, M.A. : Science Education 1952 36 259-263

7. Dunning, G.M. : Science Education 1954 38 191-211

8. Dressel, P.L. and Mayhew, L.B. : General Education - Explorations in Evaluation (Chapter 5); American Council on Education, 1954

9. Science Masters' Association : Science and Education - A Policy Statement; Murray, 1961

10. Lewis, D.G. : Educational Research 1964 7 186-199

11. Beard, R.M. : in Instructional Simulation Systems in Higher Education; Armstrong, R.H.R. and Taylor, J.L. (Eds.); Cambridge Institute of Education, 1970 p. 1-7

12. Nuffield Chemistry : Introduction and Guide; The Nuffield Foundation, 1966

13. /

13. Curriculum Papers No. 7 : Scottish Education Department, H.M.S.O., Edinburgh, 1969

14. Goodall, E.S. : Journal of Chemical Education; 1975 52 565

15. Wolke, R.L. : Journal of Chemical Education; 1975 52 153-154

16. Holliday, A.K. and Maskill, R. : British Committee on Chemical Education; The Royal Society, May 1972

17. Beard, R.M. : in Aims, Methods and Assessment in Advanced Science Education; Billing, D.E. and Furniss, B.S. (Eds.); Heyden, 1973 p. 3-15

18. Holliday, A.K. : in Aims, Methods and Assessment in Advanced Science Education; Billing, D.E. and Furniss, B.S. (Eds.); Heyden, 1973 p. 39-45

19. Hughes, N.M., Poller, R.C. and Slade, R.C. : Education in Chemistry; 1975 12 37

20. Holliday, A.K. Hughes, W.J., Maskill, R. : Education in Chemistry; 1973 10 215-216

21. Billing, D.E. : Chemical Society Curriculum Subject Group Newsletter, 1973 No. 1 p. 22

22. Bloom, B.S. (Ed.) : Taxonomy of Educational Objectives, Handbook 1, Cognitive Domain; Longmans, 1956

23. Krathwohl, D.R., Bloom, B.S. and Masia, B.B. : Taxonomy of Educational Objectives, Handbook 2, Affective Domain; Longmans, 1964

24. Mager, R.F. : Preparing Instructional Objectives; Fearon, 1962

25. Kropp, R.P., Stocker, H.W. and Bastow, W.L. : Journal of Experimental Education, 1966 34 (3) 69-73

26. /

26. Stedman; C.H. : Journal of Research in Science Teaching 1973 10 235-241

27. Lewy, A. : Journal of Experimental Education 1968 36 (3) 70-77

28. Greenwood, N.N. : Education in Chemistry 1972 9 36

29. Lord James of Rusholme : Education in Chemistry 1975 12 108-109

30. Association for Science Education : Education in Science, November, 1973

31. Thring, B. : Project Technology, Bulletin 11, November 1969

32. Hadden, R.A., Handy, J. and Johnstone, A.H. : Education in Chemistry 1974 11 206-207

33. University Grants Committee : Report of the Committee on University Teaching Methods (Chairman Sir. H.E. Hale); H.M.S.O., 1964

34. Dubin, R. and Taveggia, T.C. : The Teaching - Learning Paradox; Centre for Advanced Study of Educational Administration, Monograph 18; University of Oregon, 1968

35. McKeachie, W.J. : in Handbook of Research in Teaching; Gage N. (Ed.); Rand McNally, 1963 p. 1118-1172

36. Bligh, D.A. : What is the Use of Lectures? ; Penguin, 1972

37. Bloom, B.S. : Journal of General Education 1953 7 160-169

38. Tyler, R.W. : in The Constructs and Use of Achievement Examinations (Chapter 1); Hawkes, H.E., Lundquist, E.F. and Mann, C.R. (Eds.); Harrap, 1937

39. /

39. Hoare, D.E. and Revans, M.M. : Education in Chemistry 1969 <u>6</u> 78-80

40. Broadley, M. : University Quarterly, Summer 1970 p. 274

41. Billing, D.E. : in Aims, Methods and Assessment in Advanced Science Education; Billing, D.E. and Furniss, B.S. (Eds.); Heyden, 1973 p. 76

42. Skinner, B.F. : Harvard Educational Review 1954 <u>24</u> 86

43. Crowder, N.A. : in Automatic Teaching : the State of the Art; Glanter, E. (Ed.); Wiley, 1959

44. Bandy, R.D., Stordahl, K.E. and Carter, R.A. : Journal of Chemical Education 1974 <u>51</u> 537

45. de Winter Hebron, C.C. : Bulletin of Educational Research 1974 <u>7</u> 12-15

46. Owen, S.G., Hall, R., Anderson, J. and Smart, G.A. : Programmed Learning 1965 <u>2</u> 2-14

47. Stavert, G.S. and Wingate, T.H. : Tutor Age 1966 p. 17-27

48. Teather, D.C.B. : Journal of Biological Education 1968 <u>2</u> 119-135

49. Barrington, H. : Educational Research 1965 <u>8</u> 8-25

50. Keller, F.S. : Journal of Applied Behavioural Analysis 1968 <u>1</u> 79

51. Silberman, R. and Parker, B. : Journal of Chemical Education 1974 <u>51</u> 393-395

52. Leo, M.W. : Journal of Chemical Education 1973 <u>50</u> 49-50

53. /

53. Elton, L.R.B. : Chemistry in Britain 1973 9 164-168

54. Born, D.G. and Herbert, E.W. : Journal of Experimental Education 1971 40 6-11

55. Linder, S. and Whitehurst, C. : Journal of Experimental Education 1973 42 42-44

56. Bent, H.A. : Journal of Chemical Education 1974 51 661-664

57. Hendrick, J.L. : Journal of Chemical Education 1975 52 65

58. Young, D. : Chemistry in Britain 1973 9 168-169

59. Emerson, D.W. : Journal of Chemical Education 1975 52 228-229

60. Beard, R.M. : in Teaching and Learning in Chemistry; Trickey, D.S. (Ed.); Sheffield Polytechnic, 1972 p. 29

61. Elton, L.R.B. : Chemical Society Curriculum Subject Group Newsletter; November 1973 p. 6

62. Youmans, H.L. : Journal of Chemical Education 1973 50 565

63. Epstein, H.T. : Nature 1972 235 203-205

64. Erskine, C.A. and Tomkin, A. : Journal of Medical Education 1963 38 1036-1042

65. Tansey, P.J. and Unwin, D. : in Aspects of Educational Technology (Vol. II); Dunn, W.R. and Holroyd, C. (Eds.); Methuen, 1969 p. 171

66. Guetzkow, H. : Simulation in International Relations; Prentice Hall, 1963

67. McGarvey, D. : in Educational Aspects of Simulation; Tansey, P.J. (Ed.); McGraw Hill, 1971 p. 206

68. /

68. Bloomer, J. : Programmed Learning and Educational Technology 1973 10 224-234

69. Twelker, P.A. : First Annual Conference of the Society for Academic Gaming and Simulation in Education and Training; Berkshire College of Education, 1970

70. Twelker, P.A. : in Educational Aspects of Simulation; Tansey, P.J. (Ed.); McGraw Hill, 1971 p. 133

71. Abt, C.C. : in Simulation Games in Learning; Bovcock, S.S. and Schild, O.E. (Eds.); Sage Publishers, 1968 p. 65

72. Nesbitt, W.A. : Simulation Games for the Social Studies Classroom; Foreign Policy Association, 1956

73. Boardman, R. : Educational Research 1966 11 179

74. Fines, J. : Journal of Curriculum Studies 1970 2 23-31

75. Tansey, P.J. : in Educational Aspects of Simulation; Tansey, P.J. (Ed.); McGraw Hill 1971 p. 24

76. Walker, M. : Education in Chemistry 1974 11 58-60

77. Daniels, D.J. : in New Movements in the Study and Teaching of Chemistry; Daniels, D.J. (Ed.); Temple Smith, 1975

78. Gagne, R.M. : The Conditions of Learning (2nd Edition); Holt, Rhinehart and Winston, 1970

79. Tansey, P.J. : Simulation and Gaming in Education; Methuen, 1969

80. Cruikshank, D.R. : in Educational Aspects of Simulation; Tansey, P.J. (Ed.); McGraw Hill, 1971 p. 185

81. /

81. Bloomer, J. : in Lecture delivered at Glasgow University; June 1974

82. Fletcher, J.L. : Simulations and Games 1971 2 473-488

83. Wentworth, D.R. and Lewis, D.R. : Social Education 1973 No. 5 p. 432-440

84. Tansey, P.J. : Simulation Gaming News 1973 1 4

85. Bloomer, J. : Sagset Journal 1975 5 (1) 36-37

86. Walford, R. : Sagset Journal 1975 5 (1) 20-22

87. Kurfman, D. : Geographic Discipline and Enquiring Student; Bollier-McMillan, 1972

88. Taylor, J.L. : Programmed Learning and Educational Technology 1974 11 197-203

89. Shubik, M. : On the Scope of Gaming; Rand Corporation, 1972

90. Cowan, J. : Programmed Learning and Educational Technology 1974 11 192-196

91. Bales, R.F. : Interaction Process Analysis : A Method for the Study of Small Groups; Addison-Wesley, 1950

92. Thurstone, L.L. : Psychological Review 1929 36 232-241

93. Likert, R. : Archives in Psychology 1932 140 55

94. Osgood, C.E., Suci, G.J. and Tannenbaum, P.H. : The Measurement of Meaning; University of Illinois Press, 1957

95. Hadden, R.A. : A Study of the Affective Objectives in the Teaching of Chemistry; M.Sc. Thesis, Glasgow University, 1975

96. /

96. Handy, J. and Johnstone, A.H. : in The Discipline of Chemistry - Its Place in Education; Education Division, The Chemical Society, 1973 p. 50-53

97. Vesper, K.H. and Adams, J.L. : Engineering Education, October 1969 p. 104-106

98. Johnstone, A.H. and Percival, F. : Education in Chemistry 1976 13 49-50

99. Huck, S.W. and Long, J.D. : Journal of Experimental Education 1973 42 (1) 40-41

100. Spiegel, M.R. : Schaums Outline Series : Theory and Problems of Statistics; McGraw Hill, 1961 p. 172

101. Hartley, J. : Programmed Learning and Educational Technology 1972 9 108-112

102. Hogg, D.R. : Education in Chemistry 1973 10 7-9

103. Rae, J. : in Instructional Simulation Systems in Higher Education; Armstrong, R.H.R. and Taylor, J.L. (Eds.); Cambridge Institute of Education, 1970 p. 141-169

104. Smith, A.D. and Jepson, J.B. : The Lancet 1972 (ii) p. 585-586

105. Guide to the Use of Chemical Abstracts - A Tape/Slide Program; Southampton University, 1972

106. de Winter Hebron, C.C. : Bulletin of Educational Research 1975 9 29

107. Jones, G. : Education in Chemistry 1973 10 11

108. Steedman, W. : Education in Chemistry 1974 11 93-94

109. Parker, G.A. : Journal of Chemical Education 1973 50 606-607

110. /

110. Crombie, D.A. : Education in Chemistry 1975 12 51

111. Bartsch, R.A. : Journal of Chemical Education 1974 51 160

112. Harben, C.Y. : Education in Chemistry 1974 11 46

BIBLIOGRAPHY

Armstrong, R.H.R. and Taylor, J.L. : Feedback on Instructional Simulation Systems; Cambridge Institute of Education, 1971

Beard, R. : Teaching and Learning in Higher Education; Penguin, 1972

Beard, R. and Bligh, D. : Research into Teaching Methods in Higher Education; Society for Research into Higher Education, 1971

Bloom, B.S., Hastings, J.T. and Madaus, G.F. : Handbook on Formative and Summative Evaluation of Student Learning; McGraw Hill, 1971

Gordon, A.K. : Games for Growth; Science Research Associates Incorporated, 1972

Nisbet, J.D. and Entwhistle, N.J. : Educational Research Methods; University of London Press, 1970

Taylor, J.L. and Walford, R. : Simulation in the Classroom; Penguin, 1972

Thomas, K. (Ed.) : Attitudes and Behaviour; Penguin, 1971

Popham, W.J. and Sirotnik, K.A. : Educational Statistics - Use and Interpretation; Harper and Row, 1973

Zuckerman, D.W. and Horn, R.E. : Guide to Simulation Games for Education and Training; Information Resources Incorporated, 1970