AN INVESTIGATION OF PRACTICAL WORK IN THE S.C.E. CERTIFICATE OF SIXTH YEAR STUDIES IN CHEMISTRY.

BY

J. McGUIRE

A THESIS IN PART FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF M.Sc. AT THE UNIVERSITY OF GLASGOW.

CONTENTS

ABSTRACT

This investigation is concerned with practical work in Sixth Year Studies Chemistry and in particular with:-

(a) How much practical work is being done and under what conditions?

(b) How suitable are the experiments being used and how can they be improved?

(c) What objectives are being achieved by the practical work?

(d) Effect of the project on achievement of objectives.

(e) Preliminary investigation of assessment of skills gained through practical work by pencil and paper tests.

In 1971 a questionnaire was sent to all teachers of Sixth Year Studies Chemistry. Data obtained from this indicated that the vast majority of schools were receiving what the original planners of the course considered to be an adequate allocation of time.

The proportion of time allocated to practical work was also adequate in those terms. The number of experiments being used however fell far short of the planners' intentions. The experiments listed in the Sixth Year Studies Chemistry syllabus were tried out by the author. It was found that all but four of the experiments were well within the scope of secondary school laboratories and pupils.

Alternative experiments have been collected, rewritten and tried out by post-graduate students. They are on trial in a group of schools, before being put into general circulation.

It was found that the experiments not being used frequently in schools coincided with areas of weakness shown in the Sixth Year Studies Examinations.

The degree of achievement of some objectives of practical work in Sixth Year Studies Chemistry was investigated by sending questionnaires to pupils and teachers in ten schools during the academic year 1971 - 1972.

The pupils indicated what they thought had been achieved by each experiment after it had been completed. The teachers indicated what objectives they thought had been achieved by each experiment. Enough data was available from eighteen experiments to see trends in achievement of objectives and to compare teachers and pupils views of objectives.

Pupils tended to see properties and behaviour of substances rather than underlying concepts. There was more agreement between what objectives the pupils thought had been achieved and what the teachers thought should have been achieved when the objectives of the experiment were stated clearly.

'Encouraging further investigation' was not rated very highly as an objective by the teachers but it was rated much lower for achievement by the pupils.

The teachers rated 'reinforcing theory learned in class' high as an objective of practical work. Pupils rated it much lower and about 30% of the pupils claimed that carrying out experiments made no difference to their understanding of theory.

Further questionnaires were sent to pupils and teachers in eighteen schools in April 1972. The responses to the teachers' questionnaires indicated that practical work is not as closely integrated with theory as the responses to the 1971 questionnaires indicated.

The pupils' questionnaires tended to confirm what objectives had been achieved by practical work and to indicate that carrying out projects helped to achieve the objectives of 'increasing skills in handling apparatus' and 'introducing a variety of methods of chemical investigation'.

The teachers were asked in their questionnaire to list their pupils in order of merit for practical skills. The pupils were given a pencil and paper test to assess these skills. An order of merit was made up on the basis of the tests and compared with the teachers' orders of merit.

Ten of the schools provided data from which conclusions could be drawn. Comparing the teachers' and the test's order of merits, all showed a small positive correlation. Six were greater than 0.35 and four were less than 0.35. It would appear that further investigation of assessment of practical skills by pencil and paper tests might be worthwhile.

CHAPTER 1.

INTRODUCTION.

INTRODUCTION

In the past chemistry at sixth year level in Scottish schools was principally concerned with the needs of pupils sitting university bursary competition examinations. With the availability of larger student grants the bursary competition assumed a different role for the majority of pupils. The need for a post Higher year as a time for maturing before proceeding to a tertiary educational institution was recognised. The bursary competition was being used for this purpose. This is indicated by the drop in the number of candidates sitting Chemistry Paper I of the Glasgow University Bursary Examination on the introduction of Sixth Year Studies Chemistry in 1969.

Year	1966	1967	1968	1969	1970	1971	1972
No. of Candidates	101	111	102	86	88	72	67

Pupils were also sitting 'A' levels of English Examination Boards which, like the bursary examinations, had traditional syllabuses containing large parts of first year university courses. The introduction of the 'Alternative Syllabus' at 'O' and 'H' grade [1] made it necessary that any sixth year syllabus should show continuity of philosophy and content with the 'Alternative Syllabus'.

In 1962 the Scottish Education Department put forward proposals for 'A' levels and produced syllabuses for a number of subjects. Among these was one for chemistry.[2] These proposals received adverse criticism from interested parties and were withdrawn. Some of the criticisms took the form of counter proposals which were used in preparing Sixth Year Studies.

The guide lines for production of syllabuses were sent to the conveners of all subject panels of the Examination Board by the Scottish Certificate of Education Special Committee on Post-Higher Examination in the form of a memorandum.[3] The following extract contains what the Board considered to be the most important purpose of the course.

> The Special Committee is anxious to ensure that the examination provided by the Board should accord with the real purpose which a "proper sixth year" is intended to serve. It believes that the most important of these purposes is the development in the pupils of a greater degree of maturity of outlook than they have generally acquired by the end of the fifth year. This purpose can best be achieved through a course of study which aims partly at broadening the pupil's general outlook and partly at deepening his knowledge and understanding of a limited range of subjects.
>
> The approach to such a course should "lead the pupil into habits of positive and rewarding private study, should promote individual thinking and judgement and should develop self-reliance and responsibility in place of his almost absolute dependence on his teachers." (Report of the Advisory Council: "The Post-Fourth Year Examination Structure in Scotland" paragraph 23 ad fin.)

Some of the previous criticisms were taken into account. There was a fear, with the first proposals, that the post 'O' grade situation would deteriorate to the 'over specialisation' of the English 'A' levels where only three subjects are studied compared with five or six to the Scottish 'H' grade. This was a possibility if the Scottish 'A' level was used as a university entrance qualification.

The 'H' grade might then be devalued and possibly discontinued. Even if it was not discontinued it would mean pupils sitting three career deciding examinations in consecutive years. The syllabuses also had to ensure that the pupils were not solely memorising factual material but were being led into independence, development of critical faculties and an ability to formulate theories and supporting arguments.

It was proposed that no student should present himself for more than three subjects. These subjects should occupy one half to three fifths of the week thus allowing time for other interests. The examination was not to be used for university entrance. (A1-10 to A1-11).

All of the subjects were to be an extention of the 'H' syllabuses with a comparatively small proportion of new topics ensuring the opportunity to study some sections in depth or by projects and options. The total course time would be about seven months with examinations coinciding with the '0' and 'H' grade diet after Easter

After trials in a group of pilot schools in 1967, the chemistry syllabus was produced in 1968.[4] It consisted of a basic course of work which was expected to be covered in about 100 hours. The topics were chosen -

(a) to provide a deeper understanding of some topics from '0' and 'H' grades with more quantitative evidence than was possible at these stages, e.g. Thermodynamics, Bonding and Molecular shape with spectroscopy to provide evidence.

(b) To avoid duplicating first year university syllabuses. It had been noted that students who had covered first year university work at school often appeared to do well during their first year, but poorly during subsequent years. This may have been due to forming poor working habits while the material was familiar and required little study.

(c) To use the fact that sixth year pupils were usually in very small groups and discussion of ideas like free energy, entropy and social aspects of chemistry was possible.

The topics were set out in detail in the Certificate of Sixth Year Studies Chemistry Syllabus.[4] Since then specific as opposed to general objectives in chemistry for 'O' and 'H' grades and sixth year studies have been drawn up and may be used as a guide to modifications of all three courses. (A1 - 1 to A1 - 6).

With the topics were listed a set of experiments appropriate to each of the topics and this course work was to be taken into account for assessment. A record of practical work had to be kept. No objectives for the practical work were given with the syllabus but it was hoped that it could be used:-

(i) To raise problems that would generate discussion;

(ii) To illustrate theory;

(iii) To increase skills in measurement and in handling apparatus.

The pupils also had to carry out a project, "original as far as the pupil is concerned and detailed in a report of about 2000 words".[4] The objectives of the project work were listed with the syllabus and embodied the spirit of the 1965 Examination Board Memorandum.[3]

"The aim of project work in chemistry is the development of:-

(i) skill in devising an appropriate scheme for studying a problem in chemistry,

(ii) skill in handling, classifying, interpreting and presenting information (including graphs and quantitative results),

(iii) ability to apply previously acquired understanding to new situations and to show creative thought,

(iv) resourcefulness on the part of the pupil with a corresponding lessening of dependence on the class teacher."

It was expected that the total time allocation for Sixth Year Studies Chemistry in the school would be about 140 hours. Of this about 40 hours would be devoted to the project and the remainder to the syllabus. Of the syllabus time 5/8 would be given to practical and 3/8 to theory. (A1-11)

The syllabus was to be examined by -

(1) A three hour written paper based mainly on the sixth year work.

(2) A 1½ hour paper consisting of approximately 50 objective-type items based on the whole syllabus up to and including sixth year work

(3) A written report and oral examination on the project and course practical work.

The allocation of marks was to be -

Paper I	-	100
Paper II	-	50
Project and practical work		50

The 50 marks for project and practical work have to be awarded by an external assessor, usually another teacher involved in teaching Sixth Year Studies Chemistry. The 50 marks were allocated as follows -

Project report	-	20 marks
Oral examination	-	20 marks
Course work	-	10 marks

Fuller details of the assessment are printed in "Certificate of Sixth Year Studies Examination in Chemistry, 1970. Notes for Guidance in Project Assessment". (A1-7 to A1-9).

Since 1969 the numbers of pupils being presented are -

Year	No. of pupils presented
1969	425
1970	771
1971	1073
1972	1191

The foregoing is a summary of the history and development of Sixth Year Studies Chemistry to date. This research topic is concerned with practical work in Sixth Year Studies Chemistry and in particular with:-

(a) How much practical work is being done and under what conditions?

(b) How suitable are the experiments and can they be improved?

(c) What objectives are being achieved by the practical work?

(d) Can practical work be assessed by written tests.

POSSIBLE OBJECTIVES IN CHEMISTRY FOR 'O' AND 'H' GRADES AND CSYS

A. Pupils should acquire

1. (a) Knowledge of various symbols used by chemists (O)

   (b) Comprehension of the use of symbols by chemists in formulae and equations. (O)

   (c) Ability to apply knowledge and comprehension of chemical symbols in the writing of formulae and equations. (O)

2. (a) Knowledge of quantitative relationships in chemistry. (O)

   (b) Facility in using a variety of standard methods in chemical arithmetic. (O)

   (c) Ability to carry out relevant calculations concerning a variety of concepts. (O)

3. (a) Knowledge of systematic nomenclature applied to some chemical species. (O)

   (b) Comprehension of the principles underlying systematic nomenclature as applied to chemical species. (O)

   (c) Ability to apply systematic chemical nomenclature to the naming of various species both known and unknown. (H)

4. (a) Knowledge of fundamental concepts contained in the syllabus.(O)

   (b) Comprehension of the fundamental concepts contained in the syllabus. (O)

   (c) Ability to apply fundamental concepts contained in the syllabus. (O)

5. (a) Knowledge of the chemistry of certain elements and their simple compounds. (O)

   (b) Comprehension of the principles underlying the chemistry of certain elements and their compounds. (O)

   (c) Ability to apply knowledge and comprehension of the chemistry of the elements and their compounds in a range of situations. (H)

6. (a) Knowledge of a variety of methods of effecting chemical change (0)
   (b) Ability to apply methods of effecting chemical changes in new situations. (0)
7. (a) Knowledge of the chemistry of some industrial processes. (0)
   (b) Comprehension of the chemistry of some industrial processes. (0)
   (c) Ability to apply the knowledge and understanding of the chemistry of various industrial processes in new situations. (H)
8. (a) Knowledge of the effects of chemicals on everyday life. (0)
   (b) Comprehension of the effects of chemicals on everyday life. (0)
   (c) Ability to apply knowledge and comprehension of the effects of chemicals on everyday life to new situations. (0)
9. (a) Knowledge of the chemist's ability to produce new compounds. (0)
   (b) Comprehension of the relationship between structure and properties of various chemical substances. (0)
10. (a) Knowledge that appropriate information can be obtained from a range of sources. (0)
    (b) Ability to find various types of information from a range of sources. (0)
11. (a) Knowledge of chemical classifications. (0)
    (b) Comprehension of chemical classification. (0)
    (c) Ability to classify chemical information in various ways. (0)
12. (a) Knowledge of methods of classifying chemical information. (H)
    (b) Comprehension of methods of classifying chemical information. (H)
13. (a) Knowledge of limitations of precision involved in physical measurement. (0)
    (b) Comprehension of reasons for limitation of precision. (0)
    (c) Ability to apply a knowledge of the limitations on accuracy created in physical measurement where a range of precision levels apply. (H)

14. (a) Knowledge of laboratory equipment and techniques sufficient to enable the experimental procedures to be carried out adequately. (O)
    (b) Comprehension of laboratory techniques sufficient to enable experimental procedures to be carried out adequately. (O)
    (c) Ability to select relevant techniques to enable experimental procedures to be carried out. (O)
15. (a) Knowledge of appropriate safety regulations to be observed in the laboratory. (O)
    (b) Comprehension of the reasons underlying safety regulations in the laboratory. (O)
16. Ability to comprehend written and oral instructions. (O)
17. Ability to record and present information in various ways including graphical and diagrammatic representation as well as written statements. (O)
18. Ability to follow arguments about chemical ideas. (O)
19. Ability to criticise arguments about chemical ideas. (H)
20. Ability to consider experimental evidence in terms of two and three dimensional physical models. (O)
21. Ability to use experimental evidence to formulate hypotheses and conceptual models. (O)
22. Ability to design experiments to check predictions and hypotheses deduced from available information. (O)
23. Ability to deal with multi-variable situations. (O)
24. Ability to adopt a scientific approach in other fields of experience. (O)

B. Pupils should acquire in attitudes.

1. Awareness that chemistry can form the basis for many satisfying careers. (O)
2. Awareness of the contribution of chemistry to the full development of the individual. (O)
3. Awareness of the contribution of chemistry to the economic and social welfare of the community. (O)
4. Awareness that a number of variables can influence an experimental situation. (O)
5. Awareness of the limitations inherent in analogies as 'Models'. (H)
6. Interest and enjoyment in chemistry. (O)
7. Acceptance of the chemist's ability to produce new compounds. (O)
8. Acceptance of the importance of observation in an experimental procedure. (O)
9. Acceptance of the value of an experimental approach to problems. (O)
10. Acceptance of the desirability of working and discussing in groups in appropriate situations. (O)
11. Acceptance of responsibility for carrying out suitable safety procedures. (O)
12. Commitment to optimum precision of measurement. (O)
13. Commitment to optimum precision of statement. (O)
14. Commitment to cleanliness and neatness in experimentation. (O)
15. Commitment to the systematic recording of experimental results and other data. (O)
16. Commitment to objectivity in observation and assessment wherever possible. (O)
17. Commitment to arriving at conclusions from the information, knowledge and understanding available. (O)

18. Commitment to apply a scientific approach in other fields of experience. (0)

C. Pupils should acquire in practical skills.

1. Skill in using various pieces of equipment effectively and safely.(0)
2. Skill in drawing diagrams and visual representations of quantitive data. (0)
3. Skill in assembling relevant pieces of equipment into experimental rigs.
4. Skill in using various measuring devices to the appropriate degree of precision. (0)
5. Skill in working at adequate speed and with reasonable neatness and safety. (0)
6. Skill in handling materials with due attention to safety and economy. (0)

For CSYS, in addition to the above, pupils should also acquire

A. In knowledge and understanding -

1. ability to develop a sustained approach to a particular problem
2. ability to verbalise conceptual problems concisely (to define a problem in words)
3. ability to defend orally and in writing a given course of action and the conclusions arrived at
4. ability to work without detailed supervision
5. ability to suggest future work arising from a project.

B. In attitudes -

1. acquisitions of increasing self-confidence leading to a willingness to take decisions
2. realisation that many decisions are at best a compromise solution of conflicting interests

3. realisation that many decisions are necessarily taken on incomplete evidence
4. willingness to seek information and assistance from all appropriate sources.

SCOTTISH CERTIFICATE OF EDUCATION EXAMINATION BOARD

Certificate of Sixth Year Studies Examination in Chemistry, 1970

Notes for Guidance in Project Assessment

1. General

The assessment of projects will be based on

(1) Examination of the candidate's written report, oral examination of the candidate and inspection of the candidate's laboratory notebook - in each case by an External Assessor.

(2) The class teacher's assessment based on day to day discussions with the pupil, knowledge of the pupil and consideration of the final report.

The External Assessor is required to consult with the class teacher regarding the allocation of marks and is asked to submit an agreed mark for each candidate to the Board on Form S.Y.3 - Supplement (Chemistry). Where agreement cannot be reached, the matter is to be referred to the Board for decision by the Principal Examiner.

The oral examination of the candidate which will normally take place in the presence of the class teacher, is an important part of the assessment and only in exceptional cases, such as illness etc. will an estimate mark be accepted. In such cases, documentary evidence in support of the exceptional circumstances would require to be submitted.

2. Allocation of Marks

The 50 marks to be awarded are divided into three groups, each of which has been sub-divided into blocks carrying a maximum of 5 marks or in one case a maximum of 10 marks. Assessors will enter the award for each group in the appropriate column of the form. Marks awarded under each heading should be whole numbers. No finer divisions should be used.

(a) Project Report (20 marks)

5 marks for general layout of the report with particular attention paid to diagrams, tabulations of data, etc.

5 marks for the presentation of the report which would include such points as adequate introduction, relevance of material to theme, background information, references, conclusion.

10 marks for the experimental aspects including points such as scientific content, assessment of problems, method of tackling, design of apparatus, technique, original thought, overcoming problems.

(b) Oral Examination (20 marks)

5 marks for basic understanding.

5 marks for initiative, resourcefulness, originality, independence.

5 marks for clarity of expression.

5 marks for general estimate of the thesis including points such as an appreciation of errors, future possibility of the work.

(c) Course Work (10 marks)

5 marks for the record of the work based on points such as presentation, completeness of reports, range of work covered.

5 marks for the quality of the work based on experimental results obtained, initiative shown, development of one particular experimental line of enquiry (which could be a subject of discussion with the candidate) etc.

3. Estimate Marks

In order to provide a working basis for the assessment, the teacher is asked to provide in column (d) of Form S.Y.3 - Supplement (Chemistry) a preliminary estimate given in terms of a five point scale A - E. One copy of the form is to be sent to the Board, and the other copy to the External Assessor along with the project reports, in each case by 1st May, 1970.

The range table for the teachers' preliminary estimate on the five point scale is:-

A	40	-	50
B	30	-	39
C	20	-	29
D	10	-	19
E	0	-	9

Scottish Certificate of Education
Examination Board
140 Causewayside,
EDINBURGH EH9 1PT.

DECEMBER, 1969

SCOTTISH CERTIFICATE OF EDUCATION EXAMINATION BOARD

NEW SCOTTISH EXAMINATION

Certificate of Sixth Year Studies

The Secretary of State for Scotland, Mr. William Ross, M.P. has accepted the advice of the Scottish Certificate of Education Examination Board that an examination designed for sixth year pupils of Scottish secondary schools should be introduced. The examination is intended for pupils of a fairly wide range of ability and will cater for more practical and aesthetic as well as for more academic interests. Pupils who have pursued a sixth year of studies and taken the examination, which will begin in a limited range of subjects in 1968, will be awarded a "Certificate of Sixth Year Studies", indicating the standard reached in each subject.

The aim of this new examination is to give direction and purpose to sixth year work by encouraging pupils who have completed their main subjects at the Higher grade to engage in independent study in depth of a particular subject. The examination will not be marked on a pass/fail basis, but instead "Ranks" of attainment will be awarded, each covering a range of marks. The expectation is that candidates will not be presented for the examination in more than two or three subjects, and there should be no reason why a pupil should not enter in only one subject. As its title suggests the examination will be open only to pupils who are pursuing a course of sixth year studies in a secondary school.

For the first year the examination will be held in six subjects - Art, Commerce, English,French, Geography, Physics. Syllabuses and specimen papers in these subjects will be issued shortly. In succeeding years the range of subjects will be widened, according to the emerging needs of the schools.

The Secretary of State has asked the Board to make it clear that the new Certificate is intended, both by its character and by the conditions of its award, to supplement, not to replace, the existing Certificates. In particular the additional examination involved is in no way an alternative to the Higher grade examination: nor has the new Certificate been introduced with the intention that it should come to be regarded either by the Universities or by the professions as a formal requirement for entrance.

August, 1966.

The following is an extract from a letter sent out by Mr. A.J. Mee* on 19th April, 1968.

"(Assuming eight periods per week), it has been assumed that the time available for teaching would be 26 weeks. Out of the 208 periods available approximately one quarter, say 58 periods, would be spent on the project work, leaving about 150 periods or 100 hours for the syllabus".

You may be interested in the time allocated to the various sections in the school trials. This is as follows:-

Section 2	Energies in Macroscopic Systems	18 hours
Section 1 + 3	Practical techniques	16 hours
Section 4	Spectra and Structure	8 hours
Section 5	Energy and Bonding	6 hours
Section 6	Group IV	20 hours
Section 7	Solution Chemistry	12 hours
Section 8	Electronic Structure and Periodicity	5 hours
Section 9	Transition Elements	15 hours
		100 hours

*Then Senior Inspector of Schools, Scotland, responsible for science teaching. Letter for guidance of teachers during course on Sixth Year Studies Chemistry at St. Andrews.

CHAPTER 2.

AN EXAMINATION OF PRACTICAL WORK IN SIXTH YEAR STUDIES CHEMISTRY.

An examination of practical work in Sixth Year Studies Chemistry

The Certificate of Sixth Year Studies - Chemistry Syllabus[4] lists suitable experiments for each topic in the syllabus. In contrast with 'O' and 'H' grade, more of the experiments are of a quantitative nature There are approximately forty-five experiments listed. Some are actually a series of small experiments and so the total number could be taken as anything from forty to fifty, depending on what was considered to be an experiment. Some of the experiments could be completed in as little as ten minutes and others took up to three hours. These times are based on the experience of post-graduate students training to teach in secondary schools. (A2 - 46).

In an attempt to find what experiments were being done, and under what conditions, two types of questionnaire were sent to schools. One type asking for reactions of pupils to particular experiments carried out by them was sent to six schools during the 1970-71 session. The returns were insufficient for any conclusions to be drawn and a revised questionnaire was circulated to twelve schools (about 100 pupils) in the 1971-72 session The findings from these are discussed in chapter 3.

A general questionnaire to all teachers of Sixth Year Studies Chemistry was distributed in April 1971. This was concerned with all aspects of Sixth Year Studies Chemistry but particular sections were devoted to practical work. These were concerned with finding out the average number of experiments carried out by pupils,under what conditions of accommodation and time allocation. The experiments in the Examination Board Syllabus[4], excluding "traditional" volumetric experiments, were listed and teachers were asked to signify which experiments their pupils had attempted this year and which experiments they had carried out in previous years but not this year.

On computing, analysis gave the following information for each experiment:-

(a) Number of schools not using the experiment this year.

(b) Number of schools using the experiment this year.

(c) Number of schools in which the experiment has been used previously but not this year.

The total number of experiments was forty. Copies of the relevant section of the questionnaire and of the results of the computer analysis are in the appendix. (A2-1, A2-2).

Of the forty experiments, twenty-five were not used by about 40% of the schools. These experiments were in sections of the course in which pupils fared badly in the 1971 Sixth Year Studies examination (based on the Sixth Year Studies - Chemistry - 1971 Examiners Report[6]).

Experiments not used by 40% of schools.	Areas of weakness in the examination
Iodine coulometer.	
Gravimetric estimation of Cl^-	All quantitative work
Analysis of Ni $(NH_3)_6$ $(BF_4)_2$	
Reaction of Cl_2 and CH_4 in light.	
Reaction of Br_2 and C_7H_{16} in light	Organic
Bromination of an Alkene.	
Hydrolysis of t-butyl bromide.	
Grignard Reactions.	
Reduction of vanadium compounds.	
Oxidation states of Mn.	
Preparation of Tutton salts	Transition elements
Effect of ligand changes on colours of complexes	
Gouy balances and other paramagnetic experiments.	
All Group IV experiments	Group IV Chemistry

The experiments not used by about 40% of schools, which fell outside these areas are:-

Thermal decomposition of $NaHCO_3$
Equilibrium constant Fe^{3+}/NCS^-
Equilibrium constant. Hydrolysis of an ester.
Changes in conductivity of buffer solutions with added base/acid.

These findings were the basis of a brief research report.[7]

To find if these areas of weakness were a function of the 1971 paper, the examiners reports on Paper I (essay type) for 1969, 1970 and 1972 were also studied. (A2-42 to A2-45).

The areas of weakness were tabulated as shown:-

Areas of weakness in examination.

1969	1970	1971	1972
Organic Chemistry	Organic Chemistry Nomenclature of simple organic compounds.	Organic Chemistry	Organic Mechanisms.
Anything involving calculations.	Calculations on volumetric analysis Calculations on electrolysis.	pH calculations. Handling of logs. E^0 deduction and mole calculations.	
	Transition metals. Origins of colour.	Crystal field theory.	Transition element well done but tackled by only 24% of candidates.
		Group IV Chemistry	Dynamic equilibrium. Theory of buffer solutions.

There are factors which make it difficult to draw any 'hard' conclusions from this.

The poor response in a topic may be a function of the question.

Not all the topics were tested in each examination.

There is bound to be some element of subjectivity in the examiners reports although this is balanced by the reports having been written by different examiners.

Nevertheless it is obvious that some topics are consistently poorly tackled in the examinations namely, organic chemistry, most forms of calculations, transition element chemistry. The fact that these areas receive poor coverage in practical work need not imply that poor examination performance is due to practical coverage. There is no evidence to support this.

An international survey of comparisions of achievement in theory and practical work in school science has been made by I.U.P.A.C. and U.N.E.S.C.O. but the results have not yet been published.[8]

The objectives achieved in Sixth Year Studies Chemistry practical work will be discussed in Chapter 3, but it is not unreasonable to assume that, if pupils carried out more of the quantitative type of experiments and the associated calculations, their performance in calculations might have improved. Calculations are an area of weakness at 'O' and 'H' grade, but there is not the same emphasis on quantitative and semi-quantitative practical work at 'O' and 'H' grade as there is at Sixth Year Studies level.

The weakness in Organic and Transition Element Chemistry may be associated with the teaching order. Preliminary investigation by Miss K. Urquhart, Glasgow University, appears to indicate that the[10] majority of teachers use the 'O' and 'H' grade syllabus as a teaching order.

If this is the case Organic Chemistry would come at the end of most teaching orders in both 'O' and 'H' grades. The treatment in some schools might therefore be rushed and be providing an inadequate basis for Sixth Year Studies. The problem with transition elements is different. This is a new topic to the pupils and is unfamiliar to many teachers. Unlike most other topics in Sixth Year Studies Chemistry there has been no introduction at the 'O' and 'H' grade stage. This might make the topic inherently more difficult to the pupils. Since the transition elements do not appear as a topic at 'O' and 'H' grade few of the teachers in 1971 had much experience in teaching this topic. If the weakness was due to the inexperience of the teachers, then there should be an improvement with time. In fact the performance by candidates on this topic had improved in 1972, but the numbers choosing the question was small. It could well be that this will remain a difficult topic at this depth of treatment for Sixth Year Study pupils.

To find if unsuitability of experiments was a reason why so many of the experiments were not being used, all of the experiments were tried by the author and by post-graduate students at Notre Dame College of Education (Details in appendix A2 - 46, A2 - 47).

The criteria used in considering the suitability of the experiments were:-

safety;

availability and cost of reactants;

sophistication of apparatus required;

were the numerical results convincing?

length of time required to carry out experiment.

Comments on the individual experiments are in the appendix (A2-47 to A2-54) but the experiments which were found to be unsuitable in the secondary situation were:-

Determining equilibrium constants;

exploding methane and chlorine by initiating with U.V. light;

bromination of an alkene in the presence of the chloride ion;

hydrolysis of t-butyl bromide to illustrate S_N1 reaction mechanism.

Those were among the twenty-five experiments not used by >40% of the schools. The remainder of the twenty-five experiments were comparatively easy to do. Some are very simple experiments taking only a few minutes to carry out. Notable among those experiments not being used is the iodine coulometer. This uses electrolysis to determine the stoichiometry of the thiosulphate/iodine reaction and could be considered very important in aiding the understanding of redox reactions.

The list of experiments (A2 - 1, A2 - 2) was also examined to see if schools had tried experiments in the past and found them unsuitable. Of the twenty-five 'unpopular' experiments only eight had been tried by more than 10% of the schools in previous years and had not been repeated this year. No experiments were tried by more than 20% of the schools and then dropped. It seems therefore that the reason for omitting experiments was not that the experiment had been found unsuitable.

Analysis also gave the number of experiments completed by each school and the results are summarised here:-

No. of experiments completed.	No. of schools (~ 1000 pupils)	
0 - 5	1	38%
6 - 10	9	
11 - 15	18	
16 - 20	22	
21 - 25	29	
26 - 30	28	
31 - 35	30	
36 - 40	3	

These figures can give only an approximate picture of how much practical work was done. The volumetric experiments were omitted from the questionnaire so the number of experiments completed could be two or three more than indicated. Also an experiment is a variable unit of practical work as some take much longer to do than others. Taking this into account the amount of practical work done is much lower than it should be as about 40% of the schools completed fewer than twenty-one experiments in the year.

The questionnaire also yielded information on the time spent on Sixth Year Studies Chemistry in schools:-

Time allocation for S.Y.S. Chemistry per school.

No. of Periods	No. of Schools			
3	1			
4	3			
5	9			
6	20			88%
7	11		61%	
8	57	43%		
9	13			
10	15			
11	1			

No. of Periods	No. of Schools
12	1
15	1
	132

There was a wide variation in the time allocated. 43% of the schools had eight periods per week and 88% had six to ten periods per week. This compares favourably with time allocation of eight periods per week suggested at the planning stage and it seems that the vast majority of the schools were receiving an adequate time allocation for completion of the course.

The proportion of time spent on practical work was also obtained:-

Number of periods spent in Practical Work in 132 Schools

No. of Periods	No. of Schools	Percentage	
1	2		
2	14		
3	27	20%	
4	42	32%	63%
5	25	19%	
6	16	12%	
7	8		
9	1		
10	1		

Again there is a wide variation in the time spent in practical work per school, but 83% of schools spent between four and six periods in practical work. Comparing the time spent in practical work with total time allocation, about 60% of the total time was given to practical work. The suggested proportion at the planning stage was five periods out of eight, i.e. about 63%.

The teachers were also asked to estimate the average number of experiments performed by each pupil. These estimates would include the volumetric experiments and therefore should be greater than the number of experiments used per school derived from the forty experiments.

Average Number of Experiments Performed by Each Pupil.

No. of Experiments	No. of Schools	Percentage
1 - 5	2	1.7
6 - 10	12	10
11 - 15	21	18
16 - 20	27	23
21 - 25	15	13
26 - 30	21	18
31 - 35	10	8
36 - 40	8	7
41 - 50	0	0
46 - 50	2	2
	118	

When these were compared with the number of experiments used per school it was found that there was no significant difference.

The teachers were also asked how they organised their practical work with the following results.

Organisation of Practical Work		Percentage out of 126
Closely integrated with theory	85	67.5
Work through experiments in any order	30	23.8
Other methods	11	8.7
Non usable returns	6	

In view of the small amount of practical work that appears to have been carried out it was thought this might not be an accurate picture. Steps were taken to verify this and they are discussed in chapter 4.

Discussion.

From the survey it would appear that the vast majority of schools are receiving what the initial planners of the course reckoned to be an adequate allocation of time. The proportion of time allocated to practical work also matches the intentions of the planners. The number of experiments being used however falls far short of the planners intentions. Only a very small part of this short fall is due to unsuitability of the experiments, as, except for four experiments, all the listed experiments could be carried out comparatively quickly using simple apparatus. It may be that teachers mistakenly considered the experiments too complex but they do not appear to have tried out the experiments before deciding this. It could also be that the teachers consider some experiments unnecessary. Even if this is so, an adequate allocation of time is being made for practical work but is apparently not being efficiently used.

The experiments not being used coincide with sections of the course shown to be weak in terms of examination responses. The relationship between practical work and learning of theory has not yet been established but may become clearer when the objectives achieved by practical work are examined. There are other factors which may cause these areas of weakness, namely:-

Unpreparedness of teachers, order of teaching, new topic studied initially at too sophisticated a level, lack of mathematical ability on the part of the pupils. It seems obvious though, that time spent on quantitative experiments would improve ability in calculations if only by practice.

Questionnaire for Teachers of Sixth Year Studies Chemistry, June 1971.

Number of schools:- 130

(a) Number of schools not using the experiment this year.

(b) Number of schools using the experiment this year.

(c) Number of schools in which experiment has been used previously but not this year.

	(a)	(b)	(c)
1. Heats of combustion of a series of alcohols	26	104	13
2. Hess's Law NaOH/HCl	25	105	7
3. Hess's Law Zn/Cu^{2+}	44	86	14
4. E.m.f. of a chemical cell Zn/Ag^{+}	29	101	6
5. Comparison between ΔG and ΔH Zn/Ag^{+} reaction	29	101	6
6. $CoCl_2$ Hydrate/$SOCl_2$	47	83	7
7. Thermal decomposition of $NaHCO_3$	58	72	14
8. Equilibrium constant Fe^{3+}/NCS^{-} system (colormetric)	59	71	9
9. Equilibrium constant. Hydrolysis of an ester	61	69	14
10. Iodine Coulometer	53	77	9
11. Estimation of Cl^{-} as AgCl	57	73	9
12. Methane and Chlorine under influence of light	87	43	24
13. Bromination of heptane in light	50	80	11
14. Alkene + Br_2 + Cl^{-}	77	53	13
15. Hydrolysis of t-butyl bromide	53	77	5
16. Relative ease of displacement of halogen in RCl RBr and RI	31	99	5
17. Phenyl magnesium bromide and preparation of benzoic acid	56	74	17
18. Phenyl magnesium bromide and prepartion of triphenyl methanol	125	5	5
19. Preparation of SnI_4	64	66	7
20. Preparation of $SnCl_2$	75	55	14
21. Preparation of $PbCl_2$	88	42	10

	(a)	(b)	(c)
22. Reactions of Sn^{2+} with MnO_4^- and Fe^{3+}	69	61	6
23. Successive dilution of M/10 acids and bases	35	95	9
24. Conductivities of acid solutions	38	92	10
25. pH of acid solutions	22	108	3
26. Ka from pH of known concentrations of acids	30	100	4
27. pH of salt solutions	31	99	4
28. pH changes during acid/base titrations	29	101	2
29. Changes in pH of buffer solutions with added base/acid	35	95	3
30. Changes in conductivity of buffer solutions with added base/acid	63	67	8
31. Reduction of vanadium compounds	54	76	6
32. Oxidation states of Mn	61	69	5
33. Preparation of $FeCl_2$, $FeCl_3$	101	29	13
34. Preparation of Tutton salts	73	57	13
35. Analysis of $Ni(NH_3)_6(BF_4)_2$	92	38	10
36. Conversion of $Ni(NH_3)_6(BF_4)_2$ to NiF_2	93	37	15
37. Preparation of $Ni(NH_3)_6(BF_4)_2$	84	46	9
38. Effects of ligands on colour of complexes	56	74	4
39. Use of Gouy balance with paramegnetic substances	57	73	9
40. Magnetic properties of ferrous ammonium sulphate and potassium ferrocyanide	66	64	11

Number of experiments used per school	Number of schools		
0 - 5	1		
6 - 10	9	7%	
11 - 15	18	14%	38%
16 - 20	22	17%	
21 - 25	29		
26 - 30	28	59%	
31 - 35	20		
36 - 40	3		
	130		

A2 - 3

Chemistry

S.Y. I.

1969

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

Paper I.

Monday, 5th May—9.30 a.m. to 12.30 p.m.

Answer any FIVE questions.

Candidates are strongly recommended to spend adequate time in reading the paper thoroughly before deciding which questions to attempt.

The booklet of three-figure mathematical tables and science data for the use of candidates at Scottish Certificate of Education Examinations is provided.

T F&S 68/225 6/4/2155

Marks

1. The following data all at 298°K are obtained from tables of energies:

Energy of atomisation of sodium	$\Delta H = +25{\cdot}7$ kcal mol^{-1}
First ionisation energy of sodium	$\Delta H = +118$ kcal mol^{-1}
Energy of atomisation of chlorine	$\Delta H = +28{\cdot}9$ kcal mol^{-1} of chlorine atoms
Electron affinity of chlorine	$\Delta H = -87{\cdot}3$ kcal mol^{-1} of chlorine atoms
Energy of formation of sodium chloride	$\Delta H = -98{\cdot}2$ kcal mol^{-1}

(*a*) Write the equations for the above processes. **(2)**

(*b*) Calculate the enthalpy ΔH of the reaction
$Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g)$ **(4)**

(*c*) What is this energy called? **(1)**

(*d*) When the ions of a mole of sodium chloride are set free by solution in water about 1 kcal of energy is ***absorbed.*** Why does this experimental result differ from that calculated in (*b*)? **(3)**

(*e*) The free energy of formation, ΔG, of sodium chloride from its elements is $-91{\cdot}8$ kcal mol^{-1} at 298°K.

Calculate the entropy change, ΔS, in this reaction, stating the units in a form other than e.u. Comment on the sign and value of ΔS. **(6)**

(*f*) How would you determine experimentally the energy change referred to in (*d*)? **(4)**

2. What is meant by

(*a*) an emission spectrum;

(*b*) an absorption spectrum;

(*c*) the wave number of a spectral line? **(5)**

Calculate the frequency and the wave number of a spectral line of wavelength 3000Å. [Velocity of light $= 3 \times 10^{10}$ cm sec^{-1}] **(3)**

Account for the facts that the emission spectrum of hydrogen is a line spectrum, and that the lines come closer together at higher frequencies. **(5)**

The major infra-red absorption bands for H_2O (g) occur at 3657, 1595 and 3756 cm^{-1}.

Would you expect the corresponding bands for D_2O (g) to be at lower or higher values than these? Explain how you arrive at your answer. **(3)**

Of what value are infra-red spectra in the study of organic molecules? **(4)**

Marks

3. "The alkyl halides represent a useful class of chemicals because the halide atom may be replaced by a wide variety of other groups."

(*a*) Explain why it is easier to replace a halide atom in an alkyl halide than it is to replace a hydrogen atom in an alkane. **(4)**

(*b*) Give three examples of such replacement reactions, stating briefly how the replacement is effected in practice. **(5)**

(*c*) Indicate the importance of two of the reactions mentioned in (*b*) in organic syntheses. **(4)**

(*d*) Of what economic and social importance are the alkyl halides? **(3)**

(*e*) It is difficult to obtain a good yield of 1-bromoethane by the action of an aqueous solution of hydrogen bromide on ethanol, although this is possible by the action of potassium bromide and concentrated sulphuric acid on ethanol. Account for this. **(4)**

4. Discuss the principal physical and chemical properties of the oxides of the elements of Group IV. **(20)**

[It is suggested that before you answer this question you should marshal your facts under suitable headings, which might include

(*a*) a statement of the variation in the physical nature of the oxides through the series C–Pb;

(*b*) an explanation of this variation based on bonding;

(*c*) a statement of the main chemical properties of the oxides including acidic or basic nature, amphoterism, stability, oxidising or reducing powers, etc;

(*d*) some explanation of the variation of these properties through the series C–Pb.

You are not, however, confined to these headings and more original treatments would be welcomed. The value of the answer will be assessed on lucidity as well as accuracy.]

[Turn Over

Marks

5. (i) "A solution that tends to resist change in its pH value on addition of H^+ or OH^- is called a buffer solution."

(*a*) State the constituents of two commonly used buffer solutions. **(2)**

(*b*) Explain in the case of one of the buffer solutions mentioned in (*a*) how it works. **(2)**

(*c*) How could you show experimentally that in fact a buffer solution is effective? **(2)**

(*d*) Of what importance are buffer solutions
(1) in chemical laboratory procedures
and (2) in biological processes? **(4)**

(ii) An indicator is often used in acid-base volumetric analytical procedures.

(*a*) Indicators are weak acids or bases of which the undissociated molecule, HIn, has a different colour from the ion, In^-.

In litmus HIn is red and In^- is blue. The equilibrium constant for the reaction

$$HIn \rightleftharpoons H^+ + In^-,$$

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

is 10^{-7}.

At what pH will the concentrations of In^- and HIn be the same?

The pH range over which litmus changes colour is 5 (red) to 8 (blue).

Calculate the ratio of the concentrations of HIn to In^- when the indicator just appears (a) red and (b) blue. **(5)**

(*b*) The following table gives the pH range over which some common indicators change colour:

Bromophenol blue	1·8 — 2·7
Methyl orange	3·1 — 4·5
Methyl red	4·4 — 6·2
Litmus	5·0 — 8·0
Phenolphthalein	8·3 — 10·0
Alizarin yellow	10·0 — 12·0

Marks

Which indicator would you use for the titration of

(*α*) sodium hydroxide by hydrochloric acid

(*β*) ammonium hydroxide by hydrochloric acid

(*γ*) sodium carbonate solution by hydrochloric acid?

Give a brief reason in each case. **(5)**

6. (*a*) What is meant by hydrogen bonding? **(2)**

(*b*) What conditions govern hydrogen bonding? Illustrate your answer by considering the case of hydrogen fluoride. **(4)**

(*c*) How does the general strength of a hydrogen bond compare with that of a covalent bond and a van der Waals' force? **(1)**

(*d*) What experimental evidence is there that hydrogen bonding is stronger in water than in hydrogen sulphide? Explain how the evidence leads to the conclusion. **(4)**

(*e*) Experiments on the distribution of benzoic acid, C_6H_5COOH, between benzene and water were carried out and the ratio of the concentration of the acid in water (C_1) to that in benzene (C_2) was determined.

It was expected that the value of C_1/C_2 would have been approximately constant. It was found, however, that $(C_1)^2/C_2$ was more nearly constant.

What does this indicate about the molecular state of benzoic acid in benzene?

What explanation might be given of this behaviour of benzoic acid? **(5)**

(*f*) What part does hydrogen bonding play in the formation of natural compounds of high molecular weight, e.g. proteins and nucleic acids? **(4)**

[Turn Over

Marks

7\. (1) When an aqueous solution of ammonia is slowly added to an aqueous solution of Cu^{2+} ions there is at first a pale blue precipitate, which however dissolves as more ammonia is added to give a deep blue solution.

(*a*) What ions containing copper are present in (i) an aqueous solution of copper(II) sulphate and (ii) the deep blue solution referred to above? **(2)**

(*b*) Would the addition of ammonium chloride solution to an aqueous solution of Cu^{2+} ions produce a deep blue solution? Explain your answer. **(2)**

(*c*) Why is the colour of the "ammoniacal" solution different from that of an aqueous solution of Cu^{2+} ions? **(4)**

(2) Manganese(II) sulphate is strongly paramagnetic.

(*a*) What is meant by this statement? **(1)**

(*b*) How would you show experimentally that manganese(II) sulphate is paramagnetic? **(4)**

(*c*) What explanation can be given of this fact? **(4)**

(*d*) Which of the following would you expect to be paramagnetic?

(i) manganese(II) chloride,

(ii) copper(II) sulphate,

(iii) potassium hexacyanomanganate(III) $K_3[Mn(CN)_6]$. **(3)**

Marks

8. (i) Silicon tetrachloride is a colourless liquid, b.p. 57°C, which fumes in moist air. It can be prepared by the direct action of chlorine on heated silicon. You are faced with the problem of preparing about 10 g of silicon tetrachloride using the apparatus normally available in the laboratory. No chlorine cylinder is at hand, and consequently the gas must be made by the action of conc. hydrochloric acid on potassium permanganate. The preparation is to be carried out in the open laboratory with the minimum of inconvenience to others, so the atmosphere must not become unbearable. Bearing in mind the properties of the substance stated above devise a suitable apparatus for the preparation. A sketch of the apparatus, with the main parts labelled and substances named is required, and a statement of the reason for using each part should be given.

How would you store the product if it is not required for immediate use? **(10)**

(ii) Silicon tetrachloride is much more reactive than carbon tetrachloride, e.g. it is hydrolysed by water.

Put forward a theory (or theories) which could account for these facts. **(4)**

(iii) Silicon tetrachloride reacts with silicon at high temperatures to form a compound A. When 10·00 g of A was treated with water and the silicon dioxide formed was filtered off and dried it was found to weigh 4·46 g. Comment on the possible structure of A. **(6)**

[Turn Over

Marks

9. (i) You are asked to investigate the reaction which occurs between metallic tin and Fe^{3+} in dilute sulphuric acid at ordinary temperatures. The reaction may be one of the following:

$Sn + 2Fe^{3+} \longrightarrow Sn^{2+} + 2Fe^{2+}$
$Sn + 4Fe^{3+} \longrightarrow Sn^{4+} + 4Fe^{2+}$
$2Sn + 6Fe^{3+} \longrightarrow Sn^{2+} + Sn^{4+} + 6Fe^{2+}$

You have available
M/10 $KMnO_4$
M/10 Iodine

a solution of iron(III) sulphate in dilute sulphuric acid, which is M/10 with respect to Fe^{3+}, and
tin amalgam.

MnO_4^- oxidises both Fe^{2+} and Sn^{2+} quantitatively at ordinary temperature, whereas I_2 oxidises Sn^{2+} but has no reaction with any other ions present.

Only the tin reacts with Fe^{3+}.

Devise a series of experiments which would enable you to discover which of the above equations most closely agrees quantitatively with the reaction, and indicate how you arrive at your conclusion. **(10)**

(ii) Ammonium metavanadate containing vanadium in the oxidation state +5 is a good oxidising agent and oxidises I^- to I_2 in the presence of H^+. In an experiment to find the oxidation state of the vanadium formed in this reaction 20 ml of a M/10 solution of V_2O_5 in dilute sulphuric acid were acted upon by excess of KI. The liberated iodine required 40 ml of a M/10 solution of $S_2O_3^{2-}$ for titration. Find the oxidation state of the vanadium formed. **(10)**

[END OF QUESTION PAPER]

1970

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER I.

Marks

1. (*a*) Explain what is meant by (i) the $\triangle H$ of a reaction and (ii) the $\triangle G$ of a reaction. **(3)**

(*b*) What predictions, if any, can be made about (i) the likelihood of a reaction occurring and (ii) the rate of a reaction; given its $\triangle G$ and $\triangle H$? **(4)**

(*c*) When solid barium hydroxide, $Ba(OH)_2.8H_2O$, and solid ammonium thiocyanate, NH_4SCN, are shaken together, there is a dramatic fall in temperature while a spontaneous double decomposition (ionic interchange) reaction takes place.

(i) Write a likely equation for the reaction, and **(1)**

(ii) use it to suggest why this spontaneous endothermic reaction takes place. **(4)**

(*d*) Let us assume that the entropy change ($\triangle S$) when a liquid is changing into a gas at its boiling point is given by the Latent Heat of Vaporisation per mole divided by the boiling point (in K).

$$\triangle S = \frac{\triangle H\ vap}{T}$$

Copy this table into your answer book and fill in the blank spaces marked *.

Compound	$\triangle H$ vap (kcal mol^{-1})	B.P. (K)	$\triangle S$ (cal deg^{-1} mol^{-1})	
CCl_4	7·28	350	*	
CS_2	6·50	320	*	
H_2S	4·46	*	21·0	
C_6H_6	7·35	*	*	
H_2Te	*	271	*	**(8)**

Marks

2\. (*a*) Examine the simplified infrared spectra of some organic compounds shown on the sheet provided. Note that the C—C group does not show in the spectra.

Write down the approximate wave number(s) for the absorptions corresponding to the following groups:—

(i) C—Cl (ii) C—H (iii) C—OH (iv) C=C **(6)**

(*b*) Two infrared spectra shown on the sheet are those of a compound before and after polymerisation.

What kind of polymerisation has taken place? Give your reasoning. **(3)**

(*c*) An infrared spectrum of a compound of formula weight 92·5 is shown on the sheet. What is its most likely empirical formula? Draw the structures of and name its isomers. **(5)**

(*d*) Many organic halogen compounds are now in common use. Show clearly that you understand the social (or economic) importance of any **three** of the following:—

(i) Dichlorodiphenyltrichloroethane (D.D.T.)

(ii) Polyvinylchloride (P.V.C.)

(iii) Polytetrafluoroethylene (P.T.F.E.)

(iv) Chloromycetin

(v) Dichlorodifluoromethane (Freon)

(vi) Trichlorophenol (T.C.P.). **(6)**

[Turn Over

Marks

3\. (*a*) In a given copper(II) salt, the copper ion is complexed with ammonia. From the experimental results given below, calculate how many ammonia molecules are associated with each copper ion.

A 1 g sample of the salt was dissolved in 50 ml of M HCl and made up to 100 ml with water and mixed (Solution A). This solution was treated as follows:

(i) 50 ml of A were titrated with M NaOH to find out how much acid was left after reaction with the ammonia in the complex. 16·2 ml of the alkali were required to react completely with the excess acid.

(ii) Another 50 ml of A were titrated with a reagent called E.D.T.A., 1 mole of which is equivalent to 1 mole of copper(II) ion. It does not react with the ammonia. The volume of M/10 E.D.T.A. required was 21·7 ml. **(7)**

(*b*) (i) During the process of osmosis a pressure is built up across a membrane. This pressure is called osmotic pressure. In terms of entropy changes offer an explanation for the origin of this pressure. Are enthalpy changes likely to be important in this process? Explain. **(5)**

(ii) This part of the question deals with a situation you are unlikely to have met before. It is inserted here to test your ability to see a pattern in chemical information.

The osmotic pressure of a number of molar solutions was measured and found to be approximately as follows:—

Compound	Pressure
Glucose	1 unit
Sodium Chloride	2 units
Magnesium Bromide	3 units
Ethanol	1 unit
Sulphuric acid	3 units

In terms of particles in solution, indicate any pattern that you observe in these results. **(3)**

(iii) If a molar solution of a certain acid gives an osmotic pressure of 1·25 units, what does this suggest about the condition of the acid in solution? **(3)**

(iv) If you were going to titrate this acid with sodium hydroxide solution, which indicator would you use and why? **(2)**

[Turn Over

Marks

4. (*a*) An important industrial process is described thus.

Natural gas (CH_4) undergoes partial combustion with air in a special burner.

Reaction ①. $CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CO(g) + 2H_2(g)$.

The heat liberated is used to raise the temperature of more natural gas to bring about the reaction:—

Reaction ②. $2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$.

The questions about reaction ② refer to its going from left to right. It is assumed that $\triangle H$ and $\triangle S$ do not vary with temperature.

(i) Calculate the $\triangle H$ of reaction ②.

(ii) Estimate the temperature required to make the $\triangle G$ of reaction ② just negative.

Substance	$\triangle H_f^\circ$ (kcal mol^{-1})	S° (cal deg^{-1} mol^{-1})
$C_2H_2(g)$	+54·2	+48·0
$H_2(g)$	0	+31·2
$CH_4(g)$	−17·9	+44·5

(6)

(*b*) Indicate by means of δ^+ and δ^- the polarity of the following bonds (i) C—Br (ii) C—Li (iii) C—H. (3)

(*c*) Give the formula and name for a likely product in each case when 2-bromopropane is attacked by (i) CN^- (a cyanide ion) (ii) $Br^\cdot$ (a bromine free radical) (iii) $OC_2H_5^-$ (an ethoxide ion). (6)

(*d*) The compound ethyl lithium (C_2H_5Li) is widely used in organic synthesis. It must be kept dry and away from contact with carbon dioxide.

Indicate what might happen if these precautions were not observed. (5)

Marks

5. (*a*) "The close resemblance between elements of the same family in the Periodic Table, so obvious in Groups I and II and somewhat less evident in Group III, is even less apparent in Group IV."

Copy this grid into your answer book and set out brief comparisons between Group I and Group IV to illustrate the statement above. (A few words will often suffice.)

Property	Group I	Group IV
Oxidation state in compounds	(1)	(2)
Type of bonding between atoms in the free elements	(1)	(2)
Electrical conductivity of the elements	(1)	(2)
Stability of the chlorides to water	(1)	(3)

(*b*) Draw sketches to indicate the three dimensional structure of (i) disilane (Si_2H_6), (ii) tetramethyl tin, (iii) the ion $C(CH_3)_3^+$. **(3)**

(*c*) Disilane catches fire on contact with air to form SiO_2 and water. Assume the silicon dioxide to be separate SiO_2 molecules for the purpose of this question.

From this table of bond energies, estimate the heat of combustion of disilane.

Bond	Bond energy (in kcal mol^{-1})
Silicon—Silicon	54
Silicon—Hydrogen	76
Silicon—Oxygen	192
Oxygen—Oxygen	118
Oxygen—Hydrogen	111

(4)

[**Turn Over**

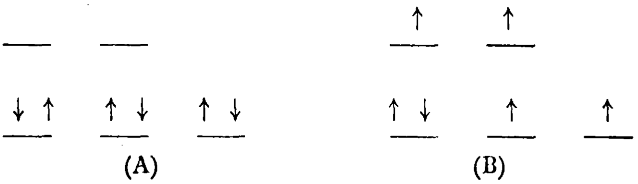
Marks

6. (*a*) What is meant by *d* orbitals being (i) degenerate, (ii) split? **(4)**

(*b*) What is the oxidation state of chromium in the chromate ion, CrO_4^{2-} ? **(1)**

This ion absorbs strongly in the blue part of the spectrum. Why might this absorption take place? **(3)**

(*c*) When an ion which has six *d* electrons is in an octahedral field these electrons can be arranged as shown in (A) and (B) below.



N.B.—These diagrams are deliberately not drawn to scale.

(i) In which of these two cases is the splitting greater? Explain your choice. **(2)**

(ii) Explain how the magnetic properties of (A) and (B) compare? **(2)**

(*d*)

Metal	At. No.	Metallic Radius (Å)
Na	11	1·86
Mg	12	1·60
Al	13	1·43
Fe	26	1·26
Co	27	1·25
Ni	28	1·24

Offer an explanation (in terms of the arrangement of electrons in shells) for the trends in atomic radius exhibited by the two groups of metals in the table above. **(4)**

Marks

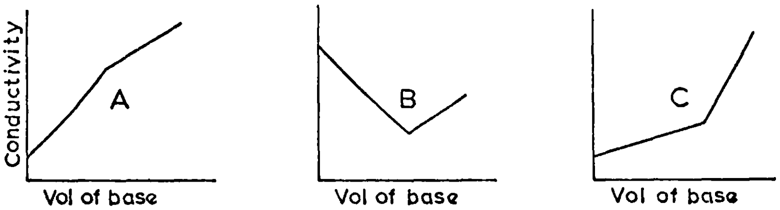
(*e*) It is possible to grow a series of isomorphous salts having the general formula $K_2SO_4.MSO_4.6H_2O$ where M is a first row transition metal in the +2 oxidation state. What property of M^{2+} is likely to permit this?

An attempt was made to grow the corresponding cadmium (II) salt, but the crystals were **not** isomorphous with those already grown from the first row transition metals. Why might this be so? **(4)**

[Turn Over

Marks

7. (*a*) Three conductivity curves are shown below which are the result of a base being added to an acid.



From this list of acids and bases, choose the pairs of reagents which would be most likely to give rise to the curves, A, B and C respectively.

Explain clearly in each case why you have made your decisions.

(i) Potassium hydroxide being added to acetic acid.

(ii) Ammonia solution being added to nitric acid.

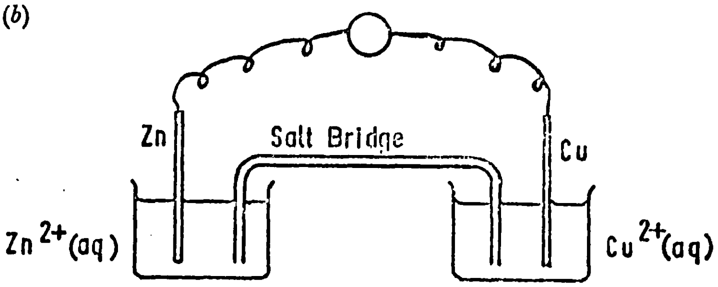
(iii) Sodium hydroxide being added to hydrochloric acid.

(iv) Strontium hydroxide being added to carbonic acid.

(v) Ammonia solution being added to acetic acid. **(9)**

Suggest a practical use for a curve of the type A. **(2)**

(*b*)



In a cell, the two half-cells are linked in two ways—by a conductor and meter, and by a salt bridge. What is the function of (i) the conductor and (ii) the salt bridge? Would a wire conductor not do instead of the bridge? Explain your answer clearly. **(6)**

Marks

(*c*) When dry powdered magnesium and dry powdered silver nitrate are mixed no reaction is seen to take place, but when a drop of water is added, a very vigorous reaction occurs and the mixture catches fire. Offer an explanation for these observed facts. **(3)**

8. (*a*) Here is a news item about the manufacture of the Prince of Wales' crown.

"The crown's designer was seeking a method which would faithfully reproduce the fine texture details of his design. The first step was to make a plastic mould of the designer's model of the crown. The inside of the mould was then sprayed with a solution of silver nitrate and a reducing agent. An electrode was attached to the mould and it was immersed in a bath of a solution of a gold salt. Electrolysis took place for two and a half days until 3 kg of gold had been deposited thus forming the crown."

(i) What was the point of spraying the plastic mould with silver nitrate and a reducing agent? **(3)**

(ii) Why was it possible to use a solution of a gold salt instead of a bath of a molten gold salt? **(3)**

(iii) If the atomic weight of gold is 197 and the gold in the bath was in the +3 oxidation state, how many moles of electrons were used in the formation of the crown? **(3)**

(iv) The electrolysis lasted for 60 hours. What was the average current (in A) during the electrolysis? **(3)**

(*b*) A sample of anhydrous europium chloride, $EuCl_3$, weighing 1 g was treated with excess silver nitrate solution and all the chloride was recovered as 1·67 g of dry silver chloride. Calculate the atomic weight of europium. **(6)**

(*c*) Europium chloride costs about £6 per gram. Suggest a chemical reason why the cost is so high. **(2)**

[Turn Over

Marks

9. (*a*) The equilibrium constants for the following reactions have been measured at 823 K.

$$CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g)\ ;\ K = 67$$

$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)\ ;\ K = 490$$

From this information, calculate the equilibrium constant of the reaction:—

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \text{ at 823 K.}$$ **(4)**

If this latter reaction were to be done industrially, what effect would (*a*) an increase in pressure and (*b*) the chilling of the products, have upon the course of the reaction. Explain your answers clearly. **(6)**

(*b*) The dissociation constant (K_a) for formic acid is $1{\cdot}8 \times 10^{-4}$. The approximate relationship between the hydrogen ion concentration and K_a is given by

$$[H^+]^2 = K_a[HA]$$

where [HA] is the molarity of the acid.

Calculate the pH of a molar solution of formic acid. **(4)**

(*c*) What change (increase or decrease) in pH, if any, would you expect to find if some solid sodium formate was added to the molar formic acid? Explain your answer clearly. **(4)**

(*d*) If you were asked to prepare some formic acid from an alcohol, which alcohol would you choose and what reagents would you use? (No experimental detail is required.) **(2)**

[*END OF QUESTION PAPER*]

A2 - 22

1971

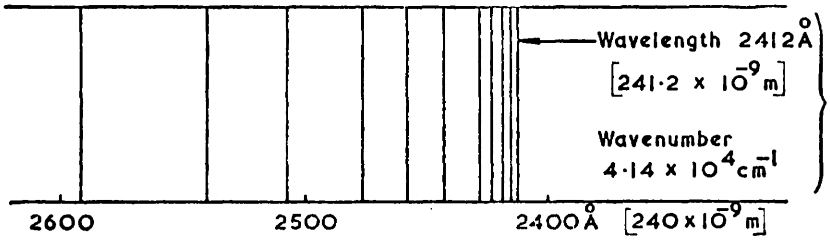
CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER I.

Marks

1. (*a*) This diagram represents a portion of the line spectrum of sodium.



(i) Describe the events which are thought to be responsible for the production of a line in the emission spectrum of sodium. **(3)**

(ii) Why are the lines closer together at the higher energy end? **(2)**

(iii) Convert the value for the energy at the convergence limit into kJ mol^{-1} (1 kcal = 4·18 kJ). **(2)**

With the help of your data book (p. 38) find out what the physical significance of this convergence limit is in terms of atoms and electrons. **(3)**

(Planck's constant, if required, is $6{\cdot}63 \times 10^{-34}$ J s).

(iv) If a bulb containing sodium vapour is placed between a source of sodium emission and the spectrograph, some of the lines in the emission spectrum are missing. Suggest why this should be so. **(2)**

(v) In terms of *s* and *p* orbitals write down the electronic configuration of sodium in the ground state. **(1)**

When an electron in one of the excited states of sodium returns to this ground state, there is a strong line in the spectrum at 5890 Å (589×10^{-9} m). In what region (i.e. ultraviolet, visible, etc.) of the electromagnetic spectrum would this line appear? **(1)**

(*b*) You are provided with a spectrometer working in the visible region of the spectrum and a series of solutions of potassium permanganate of different known concentrations. Suggest how you might use it to find the concentration of another given solution of potassium permanganate. **(6)**

Marks

2. (*a*) Draw diagrams to illustrate clearly the three-dimensional shape of a molecule of each of the following compounds:

ethene (ethylene), sulphur hexafluoride, beryllium chloride, boron trifluoride. **(8)**

(*b*) All alums have similar formulae, e.g. $K^+Al^{3+}(SO_4^{2-})_2 12H_2O$ and $NH_4^+Fe^{3+}(SO_4^{2-})_2 12H_2O$.

Alum crystals are isomorphous. Not all ions which have one or three positive charges can form an alum.

Suggest why this might be so. **(2)**

(*c*) Silica consists of a lattice of silicon and oxygen atoms. If, however, some of the silicon atoms are replaced by aluminium atoms the lattice is able to combine with cations to form a type of silicate known as a zeolite.

(i) Suggest why the replacement of silicon atoms by aluminium atoms gives the lattice this property. **(2)**

(ii) These zeolites can act as ion-exchangers. What does this mean? **(2)**

(iii) During the ion-exchange process, what condition must be met throughout the zeolite? **(1)**

(*d*) This part of the question deals with a situation you may not have met before. It is testing your ability to see a pattern in a set of results, and then use it. To answer this question you will require information in the data book on pages 36, 37 and 46.

By definition, the specific heat capacity of an element is the amount of heat required to raise the temperature of one kilogram of the element by one degree K.

(i) Either by calculation or by graph find the relationship between the atomic weight and the specific heat capacity for each of a number of metallic elements such as copper, silver, gold and uranium. **(2)**

(ii) Use these results to estimate the specific heat capacity of radium. **(1)**

(iii) Offer a possible theoretical explanation to account for your results in (i). **(2)**

[Turn over

3. (*a*) From the information given below: *Marks*

$MnO_4^-(aq) + 8H^+(aq) + 5e$
$\rightarrow Mn^{2+}(aq) + 4H_2O(l)$; E° = +1·52 V

$2CO_2(g) + 2e \rightarrow C_2O_4^{2-}(aq)$; E° = −0·49 V

decide whether or not the following reaction would be likely to go from left to right. No detailed calculation is required, but you should give reasoning to support your choice.

$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow$
$Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$. (4)

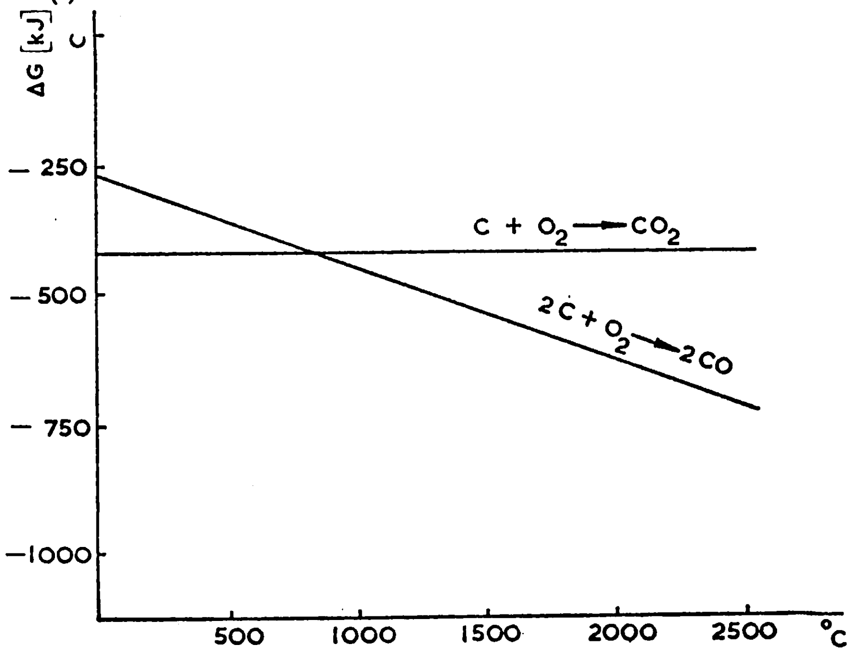
When an acidified solution of permanganate ions is added to a solution of oxalate ions ($C_2O_4^{2-}$) at room temperature the purple colour persists for a long time. If the temperature of the mixture is raised to 60°C, the purple disappears rapidly. Suggest an explanation for this. (2)

If the solution which reacted at 60°C is now cooled to room temperature and more permanganate is added, the purple disappears rapidly. Offer an explanation for this. (2)

(*b*) (i) What is meant by the free energy change (ΔG) of a reaction? (1)

(ii) From the value of ΔG what information can be obtained about the likelihood of a reaction to take place and about its velocity? (2)

(*c*)



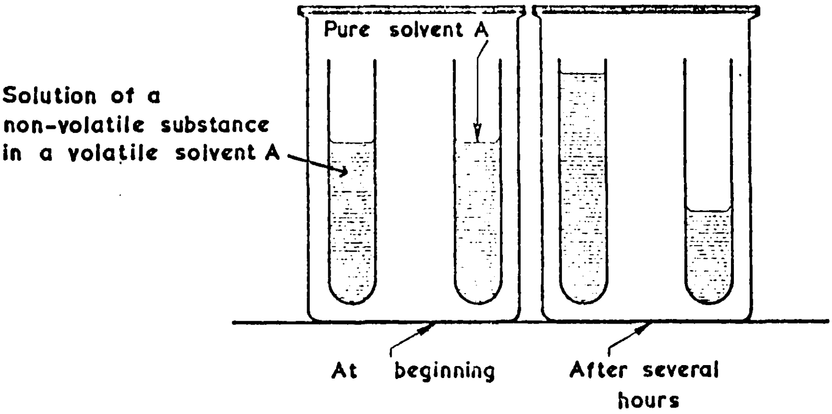
Marks

The value of $\triangle G$ for a reaction changes with temperature. This diagram shows the values for $\triangle G$ for reactions at various temperatures. Each graph shows the $\triangle G$ values when an oxide is made from an element reacting with one mole of oxygen gas.

(i) If carbon and oxygen are allowed to react at 2000°C what is the most likely product? Explain your choice. **(2)**

(ii) Carbon monoxide is frequently used as a reducing agent. Suggest why it might be found to be less effective at high temperatures, e.g. 2000°C. **(2)**

(*d*)

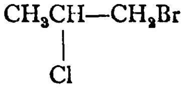


In terms of entropy and enthalpy changes, offer an explanation for the results shown above. **(5)**

[Turn over

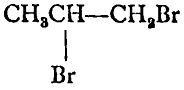
Marks

4. (*a*) When the alkene $CH_3CH{=}CH_2$ reacts with an aqueous solution of bromine saturated with potassium chloride two products are obtained:



$CH_3\underset{\substack{| \\ Cl}}{CH}-CH_2Br$

and



$CH_3\underset{\substack{| \\ Br}}{CH}-CH_2Br$

Using only the information given above, show how you can deduce something about:

(i) the way in which the Br–Br bond breaks in this reaction.

(ii) the probable way in which the bromine attacks the double bond.

Set out your reasoning clearly. **(6)**

(*b*) When an ester is hydrolysed in presence of water containing the ^{18}O isotope, the ^{18}O is found in the acid produced, but not in the alcohol.

Choosing your own ester write the equation for this reaction indicating the ^{18}O clearly. Use the experimental result quoted above to explain how information can be obtained about which bonds were broken and formed in the reaction. **(4)**

(*c*) 1·00 g of a colourless liquid containing carbon, hydrogen and oxygen only was burnt in oxygen. This produced 2·38 g of carbon dioxide and 1·22 g water. The molecular weight of the compound is 74. Calculate the following:

(i) the mass of carbon in 1·00 g of the liquid **(2)**

(ii) the mass of hydrogen in 1·00 g of the liquid **(1)**

(iii) the mass of oxygen in 1·00 g of the liquid **(1)**

(iv) the simplest formula for this compound **(2)**

(v) the molecular formula for this compound **(1)**

This highly inflammable and volatile liquid does not mix with water nor does it react with sodium. Write a structural formula for the compound and indicate by equation(s) how it could be prepared beginning with the appropriate alkyl halide and any other reagents required. **(3)**

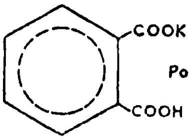
Marks

5. (*a*) Phenolphthalein is a weak acid. Its ionisation equilibrium can be represented as follows:

$$\underset{\text{(colourless)}}{\text{HPhen (aq)}} \rightleftharpoons \text{H}^+\text{(aq)} + \underset{\text{(purple)}}{\text{Phen}^-\text{(aq)}}$$

This indicator changes colour at pH 9·1. At this point the concentration of the purple and colourless forms of the indicator are equal. Calculate the ionisation constant of the indicator. (4)

(*b*) A buffer solution is often made by mixing a solution of a weak acid and one of its salts. However, a dilute solution of potassium hydrogen phthalate acts as a buffer.



Potassium hydrogen phthalate

Consider what happens to this solution when (i) a little acid is added to it and (ii) a little alkali is added to it and thus explain how it acts as a buffer. (4)

(*c*) The ionisation constant (K_a) for chloracetic acid at 25°C is $1{\cdot}38 \times 10^{-3}$. Calculate the pH of a 0·1 M solution of the acid. To do this calculation you may have to make some simplifying assumptions. If you do so, list them and explain why you employed them. (6)

(*d*) The ionisation constant (K_a) for acetic acid at 25°C is $1{\cdot}75 \times 10^{-5}$. What would be the pH of the resultant solution when equal volumes of 0·1 M sodium acetate and 0·1 M hydrochloric acid are mixed? (6)

[Turn over

Marks

6. (*a*) What is meant by the "Heat of Formation" of a compound? (2)

$$C(s) + 2Cl_2(g) \rightarrow CCl_4(l); \ \Delta H = -33{\cdot}3 \text{ kcal}$$

$$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l); \ \Delta H = -130{\cdot}3 \text{ kcal}$$

The C–Cl and Sn–Cl bond energies are very similar. What must be the prime factors in making the heats of formation of CCl_4 and $SnCl_4$ so different? Give your reasoning. (2)

(*b*) Copy this table with its information on common chlorides into your exam book and then fill it in completely.

	C	Si	Ge	Sn	Pb	
Formulae of chlorides	CCl_4	$SiCl_4$				(2)
Physical state at room temp.	liquid	liquid				(2)
Effect of water on chlorides						(3)
Mark (X) in the box corresponding to the chloride which could reduce $Hg^{2+}(aq)$ to Hg(l)						(1)

(*c*) The compound dichlorodimethylsilane $(CH_3)_2SiCl_2$ reacts with water to give a new compound which rapidly polymerises by condensation.

(i) Give a formula and name for this new compound. (2)

(ii) Give a formula for the polymer and give a name for the family of polymers to which it belongs. (2)

(iii) Mention two properties which this family of polymers usually exhibits. (2)

(*d*) "At the **low** temperatures prevalent in early cathedrals it was observed that tin organ pipes slowly developed grotesque growths called tin disease. It was blamed first of all on the devil and then on micro-organisms." Bearing in mind that tin is in the same periodic table group as carbon, suggest a more likely chemical explanation for the "growths". (2)

Marks

7\. (*a*) Iron (II) sulphate heptahydrate ($FeSO_4 7H_2O$) is green and is attracted into a magnetic field.

Potassium hexacyanoferrate(II) [potassium ferrocyanide] ($K_4Fe(CN)_6$) is yellow and not attracted into a magnetic field. In both cases iron is in the oxidation state +2.

(i) Name the ligands surrounding the iron in each of the compounds. **(2)**

(ii) In terms of electrons suggest why the compounds are coloured and why they are of different colour. **(4)**

(iii) Offer an explanation for the differences in magnetic properties. **(3)**

(*b*) A compound of cobalt has the formula $Co(NH_3)_xCl_y$. 0·500 g of it was dissolved in 50 ml M hydrochloric acid. The excess acid required 40 ml M sodium hydroxide solution to neutralise it.

Another 0·500 g portion of the compound was dissolved in water and allowed to react with excess silver nitrate solution. 0·575 g silver chloride was precipitated.

(i) Calculate the number of moles of ammonia liberated from 0·500 g of the cobalt compound. **(3)**

(ii) Calculate the number of moles of chloride ion released from 0·500 g of the cobalt compound. **(3)**

(iii) What values for x and y in the original formula do these results suggest? **(1)**

(iv) When other better methods of analysis are used, the value for y is found to be 50% greater than the value you have calculated. Offer an explanation for the two values of y. **(2)**

(v) Draw a possible structure for the complex showing the ligands surrounding the cobalt ion and also the ions required to balance the charges. **(2)**

[Turn over

Marks

8. (*a*) Use your data book (p. 41) to help you to explain the following observations in terms of E° values.

   (i) In the extraction of bromine from sea water, bromine is displaced from bromide ions by chlorine. Bromine is converted back to bromide ions by the action of an aqueous solution of sulphur dioxide. **(4)**

   (ii) During the electrolysis of an aqueous solution of manganese (II) sulphate, manganese does not appear at the cathode, but a dark brown deposit appears on the anode. **(4)**

   (iii) Molar potassium bromide solution is electrolysed between porous carbon electrodes for some time. When the current is switched off and the electrodes are attached to a voltmeter a reading in the region of one volt is obtained. **(3)**

   (iv) $Cr^{3+}(aq) + 3e \rightarrow Cr(s)$; $E^\circ = -0{\cdot}74$ V

   $Ni^{2+}(aq) + 2e \rightarrow Ni(s)$; $E^\circ = -0{\cdot}23$ V

   $Fe^{2+}(aq) + 2e \rightarrow Fe(s)$; $E^\circ = -0{\cdot}44$ V

   Chromium and nickel are both used as platings for iron. Indicate the importance of each in terms of the type of protection which they give to iron. **(5)**

(*b*) A solution of a molybdate contains molybdenum in the +6 oxidation state. 20·0 ml of this solution was shaken with concentrated hydrochloric acid and mercury. After filtration, the filtrate and the washings required 27·1 ml of 0·015 M permanganate solution to reoxidise the molybdenum to its original oxidation state (+6).
20·0 ml of the same molybdate solution was mixed with dilute hydrochloric acid and zinc amalgam. After filtration, the filtrate and washings required 81·4 ml of the same permanganate solution to reoxidise it to the original oxidation state (+6).

From your calculation suggest the two most likely oxidation states to which the molybdenum was reduced by the two reducing agents. Set out your reasoning clearly. **(4)**

[*END OF QUESTION PAPER*]

1972
CERTIFICATE OF SIXTH YEAR STUDIES
CHEMISTRY
PAPER I.

Marks

1. (*a*) What is meant by (i) $\triangle G$, the Free Energy Change, and
(ii) $\triangle H$, the Enthalpy Change, for a reaction? **(2)**

(*b*) What do the values of $\triangle G$ and $\triangle H$ tell about
(i) the likelihood of a reaction occurring, and
(ii) the rate at which it occurs? **(4)**

(*c*) For the reaction

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

calculate a value for $\triangle H$. The heats of formation of ethene (ethylene) and ethane are $+52{\cdot}3$ kJ mol^{-1}($+12{\cdot}5$ kcal mol^{-1}) and $-84{\cdot}4$ kJ mol^{-1}($-20{\cdot}2$ kcal mol^{-1}) respectively. **(4)**

(*d*) Nickel speeds up the rate at which the hydrogenation of ethene occurs.

(i) Indicate briefly how nickel might catalyse the reaction. **(1)**

(ii) What is the effect of the catalyst on $\triangle H$ for the reaction? Give your reasoning. **(2)**

(iii) What is the effect of the catalyst on $\triangle G$ for the reaction? Give your reasoning. **(2)**

(*e*) A hydrogenation reaction of commercial importance is

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOR(l) + H_2(g)$$
$$\rightarrow CH_3(CH_2)_{16}COOR(s)$$

(i) What is the commercial importance of a reaction of this type? **(1)**

(ii) How will $\triangle H$ for this reaction compare with $\triangle H$ for the hydrogenation of ethene? Give your reasoning. **(2)**

(iii) Suggest how the entropy factor for this reaction might compare with the entropy factor for the hydrogenation of ethene. Give your reasoning. **(2)**

Marks

2. (*a*) Helium was discovered in the Sun before it was found on Earth.

(i) What is likely to happen to helium atoms at the temperatures which exist in the Sun? **(2)**

(ii) How could this enable us to decide that helium is present in the Sun? **(3)**

(*b*) The simplified spectra shown on the worksheet are part of the infra-red spectra of a series of solutions of cyclohexanol in tetrachloromethane (carbon tetrachloride).

The absorption bands shown are due to free O—H groups and hydrogen bonded O—H groups.

(i) Identify the wavenumber of the absorption due to the free O—H groups. Give your reasoning. **(3)**

(ii) In the spaces provided on the worksheet draw the spectra you would expect to obtain over the same region for

(A) cyclohexanol at room temperature **(1)**

(B) cyclohexanol in the vapour phase. **(1)**

In the answer book give your reasons for your answers. **(2)**

(*c*) The following diagrams are representations of the X-ray diffraction pattern formed by a number of crystalline substances.

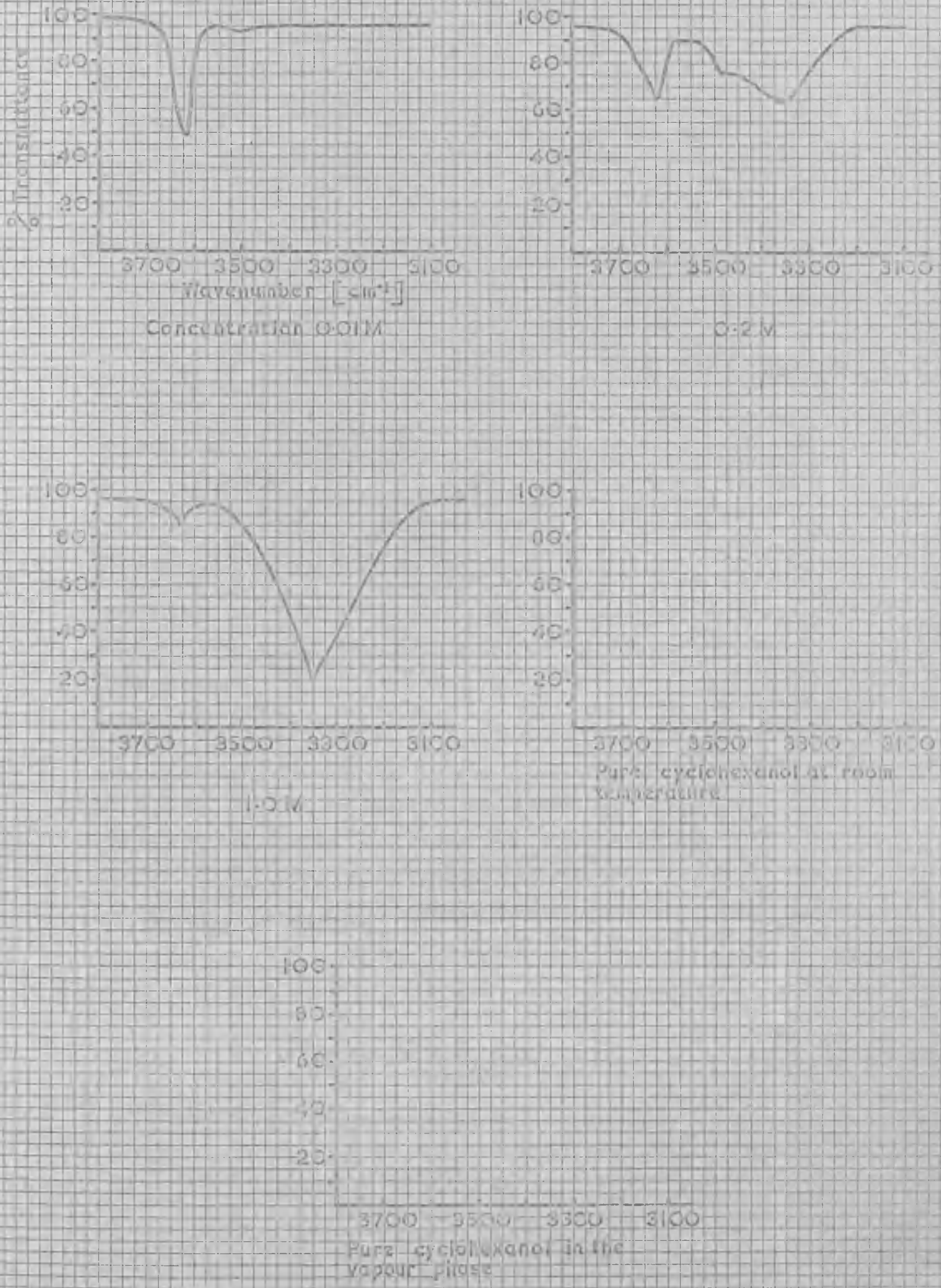
(i) What pieces of information could a chemist derive from a study of the X-ray diffraction pattern of a crystal? **(2)**

(ii) By comparing the X-ray pattern for silver chloride with those of sodium chloride and caesium chloride, what can be deduced about a silver chloride crystal? Give your reasoning. **(3)**

(iii) Suggest what happens to the structure of ammonium chloride as it is heated from 20°C to 250°C. **(3)**

[Turn over

2[b] Solutions of cyclohexanol in tetrachloromethane



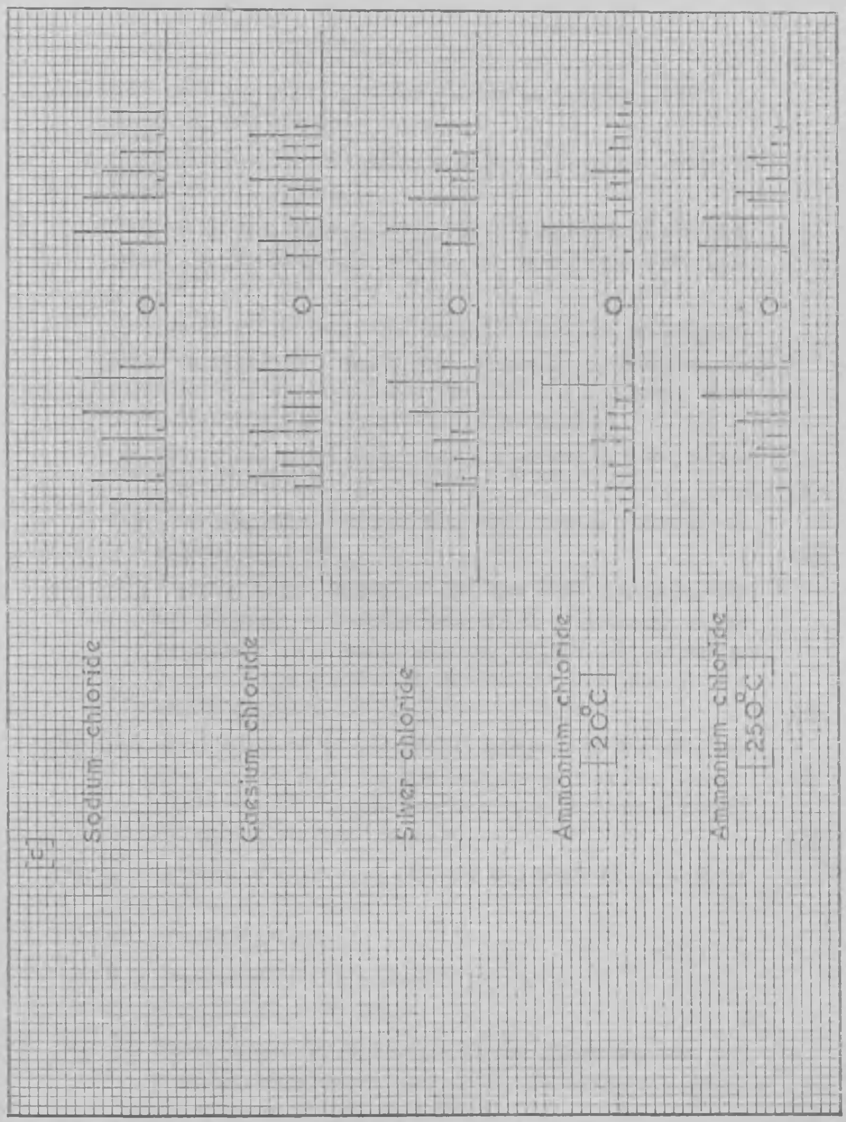
Concentration 0.01M

0.2 M

1.0 M

Pure cyclohexanol at room temperature

Pure cyclohexanol in the vapour phase


E
Sodium chloride
Caesium chloride
Silver chloride
Ammonium chloride
20°C
Ammonium chloride
250°C
O

Marks

3. (*a*) The table on page 41 of the data book may be helpful in answering this question.

A solution is known to contain iron(II) sulphate and iron(III) sulphate.

50·0 ml of this solution required 20·0 ml 0·02 M acidified potassium permanganate solution to oxidise the Fe^{2+} ions present.

50·0 ml of the original solution, after reduction with tin(II) chloride, required 41·6 ml 0·01 M acidified potassium dichromate solution to oxidise the Fe^{2+} ions present. Any excess tin ions do not react with dichromate ions.

(i) How many moles of Fe^{2+} ions are present in 1 litre of the original solution? **(4)**

(ii) How many moles of iron ions are present in 1 litre of the original solution? **(4)**

(iii) Use the table on page 41 of the data book to explain why the presence of chloride ions makes it necessary to use potassium dichromate solution instead of potassium permanganate solution to oxidise the Fe^{2+} ions in the second titration. **(4)**

(iv) What happens to the tin(II) chloride in the reaction which results in all the iron being present as Fe^{2+} ions? **(1)**
Could lead(II) chloride have been used in place of tin(II) chloride? Give your reasoning. **(1)**

(*b*) A compound of chromium, chlorine and water exists in three isomeric forms. These are

A $[Cr(H_2O)_6]^{3+}(Cl^-)_3$
B $[Cr(H_2O)_5Cl]^{2+}(Cl^-)_2\ H_2O$
C $[Cr(H_2O)_4Cl_2]^+Cl^-\ 2H_2O$

(i) Three equimolar solutions of the above isomers are provided. How would conductivity measurements enable you to determine which is which? **(2)**

(ii) 100 ml of an aqueous solution containing 2·665 g of one of the isomers, when treated with silver nitrate solution, gave 2·870 g silver chloride. Which one of the isomers was in solution? **(4)**

[Turn over

4. (*a*) "It is difficult at first to see how the inclusion of carbon and lead in the same Group can be justified."

Copy this grid into your answer book and set out brief comparisons between carbon and lead to illustrate the statement above.

Property	*Carbon*	*Lead*
Bonding in the free elements.	(1)	(1)
Most stable oxidation state in halides.	(1)	(1)
Ability to form chains with itself in compounds with hydrogen.	(1)	(1)

(*b*) For the reaction

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

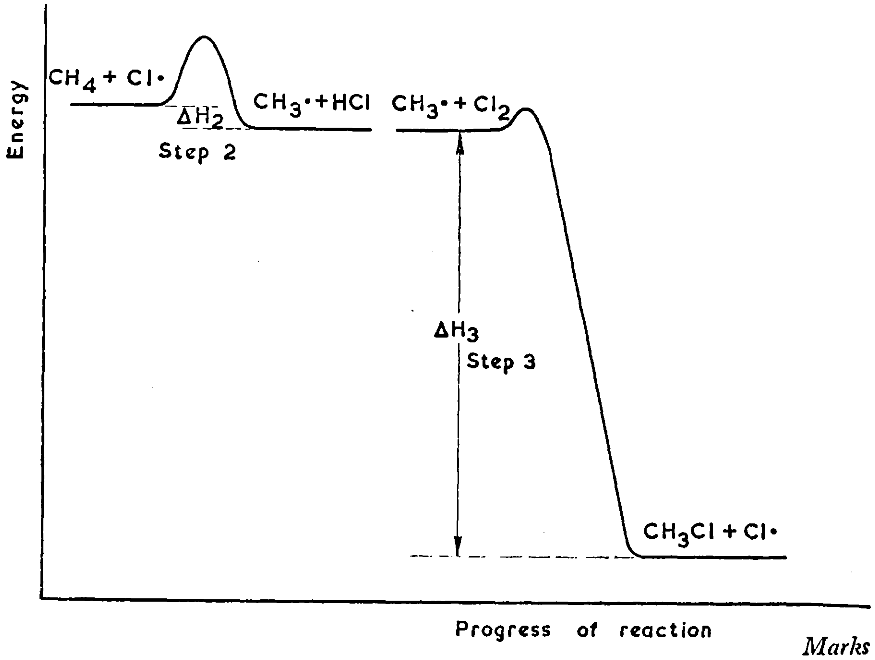
the following chain mechanism has been proposed.

STEP 1. $Cl_2 \rightarrow 2Cl\cdot$

STEP 2. $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$

STEP 3. $CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$

The enthalpy changes in Steps 2 and 3 can be represented diagrammatically as follows:—



Marks

(i) Use the table of bond energies on page 40 of the data book to determine the approximate $\triangle H$ for Steps 2 and 3 ($\triangle H_2$ and $\triangle H_3$ in the diagram). **(4)**

(ii) Step 2 is slower than Step 3. Suggest a reason for this. **(1)**

(iii) An alternative mechanism for Steps 2 and 3 is

STEP 2. $CH_4 + Cl\cdot \rightarrow CH_3Cl + H\cdot$

$\triangle H = +88$ kJ mol^{-1}($+21$ kcal mol^{-1})

STEP 3. $H\cdot + Cl_2 \rightarrow HCl + Cl\cdot$

$\triangle H = -188$ kJ mol^{-1}(-45 kcal mol^{-1})

Suggest why this is a less likely mechanism. **(2)**

(iv) The reaction does not occur in the dark until 300°C. If tetramethyl lead is added the reaction occurs at 150°C. Suggest why this compound should have such an effect. **(2)**

(v) Step 1 can be carried out at room temperature in the presence of bright sunlight. From the bond energy of the Cl—Cl bond find

(*a*) the energy required to dissociate one **molecule** of chlorine. **(1)**

(*b*) the wavelength of the radiation responsible for this dissociation. **(4)**

(Planck's Constant $6{\cdot}63 \times 10^{-34}$ J s; 1 calorie = $4{\cdot}18$ J; Velocity of light $3{\cdot}00 \times 10^{8}$ m s^{-1})

5. (*a*) Offer an explanation of the following:— *Marks*

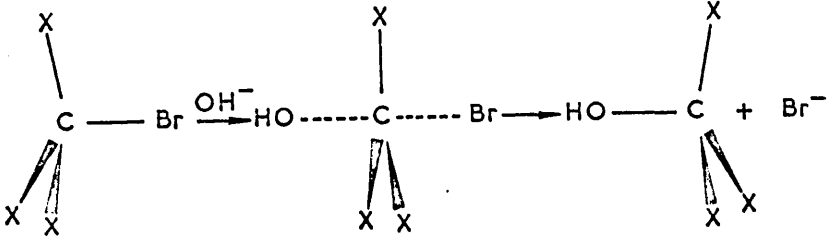
(i) When a crystal of sodium chloride is kept in a saturated solution of sodium chloride maintained at constant temperature, the crystal gradually changes shape. **(2)**

(ii) The solubility of silver chloride in water at 25°C is very much higher than its solubility in M sodium chloride solution at the same temperature. **(4)**

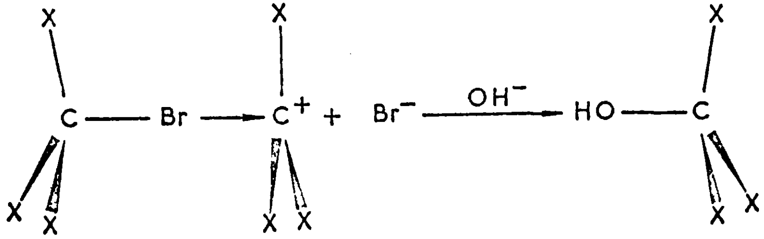
(iii) When an ammonia solution is added to an aqueous solution containing ions of a metal X, the hydroxide of X is precipitated. If ammonium chloride is first added to the metal ion solution there is no precipitate when the ammonia is added. **(5)**

(*b*)

Mechanism 1



Mechanism 2



The diagrams above show two possible mechanisms by which an alkyl bromide can be hydrolysed when treated with sodium hydroxide solution.

When X is $-C_2H_5$ the rate of hydrolysis is found to depend only on the concentration of the alkyl bromide.

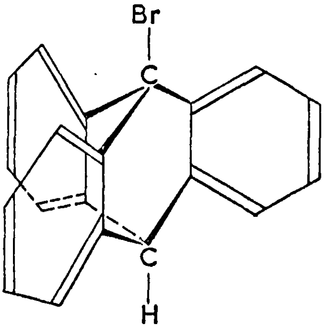
(i) Give the systematic name for $(C_2H_5)_3C.OH$, which is the product of the hydrolysis of $(C_2H_5)_3CBr$. **(1)**

(ii) In the compound $(C_2H_5)_3CBr$ what are the polarities of the bonds C—H and C—Br? **(2)**

(iii) Suggest by which of the above mechanisms the hydrolysis of $(C_2H_5)_3CBr$ occurs. Give a reason for your answer. **(2)**

Marks

(iv) The bromine atom in the compound shown is **not** easily removed by reaction with hydroxide ions. By considering the two mechanisms above, offer a possible explanation of this inactivity. **(4)**



6. (*a*) 0·56 g of a primary amine (A) was dissolved in water giving 100 ml solution. 25·0 ml 0·1 M hydrochloric acid was neutralised by 20·0 ml of this solution.

(i) If 1 mole of A is neutralised by 1 mole of hydrochloric acid calculate the molecular weight of A. From your result suggest a name and formula for A. **(6)**

(ii) Could phenolphthalein be used as an indicator for the neutralisation reaction? Explain your reasoning. **(3)**

(iii) The aqueous solution of A gives a deep blue colour when added to a solution containing Cu^{2+}ions. Tetramethylammonium hydroxide does not give this blue colour with Cu^{2+} ions in solution. Suggest an explanation for this difference. **(3)**

(*b*) Consider the data for the following reactions at 25°C

A $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $K_a = 1{\cdot}74 \times 10^{-5}$; $\Delta H = 0$ kJ mol^{-1}

B $CCl_3COOH \rightleftharpoons CCl_3COO^- + H^+$ $K_a = 2{\cdot}24 \times 10^{-1}$; $\Delta H = 0$ kJ mol^{-1}

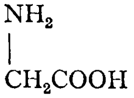
ΔH refers to the reaction from left to right.

(i) Calculate the pH of a 0·1 M solution of acetic acid. **(4)**

(ii) ΔG for reaction A has a more positive value than ΔG for reaction B. How can this difference be accounted for in terms of entropy or enthalpy changes? **(2)**

(iii) From your answer to (ii) suggest a reason in terms of the structure of the particles present for the large difference in K_a values. **(2)**

Marks

7. (*a*) Glycine  $\underset{CH_2COOH}{NH_2}$ dissolves in water giving a solution which has a buffering action. Show what is meant by buffering, indicating what might happen when
(i) a little acid
(ii) a little alkali is added to an aqueous solution of glycine. **(4)**

(*b*) Glycine is a crystalline solid with a fairly high melting point. (230°C). By comparison the melting point of $CH_2(OH)COOH$, which has almost the same molecular weight, is 63°C. Glycine is almost insoluble in solvents such as methanol and diethyl ether.
(i) What type of bond[illegible] of glycine? **(1)**
(ii) Suggest how such b[illegible] glycine. **(3)**

(*c*) Write structural formulae for the main organic products of the reaction of glycine with (i) ethanol
(ii) sodium hydroxide. **(2)**

(*d*) Methylmagnesium iodide can be used to determine the number of —OH groups in a compound of known molecular weight. When the compound containing —OH groups is added to methylmagnesium iodide, 1 mole of —OH groups liberates 1 mole of methane.

An organic compound on analysis gave the following results:
A It contained 39·1% carbon, 52·2% oxygen and 8·7% hydrogen.
B The molecular weight was 92.
C 0·1 g of the compound yielded 73 ml methane (measured at s.t.p.) when added to excess methylmagnesium iodide in an ether.

From these results find
(i) the molecular formula of the compound. **(3)**
(ii) the number of —OH groups in one molecule of the compound. **(3)**
(iii) a possible structural formula and systematic name for the compound. **(2)**
(iv) The viscosity of this compound is very much greater than that of toluene ($C_6H_5CH_3$) which has the same molecular weight. Suggest a reason for this. **(2)**

Marks

8. (*a*) "While we find noticeable similarities between many of the transition metals, there is at the same time an enormous range of properties displayed by these elements."

Reference to pages 36-39 of the data book may be helpful in answering the following questions.

(i) Account for the following similarities.

	Fe	Co	Ni	
1st ionisation energy ($J\ mol^{-1} \times 10^3$)	760	760	740	
Covalent radius of atom ($m \times 10^{-10}$)	1·16	1·16	1·15	**(3)**

(ii) Account for the following differences

	Sc	Mn	
Oxidation states	$+3$	$+2, +3, +4, +5, +6, +7$.	**(2)**

(iii) Suggest the likely maximum oxidation state of osmium (Atomic number 76). **(1)**

(*b*) A ruby is composed of aluminium oxide containing occasional Cr^{3+} ions in place of Al^{3+} ions. The environment of the Cr^{3+} ions is an octahedron of oxide ions. Because of this the *d* orbitals are no longer degenerate, but split.

(i) Show by a three dimensional diagram the environment of a Cr^{3+} ion in a ruby crystal. **(2)**

(ii) What is meant by saying "the *d* orbitals are no longer degenerate, but split."? **(4)**

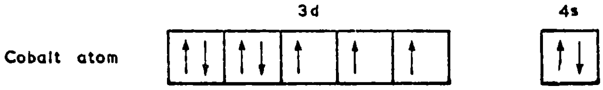
(iii) The Cr^{3+} ions distort slightly the aluminium oxide structure. Suggest a reason for this. **(2)**

(iv) Suggest why aluminium oxide is colourless, while a ruby is coloured. **(3)**

[Turn over

Marks

(*c*) The structure of the outer electron levels of cobalt can be represented in the following manner:—



The $[Co(NH_3)_6]^{3+}$ ion is diamagnetic; the $[CoF_6]^{3-}$ ion is paramagnetic.

Draw diagrams to represent the likely outer electronic configurations for cobalt in

(i) the $[Co(NH_3)_6]^{3+}$ ion

(ii) the $[CoF_6]^{3-}$ ion.

Give reasons for your answers. **(3)**

[*END OF QUESTION PAPER*]

Summary of Examiners Reports on Paper I (Essay Type) Sixth Year Studies Chemistry

1969. 425 Candidates

Paper I.

The comparative weakness of organic chemistry.

The difficulty caused by even the simplest calculation.

Many candidates seemed to be afraid to attempt questions which involved calculations.

1970. 771 Candidates

Paper I.

Question 1. Thermodynamics. Popular and well done, showing that pupils were getting a good grasp of basic concept. Where a bad performance occurred it was seen throughout the school.

Question 2. Spectroscopy. Popular and well handled. Pupils grasp of nomenclature of simple organic compounds was weak.

Question 3. Calculations on Volumetric Analysis. Deductions from osmotic pressure. Lowest in the popularity list. Examiners reported that only two candidates succeeded in getting the calculations correct although it was parallel to the calculation recommended in the practical work. The answers to the second part of the question involving deduction and extrapolation were quite good.

Question 4. Organic with some thermodynamics. Only moderately well done. Again the weakness in organic nomenclature was in evidence. The majority of the candidates thought that 2- bromopropane was $C_3H_6Br_2$. The ability to extend their knowledge of grignard reagents to the likely reactions of an alkyl lithium compound was poor.

Question 5. Relationships within groups in the periodic table with particular reference to group IV. This was an experimental question which candidates were asked to answer in a grid to cut down the random verbiage ~~verbago~~ so often found in answers on comparative chemistry. It was popular and well done when candidates took care to read the captions. For example some candidates gave adequate answers about the properties of Group IV compounds when the question asked for information about Group IV elements. The calculation at the end on bond energies was feebly done.

Question 6. Transition metals. This question was not very popular. The candidates ideas of the origin of colour in transition element compounds were, to say the least, unorthodox. This part of the work had clearly not been well taught or understood.

Question 7. Conductivity curves, Zn/Cu cell, reaction between Mg and $AgNO_3$ powder when water is added. Quite popular. The conductivity parts of the question were generally well done. Surprisingly few candidates could put forward a reasonable explanation for the function of water in the reaction between magnesium and silver nitrate.

Question 8. Electrolysis and simple calculations. This question required the ability to marshal facts and extend knowledge into an 'unseen' situation. Some parts of the question were very well done, but, as usual, the calculation was weak.

Question 9. Equilibria and solution chemistry. A very popular and well done question.

1971. 1073 Candidates.

Paper I.

Mean score less than mean score for 1970. The paper was generally too difficult this year for most candidates. The reaction was very much according to schools in that some schools did uniformly well while others performed at a very low level. Allowing for the searching nature of the paper there was an evident unpreparedness among the candidates even for "routine bookwork".

Question 1. Spectroscopy. Quite satisfactory

Question 2. Structure and 'unseen'. Well done on the whole. The unseen was tackled and solved with considerable ingenuity.

Question 3. Thermodynamics and difficult 'unseen'. Few candidates obtained full marks for the unseen, but there was evidence of some quite mature thought. Schools are evidently teaching that ΔG values are related to reaction rate. Some teacher re-education is necessary here.

Question 4. Organic. Mean score less than 9. Section (a) which was "bookwork" was very loosely done. Pupils were trotting out a potted answer with no reference to the experimental evidence. (c) The stepwise calculation was done adequately, but the chemical conclusions arising from it were often nonsensical.

Question 5. pH calculations. Mean score less than 8. Section (b) This 'comprehension type' question revealed little real understanding of how a buffer works. (c) and (d). Many pupils could not handle logs.

Question 6. Extension to Group IV. Mean score less than 8.

Question 7. Crystal field theory and mole calculations. Mean score less than 8.

(a) Crystal field theory is not being taught clearly in most schools. Any resemblance between most answers and the accepted answer was purely coincidental. (b) Only a handful of pupils made anything of the calculations despite its simple figures.

Question 8. E^o deductions and mole calculation. Mean score less than 8. (a) The answers showed again the poor grasp that pupils got of the meaning and use of E^o values. (b) Arithmetic defeated most candidates. These disappointing results might give us cause to ask if we are teaching chemistry which is meaningful to most candidates, or are candidates treating the course so lightly that a basic modicum of work is not being done.

Questions 5, 7 and 8 were tackled by less than 50% of pupils.

1972. 1191 Candidates

Question 1. Thermodynamics. On the whole this was well done. A number of schools still link values of ΔG and ΔH with rate.

Question 2. Spectroscopy, I.R. and X-ray. The eight marks for the X-ray part of the paper were lost by the majority of candidates. It was clear that this piece of work had not been taught in most schools.

Question 3. Calculations on Transition Element Chemistry. Attempted by only 24% of candidates. Those who attempted it scored quite well.

Question 4. Group IV and 5th year kinetics. Well done.

Question 5. Solubility and equilibrium and organic mechanisms. This was disastrous. 5(a) based on the ideas of dynamic equilibrium was uniformly badly done. In 5(b) few pupils could distinguish between S_N1 and S_N2 reactions and the deductive part (IV) was a mystery to most candidates. It seems almost certain that this section of the work is taught without the aid of models.

Question 6. Solution chemistry. This was fairly well answered although few pupils read b(iii). Instead they trotted out a pat answer to quite a different question.

Question 7. Buffers. Calculation for deduction of structure. The first half of this question was very poorly done. The action of a buffer (other than the text book standard examples) was not understood. The latter part of the question was better although the systematic nomenclature left much to be desired.

Question 8. Transitional metal chemistry and origin of colour. The ideas on the origin of colour have improved compared with previous years, but we still have a long way to go to clarify this area.

Evaluation of Experiments

Details of some experiments were circulated to teachers of Sixth Year Studies in a memorandum from the Scottish Education Department. Most of the experiments were tried by the author and their suitability for normal school laboratory use evaluated on the following criteria:-

safety;
availability and cost of reactants;
sophistication of apparatus required;
were the numerical results convincing?
length of time required to carry out experiment.

Only a few experiments were found to be unsuitable namely :-

determining equilibrium constants;
exploding methane and chlorine by initiating with U.V. light;
bromination of an alkene in the presence of the chloride ion;
hydrolysis of t-butyl bromide to illustrate S_N1 reaction mechanism.

Others were suitable but the instructions were lacking in clarity and detail, and less sophisticated apparatus could have been used. (Observations on the individual experiments are listed separately). Some alternative experiments, written or modified by the author, were tried during the period late 1970 to early 1972. Where alternative experiments were found, they were assessed by the Chemistry post-graduate students at Notre Dame College of Education in May, 1972. They were then rewritten and circulated to a group of Glasgow schools for use by their Sixth Year Study pupils during the 1972-73 session. Questionnaires were circulated with the experiments and it is hoped to obtain details of time required to complete experiments, numerical results and difficulties encountered. After any necessary alterations, details of the experiments will be passed to the Scottish Certificate of Education Examination Board. Details of the experiments on trial are on pages A2 - 55 to A2 - 92.

The teachers of Sixth Year Studies Chemistry from the Glasgow schools are also attempting to rewrite the experiments in a structured form. The writing is being edited by R. Stewart and J. McGuire. It is hoped that the structured format will make the pupils more aware of the objectives of the experiment and less likely to follow the instructions simply as a recipe.

Experiments Evaluated

Heats of combustion of alcohols. The simple heating of a beaker containing a fixed weight of water by a series of alcohols (methanol, ethanol, propanol and butanol in spirit burners), yielded reasonably constant stepwise increases in the heats of combustion of the alcohols provided simple precautions were taken

The actual heats of combustion were only about 50% of the literature values due to heat losses and to not considering heat absorbed by container. These losses are the same for each alcohol provided the same mass of water and container are heated over the same temperature range by each alcohol.

Using a simple heats of combustion apparatus (A2 - 58).

the author obtained heats of combustion of 95%,82% and 62% of the literature values for ethanol, propanol and butanol respectively.

The sample results on page A2-56 are those obtained by the author.

This appartus however has had very limited success in the hand of pupils. It was used in seven schools during the 1971-72 session and produced results little better than that of simply heating beakers.

The extra time involved using this does not seem to be worthwhile in relation to the aim of the experiment, i.e. showing there is a stepwise increase in the heats of combustion of the alcohols.

Hess's Law. Both experiments listed in the syllabus provide good results. The NaOH (solid)/H_2O, NaOH(solid)HCl , NaOH (solution)/HCl might be preferred to the Zn/Cu^{2+}, Cu/Ag^+, Zn/Ag^+ experiment. The former uses reactions which are possibly more familiar to the pupils. The latter uses quantities of molar silver nitrate solution. This is fairly expensive in terms of school chemicals budgets. The cost could be cut by recovering the silver but very few Scottish schools appear to do this.

Measurement of the e.m.f. of a chemical cell. The Zn/Ag^+ cell provides no problems except that of cost of silver nitrate. This is offset by the fact that the results can also be used for the comparison of ΔG and ΔH The author measured the e.m.f. using a high resistance voltmeter(1000 ohms/volt) a pH meter (calibrated in millivolts) and a potentiometer. These were all of patterns likely to be supplied to schools. The values agreed to within 1%. It appears that sophisticated apparatus is not required for this experiment.

Comparison of ΔG and ΔH. A number of metal displacement type reactions were tried by the author. Only those involving a change in the oxidation number greater than one produced results in which the difference between ΔG and ΔH lay outside the limits of experimental error, e.g. Zn/Ag^+ and Cu/Ag^+. The rate of reaction for Zn/Ag^+ is faster than Cu/Ag^+ and is therefore probably preferrable.

The reaction Al/H^+ was also tried by the author. A known weight of aluminium was put on 6M HCl in a vacuum flask and the heat of reaction measured. ΔG was calculated using the Al/Al^{3+} E^0 value obtained from the data book. The experiment is cheap to carry out, provides a large difference between ΔG and ΔH but is complicated by a $P\Delta V$ factor due to the generation of $H_{2(g)}$.

Spontaneous Endothermic Reactions. Both the $CoCl_2$ hydrated/$SOCl_2$ and $Ba(OH)_2/NH_4SCN$ produce temperature drops in excess of 20°C. The latter may be preferrable because a fume cupboard is not required. The reaction of ammonium carbonate with ethanoic, propanoic, butanoic, pentanoic or hexanoic acid[11] could also be used. The reactants are readily available and the products are non-toxic.

Prediction of Transition Temperatures. Both the decomposition temperature of $NaHCO_3$ and the transition temperature of $Na_2SO_4 10H_2O$ can be found using simple apparatus. Plotting the data and interpreting the graph are also useful skills for the pupils to acquire.

The decomposition temperature of ammonium chloride is not so conveniently found. If ammonium chloride is heated in a test-tube the decomposition is not noticeable until the NH_3 and HCl recombine in the cooler parts of the tube. There is therefore a delay before the decomposition temperature is noted. Even using electrically heated melting point apparatus the author could not obtain a sharp decomposition temperature. The decomposition took place over a range of about 5°C.

Equilibrium Constants. The two experiments listed in the syllabus[4] are the colorimetric determination of the $Fe^{3+}NCS^-$ system equilibrium constant and the hydrolysis of an ester. Neither have proved satisfactory in the school situation.

Where the Fe^{3+}/NCS^- system has been used in schools teachers have adopted variations on two of the following methods:-

(a) Visual matching of colour intensity in the test-tubes[12,]

(b) Colorimetric estimation of colour intensity.

Both methods are tedious and even method (b) does not produce good results.

The hydrolysis of an ester requires great care experimentally; it requires the use of a good thermostatical controlled bath; it takes a long time to complete; the presence of an acid to act as a catalyst confuses the situation and makes the arithmetic more complex.

Both of these experiments are demanding in time, are complicated for sixth year pupils and do not yield constants in the school situation. There is also the possibility of pupils losing sight of the objectives because of the complexity of the experiments. This is discussed in relation to all the experiments in chapter 3, but none of the schools completing questionnaires used the hydrolysis of an ester experiment and there was insufficient data on the Fe^{3+}/NCS^- reaction. It is doubtful if any good purpose is served by carrying out these two experiments at school level and alternative experiments have been sought by the author.

Determining an equilibrium constant for the $KI_3 \rightleftharpoons KI + I_2$ reaction (A2 - 63 to A2 - 67) has been tried in the group of Glasgow schools after evaluation by a post-graduate student at Notre Dame College. The particular post-graduate student who evaluated this experiment is a former supervisor of an I.C.I. standards laboratory and a very skillful practical chemist. He obtained values of 1.74×10^{-3}, 1.75×10^{-3} and 1.82×10^{-3} for the equilibrium constant but it took him a full day to complete the experiment. Only one report has been returned from a Glasgow school and they abandoned the experiment after three groups each of three persons had taken 100 minutes simply to find the distribution constant. They also commented on the complexity of the experiment and the arithmetic.

It would appear that this is another experiment which does not fit the school situation.

An experiment to determine the equilibrium constant of the reaction;

$$PbSO_{4(S)} + 2\ NaI_{(aq)} \rightleftharpoons PbI_{2(S)} + Na_2SO_{4\ (aq)}$$

is now on trial in the Glasgow schools. The following results have been obtained by one school.

Expt 1. Varying amounts of $PbSO_{4(s)}$ + 200 cm^3 0.1M NaI

Sample .	Wt. of $PbSO_4$ used g.	Kc
1	5	4.6
2	10	6.3
3	15	7.0
4	25	6.9

Expt. 2. Varying amounts of 0.1 M NaI + 10g $PbSO_4$

Sample.	Vol. of 0.1M NaI used.	Kc
1	50	6.6
2	100	6.6
3	150	6.7
4	200	6.4

Both the experiments were carried out at 21°C. No mechanical stirrer was available. Total time taken was approximately 90 minutes. The variation in the values of Kc in the first experiment could well be due to unfamiliarity with this type of indicator. If an exercise using this type of indicator was given earlier in the course, and the laboratory instructions were rewritten in a clearer form then this would appear to be a very promising experiment.

There is also the possibility of delaying the experimental determination of an equilibrium until the section on solution chemistry where experiments suitable to the secondary school are available.

Iodine Coulometer. Determination of the stoichiometry of the $Na_2S_2O_3/I_2$ reaction by electrolysis.

Purpose built apparatus is available for this experiment but the postgraduate students found that a variety of apparatus and constant current sources gave acceptable results. This makes it all the more extraordinary that an experiment so important in redox reaction study should be so neglected.

The stoichiometry of the MnO_4^-/Mn^{2+} and Fe^{2+}/Fe^{3+} are well tried experiments and produced no problems.

Ignition of $BaCl_2 \cdot H_2O$ and the estimation of Cl^- as AgCl.

These are standard gravimetric experiments and require only mastery of the experimental techniques.

Exploding Methane with Chlorine under the influence of Light.

This is a demonstration experiment. When it works it is spectacular but it requires careful preparation. The reaction proceeds explosively only if the methane and chlorine are pure and dry. Both the methane and chlorine have to be prepared in the laboratory. In relation to the amount of preparation required this experiment appears to be an uneconomic use of time and a certain amount of risk is involved.

Bromination of Heptane in Light. As opposed to the preceeding demonstration experiment, this can be carried out by the pupils. The reagents need very little preparation and the experiment is very quickly carried out. The hazards can be minimised by supplying the pupils with the bromine solution instead of asking them to make it up and cautioning them on the use of U.V. light sources. The absence of reaction when light is excluded is shown at the same time. This experiment seems preferable to exploding methane and chlorine.

Bromination of an Alkene in the presence of a Chloride. Neither of the experiments described in the memorandum are particular suited to school use. The first involves the purchase of cylinders of ethene and nitrogen and setting up a heated G.L.C. column. Since the column is unlikely to be used for any other experiment this is probably an uneconomic use of time and money.

The samples could of course be sent to a friendly neighbourhood University for chromatographic analysis, but this deprives the pupils of seeing the experiment through to the end. The second experiment can be completed in school but involves a sodium fusion test. Since some Sixth Year Study Chemistry practical is unsupervised, this is too dangerous for school use.

An alternative experiment using hexene (A2 - 79, A2 - 80) has been designed by the author, and is on trial in the schools. Analysis of the products is by T.L.C. on precoated silica gel sheets. This should make it suitable for schools in terms of financial cost and time.

Hydrolysis of t-butyl bromide to illustrate S_N1 reactions.

No suitable experiment was found to illustrate this and the experimental ~~24~~ 13 proof has now been dropped from the syllabus.

Relative Ease of Displacement of Halogen in RCl, RBr and RI

This experiment has been rewritten by the author and is on trial in the schools. Post-graduate students and teachers on in-service courses at Notre Dame College have had no difficulty with this experiment.

Grignard Reaction

Both a large scale and small scale preparation of benzoic acid were evaluated by post-graduate students. It was found that, provided all moisture was excluded the small scale experiment was satisfactory. The instructions have been rewritten (A2 - 78) and the experiment is on trial in the schools. Since this experiment so readily illustrates the use of organomagnesium halides as sources of ~~nucleophile~~s nucleophiles there seems little purpose in preparing triphenyl methanol for the same purpose.

Preparation of SnI_4, $SnCl_2$ and $PbCl_2$.

No difficulties were experienced with these experiments on evaluation. They have been rewritten by the author to a common format using quantities suitable for individual experiments.

Reactions of Sn^{2+} with MnO_4^- and Fe^{3+}.

These are straightforward test tube reactions and no difficulties were found.

Oxidation States of Vanadium and Maganese.

These were evaluated by post-graduate students and rewritten by the author to a common format.

Preparation of Tutton Salts.

These are very simple inorganic preparations. Recipes were made up by the author and tried out by a post-graduate student.

Preparation and Analysis of $Ni(NH_3)_6(BF_4)_2$.

The preparation is quite straight forward and presents no problems. This was one of the 'unpopular' experiments and this may be partly due to the analysis. Analysis for the NH_3 is a normal acid-base titration. The Ni can also be determined simply by titrating with E.D.T.A. Problems may have arisen through schools determining Ni gravimetrically. This like most gravimetric work is time consuming and requires a fair degree of manipulative skill. This aspect of the experiment may have contributed to the unpopularity.

EXPERIMENTS ON TRIAL.

Heats of Combustion of Alcohols

The heats of combustion of a series of alcohols increase by constant amounts as the number of carbon atoms increases. The heats of combustion can be determined by burning a known weight of alcohol and measuring the temperature rise produced. This can be carried out using (a) low heat capacity containers (e.g. aluminium beakers) containing known weight of water or (b) a heat of combustion apparatus which is easily constructed. Both methods will give an ascending order of heats of combustion provided simple precautions are taken.

Shield the apparatus from draughts.

Measure the temperature rises over similar ranges in temperature.

Use fibreglass wicks approximately ⅛" diameter. (If not available strands of fibreglass can be twisted together).

Keep flames approximately the same height. (n-butanol will give the smallest flame, so it is advisable to check all the flame heights against that of n-butanol before starting the experiment.)

Weigh burners immediately after extinguishing to minimise loss by evaporation.

Use a balance accurate to 10mg.

(a) Since no account is take of heat losses and heat capacity of beaker, heats of combustion will not approach literature values but constant differences between pairs of alcohols should be found.

Place 100 cm^3 of water in the beaker. Weigh the burner and alcohol. **Take** the initial temperature of the water. Light the burner and heat the water to raise the temperature by about 15^oC. Measure the final temperature accurately. Extinguish the flame and reweigh the burner immediately. Calculate the heat obtained by burning 1 mole of the alcohol. Repeat for the other alcohols in the series.

(b) This method involves finding the heat capacity of the appartus by using the literature value for the heat of combustion of methanol. No precautions are taken to cut down heat losses, but the heat loss should be approximately the same for each alcohol. The obtained values for the heats of combustion should be closer to the literature values with this apparatus.

(i) Heat capacity of appartus.

Weigh burner containing methanol and find initial temperature of water. Light the burner and draw the combustion products gently through the apparatus. Stir the water and allow the temperature rise of 15-20°C. Extinguish the burner and weigh quickly. Note the final temperature of the water.

e.g. Initial weight of burner + CH_3OH = 146.27g.
Final weight of burner + CH_3OH = 144.70g.
Weight of CH_3OH = 1.57g.

Final temperature of water = 41.2°C
Initial temperature of water = 22.2°C
19.0°C

$$\text{Heat capacity} = \frac{715}{32.05} \text{ X } \frac{1.57}{19}$$

$$= 1.85\ \text{kj.C}^{o-1}$$

(ii) Heat of combustion of ethanol.

Mark water level in apparatus. Remove some of the warm water by syringe and replace with cold water to bring temperature back to approximately initial temperature in (a). Using method for (a) find heat of combustion. e.g. Initial weight of burner + C_2H_5OH = 144.08g.

Final weight of burner + C_2H_5OH = 142.96g.
Weight of C_2H_5OH burned = 1.12g.
Final temperature of water = 41.4°C
Initial Temperature of water = 21.8°C
Temperature rise = 19.6°C

Heat given out by ethanol = 19.6 x 1.85

= 36.26kj.

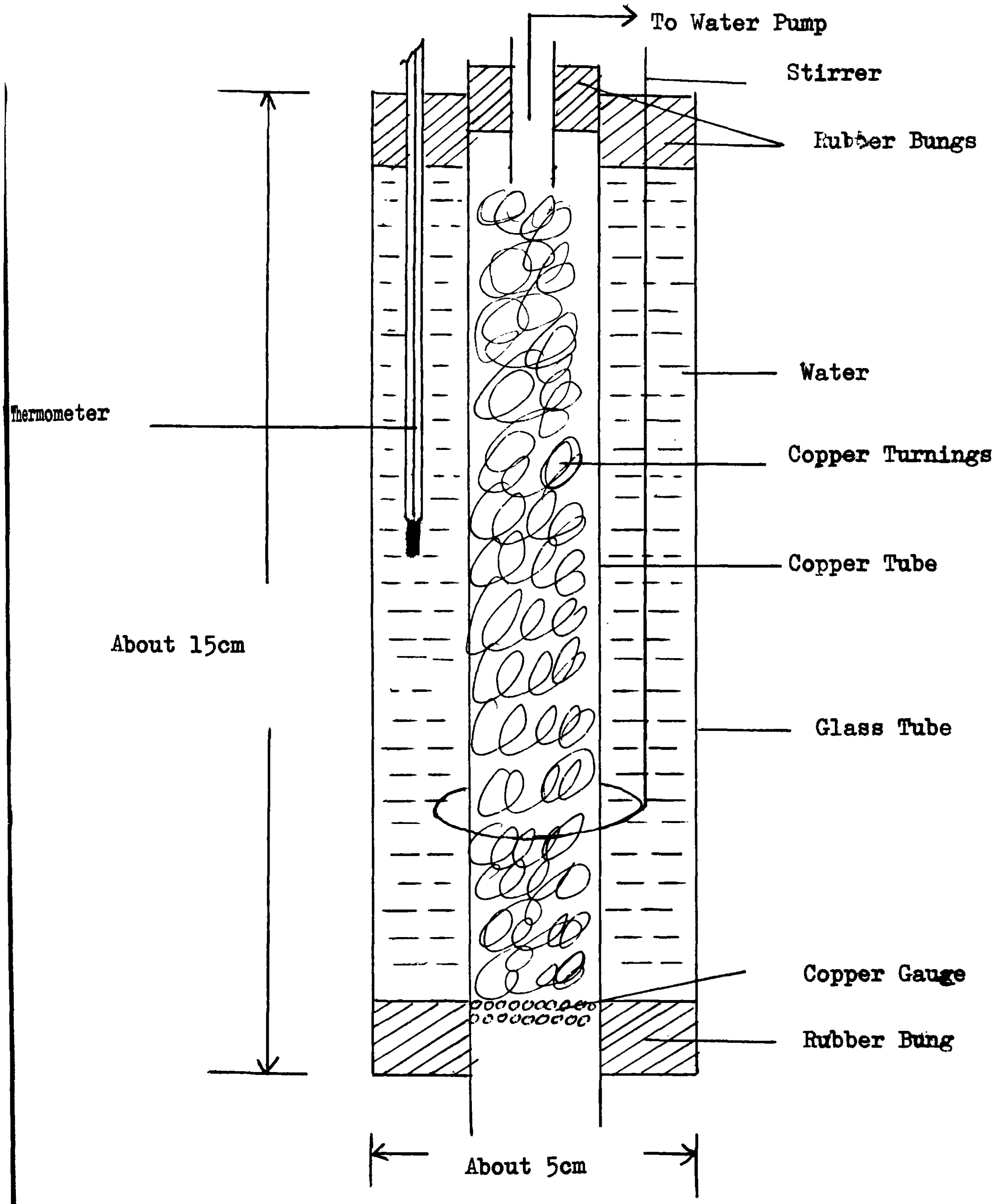
1.12g of ethanol on combustion produces 36.26kj.

40.048g of ethanol on combustion produces $\frac{36.26 \times 40.048}{1.12}$

= 1310.54kj.

∴ Heat of combustion of ethanol = 1310.54kj. mole^{-1}

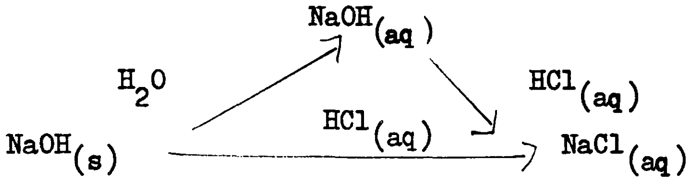
Repeat for propanol and butanol.



The metal tube need not be copper and coiled strips of aluminium foil could be substituted for the copper turnings. The glass chimney from Griffin & George ventilation apparatus is a suitable size for the large glass tube (Cat.No. L44-780). Care must be taken in positioning the spirit burner to prevent rapid deterioration of the stopper.

VERIFICATION OF HESS'S LAW

If a chemical change can occur by two or more paths, the amount of heat absorbed or evolved in the total change must always be the same, independent of pathway. This can be illustrated by the following reactions.



$NaOH_{(s)} + H_2O \longrightarrow NaOH_{(aq)}$ ΔH_1

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O$ ΔH_2

$NaOH_{(s)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O$ ΔH_3

If similar quantities react then, according to Hess's Law

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

Procedure

ΔH_1 Find the temperature of 100cm^3 water in a vacuum flask,* add 2g of sodium hydroxide. Stir and note rise in temperature.

ΔH_2 Find temperature of 50cm^3 1M sodium hydroxide in a vacuum flask. Find temperature of 50cm^3 1M hydrochloric acid and add to the flask. Note the temperature rise.

ΔH_3 Find the temperature of 100cm^3 0.5M hydrochloric acid in a vacuum flask. Add 2g sodium hydroxide. Stir and note the rise in temperature.

Compare $\Delta H_1 + \Delta H_2$ with ΔH_3.

*The small vacuum flasks supplied by Woolworths are very suitable for this type of experiment. Reasonably small amounts of solution can be used and standard thermometers can be conveniently read over the temperature ranges expected.

COMPARISON OF ΔG AND ΔH

There are few reactions which can be carried out in schools, in which the difference between ΔG and ΔH is greater than the experiment errors. Some of the possibilities are Zn/Ag^+ (ii) Cu/Ag^+ and (iii)Al/H^+. In the latter case ΔG has to be calculated from E^0 values for $Al^{3+} + 3e \rightarrow Al$. In all those cases ΔH should be measured in a vacuum flask of known heat capacity.

Thermal Capacity of Flask

Note the temperature of 100 cm^3 of M HCl in the vacuum flask and 100 cm^3 of M NaOH in a measuring cylinder. Add the NaOH to the flask, stir and note the temperature. From the literature value of the heat of neutralisation, calculate the amount of heat required to raise the temperature of the flask and contents through 1°C

(i) ΔH $Zn + 2Ag^2 \rightarrow Zn^{2+} + 2Ag$.

Note the temperature of 200 cm^3 of 1M $AgNo_3$ in the vacuum flask. Add about 5g of granulated zinc, weighed accurately. Stir and note the highest temperature reached. From the temperature rise and the known thermal capacity of the flask, calculate the amount of heat given out in the reaction and hence ΔH for one mole of zinc.

ΔG. Using molar solutions of zinc nitrate and silver nitrate with zinc and copper foil set up a cell. A strip of filter paper folded several times and soaked in ammonium nitrate solution makes an adequate salt bridge for short term use. The e.m.f. of the cell should be measured with a potentionmeter (Why) but a high resistance voltmeter or pH meter with a millivolt scale will give results which are sufficiently accurate. Note the temperature of the solutions.

Calculate ΔG from the equation $\Delta G = -nFE$. ΔS can now be calculated from $\Delta G = \Delta H - T\Delta S$.

(ii) $Cu + 2Ag^{+} \longrightarrow Cu^{2} + 2Ag$.

Procedure as for (i) using 5g of copper powder, molar copper nitrate and copper foil instead of granulated zinc, zinc nitrate and zinc foil.

(iii) Note the temperature of 200ml of 6M.CL in the vacuum flask. Accurately weigh approximately 0.5g of aluminium foil and place in the flask. Loosely plug the thermos flask with cotton wool around the thermometer. Stir gently and note the highest temperature reached. There is usually a considerable delay before the reaction becomes vigorous. From the known thermal capacity of the flask and the rise in temperature calculate ΔH for 1 mole of aluminium. This should be greater than ΔG for the reaction calculated from the E^{o} value for $Al^{3+} + 3e \rightarrow Al$.

In this reaction $\Delta G = \Delta H - T\Delta S + P\Delta V$. ΔV can be calculated from the reacting weight of aluminium.

Decomposition Temperature of Sodium Bicarbonate.

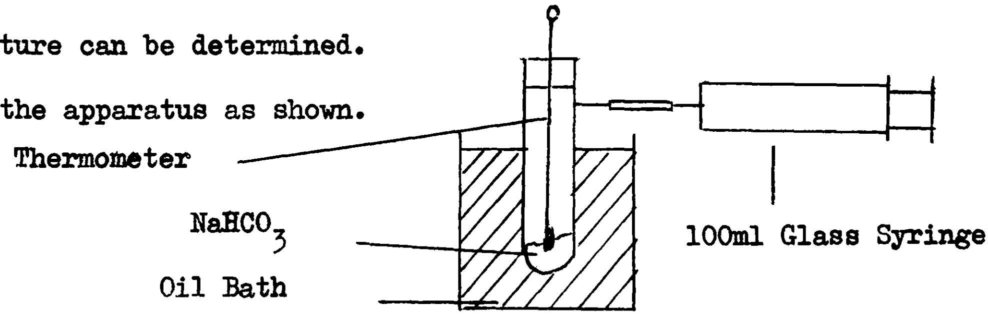
$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

In the relationship $\Delta G = \Delta H - T\Delta S$ at equilibrium $\Delta G = 0$

$$\therefore \quad \Delta H = T\Delta S \text{ and } T = \frac{\Delta H}{\Delta S}$$

If the heats of formation and standard entropies of reactants and products in a reaction can be found then the transition or decomposition temperature can be determined.

Set up the apparatus as shown.



Ensure that the piston can move freely and that there are no leaks. Place approximately 0.25g of sodium carbonate in the tube and that the syringe is fully closed. Heat the oil bath and plot gas volume in the syringe against temperature over the sodium bicarbonate. Decomposition temperature is the temperature at which the gas volume begins to increase rapidly. Compare experimental and calculated decomposition temperatures.

Transition temperature of sodium sulphate decahydrate

$$Na_2SO_4 + 10H_2O \rightleftharpoons Na_2SO_4.10H_2O$$

Half fill a boiling tube with sodium sulphate decahydrate crystals. Place a thermometer in the tube and heat in a water bath until all the crystals have dissolved (about 50°C). Remove the boiling tube, dry the outside, and place in an empty beaker or larger tube to protect from draughts. Allow to cool, noting the temperature every minute and stirring before each reading. When the temperature falls below 35°C it may be necessary to add small crystals of sodium sulphate at intervals to prevent the solution becoming super saturated. The temperature should stop falling when the heat being evolved balances the heat being lost in cooling. Plot temperature against time. What is the transition temperature in °K. Using the data book calculate the transition temperature in °K.

Is any of the data used in the calculation a possible source of disagreement between the calculated and experimental results?

Spontaneous endothermic reactions.

(a) $Ba(OH)_2.\ 8H_2O + 2NH_4SCN \longrightarrow Ba(SCN)_2 + 2NH_3 + 10H_2O$.

add 16g of $Ba(OH)_2.8H_2O$ to 8g of NH_4SCN in a dry flask, loosely stoppered with cotton wool. Wet the outside of the flask, with water, and leave on a wooden block. Ice will form on the outside of the flask and the flask will freeze to the wood indicating that the reaction is endothermic.

The reactants are crystalline and the products form an aqueous solution so the increase in entropy is great enough for ΔG to be negative in spite of a positive ΔH.

$$\Delta G = \Delta H - T\Delta S.$$

(b) $CoCl_2.6H_2O + 6SOCl_2 \longrightarrow CoCl_2 + 12HCl + 6SO_2$.

This experiment must be carried out in a fume cupboard. Goggles and rubber gloves must be worn when handling thionyl chloride.

Place about 1g of $CoCl_2.6H_2O$ in a test tube containing a -10/110°C thermometer. Add 3 to 5 cm^3 $SOCl_2$. There is a large evolution of gas and the temperature falls rapidly. The presence of SO_2 and HCl in the evolved gases can be established by passing them through test tubes containing potassium dichromate paper and silver nitrate solution or by holding the paper in the gas and by suspending a drop of silver nitrate solution on a rod in the gas.

Again this reaction proceeds because of the large increase in entropy due to the formation of gaseous products. The influence of the $T\Delta S$ factor in the equation can be further emphasised by immersing the test tube in a suitable freezing mixture. If the temperature is low enough the reaction will stop.

Similar reactions occure with $MnCl_2.4H_2O$, $FeCl_2.4H_2O$, $FeCl_3.6H_2O$ and $NiCl_2.6H_2O$.

Determination of the Equilibrium Constant for the Reaction $KI_3 \rightleftharpoons KI + I_2$

In solutions of iodine in potassium iodide part of the iodine has been converted into KI_3.

The equilibrium constant for the reaction is expressed as

$$K_c = \frac{[KI] . [I]}{[KI_3]}$$

The conversion of reactants to products and vice versa is so rapid that no chemical method can be used to determine their concentration in the mixture. The concentration of the iodine in the aqueous solution can however be determined by physical means without disturbing the equilibrium. If aqueous KI solution is shaken with CCl_4 the iodine (I_2) is distributed between the aqueous and the CCl_4 layer according to the partition or distribution coefficient.

If this partition coefficient has already been established titration of portions of the aqueous and CCl_4 layers with sodium thiosulphate will establish the concentration of the reactants and products in the aqueous layer.

The experiment falls into two parts. (a) Determining the distribution coefficient of iodine between carbon tetrachloride and water, and (b) determining the equilibrium constant for the reaction $KI_3 \rightleftharpoons KI + I_2$. This involves either two laboratory sessions or working in partnership. A safety pipette must be used with carbon tetrachloride and the laboratory must be well ventilated.

(a) The Distribution of Iodine between Carbon Tetrachloride and Water.

A pipette is calibrated for use with carbon tetrachloride. A saturated solution of iodine in carbon tetrachloride is shaken with water, allowing sufficient time for equilibrium to be reached. Samples from each layer are withdrawn by means of a pipette, and run into a solution of potassium iodide; the iodine content of each layer is determined by titration with sodium thiosulphate using starch indicator.

Clean and dry a $2cm^3$ pipette. Calibrate it for use with carbon tetrachloride by filling to the mark with carbon tetrachloride, discharging the contents into a previously weighed stoppered weighing bottle and reweighing (the density of carbon tetrachloride at 20°C is $1.595g/cm^3$).

Shake $20cm^3$ of a saturated solution of iodine in carbon tetrachloride with $250cm^3$ distilled water in a $500cm^3$ stopped flask. After 20 minutes shaking allow 10 minutes for the layers to settle. Using a safety pipette withdraw $2cm^3$ of the carbon tetrachloride layer. Air pressure within the pipette has to be increased slightly while passing through the aqueous layer to prevent water entering the pipette. Discharge the pipette into a conical flask containing approximately $50cm^3$ of 10% potassium iodide solution. Determine the iodine constant by titration with 0.01 M sodium thiosulphate. The starch indicator is added when the solution in the flask turns a pale straw colour.

Withdraw 100cm^3 of the aqueous layer by pipette and determine its iodine content using 5cm^{3}of 10% potassium iodide and titration with 0.01M sodium thiosulphate.

Repeat the experiment a further two times by pouring out from the bottle as much of the aqueous layer as can be done without losing any of the carbon tetrachloride layer, adding a fresh 250cm^3 of distilled water and shaking as before.

Calculate the distribution coefficient D for each of three sets of data.

$$D = \frac{\text{litre of carbon tetrachloride solution} \times 100}{\text{litre of aqueous solution} \times V}$$

(v = volume of 2cm^3 pipette obtained by calibration).

(b) Equilibrium Constant for the Reaction $KI_3 \rightleftharpoons KI + I_2$

The equilibrium constant for the reaction is determined by shaking a saturated solution of iodine in carbon tetrachloride with 0.1M potassium iodide, and the iodine content determined by titration with sodium thiosulphate. The experiment is repeated with 0.05 M and 0.02 M potassium iodide.

Make up 500cm^3 of 0.1 M potassium iodide solution accurately from solid potassium iodide. Shake 20cm^3 of saturated iodine in carbon tetrachloride with 100cm^3 of 0.1 M potassium iodide for 20 minutes and allow the layers to settle for 10 minutes. Using calibrated pipette withdraw 2cm^3 of the carbon tetrachloride layer (actual volume will be Vcm^3), and discharge into a conical flask containing 5cm^3 10% potassium iodide solution. Withdraw 25cm^3 of the aqueous layer and discharge into a conical flask containing 5cm^3 10% potassium iodide solution. Titrate both with 0.01M sodium thiosulphate solution. Repeat the experiment with 0.05 M and 0.02 M potassium iodide solution.

Since KI and KI_3 are insoluble in carbon tetrachloride, all the iodine in the carbon tetrachloride layer is present as I_2 molecules. In the aqueous layer, the titratable iodine is present partly as free I_2 molecules and partly combined with KI to form KI_3.

Since I_2 molecules in the carbon tetrachloride are in direct equilibrium across the boundary with the free I_2 molecules in the aqueous layer, it follows that the concentration of free iodine in the aqueous layer equals the concentration of iodine in the carbon tetrachloride layer divided by the distribution coefficient D.

THUS

If $V cm^3$ extract from CCl_4 layer $\equiv$ $x cm^3$ 0.01 M sodium thiosulphate (i)

and 25 cm^3 extract from aqueous layer $\equiv$ $y cm^3$ 0.01M sodium thiosulphate (ii)

concentration of free I_2 in aqueous layer = $\frac{x\ 0.01}{2\ VD}$ moles. litre $^{-1}$

$$\text{i.e.} \left[I_2\right] = \frac{x\ 0.01}{2VD} \quad \text{moles.litre}^{-1}$$

and from (ii)

$$\left[I_2\right] + \left[KI_3\right] = \frac{y\ 0.01}{50} \text{ moles. litre}^{-1}$$

$$\therefore \left[KI_3\right] = \frac{y\ 0.01}{50} - \frac{x\ 0.01}{2\ VD}$$

In the reaction $KI_3 \rightleftharpoons KI + I_2$

For every molecule of KI_3 formed one molecule of KI is used up.

Let c = original concentration of KI in moles. litre $^{-1}$

$\therefore$ at equilibrium

$$\left[KI\right] = c - \left[KI_3\right]$$

$$\left[KI\right] = c - \left(\frac{y\ 0.01}{50} - \frac{x\ 0.01}{2\ V\ D}\right)$$

Values for $\left[I_2\right]\left[KI_3\right]$ and $\left[KI\right]$ can now be substituted in the equation $K = \frac{\left[KI\right]\left[I_2\right]}{\left[KI_3\right]}$ thus giving three values for the equilibrium constant starting with 0.1 0.05 M and 0.02 M potassium iodide.

Apparatus and Chemicals

Pipettes	2cm^3, 25cm^3
Measuring cylinders	25cm^3, 100cm^3, 250cm^3
Graduated Flasks	100cm^3, 250cm^3, 500cm^3
Burette	50cm^3
Conical Flasks	100cm^3, 250cm^3
Stoppered Weighing Bottle	
Glass/Plastic Stoppered Bottle	500cm^3

Soluble starch, potassium iodide, iodine, carbon tetrachloride, 0.01 M so~~l~~dium thiosulphate.

SCHOOL SCIENCE REVIEW, DECEMBER 1972

A Quantitative Study of the Equilibrium: $PbSO_4(s) + 2NaI(aq) \rightleftharpoons PbI_2(s) + Na_2SO_4(aq)$.

J.W. Turner, Caerleon College of Education, Newport, Monmouthshire.

When sodium iodide solution is mixed with solid lead sulphate, a bright yellow precipitate of lead iodide is thrown down and sodium sulphate is formed in solution. When both solids are allowed to settle and the clear solution tested, both iodide and sulphate ions are found to be present, indicating that the equilibrium:

$$PbSO_4(s) + 2NaI(aq) \rightleftharpoons PbI_2(s) + Na_2SO_4(aq)$$

had been established. Exactly the same equilibrium is produced when solid lead iodide and sodium sulphate solution are mixed.

The reversibility of the reaction is easily demonstrated quantitatively. Addition of excess sodium iodide solution to a mixture of both solids results in the lead sulphate being almost totally converted to lead iodide, whilst addition of a large excess of sodium sulphate results in the consumption of the yellow lead iodide to give lead sulphate. The equilibrium may also be studied quantitatively and used to illustrate the following principles:

(a) The equilibrium law holds reasonably well over a range of concentrations.

(b) In heterogeneous equilibria such as this, the concentrations of the solids in the aqueous phase are effectively constant.

(c) The same equilibrium position may be established starting either from reactants or products.

PROCEDURE.

Standard solutions of sodium iodide and sodium sulphate are prepared and reaction mixtures of $NaI(aq) + PbSO_4(s)$ and $Na_2SO_4(Aq) + PbI_2(s)$ are made up in labelled 250cm^3 conical flasks. The flasks are stoppered with rubber bungs and well shaken. Attainment of equilibrium is facilitated by continuous stirring for an hour or so using a magnetic stirrer.

The equilibrium concentration of iodide ions is then determined in the following manner. After stirring, the solids are allowed to settle out and $25cm^3$ aliquots of the clear solution removed and titrated with standard silver nitrate using fluorescein as indicator. As both solids are left behind on removal of aliquot, the equilibrium is effectively 'frozen' and no change in the concentration of I^- and SO_4^{2-} can occur as a result of disturbance of the equilibrium by the analysis.

RESULTS.

1. Experiments starting from Nal(aq) + $PbSO_4$(s) mixtures .

(a) Initial concentration of Nal 0.099 M

Experiments showed that the equilibrium constant defined as:

$$K_c = [SO_4^{2-}]eqm / [I^{-\,2}]eqm$$

at a given temperature was independent of the volume of Nal solution mixed with a fixed weight of lead sulphate (Table I) and of the weight lead sulphate used with a fixed volume of Nal solution (Table II). The equilibrium constant was found to decrease with increasing temperature. In the table below errors quoted for average titre values represent the maximum variations in the end point readings from sample to sample, not errors in the titration technique itself.

TABLE I

Mixture of 0.099M Nal + 10g of $PbSO_4$ at 20°C

Sample	Vol. of Nal used/cm^3	Volume of 0.05_3M Ag^+ reqd. for $25cm^3$ sample	Value of K_c
1	50	31.10	4.75
2	100	31.05 ± 0.1	4.77 ± 0.06
3	150	31.10	4.75
4	200	31.20 ± 0.2	4.31 ± 0.1

TABLE II

Mixtures of 200cm^3 0.099M NaI + $PbSO_4(s)$ at 31°C

Sample	Wt. of $PbSO_4$ used/g	Volume of 0.05M Ag^+ reqd. for 25cm^3 sample	Value of K_c
1	5	36.45 ± 0.2	2.42 ± 0.1
2	10	36.40 ± 0.2	2.47 ± 0.1
3	15	36.40	2.47
4	25	26.20 ± 0.3	2.54 ± 0.15

(b) Values of K_c at different starting concentrations of NaI.

These are tabulated in TABLE III.

TABLE III

Mixture of 200cm^3 of NaI Solution 10g $PbSO_4$ at 31°C

Starting conc. of NaI soln.	Strength of Ag^+ used in titration	Average titre/cm^3	Value of K_c
0.1976M	0.1M	29.3 ± 0.5	2.92 ± 0.2
0.099M	0.05M	36.20 ± 0.4	2.54 ± 0.2
0.0496M	0.05M	21.15 ± 0.1	2.04 ± 0.1

2. Experiments starting from Na_2SO_4 (aq) + $PbI_2(s)$ mixtures. These are shown in TABLE IV.

TABLE IV

Mixtures of 200cm^3 Na_2SO_4 solution + 10g PbI_2 (s) at 20°C

Starting concn. of Na_2SO_4	Strength of Ag^+ used in titration	Average titre/cm^3	Value of K_c
0.05M	0.1M	15.65 ± 0.1	4.77 ± 0.1
0.1M	0.2M	12.50 ± 0.2	5.00 ± 0.3

DISCUSSION

The results show that the value of K_c is constant to a first approximation over the range of concentration studied, although there appears to be a real decrease at lower ionic concentrations. A variance was also reported in an earlier study of this system (1). An order of magnitude estimate of the limiting value of K_c can be obtained from a knowledge of the solubility products of lead sulphate and lead iodide. It can easily be shown that K_c as defined above is also equal to the ratio of the solubility product of lead sulphate to that of lead iodide, i.e.

$$K_c = (SO_4^{2-})_{eqm}/(I^-)^2_{eqm} = S_{PbSO_4}/S_{PbI_2}$$

Values for these (2) in the temperature range of the experiments were taken as

$$S_{PbSO_4} = 1.3 \times 10^{-8}$$

$$S_{PbI_2} = 8.3 \times 10^{-9}$$

thus giving a value for K_c of 1.6, which is in approximate agreement with experimental values.

REFERENCES.

1. Glasstone, S., A Textbook of Physical Chemistry, 2nd edition (Macmillan, 1962) P.852.
2. Tuffnall, R., and D.J. Luke, Nature of Physical Chemistry (Arnold, 1969), p. 193.

Determination of the Stoichiometry of the Thiosulphate Iodine Reaction - Iodine Coulometer.

Sodium thiosulphate reacts with iodine to produce sodium iodide and sodium tetrathionate.

$$2Na_2S_2O_3 + I_2 \longrightarrow 2\ NaI + Na_2S_4O_6$$

Ionic equations.

$$2\ S_2O_2{}^{2-} \longrightarrow S_4O_6{}^{2-} + 2e$$

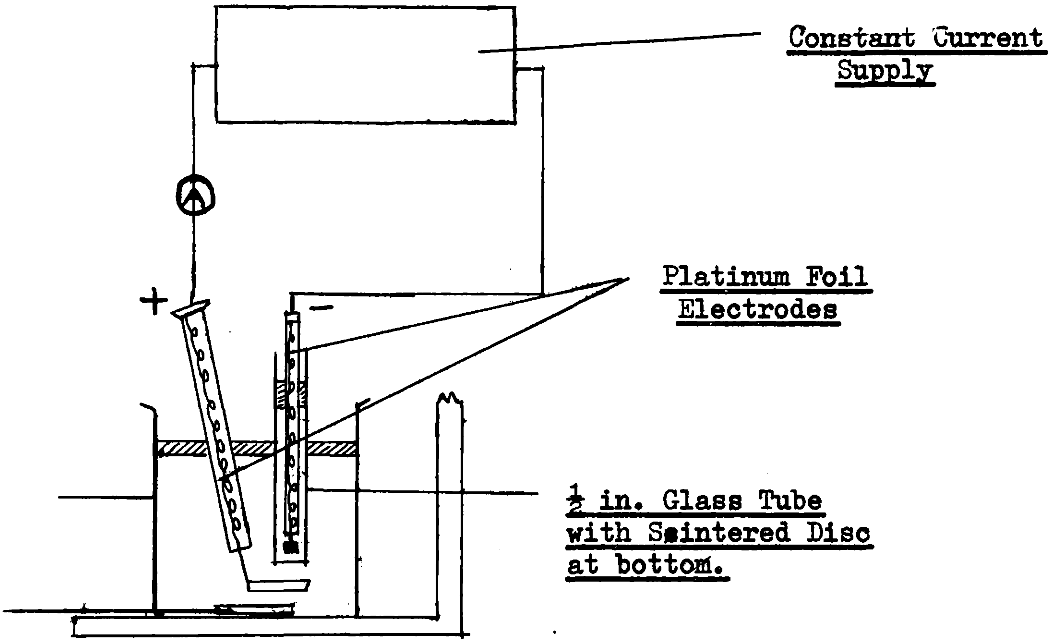
$$I_2 + 2e \longrightarrow 2I^-$$

The iodine can be produced by electrolysis of potassium iodide. The iodine produced will react with the sodium thiosulphate as long as there is thiosulphate present. The presence of free iodine is then detected with starch solution. If the current and the time for which it flows is noted, the number of electrons used in the reaction can be calculated.

If we assume the relationship $\frac{1}{2}I_2 + e \longrightarrow I^-$ the number of moles of electrons which react with one mole of sodium thiosulphate can be calculated.

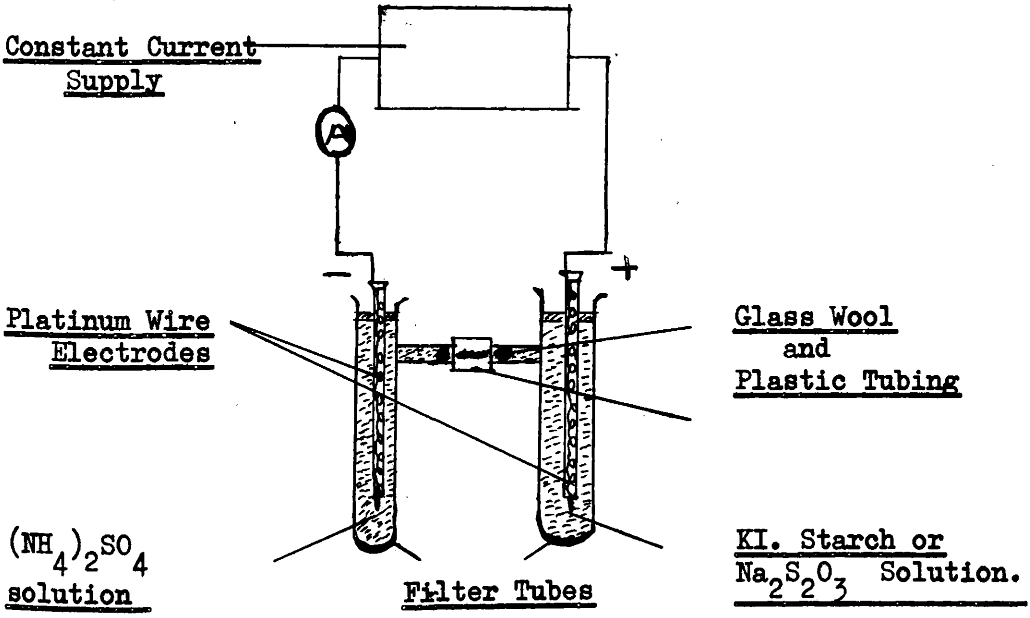
The experiment can be carried out using several different sets of apparatus. The most convenient is probably the Griffin & George Coulometric Titration Cell (S76-126). The electrodes supplied require mercury for making contacts. This can be avoided by using electrodes with 4mm plug connections. The apparatus in diagram B produces fairly satisfactory results. Finlay's Transport Number Apparatus can also be used. The experimental instructions refer to the apparatus in diagram A.

Diagram A.



Magnetic Stirrer and Stand

Diagram B.



Filter Tubes

Place approximately 0.1M $(NH_4)_2SO_4$ solution in the central compartment and approximately 0.1M KI solution in the beaker until the electrodes are well covered. Add $1cm^3$ of approximately 0.01M standard $Na_2S_2O_3$ solution to the KI solution together with one or two drops of freshly prepared starch solution. Make the electrode in the beaker the anode. Start the magnetic stirrer and set the constant current unit to 10mA. Switch on the stop clock and current simultaneously. When the whole solution just achieves a permanent blue colour stop the current and the clock.

1. How many coulombs of electricity have passed through the cell?
2. If 96,500C are carried by one mole of electrons, calculate the number of moles of electrons passing through the cell.
3. How many moles of electrons have been removed at the anode, converting iodide ions into iodine?
4. During the titration, these electrons are replaced by the sodium thiosulphate solution. How many moles of sodium thiosulphate were needed?
5. How many moles of electrons can be supplied by one mole of thiosulphate ions in this type of reaction?

<u>Sample set of results</u>

Current = 10mA.

Time till development of blue colour = 98 seconds.

$1cm^3$ of exactly 0.01 M $Na_2S_2O_3$ solution used.

1. Number of coulombs added $= \frac{10}{1000} \times 98$ C

$$= 9.8 \times 10^{-1} \text{ C}$$

2. Number of moles of electrons passed through cell

$$= \frac{9.8 \times 10^{-1}}{96{,}500} \text{ moles}$$

$$= 1{,}015 \times 10^{-5} \text{ moles.}$$

3. Number of moles of electrons removed at anode = 1.015×10^{-5} moles.
4. Moles of thiosulphate required $\equiv 1cm^3$ of 0.01 M $Na_2S_2O_3$

$$= 1.0 \times 10^{-5} \text{ moles.}$$

5. Within experimental error of measuring out correctly 1cm^3 of 0.01M $Na_2S_2O_3$ solution, one mole of thiosulphate will supply one mole of electrons.

Note. Assuming the charge on the electron to be 1.6×10^{-19}C, Avagadro's number can be calculated from the above results.

Determination of the Stoichiometry of the Permanganate-Iodide Reaction.

In an acid solution potassium permanganate will react with potassium iodide to form iodine. The amount of iodine produced can be found by titrating it with standard ~~soldium~~ sodium thiosulphate. The number of moles of thiosulphate which are equivalent to one mole of permanganate ion can then be calculated.

Procedure.

Weigh out accurately about 0.1g of potassium permanganate and dissolve it in 20cm^3 M H_2SO_4 in a conical flask. Add 10% W/V KI till no more iodine forms, then titrate with 0.1 M $Na_2S_2O_3$ solution using starch solution as an indicator when near the end point.

1. How many moles of potassium permanganate did you weigh out?
2. How many moles of thiosulphate are equivalent to one mole of permanganate?
3. How many electrons combine with each permanganate ion in this reaction?

ESTIMATION OF Cl^- AS AgCl

Chloride can be analysed by conversion to an equivalent amount of silver chloride, which is very insoluble and readily collected by filtration.

$$Cl^-_{(aq)} = AgNO_{3(aq)} \longrightarrow AgCl_{(s)} + NO_3^-{}_{(aq)}$$

Silver Chloride is photosensitive, so strong light should be avoided where possible. Distilled or deionised water should be used in this experiment.

Weigh accurately a sample of pure dry metal chloride into a 500cm^3 beaker. (W_2). The weight of the sample should be about 0.5g for the chlorides of 'light' elements and about 1g for the chlorides of 'heavy' elements. Dissolve the chloride in about 20cm^3 of deionised water, warming if necessary. Dilute to about 100cm^3 with deionised water. Any solution adhering to the stirring rod should be rinsed into the beaker if it is necessary to remove the stirring rod. Acidify the solution with about 1cm^3 of concentrated nitric acid. Add about 25cm^3 of 0.5M silver nitrate solution SLOWLY WITH STIRRING. There should be an excess of silver nitrate and the silver chloride formed should coagulate. Allow the precipitate to settle and add another 1 drop of silver nitrate solution. If no further precipitate forms the silver nitrate solution is in excess. If further precipitate forms, silver nitrate solution should be added until it is in excess.

Weigh a sintered-glass crucible (W_2) and place it on a Buchner filter flask. Transfer the precipitate carefully to the crucible and wash with several portions of dilute nitric acid (approximately 0.01 M). Continue washing with nitric acid until the filtrate remains clear when added to 2 M hydrochloric acid. Wash with two portions of methanol to remove acid and facilitate drying.

Place the crucible in a suitable container and cover with a clock glass. Dry to constant weight in an oven at about 120°C. The drying takes a considerable time and might best be done overnight. Allow the crucible and contents to cool to room temperature and weigh accurately. (W_3)

The formula weight of the metal chloride or the weight of chlorine in the metal chloride can then be calculated.

$$\frac{\text{Formula wt. of metal chloride}}{\text{Formula wt. of silver chloride}} = \frac{\text{wt. of metal chloride}}{\text{wt. of silver chloride.}}$$

$$= \frac{W_1}{W_3 - W_2}$$

$$\therefore \text{Formula wt. of metal chloride} = \frac{W_1}{W_3 - W_2} \text{ X Formula wt. of silver chloride.}$$

or
$$\frac{\text{Wt. of Chlorine in silver chloride}}{\text{Wt. of silver chloride}} = \frac{\text{At. wt. of chlorine}}{\text{Formula wt. of silver chloride}}$$

$$\therefore \text{Wt. of chlorine in silver chloride} = \frac{35.5}{143.3} \text{ X } (W_3 - W_2)$$

but Wt. of chlorine in silver chloride = Wt. of chlorine in metal chloride.

$$\therefore \text{Wt. of chlorine in metal chloride} = \frac{35.5}{143.3} \text{ X } (W_3 - W_2)$$

Determination of Water in $BaCl_2.2H_2O$

Barium chloride dihydrate loses its water of crystallisation above 100^oC and the anhydrous salt is stable up to 850^oC. The weight of water of crystallisation can therefore be readily determined without excessive heating.

Heat a clean crucible and lid to dull red heat for a few minutes, allow to cool in a desiccator, and ~~wiegh~~ weigh at room temperature. Put about 1.5g of barium chloride dihydrate in the crucible and reweigh the crucible and lid. Transfer to a pipe clay triangle and heat gently with a small non-luminous flame for a few minutes. Gradually increase the height of the flame to about 6 cm. Tilt the crucible lid to give a small opening. Heat for about 20 minutes. Transfer to a desiccator to cool and weigh at room temperature. Repeat the heating process until a constant weight is obtained.

Calculate the percentage weight of water of crystallisation in barium chloride dihydrate and compare with the theoretical value.

(Further details from Practical Inorganic Chemistry - B.E. Dawson, Methuen.)

Grignard preparation of Benzoic Acid

Since diethyl ether is used in this experiment all flames in the laboratory should be extinguished.

The initiation of the Grignard reaction may be inhibited by traces of water so all reactants and apparatus must be carefully dried. The apparatus can be oven-dried. The magnesium turnings can be dried by warming. The bromobenzene can be dried over magnesium sulphate and the ether can be dried over sodium wire.

Method: Put 0.1g dried magnesium turnings in a dry test-tube. Add about 7cm^3 dry ether then 0.4cm^3 dry bromobenzene. Place a loose plug of cotton wool in the mouth of the tube, and warm the tube gently in a warm water-bath until the reaction starts. It may be necessary to grind the magnesium turnings together with a glass rod to initiate the reaction. When the reaction starts it should proceed without further heating. When the reaction is complete, allow the mixture to stand for about 15 minutes and then pour it on to crushed solid carbon dioxide, about 1g in a 100cm^3 beaker. Allow the mixture to warm up to room temperature, carefully add 5cm^3 of 2M hydrochloric acid, transter the mixture to a small separating funnel, shake and separate the layers. Collect the ether layer and add 5cm^3 2M sodium carbonate solution to extract the benzoic acid from the ether layer. Acidify the sodium carbonate portion with the minimum amount of concentrated hydrochloric acid. Filter off the benzoic acid and recrystallise it from water. Filter the solution under suction. Press the crystals between filter papers to remove any residual water and finally spread the crystals on a watch-glass to dry at room temperature. Find the melting point (pure benzoic acid melts at 122°C).

Relative Ease of Hydrolysis of Alkyl Halides.

Dissolve 2cm^3 each of 1-iodo, 1 - bromo, 1 0 chlorobutane, in 2cm^3 ethanol in a test-tube. Add 2cm^3 of aqueous silver nitrate solution to each test-tube. Shake and observe the time taken for each precipitate to form.

Bromination of an Alkene in the presence of an Anion.

1. Alkenes can be brominated in the presence of the chloride ion by shaking the alkene with a saturated aqueous solution of bromine and sodium chloride. The saturated solution is prepared by adding bromine to a saturated solution of sodium chloride and shaking or stirring the solution till it has become saturated with bromine. The solution is then decanted from the undissolved reagents.

Add a few drops of the bromine/chloride solution to 5cm^3 hexene in a stoppered flask and shake till the colour of the bromine disappears. Make further additions of the bromine/ chloride solution with shaking until the bromine colour just persists. Transfer the mixture to a separating funnel containing 50cm^3 10% sodium thiosulphate solution. Rinse out the reaction vessel with 20cm^3 ether and add to the separating funnel. Shake well. Allow the layers to separate and run off the aqueous layer. Dry the ethereal solution over anhydrous magnesium sulphate.

The presence of more than one product in the ethereal solution can be illustrated conveniently using thin layer chromatography with the Kodak Eastman 'Chromagram' Kit or any precoated silica gel sheets.

Activate a silica gel 'Chromagram' sheet by placing in an oven at 100 - 120°C for 30 minutes. This can be done while the bromination is taking place. Draw a pencil line at least 1.5cm from the bottom of the sheet. Spot a little of the ethereal solution on the line taking care not to damage the surface of the layer. Spot some dibromohexane in ether solution on to the line about 15mm from the first spot. If no dibromohexane is available it can be quickly made by adding drops of bromine carefully to some hexene (Fume cupboard).

Using 60-80 petroleum ether as an eluent, allow the eluent to migrate to about 10mm from the top of the sheet. Remove the sheet, allow it to dry and stand in a covered beaker with a crystal of iodine. Brown stains develop indicating the components. The product from the bromine/ chloride solution yields 3 spots.

The furthermost spot matches that of the dibromohaxane. The next spot is chlorobromohexane and the spot almost on the base line is probably a bromohydrin.

This is not a direct proof of the mechanism of the reaction but is good circumstantial evidence.

Bromination of Heptane in Light.

The halogenation of an alkane at room temperature in the presence of light takes place by a free radical chain mechanism. The process takes place in three stages; initiation, propogation and termination. Some of the possible stages in the chlrination of methane could be:-

Initiation. The U.V. part of the spectrum excites the chlorine molecule causing it to undergo homolytic fission and produce free radicals.

$$Cl : Cl \longrightarrow \cdot Cl + \cdot Cl$$

Propogation. A chain reaction follows by free radical attack on the methane molecule with the production of more free radicals

$$\cdot Cl + CH_4 \longrightarrow \cdot CH_3 + HCl$$
$$\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + \cdot Cl$$
$$\cdot Cl + CH_3Cl \longrightarrow \cdot CH_2Cl + HCl$$
$$\cdot CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + \cdot Cl$$

These are only some of the possible steps.

Termination. This occurs by the combination of free radical pairs e.g.

$$\cdot Cl + \cdot Cl \longrightarrow Cl_2$$

The role of light in the bromination of heptane can be illustrated by setting up two identical sets of reactants and excluding light from one of them A U.V. source should be used but any strong light, e.g. a photoflood will do. Looking directly at a U.V. source can cause eye injury.

Take two thin walled pyrex test tubes (20cm x 3.8cm) and make one light tight by wrapping black adhesive tape around it. Place them in a test tube rack or clamp stands equidistant (about 5cm) from the U.V. lamp. Add $25cm^3$ of heptane to each, followed by $5cm^3$ of a 1% W.V. solution of bromine in tetrachloremethane. ($1cm^3$ bromine in $200cm^3$ tetrachloromethane) Stopper both test tubes and switch on the lamp. After a short time the solution in the unwrapped tube will be decolorised. Switch off the lamp and empty the contents of the light tight tube into a clean test tube. The bromine colour will still be evident. The presence of hydrogen bromide in the unwrapped tube can be indicated by holding moist blue litmus paper in the mouth of the tube and by holding a glass rod moistened with concentrated ammonia solution at the mouth of the tube.

Preparation of Tin (IV) Iodide

Tin (IV) iodide can be prepared by the direct combination of tin with iodine in an organic solvent.

$$Sn + 2I_2 \longrightarrow SnI_4$$

This experiment must be carried out in a fume cupboard.

Dissolve 2.5g of iodine in $50cm^3$ of benzene in a $100cm^3$ beaker. Add 0.5g of powdered tin. Place in a container of warm water and stir gently for 5 minutes. Allow the benzene to evaporate in the fume cupboard and leave overnight. The excess iodine will have sublimed leaving tin (IV) iodide. Examine the crystals with a hand lens and find their melting point. If necessary the product can be recrystallised from tetrachloromethane. A fume cupboard must also be used at this stage.

Preparation of Lead (II) Chloride

Lead (II) chloride can be prepared by adding dilute hydrochloric acid to a solution of lead nitrate.

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + \overset{2HNO_3}{\cancel{2HCO}_3}$$

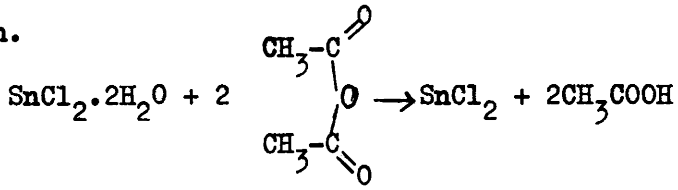
Dissolve about 5g of lead nitrate crystals in 50cm^3 water. Add bench hydrochloric acid to the solution until no more lead chloride precipitates. Collect the precipitate by filtering through a Buchner funnel. Dissolve the precipitate in hot water. Allow to cool and white needles of lead chloride appear. Collect crystals in a Buchner funnel and dry in a desiccator.

Preparation of Tin (II) Chloride

Tin (II) chloride dihydrate is prepared by dissolving tin in concentrated hydrochloric acid.

$$Sn + 2HCl \xrightarrow{H_2O} SnCl_2.2H_2O + H_2$$

The dihydrate is recovered and added to acetic anhydride. The water molecules are removed and the anhydrous tin (II) chloride is recovered by filtration.



Dissolve 5g of tin foil in approximately 20cm^3 of concentrated hydrochloric acid. The mixture has to be warmed to complete the reaction. Transfer the solution to an evaporating basin and reduce to about one fifth its original volume by heating gently. Allow to cool. If no crystallisation occurs, reduce the volume till crystallisation does occur on cooling. Filter off the crystals and dry in a desiccator. Find the melting point. (37°C).

Add the dihydrate to about 5cm^3 of acetic anhydride in a beaker. This should be carried out in the fume cupboard. Stir and collect the product on a Buchner funnel. Wash with a little ether and dry on the filter paper. Find the melting point. (247°C).

SOLUTION CHEMISTRY

1. **The pH of Hydrochloric Acid, Ethanoic Acid and Sodium Hydroxide at successive tenfold dilutions.**

Measure the pH of 70cm^3 of 0.1M hydrochloric acid in a 100cm^3 beaker. Use pH paper or a meter with a combined electrode. Using a measuring cylinder dilute 10cm^3 of the 0.1M solution to 100cm^3 with deionised water to give 0.01M hydrochloric acid. Measure the pH and dilute further to give 0.001M hydrochloric acid.

Repeat the series of measurements with successive dilutions of ethanoic acid and sodium hydroxide.

Compare the pH values obtained.

2. **The Dissociation Constants of Weak Acids.**

(a) Prepare 0.1M solutions of ethanoic acid, propanoic acid and monochloroethanoic acid.

Measure the pH of each solution. Using the equation $K_a = \frac{[H^+]^2}{c}$ or $pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$, calculate the dissociation constant for each acid. (c = initial concentration of acid).

(b) **The Dissociation Constant for Ethanoic Acid.**

(i) As in (a) find the dissociation constant for 0.1M and 0.01M ethanoic acid,

(ii) To 10cm^3 of 0.2M sodium acetate add 10cm^3 of 0.2M hydrochloric acid. Find the pH and calculate the dissociation constant for ethanoic acid using $pH = \frac{1}{2}pK - \frac{1}{2}\log NaAc$

This assumes that the ethanoic acid formed will be only slightly dissociated and hence $[HAc]$ will approximate to $[NaAc]$ or $[HCl]$.

Repeat using 0.02M solutions.

3. **Salt hydrolysis. NaCl, NH_4Cl, CH_3COONa, CH_3COONH_4.**

Measure the pH of the molar solutions provided. From the data book find the dissociation constant of any substance you think has been formed in the aqueous solution.

4. Titrations followed by pH Measurement.

Pipette 25cm^3 of 0.1M HCl into a 100cm^3 beaker. Add 25cm^3 of water. Stir and measure the pH. Add 30cm^3 of 0.1M NaOH from a burette in 2cm^3 portions. Stir and measure the pH after each addition. Plot pH against cm^3 of NaOH added.

Repeat the experiment titrating 0.1M CH_3COOH with 0.1M NaOH
0.1M HCl with 0.1M NH_4OH
0.1M CH_3COOH with 0.1M NH_4OH

Measuring Ka for Indicators and Weak Acids.

For an indicator, HIn

$$pH = -\log Ka - \log\frac{[HIn]}{[In^-]} \qquad (a)$$

Ka for the indicator can be calculated if the ratio $\frac{[HI]}{[In^-]}$ is found and the pH of the solution is known.

A solution of known pH can be made using a buffer solution. A buffer solution consists of a mixture of equal volumes of equimolar solutions of a weak acid and a salt of the weak acid.

For a weak acid HA

$$pH = -\log Ka - \log\frac{[HA]}{[A^-]} \qquad (b)$$

In a buffer solution $[HA] = [A^-]$

$$\therefore \quad pH = -\log Ka \qquad (c)$$

The ratio $\frac{[HIn]}{[In^-]}$ can be obtained by preparing test tubes containing solutions of known $[HIn]$ and $[In^-]$. When the tubes containing known amounts of In^- are viewed through tubes containing known amounts of HIn a series of $\frac{[HIn]}{[In^-]}$ ratios are obtained.

Visual comparison with these tubes can establish the $\frac{[HIn]}{[In^-]}$ ratio for the solution being investigated.

Ka for Bromophenol Blue

HIn Solution. Add one drop of concentrated hydrochloric acid to $5cm^3$ of bromophenol blue solution.

In^- Solution. Add one drop of 4M sodium hydroxide solution in $5cm^3$ of bromophenol blue solution.

Arrange 18 test tubes in nine pairs one behind the other in test tube racks so that, when looking through a pair of tubes the colour seen will be due to the solutions in both tubes.

Put $10cm^3$ distilled water into each of the test tubes and drops of HIn solution and In^- solution as follows:-

Tube	1	2	3	4	5	6	7	8	9
Drops of HIn solution	1	2	3	4	5	6	7	8	9
Tube	10	11	12	13	14	15	16	17	18
Drops of In^- solution	9	8	7	6	5	4	3	2	1
$\frac{HIn}{In^{-1}}$	$\frac{1}{9}$	$\frac{1}{4}$	$\frac{3}{7}$	$\frac{2}{3}$	$\frac{1}{1}$	$\frac{3}{2}$	$\frac{7}{3}$	$\frac{4}{1}$	$\frac{9}{1}$

Add $5cm^3$ 0.02M methanoic acid to $5cm^3$ 0.02M sodium methanoate in a test tube of the same size as those in the rack. Calculate the pH of this solution using equation (c). (Ka for methanoic acid is 2×10^{-4} mol dm^{-3}).

Add 10 drops of bromophenol blue solution to the test tube and shake to mix the contents. Compare the colour of the mixture with the colours seen by looking through the pairs of test tubes in the rack.

Which pair of tubes matches most closely the colour in the methanoic acid/sodium methanoate mixture?.

What is the ratio $\frac{[HIn]}{[In^-]}$ in the methanoic acid/sodium methanoate mixture?

Calculate Ka for bromophenol blue using equation (a), the ratic $\frac{[HI]}{[In^-]}$ you have found and the calculated pH of the methanoic acid/sodium methanoate solution.

(Ka for bromophenol blue can be calculated at different pH values by using similar quantities of other buffer solutions in place of the methanoic acid/sodium methanoate solution.)

Ka for Benzoic Acid

Mix 5cm^3 0.02M benzoic acid and 5cm^3 0.02M sodium benzoate in a test tube, add 10 drops bromophenol blue solution. Compare the colour of the mixture with that seen through the pairs of test tubes in the rack. Using equation (a), Ka for bromophenol blue and the ratio $\frac{[HIn]}{[In^-]}$ you have found with the benzoic acide/benzoate mixture, find the pH of the benzoic acid/sodium benzoate mixture.

Using equation (c) calculate Ka for benzoic acid.

Note. The tubes are best observed against a strongly illuminated white background.

Oxidation States of Vanadium

Vanadium can appear in four oxidation states and a particular colour is associated with each ion in aqueous solution.

V^{+5}	Yellow
V^{+4}	Blue
V^{+3}	Green
V^{+2}	Violet

These oxidation states can be obtained and the colours observed by taking a solution of ammonium metavanadate and reducing it.

Dissolve 1.5g of ammonium metavanadate in 20cm^3 2M sodium hydroxide solution. Add 40cm^3 of M sulphuric acid and dilute to 250cm^3 with distilled water. To 30cm^3 of this solution in a 150cm^3 conical flask add 2g zinc dust. Add dilute sulphuric acid (approximately 4M) dropwise with constant stirring. The solution is yellow at first due to V^{+5} ions. As some of these are reduced to V^{+4} ions the solution will turn green due to the combination of yellow and blue. As the concentration of the V^{+4} ions increases the solution will become blue. As the V^{+4} ions are reduced to V^{+3} the solution becomes green and then violet as V^{+2} ions are produced.

The process can be reversed by progressively oxidising the V^{+2} ions by the slow addition of dilute nitric acid. Stirring of the solution would be most conveniently done by a magnetic stirrer.

Reactions of Sn^{2+} with MnO_4^- and Fe^{3+}

Prepare an approx. 0.1M solution of $SnCl_2 \cdot 2H_2O$ in 2M HCl. If the $SnCl_2 \cdot 2H_2O$ is not fresh stock it may be difficult to prepare a clear solution, but the reactions will still take place even if the solution is cloudy. The solution can of course be prepared by adding a measured amount of granulated tin to concentrated hydrochloric acid and diluting to the appropriate concentration once the tin has dissolved.

Add a few drops of the Sn^{2+} solution to some very dilute potassium permanganate solution (approx. 0.001M) in a test tube. The permanganate ~~soltuion~~ solution will be rapidly decolourised.

$$5Sn^{2+} + 2\,MnO_4^- + 16H^+ \longrightarrow 5\,Sn^{4+} + 2\,Mn^{2+} + 8H_2O.$$

Prepare solutions of Fe^{3+} and Fe^{2+} ions in water. The Fe^{3+} solution can be prepared by dissolving a few crystals of iron (III) ammonium sulphate in a test tube of water. The Fe^{2+} solution can be prepared by putting some crystals of iron (II) sulphate in a test tube and rinsing the crystals twice with a little water to remove any Fe^{3+} ions. The crystals can then be dissolved in water.

Add a few drops of ammonium thiocyanate solution to test tubes containing Fe^{3+} and Fe^{2+} solutions respectively. The Fe^{2+} solution should remain colourless but may be slightly coloured due to traces of Fe^{3+}. The Fe^{3+} solution gives a deep red colour. Add a few drops of Sn^{2+} solution to both tubes and the colour disappears as Fe^{3+} ions are reduced to Fe^{2+} ions.

$$Sn^{2+} + 2\,Fe^{3+} \longrightarrow Sn^{4+} + 2\,Fe^{2+}$$

Add a few drops of potassium hexacyanoferrate (III) solution to test tubes containing Fe^{3+} and Fe^{2+} solutions respectively. The Fe^{3+} solution remains colourless. (There may be a slight brown colour) and the Fe^{2+} solution turns deep blue. On adding a few drops of the Sn^{2+} solution the Fe^{3+} solution also turns a deep blue colour as the Fe^{3+} ions are reduced to Fe^{2+}.

Oxidation States of Manganese

Manganese exhibits several oxidation numbers. The most familiar are:-

Mn^{2+}	Simple salts	Pink
Mn^{3+}	Stable only in complexes and insoluble compounds.	
Mn^{4+}	Oxide	
Mn^{6+}	Disproportionates to Mn^{7+} and Mn^{4+} except under strongly alkaline conditions.	Green
Mn^{7+}	Permanganate ion	Purple

The different oxidation states are not so easily obtained as those of vanadium. Some of the conditions are extreme involving highly concentrated strongly alkaline solutions. The use of gloves and safety spectacles is advised.

Conversion of Mn^{2+} to Mn^{4+}

$$MnSO_4 \xrightarrow{NaOH} Mn(OH)_2 \xrightarrow{H2O2} MnO_2 + O_2$$

Dissolve a few crystals of any Mn^{2+} salt in about 25cm^3 water. Add a small excess of 2M sodium hydroxide solution and 2M (20 volume) hydrogen peroxide. A black precipitate of manganese (IV) oxide appears and oxygen is evolved. If required, the oxide can be recovered by filtration (funnel and paper), washing with ethanol and drying in an oven at about 120°C.

Conversion of Mn^{7+} to Mn^{6+}

$$MnO_4^- + e \longrightarrow MnO_4^{2-}$$

Put 2-3cm^3 0.01M potassium permanganate solution in a boiling tube and add 15-20 potassium hydroxide pellets. The solution slowly changes colour. The green colour of the MnO_4^{2-} ion may be more noticeable on diluting a small amount of the solution. The colour change can be hastened by warming the boiling tube in a beaker of hot water. The purple colour of the MnO_4^- ion can be recovered by carefully acidifying a portion of the strongly alkaline solution with dilute sulphuric acid.

In neutral or slightly acid solutions Mn^{6+} disproportionates to Mn^{7+} and Mn^{2+}.

$$3\ MnO_4^{2-} + 2H_2O \longrightarrow 2\ MnO_4^- + MnO_2 + 4OH^-$$

Manganese (IV) oxide is precipitated as the solution becomes purple.

<u>Preparation of Mn^{3+}</u>

Mn^{3+} is unstable but it can be stabilised by complexing. Dissolve 0.5g of hydrated manganese (II) sulphate in 2cm^3 dilute sulphuric acid. Carefully add 10 drops of concentrated sulphuric acid. Cool the tube and add 2cm^3 0.1M potassium permanganate solution. The solution becomes deep red due to the presence of Mn^{3+} ions.

$$Mn^{2+} + Mn^{7+} \xrightarrow{H^+} Mn^{3+}$$

If some 0.1M EDTA solution is added the solution is decolourised as the EDTA complexes with the Mn^{3+} ions.

A complex containing Mn^{3+} ions, viz. Tris (acetylacetanato) manganese (III) can be isolated. Mn^{2+} is oxidised to Mn^{3+} in the presence of a slighly alkaline solution of acetyl acetone by potassium permanganate. The Mn^{7+} in the potassium permanganate is itself reduced to Mn^{3+}. The reaction is carried out by first forming Bis (acetylacetanato) manganese (II) and then allowing it to react with potassium permanganate.

$$MnCl_2 + 2CH_3COCH_2\ COCH_3 + 2CH_3COONa.$$
$$\longrightarrow Mn(CH_3COCHCOCH_3)_2 + 2NaCl + 2CH_2COOH$$

$$4Mn(CH_2COCHCOCH_3)_2 + KMnO_4 + 7CH_3COCH_2COCH_3 + CH_3COOH$$
$$\longrightarrow 5Mn(CH_3COCHCOCH_3)_3 + CH_3COOK + 4H_2O$$

Dissolve 2.5g of manganese (II) chloride tetrahydrate in 100cm^3 water and add 6.6g of sodium ethanoate trihydrate. When this has dissolved add 10cm^3 of acetylacetone and mix thoroughly. Dissolve 0.5g of potassium permanganate in 25cm^3 water and add slowly to the solution with stirring. Dissolve 6.6g of sodium ethanoate trihydrate in 25cm^3 water and add to the solution. Heat the mixture in a boiling water bath for about 10 minutes, cool and leave in an ice bath. Filter off the crystals and allow them to dry. If a few of the crystals are added to water a brown precipitate is forms. $Mn^{3+} \longrightarrow Mn^{2+} + Mn^{4+}$

Preparation of Tutton Salts

The general formula of a Tutton salt is $M(H_2O)_6K_2(SO_4)_2$, i.e. Tutton salts contain the complex cation $M(H_2O)_6^{2+}$, where M = Mn. Fe, Co, Ni, Cu, Zn. Since the sizes of Mn^{2+}, Fe^{2+} etc. are very similar, there is little variation in the size of $M(H_2O)_6^{2+}$ and Tutton salts are therefore isomorphic.

Crystalline samples of Tutton salts can be prepared in the following way. Make up 150cm^3 of a 0.5M solution of potassium sulphate and 25cm^3 of 0.5M solution of each of the following:- manganese (II) sulphate, iron (II) sulphate, cobalt (II) sulphate, nickel (II) sulphate, copper (II) sulphate, zinc sulphate.

Put a 10cm^3 sample of each of these solutions in a labelled crystallising dish. To each solution add 10cm^3 0.5M K_2SO_4 solution and leave aside to crystallise. Compare the crystal shapes.

Solubilities and Formula weights:-

Salt	Solubility (g. per litre)	Formula weight
K_2SO_4	120	174.3
$MnSO_4 \cdot 4H_2O$	105.3	223.1
$FeSO_4 \cdot 7H_2O$	156.5	278.0
$CoSO_4 \cdot 7H_2O$	604	281.1
$Ni.So_4 \cdot 6H_2O$	620	263.0
$CuSo_4 \cdot 5H_2O$	316	249.7
$ZnSO_4 \cdot 7H_2O$	965	289.5

Preparation of $[Ni(NH_3)_6](BF_4)_2$, Hexammino-Nickel Fluoroborate.

Dissolve $NiCl_2 \cdot 6H_2O$ (~6g) in water (10cm^3). Add 0.880 ammonia (about 12cm^3) till the green precipitate of nickel hydroxide has dissolved and violet crystals have formed. This should be carried out in a fume cupboard. The crystals are hexammino - nickel chloride $[Ni(NH_3)_6]Cl_2$. Redissolve the crystals by the gradual addition of cold water (15-17cm^3) while stirring. Filter the solution and to the filtrate add a solution of ammonium fluoroboarate in dilute ammonia (5g NH_4BF_4 in 20cm^3).

The precipitated complex is difficult to see but can be filtered off immediately. Wash the product with dilute aqueous ammonia till the filtrate is colourless, then with acetone.

Dry in air at room temperature.

Note: After prolonged exposure the violet $[Ni.(NH_3)_6](BF_4)_2$ loses to molecules of ammonia to give green $[Ni.(NH_3)_4](BF_4)_2$, tetrammino-nickel fluoborate. Heating $[Ni(NH_3)_6](BF_4)_2$ gives a sublimate of NH_3BF_3 and a yellow infusible residue of NiF_2.

Analysis of $[Ni(NH_3)_6](BF_4)_2$, Hexammino-nickel fluoborate

Volumetric analysis can be used to determine the ammonia and the nickel content of this complex.

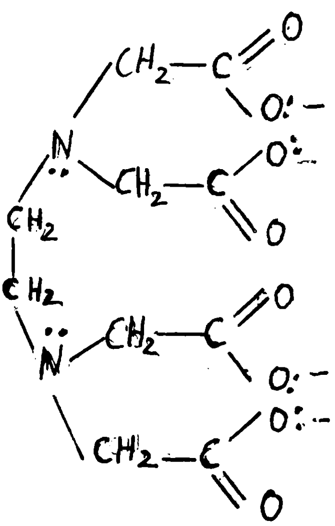
Determination of Ammonia.

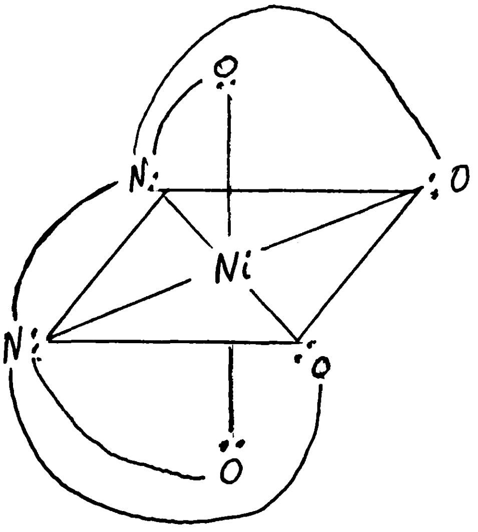
Weigh out accurately approximately 0.3g of the complex. Dissolve this in exactly $25cm^3$ M HCl. Titrate with M NaOH using methyl orange indicator. The ammonia in the complex is equivalent to the difference between the $25cm^3$ M HCl and the titre of M NaOH.

Since one mole of HCl $\equiv$ 17g NH_3 the weight of ammonia in the complex can be calculated.

Determination of Ni^{2+}

Ethylene diamine tetracetic acid (EDTA) has six atoms with lone pairs capable of linking with Ni^{2+}. The acid molecule forms an octahedral complex with Ni^{2+}





One mole of the acid $\equiv$ one mole of Ni^{2+}

Since the acid is not readily soluble in water E.D.T.A. is usually supplied as the sodium salt. This does not alter the stoichiometry.

Weigh out accurately approximately 0.6g of the fluoborate. Dissolve it in the minimum quantity of bench HCl. Dilute the solution to about 100cm^3 with distilled water. Add 10cm^3 of approximately M NH_4Cl and a small amount of murexide indicator. Add 0.88 NH_3 dropwise until the pH is 7. Titrate with 0.1M E.D.T.A. until about 10cm^3 have been added, then make the solution strongly alkaline by adding 10cm^3 0.88 NH_3. Continue titrating until the solution just turns blue-violet.

Note: Murexide indicator has a limited life as an aqueous solution and so it is used as a solid. Since very little is required it is diluted by mixing solid murexide with sodium chloride. About 0.1g of this solid mixture is then used.

CHAPTER 3.

OBJECTIVES OF PRACTICAL WORK AND THEIR ACHIEVEMENT.

OBJECTIVES OF PRACTICAL WORK AND THEIR ACHIEVEMENT.

In recent years there have been several published investigations into practical work in chemistry at secondary level. The most extensive study was that of J.F. Kerr.[~~15~~ 14] This was a report on an enquiry into the nature of practical work in school science teaching in England and Wales. The enquiry was limited to secondary schools following a grammar school type curriculum and the data was provided by teachers and former pupils. Seven hundred and one science teachers in one hundred and fifty-one schools were involved.

The results of an enquiry on practical work in sixth-form chemistry courses was published by J.G. Buckley and R.F. Kempa in 1971.[~~16~~ 15] The data were provided by two hundred and thirty-six teachers from seventy-four schools in the London area. The objectives of the enquiry were:

(i) to obtain information about the type of practical work currently undertaken in sixth-form chemistry courses, and the working conditions under which this is carried out;

(ii) to obtain teachers' views on the possible aims and objectives of practical work at sixth-form level and on the relationship between such objectives and the existing forms of examination;

(iii) to obtain teachers' views on alternative schemes for the assessment of practical abilities at sixth-form level.

The most recent enquiry is that of R.W. West [~~17~~ 16] into practical work in chemistry in years one to five (age range 11 - 16). The data were provided by thirty-one chemistry teachers in seventeen schools situated in urban areas in England. The questions were aimed at finding:-

A. The purpose of practical work in chemistry.

B. The kinds of practical work used in chemistry.

The findings were compared with those of R.F. Kerr[~~15~~ 14] to find what changes in the approach to practical work had been caused by the development of Nuffield courses.

The latter two investigations were running more or less concurrently with that being carried out by the author. Although there is obviously some common ground there is a difference of approach and because of other factors the findings are not directly comparable. R.W. West's enquiry[~~27~~/16] was concerned with up to fifth year (English 'O' Level). The author was concerned with Sixth Year Studies where the objectives could be considered to be somewhat different as the pupils had already enquiry[~~26~~/15] was concerned with sixth-form but in an English 'A' Level

enquiry[~~26~~/15] was concerned with sixth-form but in an English 'A' Level

situation where the pupils take a three hour practical examination as part of their assessment. J.F. Kerr [~~25~~/14] found that practical examinations greatly influenced the type of practical work carried out. This constraint does not apply to Sixth Year Studies where the course practical work is not assessed by a practical examination, and so the teacher has a wider choice of practical work. These factors have to be taken into account when any reference is made to the above investigations.

The author's investigation differed from previous investigations in that teachers were being asked what they thought the objectives of a particular experiment were before the pupils carried out the experiment. The pupils were asked what objectives had been achieved by the experiment after they had completed it. It was hoped that from this some of the functions of particular experiments and of a course of practical work might become clear. It was also hoped that any divergence between teachers and pupils views of the functions of practical work would be apparent.

Approximately one hundred pupils from ten schools were involved in the investigation (approximately 1200 pupils sat Sixth Year Studies Chemistry that year). Each pupil was asked to complete a questionnaire on each experiment, and a pupil could carry out in excess of forty experiments.

To have any hope of pupils completing questionnaires, the number of questions, and therefore the number of objectives examined, had to be kept down to a reasonable number. Similar constraint applied to the teachers' questionnaire.

There were no stated aims for course practical work in Sixth Year Studies Chemistry. In comparable English courses, i.e. Nuffield 'A' Level Chemistry ~~[18]~~ [17] and Nuffield 'A' Level Physical Science ~~[19]~~ [18] only very general statements are made on the objectives of course practical work (A3 - 1, A3 - 2).

An initial choice therefore had to be made as to what were the objectives of practical work. The objectives as tested by Kerr ~~[15]~~ [14] could have been taken or the opinions of a large number of teachers could have been taken. If the latter course had been adopted the opinions would have been collated and a short list of objectives drawn up. There would probably have been an element of subjectivity in producing the short list. There was probably a similar element of subjectivity in Kerr's list. The author therefore decided to make a personal list of objectives. The frequency of teachers responses on the individual objectives in questionnaires would indicate whether they agreed with the relative importance of the author's objectives, and the pupils' questionnaire would indicate how far these objectives were being achieved.

Some problems associated with this approach are:-

(a) Relevant objectives may have been missed. (On completing the questionnaire only one teacher out of twenty-one suggested another objective. This is taken up in chapter four):

(b) Teachers may not have considered an objective until they saw it in the questionnaire:

(c) Pupils learn the objectives after they have completed a few questionnaires and start to look for these objectives in the experiments.

It would be difficult to circumvent (b) and (c), and they have to be accepted as slightly widening the limits of experiment error.

The objectives decided upon are those listed in the teachers' questionnaire (A3 - 3). The pupils' questionnaire (A3-4, A3-5) included these objectives but attempted to obtain other information e.g.,

Whether the experiment was achieving the objective the pupils expected it to do.

A credibility level for numerical results.

Were the pupils 'lost' during long experiments?

Did the experiments aid the pupils' understanding of theory or were they a source of confusion.

The item numbers on the pupils' questionnaire corresponding to the objectives on the teachers' questionnaire are as follows:-

Teachers' Questionnaire.	Pupils' Questionnaire.
1	1
2	2a
3	3a
4	5a
5	6
6	8
7	9
8	10

The schools taking part in the enquiry were chosen to give a reasonable approximation to a cross-section of schools doing Sixth Year Studies Chemistry.

Glasgow.	Two, boys, selective. Two, mixed, comprehensive. (one > 2000 pupils)
Dunbartonshire and Stirlingshire.	Five, mixed, comprehensive. The schools were in towns with difference economic and social backgrounds. One, mixed, selective.

The total number of pupils involved was approximately one hundred.
The response from some schools was disappointing, but by the summer of 1972, eight hundred and forty-one questionnaires had been returned by pupils. From these it was possible to collect eighteen experiments which had been performed by twenty or more pupils. It was considered that this was the lowest number of responses per experiment from which any reasonable conclusions could be drawn.

The number of teachers involved was less than the pupils (approximately twenty). Since the experiments were not used by all the teachers it was necessary to enlarge the teacher sample. Accordingly, questionnaires on the eighteen experiments were sent to a further group of experienced teachers. When these were included, the teachers' responses on each of the eighteen experiments varied from sixteen to twenty-one.

The eighteen experiments were divided into experiments involving numerical data, experiments not involving numerical data and unclassified experiments as follows:-

Reactions involving Numerical Data.

Iodine coulometer.

Comparison of ΔG and ΔH. Al/HCl

Comparison of ΔG and ΔH $Cu/AgNO_3$

Decomposition temperature of $NaHCO_3$

Verification of Hess's Law.

Partition co-efficient.

Heat of combustion of alcohols.

Transition temperature of Na_2SO_4. 10 H_2O

pH acid/base titration curves.

Ka for a week acid from pH.

Reactions not involving Numerical Data.

Oxidation states of vanadium.

Preparation of benzoic acid using Grignard reagent.

Preparation of Tutton salts.

Alkene + halogen in U.V. light.

Ligands and colour change.

Unclassified.

Paramagnetism of transition elements.

Ignition of $BaCl_2 . 2H_2O$

Spontaneous endothermic reaction.

Both the pupils' and the teachers' questionnaires were treated similarly. Questions on individual experiments were collected and summarised. For comparison between teachers' and pupils' reactions only those questions in common were considered (see page 3-4)
The answers to each question were expressed as a percentage of the total pupil or teacher response on that experiment. Graphs comparing pupil and teacher responses were drawn for each of the eighteen experiments. The answers to the eighteen experiments were amalgamated, and a graph comparing the pupil and teacher responses was drawn. Graphs were also drawn for the combined reactions involving numerical data and for those not involving numerical data.
When examining the collected responses it must be recognised that they can only have a limited accuracy in specifying what objectives have been achieved. Some of the factors which limit the accuracy are:-

Subjectivity of answers,

indiscriminate answering,

variation in methods of doing experiments, e.g. method of instruction of pupils; teacher supervision of pupils, type of apparatus and availability,

whether experiments were done before or after theory,

whether experiments were discussed with teacher or not.

The objectives were also selected in a subjective manner. When comparing pupils' objectives achieved and teachers' expected objectives, the following points should be noted:-

The data are expressed as percentages of the total responses.

In some cases the total numbers of responses are small and an indiscriminate answer could make a considerable difference to the percentages.

The numbers of the pupil responses are usually approximately twice the numbers of the teacher responses. Care must therefore be taken in making direct comparisons.

The eighteen experiments happen to be drawn from all sections of the course and should give a reasonable cross section of the types of experiment likely to be tackled by a school. The total impact of these experiments should therefore be an approximation to the impact of the total course practical work (excluding project). The effect of experiments involving numerical data, those not involving numerical data, and of individual experiments can be examined separately.

Graphical Comparison of Pupils' and Teachers' Responses.

Examination of the graphs (A3 - 7 to A3 - 24) for the individual experiments shows both the pupils' and the teachers' graphs following similar trends with occasional differences. However in only one case was there a very good fit between the graph of the pupils' responses and that of the teachers' responses. This was for the verification of Hess's Law (A3 - 11).

Because of the limitations pointed out at the beginning of the chapter, it is difficult to decide whether the differences, even when they appear large graphically, are significant. However one difference shows consistently. In response to question 8, the pupils only once agreed with the teachers that carrying out an experiment encouraged further investigations. This is not to say that teachers were optimistic on this point.

On only two occasions did more than 30% of the teachers consider that experiments encouraged further investigations, i.e.

Comparision of ΔG and ΔH Al/HCl	31%	(0%)
Spontaneous endothermic reaction	40%	(8%)

The corresponding percentages of pupils' responses are shown in brackets.

Statistical Comparison of Pupils' and Teachers' Responses.

To establish the significant differences Z values were calculated, where possible for each of the eighteen experiments, and for the combined returns on the eighteen experiments, the ten experiments involving numerical data and the five experiments not involving numerical data. Product moment correlations were also calculated between the pupils' responses and the teachers' responses. The Z and r values are detailed on A3-29 to A3-32 and summarised on 3 - 9.

All the correlations between pupils' and teachers' responses were positive. The lowest value was 0.22 for the experiment on pH acid/base titration curves. The only other value less than 0.50 was 0.39 for the experiment to determine the decomposition temperature of $NaHCO_3$.

+ Indicates difference significant at 5%. Pupil response greater.

++ Indicates difference significant at 1%. pupil response greater.

- Indicates difference significant at 5%. Teacher response greater.

-- Indicates difference significant at 1%. Teacher response greater.

	1. Illustrates a property of a particular substance or group of substances.	2. Test an explanation of chemical behaviour.	3. Test a theory or Law given in class	4. Reinforce theory learned in class.	5. Encourage accurate measurement.	6. Increase skill in handling apparatus.	7. Introduce another method of chemical investigation.	8. Encourage further investigation.	r
Iodine coulo~~colour~~meter							--		0.57
Comparison of $\Delta G + \Delta H$, Al/HCl									0.78
Comparison of $\Delta G + \Delta H$, Cu/$AgNO_3$		++							0.62
Decomposition Temp. $NaHCO_3$	++				++				0.39
Verification of Hess's Law.									0.99
Partition coefficient	++	++							0.53
Heat of combustion of alcohols.			++	--	+				0.50
Transition temp. $Na_2So_4 \cdot 10H_2O$.									0.81
pH acid/base titration curves	++					--	--		0.22
Ka weak acid for pH				--					0.61
Oxidation states of vanadium									0.88
Benzoic acid by Grignard	++	++							0.78
Prep. of Tutton Salts		+							0.84
Alkene/Halogen in U.V.		++							0.87
Ligands and colour change									0.91
Paramagnetism. Gouy balance									0.85
Ignition of $BaCl_2 \cdot 2H_2O$	+			++		--			0.73
Spontaneous endothermic		+							0.69
Eighteen experiments	++	++	+		+			--	0.79
Ten with numerical data	++	++		-	++			--	0.79
Five without numerical data		++						--	0.89

Significant differences between Pupils' and Teachers' Responses on Individual Experiments.

The significance of the differences between some responses could not be calculated because of the small number of responses, but trends could be seen.

In five experiments there were no significant differences between pupils' and teachers' responses. These were:-

(a) Comparison of ΔG and ΔH, Al/HCl;

(b) verification of Hess's Law;

(c) transition temperature of $Na_2SO_4 . 10 H_2O$;

(d) oxidation states of vanadium;

(e) ligands and colour change;

(f) paramagnetism of transition elements using a Gouy balance.

In at least (a) and (b) the objective of the experiment would appear to be stated in the title of the experiment. In the case of (b) no z value was greater than 0.8 so the possibility of a significant difference between the pupils' and teachers' responses was very small. From the summary on pages 3 -9 it can be seen that there are a greater number of calculable significant differences among the experiments involving numerical data than among those not involving numerical data (1.3 mean as opposed to 0.8 mean). The differences occur in the pupils making more responses than the teachers on objectives:-

1. Illustrating a property of a particular substance or group of substances.
2. Testing an explanation of chemical behaviour.

They also occur in the pupils making less responses than the teachers on objectives:-

4. Reinforcing theory learned in class.
7. Introducing another method of chemical investigation.

Significant differences between Pupils' and Teachers' Responses on Combinations of the Eighteen Experiments.

When the composite of the eighteen experiments is examined the significance of the differences between the pupils' and the teachers' responses to each objective can be calculated because of the greater number of responses.

Again objectives 1 and 2 are seen more clearly as objectives by the pupils than by the teachers. Objectives 3 and 5 were also favoured by the pupils.

With regard to objective 8 (encouraging further investigation), the trend seen in the graphs becomes definite. Pupils simply are not encouraged to further investigation by course practical work. (The Z value of 6.3 was the highest found in this investigation). This is true also when the experiments involving numerical data and those not involving numerical data are considered separately (Z values of 4.92 and 2.6 respectively).

When the ten experiments involving numerical data are considered separately a similar pattern to that for the composite of eighteen experiments appears. There are however changes in that the pupils now agree with the teachers on the responses on objective 3 (testing theory or Law given in class), but the teachers are more optimistic than the pupils in objective 4 (reinforcing theory learned in class).

With the five experiments not involving numerical data there is much more agreement between pupils and teachers. The pupils still see 2 (testing an explanation of chemical behaviour) more as an objective than the teachers see it. The teachers are still more optimistic than the pupils with 8 (encouraging further investigation), but the difference is not as great as when the experiments involving numerical data are examined.

From this it appears that the divergent views of objectives mostly occur with the experiments involving numerical data.

Rank Order of Objectives Based on Pupils' and Teachers' Responses.

If the composite of the eighteen experiments is considered as being a typical cross section of the course practical work, examination of this should provide a guide to the rank order of the objectives of the course as seen by the pupils and by the teachers.

The rank order of objectives for the pupils and the teachers was tabulated as shown below. The total responses on the eighteen experiments from the pupils was 526 and from the teachers 335. The figures in brackets are the percentage of the responses from the pupils and teachers respectively.

Objectives (numbered as in Teachers' Questionnaire).	Rank Order of Objectives	
	Pupils	Teachers
1. Illustrate a property of a particular substance or group of substances.	1 (56.1)	4 (59.4)
2. Test an explanation of chemical behaviour.	4 (52.9)	1 (44.5)
3. Test a theory or Law given in class.	2 (51.1)	3 (40.3)
4. Reinforce theory learned in class.	3 (48.3)	5 (39.7)
5. Encourage accurate measurement.	5 (47.7)	6 (36.1)
6. Increase skill in handling apparatus.	6 (30.8)	2 (30.4)
7. Introduce another method of chemical investigation.	7 (16.7)	8 (21.2)
8. Encourage further investigation.	8 (6.7)	7 (19.7)

A rank order correlation was calculated and a value of +0.5 was obtained showing there was fairly good agreement. Differences where they occurred were principally in the following:-

'Illustrate a property of a particular group of substances'.

This came first with the pupils and second with the teachers. The difference between the percentage responses of 56.1 and 44.5 respectively was significant at better than 1% ($z = 3.31$).

'Test an explanation of chemical behaviour'. This came third with the pupils and sixth with the teachers. The difference between the percentage responses of 51.1 and 30.4 respectively was significant at better than 1% ($z = 5.91$).

These confirm the differences noted on page 3 -11 and indicate that pupils seem to be seeing properties and behaviour of substances rather than concepts.

The difference in responses on 'encourage further investigation' is again evident. Although both the pupils and the teachers place this low in their order of objectives achieved, the teachers are still much more optimistic than the pupils.

Analysis of Responses to Pupils' Questionnaire.

As indicated on page 3 - 4 the pupils' questionnaire (A3-4, A3-5) was designed to obtain more information than the teachers' questionnaire. It attempted to find:-

What the pupil thought the objective of the experiment was and whether that objective was achieved;

how close experimental results had to approach theoretical values before they became acceptable to the pupils;

if pupils were aware of what they were doing throughout the experiment;

if the experiment aided or hindered the pupils' understanding;

what experiments encountered problems in their execution.

The data obtained from the questionnaires is summarised on page A3 - 28 and is expressed as percentages of responses made.

Returns on individual experiments were too small to produce conclusive results. Only two experiments had greater than forty responses. Those were the verification of Hess's Law and a spontaneous endothermic reaction. Results from these experiments have a reasonable chance of being significant, but the results from the other experiments taken individually can only be of limited significance though they are worth examining. (For the sake of brevity questions will be referred to by number. To assist with the interpretation a copy of the questionnaire is included).

Although pads and carbon papers were provided very few schools returned details of numerical data so it was impossible to establish the credibility of the data, i.e. from the answers to 3(a) and 3(b) how 'good' the results had to be before the pupils were convinced.

Verification of Hess's Law.

2 a	45.2%	3 a	97.6%	4 a	95.2%	5a	66.7%
2 b	40.5%	3 b	92.9%	4 b	90.5%	5c	28.6%
7	42.9%						

This looks to be the most successful experiment of the eighteen.

The pupils appear to be convinced by the experimental results and a considerable proportion 66.7% thought the experiment helped their understanding of the theory. The percentage of 42.9 for question 7 is not high in comparison to those others involving numerical data.

Spontaneous Endothermic Reaction

2a	72%	3a	42%	4a	81.7%	5a	56%	7	20%
2b	62%	3b	18%	4b	75.9%	5c	26%		

Again this seems to be a reasonably successful experiment. The difference in 3a and 3b may be due to the fact that numerical data are collected in some schools and not in others.

From the remainder of the eighteen experiments only those showing differences which are large are now discussed. In view of the small number of responses these are more likely to be significant.

Iodine Coulometer

2a	54.8%	5a	58.1%	7	80.6%
2b	32.3%	5c	29%		

From the percentage responses to 2a, 2b and 7 this would appear to have not been so successful. The results were not so convincing to the pupils and they seem to have had a fair amount of trouble, 80.6% for question 7.

Comparison of ΔG and ΔH. Al/HCl

3a	70%	5a	35%
3b	40%	5c	45%

The pupils were not convinced by the numerical results and it did not help them to understand the theory.

Heat of Combustion of Alcohols.

3a	62%	5a	38.2%	5b	11.8%
3b	44%	5c	35.3%		

The pupils were not convinced by the numerical results and it did not help them to understand the theory. The 11.8% percentage of responses for 5b was the only figure greater than 8% for this question.

Transition Temperature of $Na_2SO_4 . 10H_2O$

2a	42.9%	3a	71.4%	5a	60.7%	7	57%
2b	25%	3b	32.1%	5c	32.1%		

In this experiment it appears that the pupils were not convinced by the numerical results but still thought carrying out the experiment helped them understand the theory

Ka for a Weak Acid from Measurement of pH.

2a	40.9%	3a	63.6%	5a	36.4%
2b	27.3%	3b	27.3%	5c	54.5%

The pupils were not convinced by the results in this experiment and it did not help them understand the theory.

Preparation of Tutton Salts.

2a	57.7%	5a	23.1%
2b	34.6%	5c	65.4%

The pattern of the responses for what is a simple experiment are disappointing. The students were not convinced by the results and the highest proportion for any of the eighteen experiments thought the experiment made no difference to their understanding.

Reaction between an Alkene and a Halogen in U.V. Light.

2a	85.2%	5a	44.4%	7	29.6%
2b	55.6%	5c	25.9%		

The pupils were not convinced by the results that the explanation was correct, but thought that carrying out the experiment helped their understanding.

Ligands and Colour Change.

2a	66.7%	4a	85.7%	5a	71%
2b	57.1%	4b	52.4%	5c	19%

The pupils thought that carrying out this experiment helped them understand the theory. This is the only experiment which produced a large difference between 5a and 5c. This may be an indication that the students were not clear on what the objectives were before starting the experiment.

Paramagnetism of Transition Metals using a simple Gouy Balance.

2a	43.3%	3a	63.3%	4a	76.7%	5a	53.3%
2b	33.3%	3b	23.3%	4b	60%	5c	46.7%

The pupils do not appear to have been convinced by the experimental results, and the number whose understanding was no better through carrying out the experiment approached that of those who had benefited. The significance of the above conclusions must be suspect because of the small number of responses, but if we examine the percentage responses from the composite of the eighteen experiments the significance is likely to be more certain because of the larger number.

Eighteen Experiments where Responses made by > 20 Pupils.

2a	51.1%	3a	48.3%	4a	81.7%	5a	52.9%
2b	41.3%	3b	30.4%	4b	75.9%	5b	34%

From questions 2 and 3 it seems that a number of pupils were not convinced by the results of experiments. A better idea of the numbers involved can be obtained when the experiments involving numerical data and those not involving numerical data are compared. From question 5 it can be seen that about 30% of the pupils claim that carrying out the experiment makes no difference to their understanding. Even allowing for the subjectivity of the answers this is a rather high ~~proportion~~.

From the answers to question 4, it would appear that the percentage of pupils who 'were not aware of the aim of the experiment throughout the experiment' was less than 20%.

Experiments involving Numerical Data and Experiments not involving Numerical Data.

When we consider these experiments separately to decide on whether the experiments are convincing to the pupils or not, question 3 is more likely to be relevant to the numerical data experiments and question 2 more likely to be relevant to the non-numerical data experiments. There should have been no responses to question 3 for the non-numerical data experiments, but in fact some were made. This is probably due to a spectrophotometer having been used in some school when examining ligands and colour change.

Numerical Data Experiments.			Non-Numerical Data Experiments.		
3a	56.1%	Difference 12.2%	2a	66.2%	Difference 17%
3b	43.9%		2b	49.2%	

Percentage of pupils not convinced by results of experiment:-

21.7%	25.7%

To check if there was any significant difference between these two figures a z value was calculated and was found to be 0.9. This means that there is no significant difference. Therefore, regardless of whether the experiments involve numerical data or not, about 20% of the pupils state that they are not convinced by the results of the experiment.

To find whether the 34% of pupils claiming that carrying out experiments makes no difference to their understanding, was affected by whether the experiments involved numerical data or not, the answers to question 5 were also compared:-

	Numerical Data Experiments	Non-Numerical Data Experiments
5a	54.1%	49.2%
5c	32.8%	37.7%

z values were calculated for the percentage responses to 5a and 5c. They were 0.93 and 0.98 respectively showing there is probably no significant difference between experiments involving numerical data and those not involving numerical data as far as aiding understand is concerned, in the pupils view.

Discussion.

The objectives listed could be classified as general as opposed to those specific to a particular experiment. A fair degree of agreement could therefore be reasonably expected between pupils and teachers. This is borne out by product moment and rank correlations of 0.79 and 0.5 respectively for the composite of eighteen experiments. Although there is general agreement, differences do exist.

More differences between expected and achieved objectives are found among the experiments involving numerical data than among those not involving numerical data. They appear to arise from the pupils seeing properties and behaviour of substances rather than concepts. This substantiates the need for ensuring that the objectives of an experiment are stated clearly. Where the objectives are implicit in the title of the experiment there appear to be fewer differences. Similar evidence has been produced by Miss M.A. McCallum.[~~20~~ 19] It also indicates that substances familiar to the students should be used when establishing concepts or substantiating theories. Pupils are not then distracted from the point of the experiment by unfamiliar compounds, names and equations.

Although 'encouraging further investigation' was not rated very highly by the teachers, the pupils rated it much lower. The limited success of achievement of this objective may be due more to the influence of the teacher than to the actual experiments. It may be that the best hope for achieving this objective is in project work.

The teachers were also more optimistic than the pupils in thinking that practical work would reinforce theory learned in class. This was their most frequently noted objective by a margin of 15% over their next most frequently quoted objective.

The difference in belief in the efficacy of practical work in reinforcing theory learned in class is also evident when the responses to the pupils' questionnaires are analysed.

About 30% of the pupils claim that carrying out experiments made no difference to their understanding of theory. Also about 20% of the pupils claimed that the results of the experiment were not convincing to them. In this there was no difference between the experiments involving numerical data and those not involving numerical data. Course practical work then has limited success in helping with the understanding of theory. This difference between stated aims and actual achievements was also noted in the surveys mentioned at the beginning of this chapter.[14,15,16,17] Since about 60% of the total time allocated to Sixth Year Studies Chemistry is devoted to course practical work (page~~s~~ 2 - 8) the tangible results do not seem commensurate with the time allocation. Some improvement could be made towards a greater achievement of the objectives listed by improving the experiments through:-

Stating clearly to the pupils the objectives for each experiment;

structuring the instructions so that pupils work to achieve the objectives;

familiarising pupils with the properties of substances and with experimental techniques before they are used to substantiate a theory.

Even if the achievement of set objectives is not totally effective there may be other less tangible functions of practical work. The following is an extract from an article by W.R. Russell.[20] "Most young people cannot absorb information usefully from books and lectures for more than three or four hours in the 24, and the consolidation of this new knowledge might well occur more effectively if the remaining hours of the working day were spent in practical physical tasks. Clearly the scientific university courses which demand an integrated balance of bookwork, lecture, laboratory or work-shop education are at an advantage in this respect when compared to the arts courses.

I would suggest, therefore, in the planning of higher education for the future, that there should be a balance of theoretical and practical experience provided in the most appropriate way to meet the objectives of the particular course of education. While it may be advantageous for the theory and practical to be related, this will not always be possible nor indeed is it essential."

There is no reason why the theory and practical should not be related in the Sixth Year Studies Chemistry course but, if success in achieving stated objectives is not great, a useful function is still being performed by practical work.

Extract from Nuffield Advanced Science, Chemistry. Teachers' Guide 1. p10.

"The integration of theory and practical work. Chemistry is predominanly an experimental subject and can only be fully understood by frequent recourse to the laboratory bench. Consequently, in this course, the theory and relevant practical experience are integrated as fully as possible. In a few areas, in particular when dealing with structure, the practical work is somewhat meagre, but these are rare. As the course proceeds students gain experience in using theoretical principles to predict the outcome of reactions, and in testing their predictions experimentally. This close integration of experiment and theory involves the abandonment of formal practical exercises, such as unrelated preparative work and formal volumetric or quanlitative analysis. This does not mean that the techniques involved in those areas of practical work are neglected; they are used when the necessity for them arises."

Extract from Nuffield Advanced Science, Physical Science, Introduction and Guide pp.26,27.

Following a decision not to have a formal practical test. "This decision meant that whatever practical work was done, could be completely integrated with the overall development of the course; there would never be any question of doing experiments as a drill for a practical examination.

What other functions are served by practical work? Its main function can hardly to be to teach students practical techniques, since far too little time can be spared in a sixth-form course for any type of experiment or measurement for students to become really proficient in it. Its PRINCIPAL purpose must surely be to give students something of the flavour of scientific discovery - to let them share, in however small a way, the experience of the scientist carrying out original research. This most important aspect of school practical work will not be considered further here, for it is discussed at some length in chapter 4, which deals with the physical science project.

The other main reason commonly given for doing practical work, is that students can best come to understand scientific facts and principles in this way. This ought certainly to be the case, but even so such an assertion calls for some examination. For instance, every teacher has the experience of carefully explaining an experiment, and of ensuring that the class carries it out conscientously, works out the results, and answers questions on it - only to discover a week later that they have only the haziest recollection of what they have done. Also, experiments have a tiresom way of going wrong, and students an annoying habit of making misleading observations.

For all that, experiments of this type have an important place in science courses."

University of Glasgow   Research in Chemical Education

Sixth Year Studies in Chemistry

Please indicate with a tick the statements which you think apply to each experiment completed by your pupils.

NAME: SCHOOL:

TITLE OF EXPERIMENT:

This experiment was intended to -

1. Illustrate a property of a particular substance or group of substances. ☐
2. Test an explanation of chemical behaviour. ☐
3. Test a theory or Law given in class. ☐
4. Reinforce theory learned in class. ☐
5. Encourage accurate measurement. ☐
6. Increase skill in handling apparatus. ☐
7. Introduce another method of chemical investigation. ☐
8. Encourage further investigations. ☐

Thank you.

University of Glasgow Research in Chemical Education

Sixth Year Studies in Chemistry

After you have completed each experiment, please fill in a copy of this form and give it to your class teacher. The object of this is to provide a clear picture of how useful and successful the practical work of S.Y.S. is. On the basis of your comments, future modifications will be made.

Please fill in the form independently and frankly.

NAME: SCHOOL:

TITLE OF EXPERIMENT:

Please indicate with a tick where you think the question refers to the experiment you have just completed.

1. This experiment illustrated a property of a particular substance or group of substances. ☐

2.(a) An explanation of chemical behaviour was tested in this experiment. ☐

(b) From the results of the experiment I was convinced that the explanation was correct. ☐

3.(a) This experiment tested a theory or Law given in class. ☐

(b) The numerical results obtained from this experiment convinced me of the truth of the Law. ☐

4.(a) I was aware of the aim of the experiment throughout the experiment. ☐

(b) I was aware of the reason for carrying out each stage of the experiment during the experiment. ☐

5. Carrying out this experiment ☐

(a) Helped me to understand the theory. ☐

(b) Confused me. ☐

(c) Made no difference to my understanding. ☐

6. This experiemnt made me aware of the need for accurate measurement. ☐

Sixth Year Studies in Chemistry (cont'd.) ☐

7. During the experiment other problems became apparent. ☐

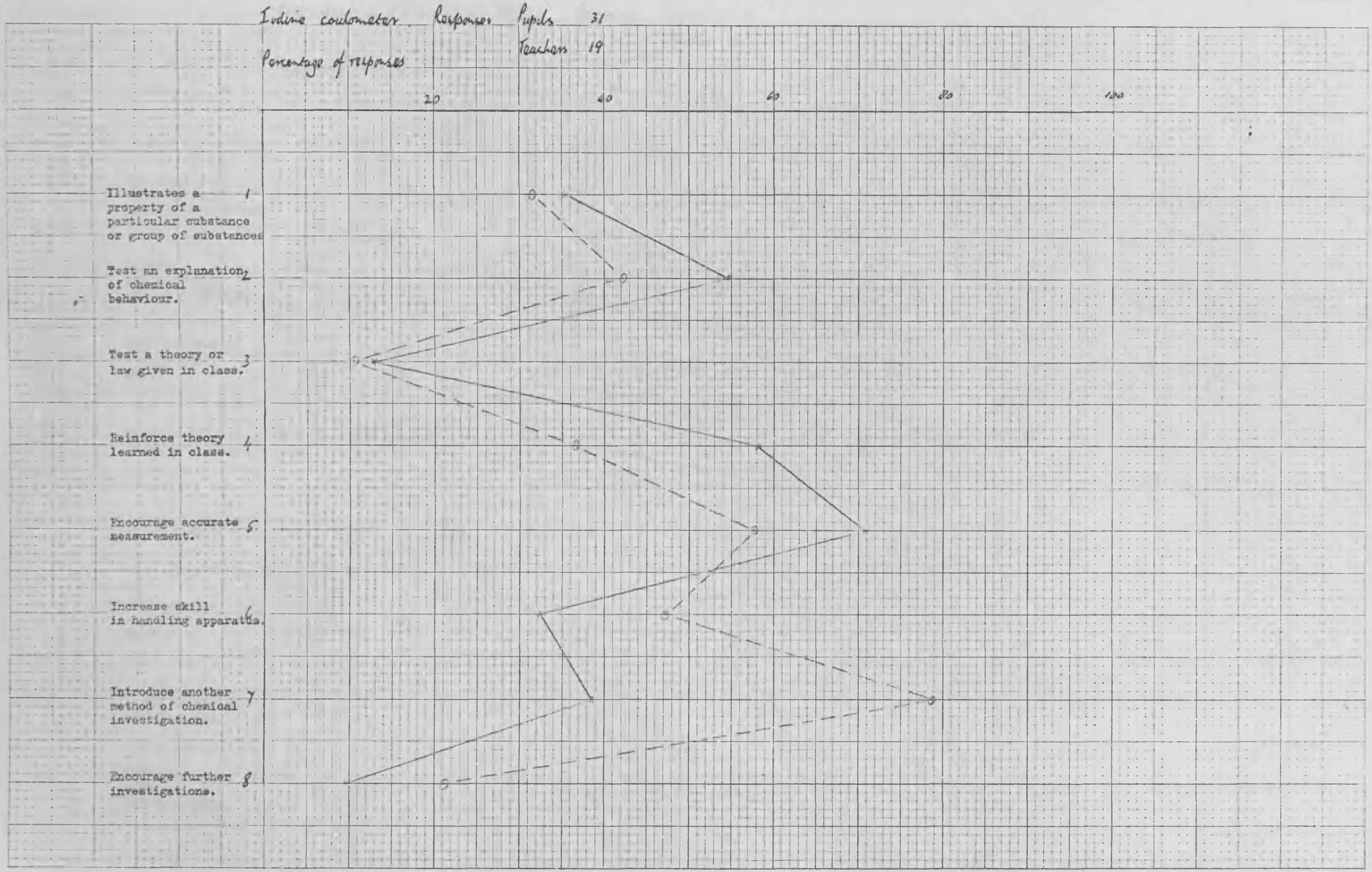
8. Carrying out this experiment increased my skill in handling apparatus. ☐

9. I learned a new method of chemical investigation during this experiment. ☐

10. Carrying out this experiment interested me in making further investigations. ☐

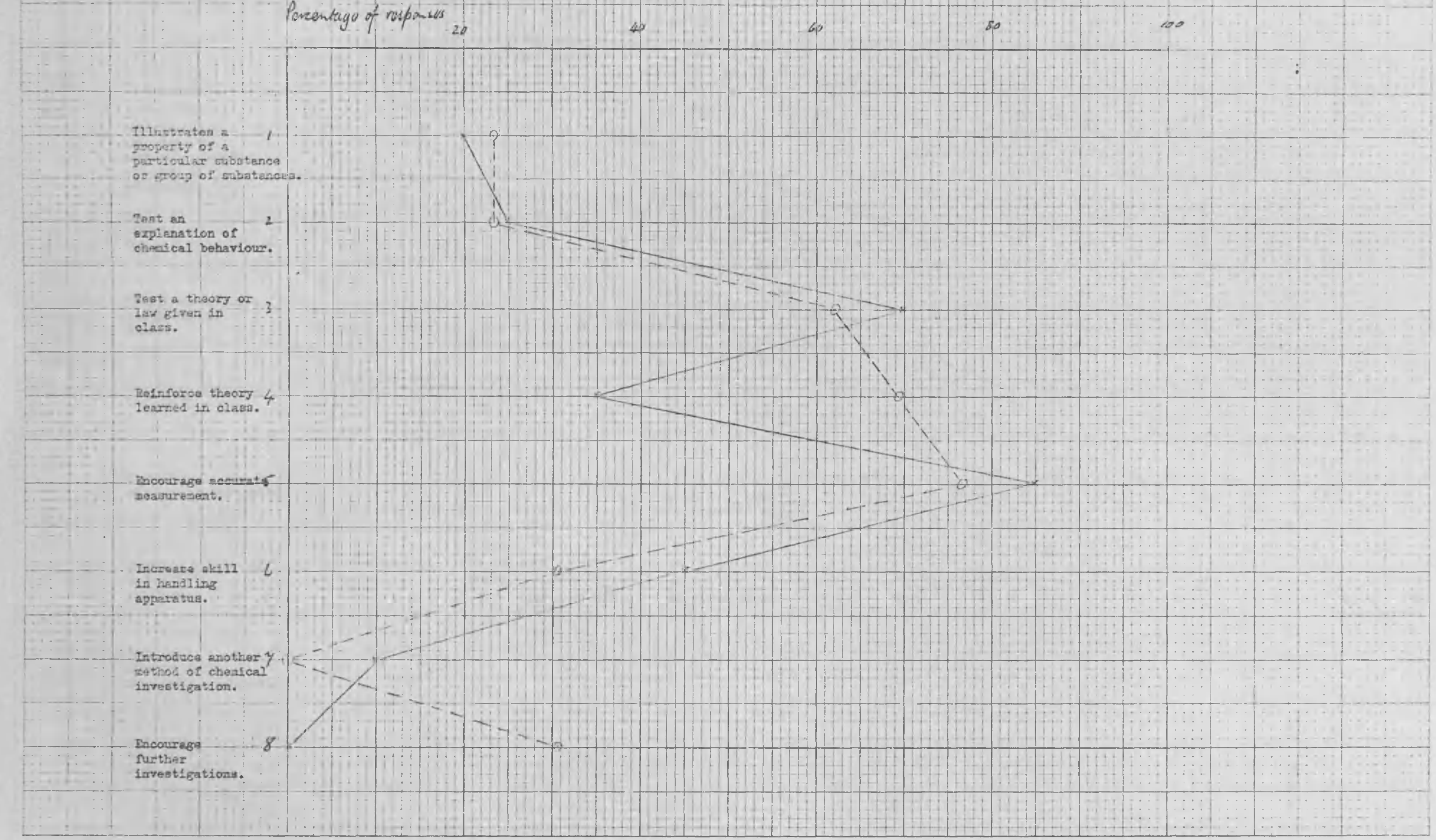
GRAPHICAL COMPARISON OF PUPILS' AND TEACHERS' RESPONSES.

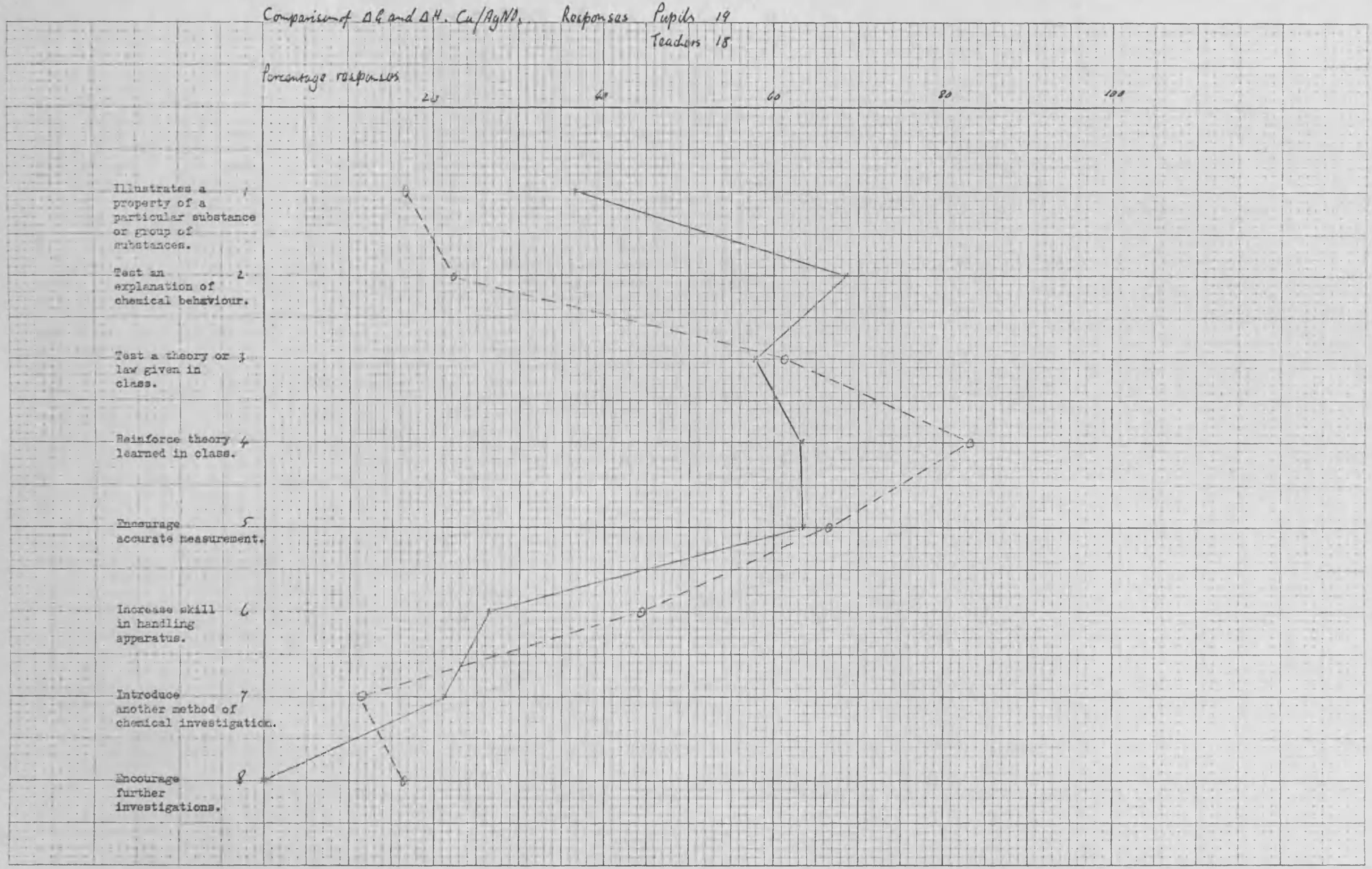
A3 - 7



Iodine coulometer Responses Pupils 31
Teachers 19

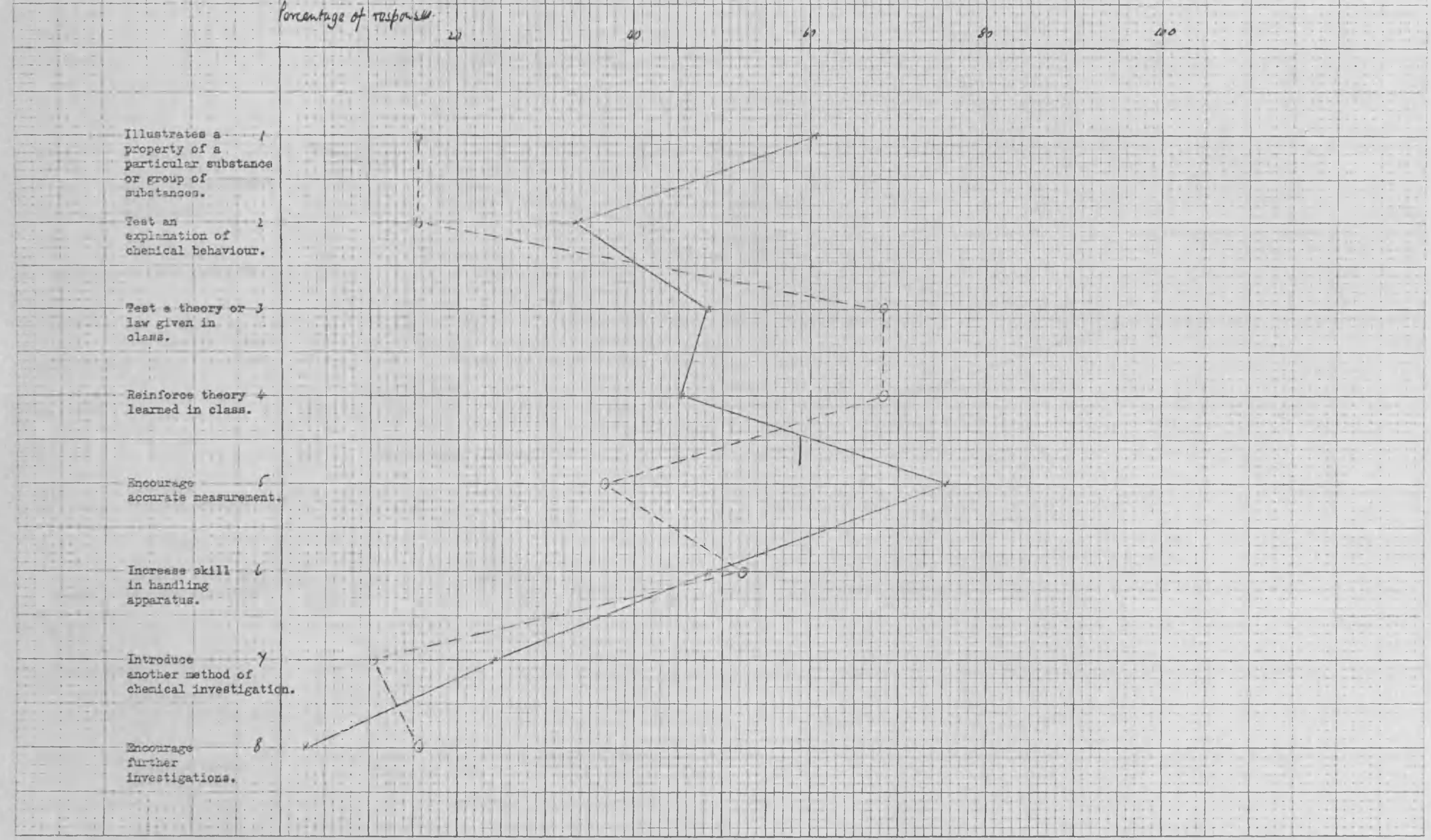
Comparison of ΔG and ΔH Al/HCl Responses Pupils 20
Teachers 13.



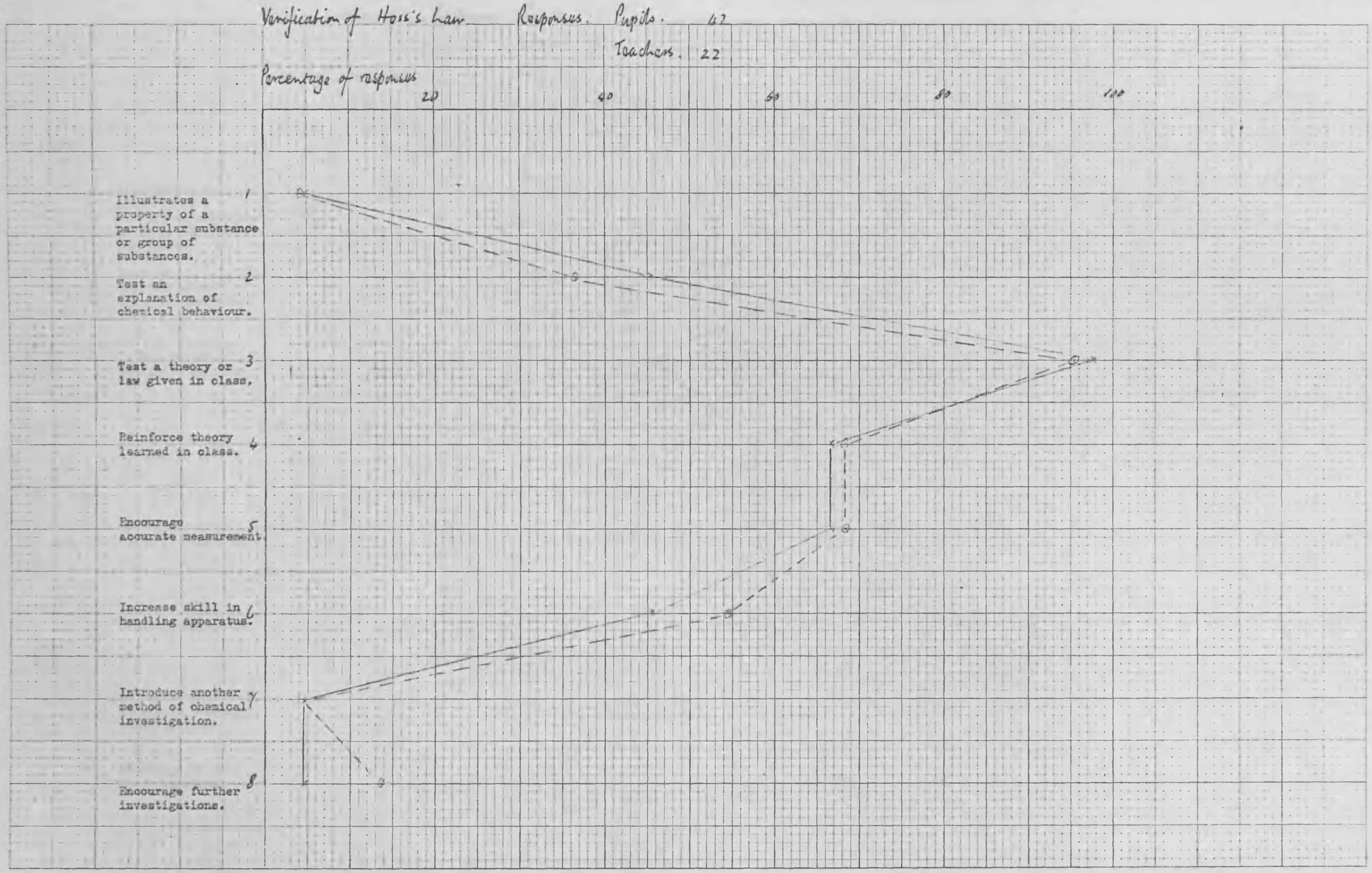


Comparison of ΔE and ΔH. Cu/AgNO₃. Responses Pupils 19
Teachers 18

Decomposition temperature of $NaHCO_3$. Responses Pupils 33
Teachers 19.

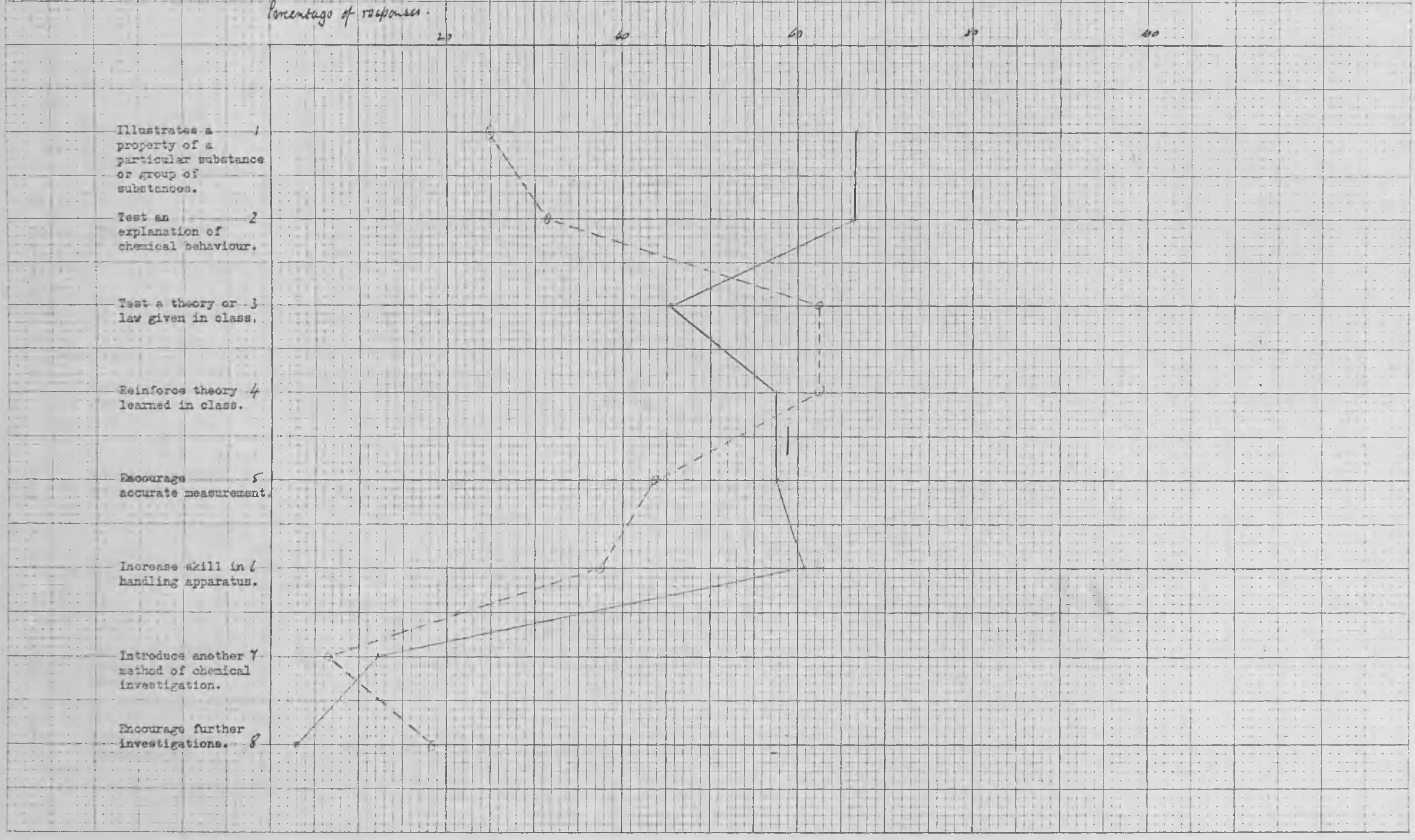


A3 - 11



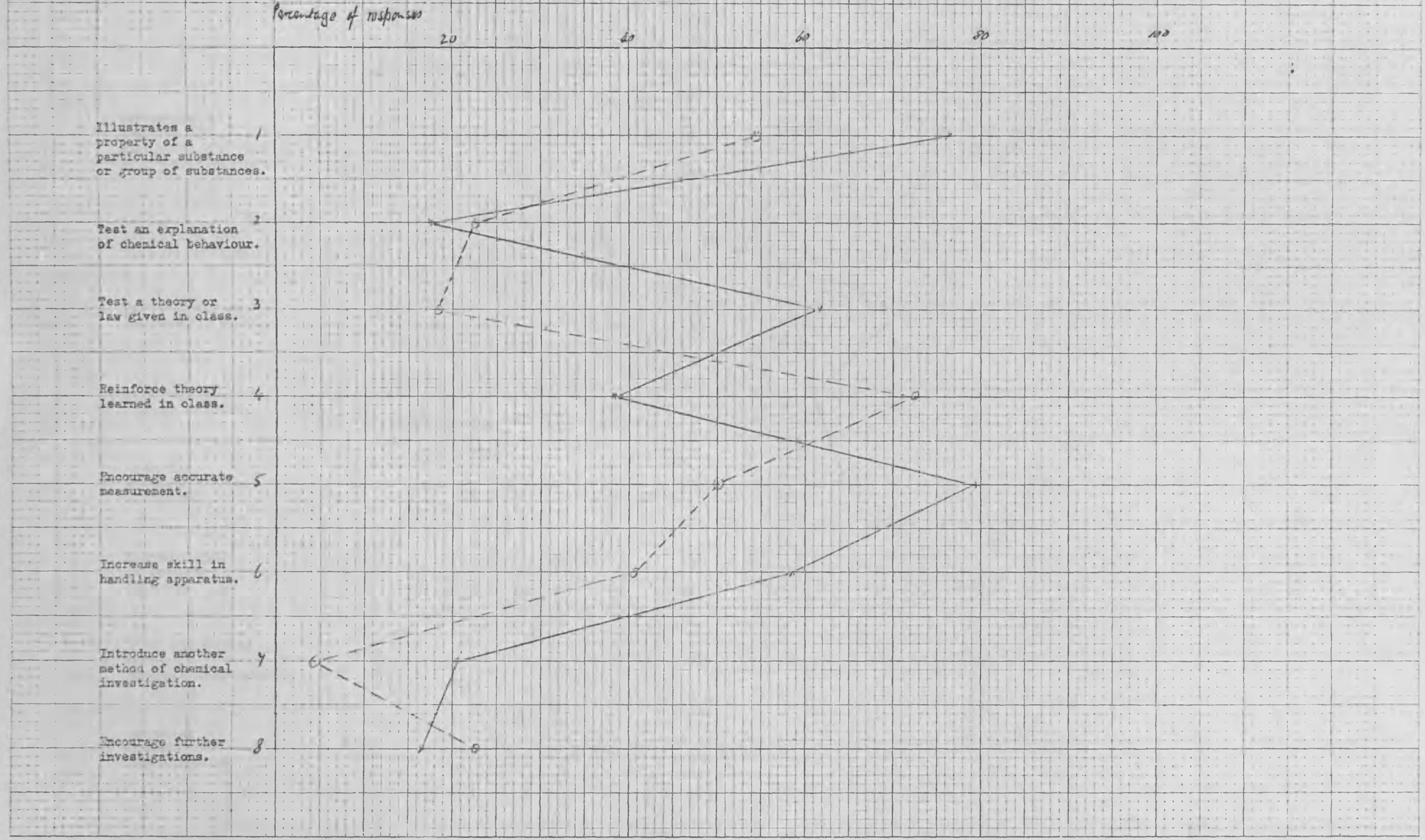
Verification of Hess's Law Responses. Pupils. 47
Teachers. 22

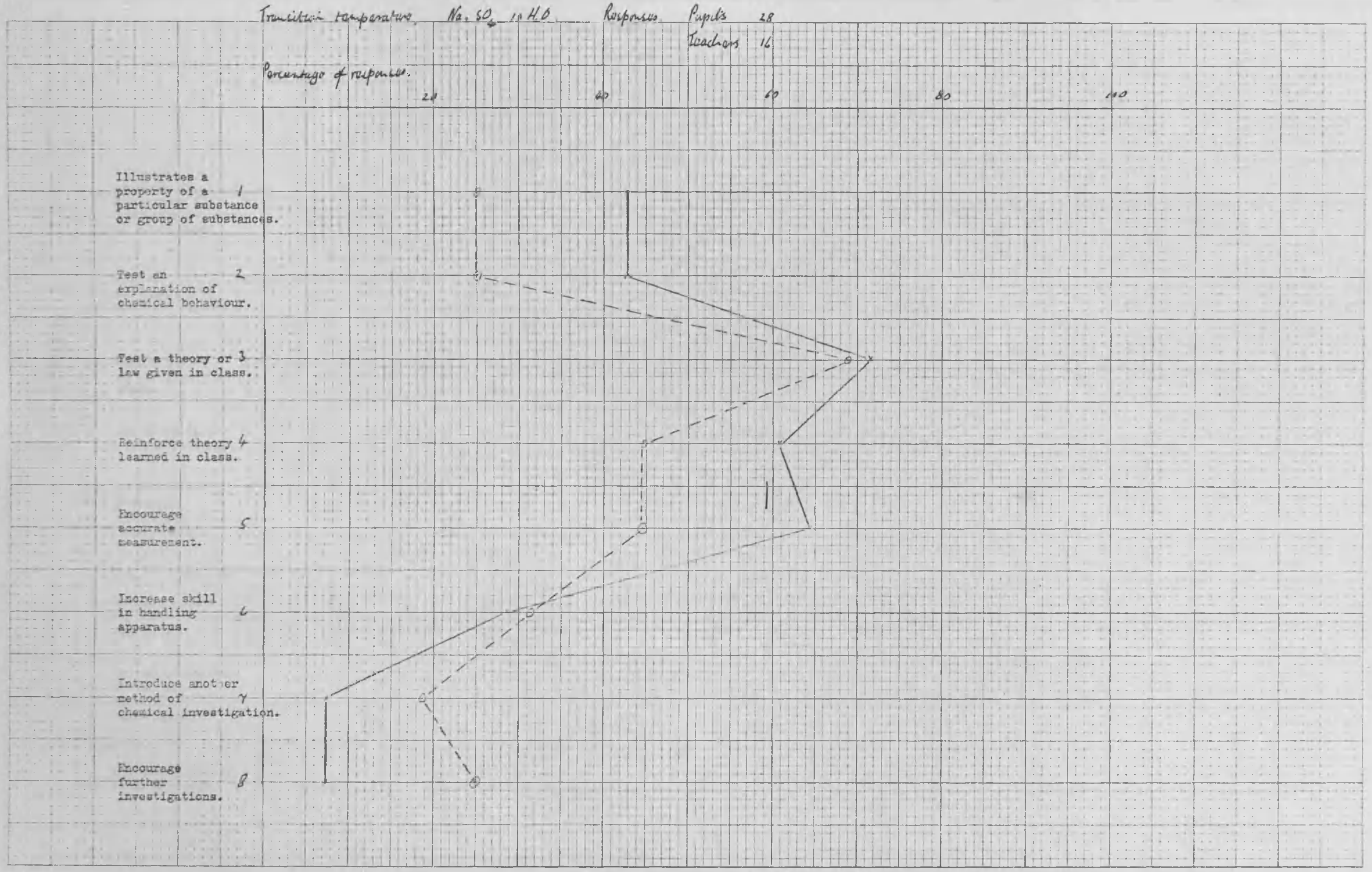
Partition coefficient. Responses. Pupils 33
Teachers 16



A3 - 13

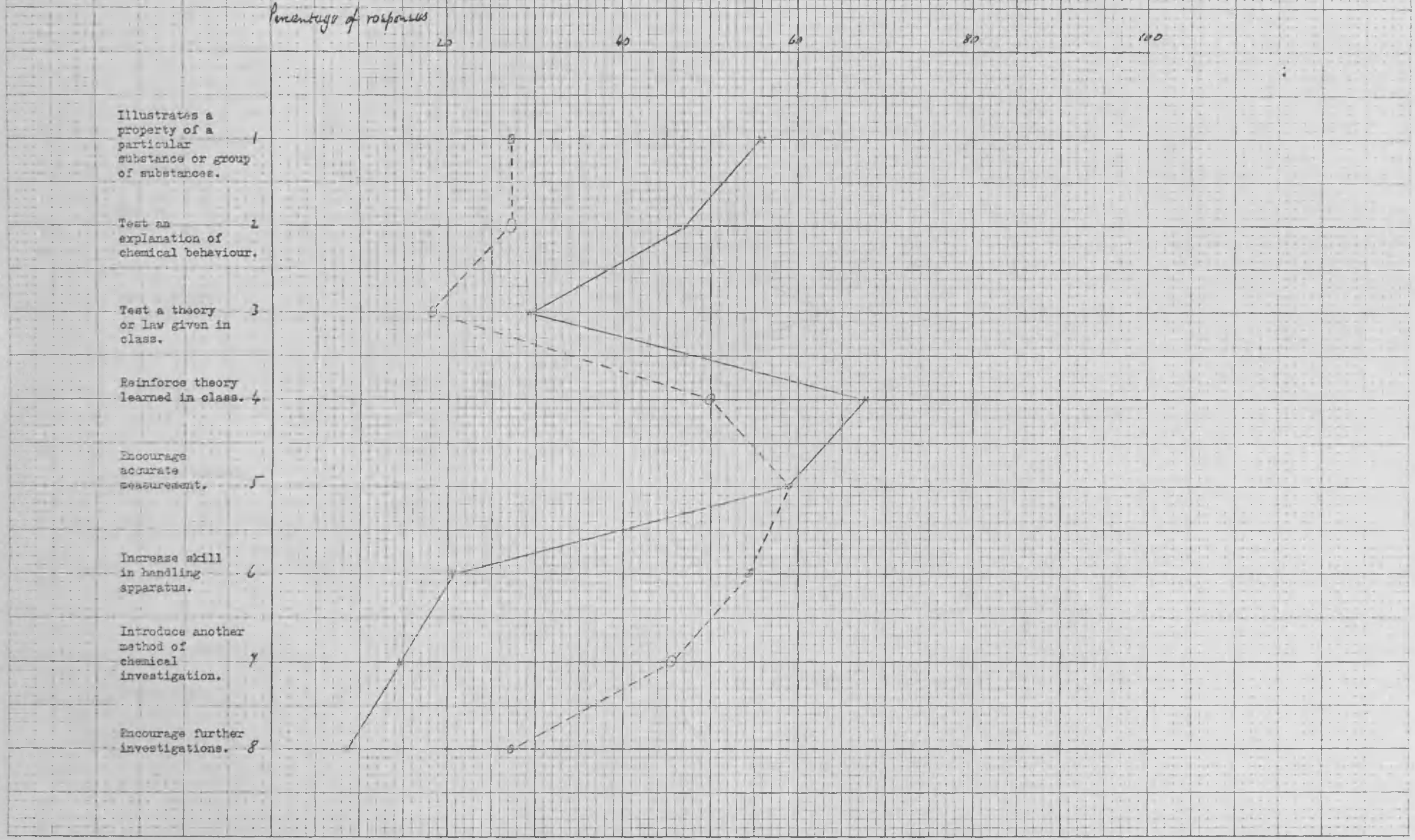
Heat of combustion of alcohols. Responses. Pupils. 34
Teachers. 22.




Transition temperature. Na_2SO_4 10 H_2O
Responses Pupils 28
Teachers 16
Percentage of responses.
20
40
60
80
100
Illustrates a property of a particular substance or group of substances. 1
Test an explanation of chemical behaviour. 2
Test a theory or law given in class. 3
Reinforce theory learned in class. 4
Encourage accurate measurement. 5
Increase skill in handling apparatus. 6
Introduce another method of chemical investigation. 7
Encourage further investigations. 8

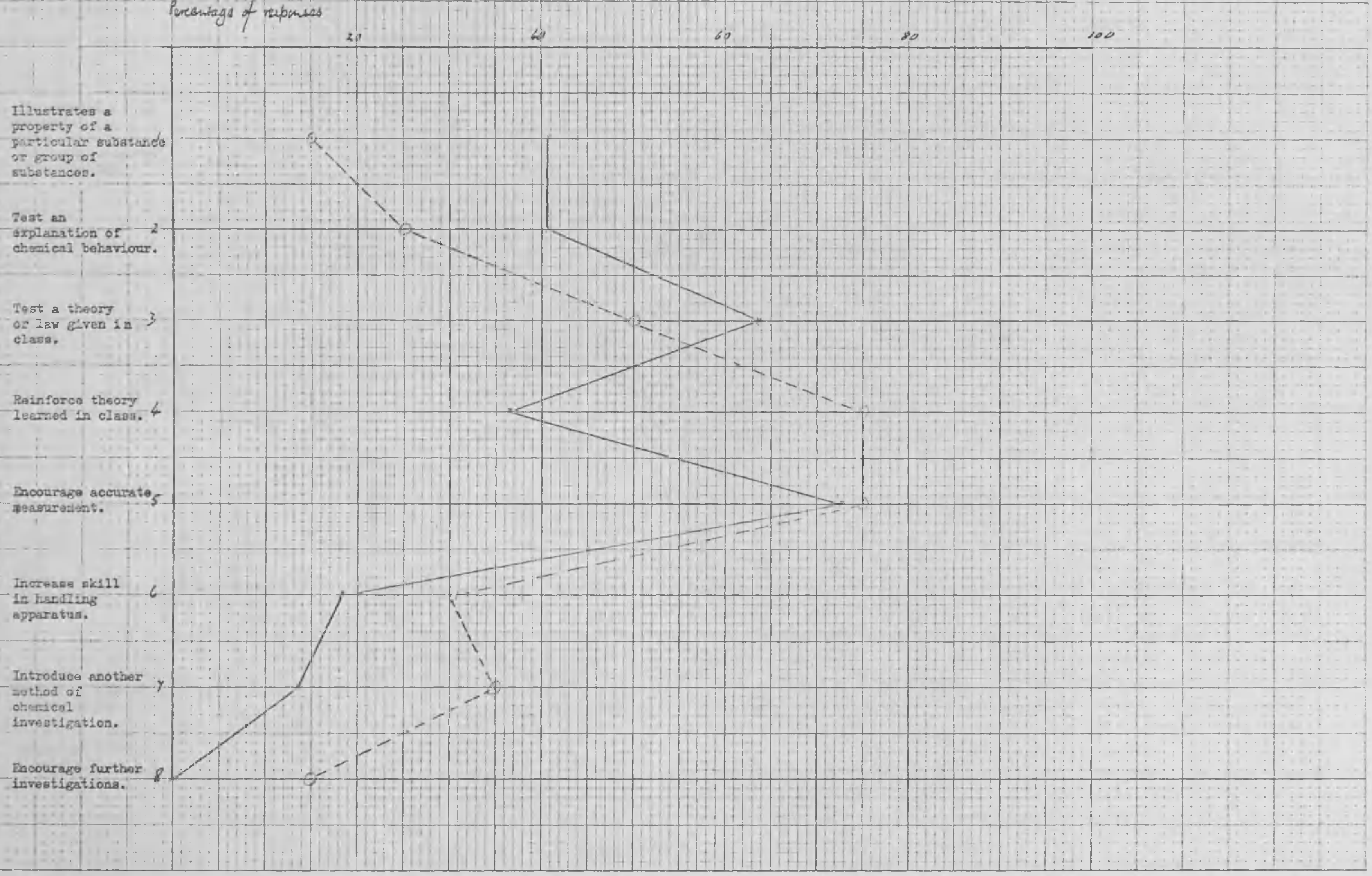
13 - 15

pH acid/base titration curves. Responses Pupils 34
Teachers 21

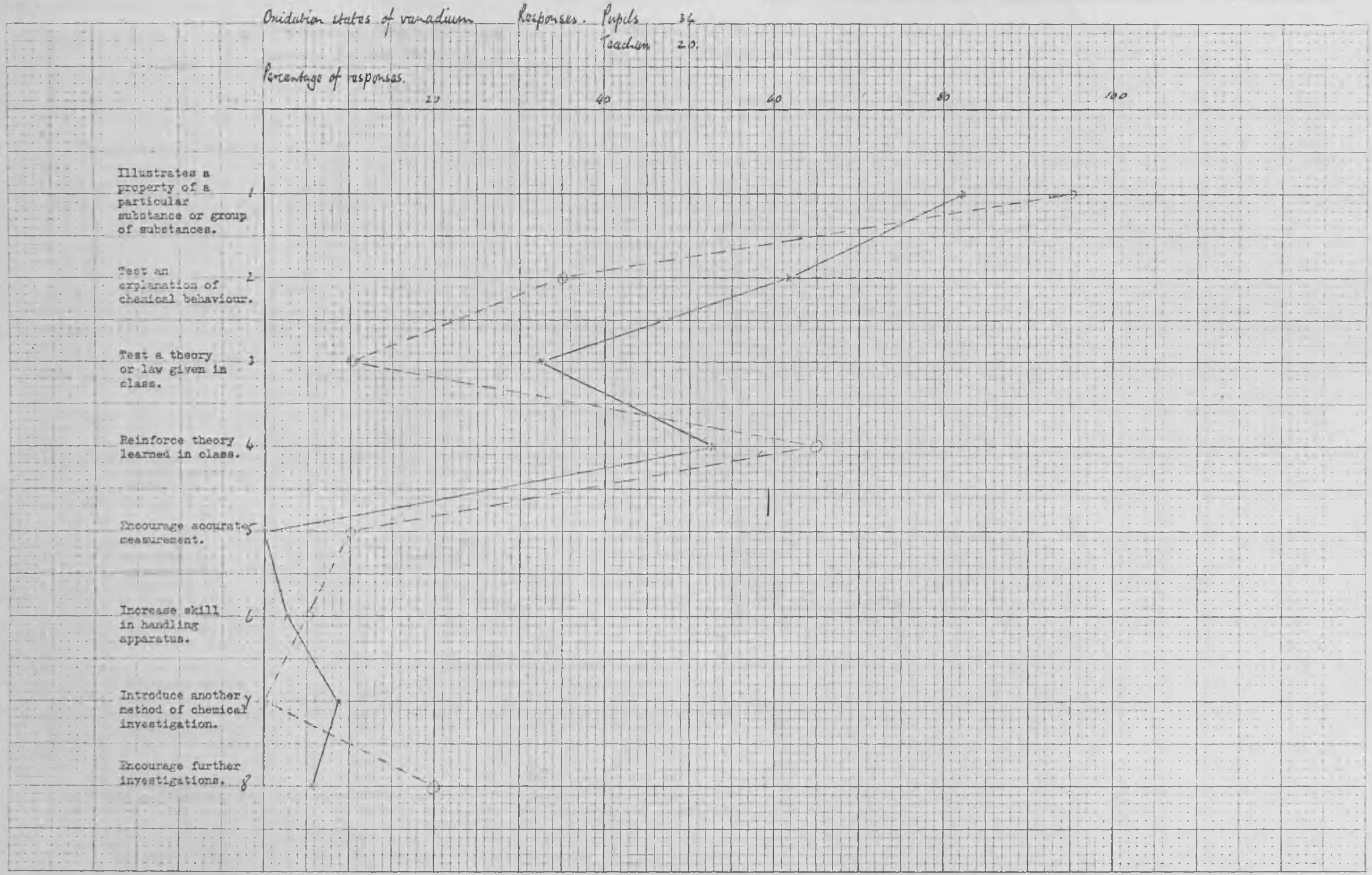


Finding Ka for a weak acid from pH measurement.

Responses. Pupils. 22
Teachers 20



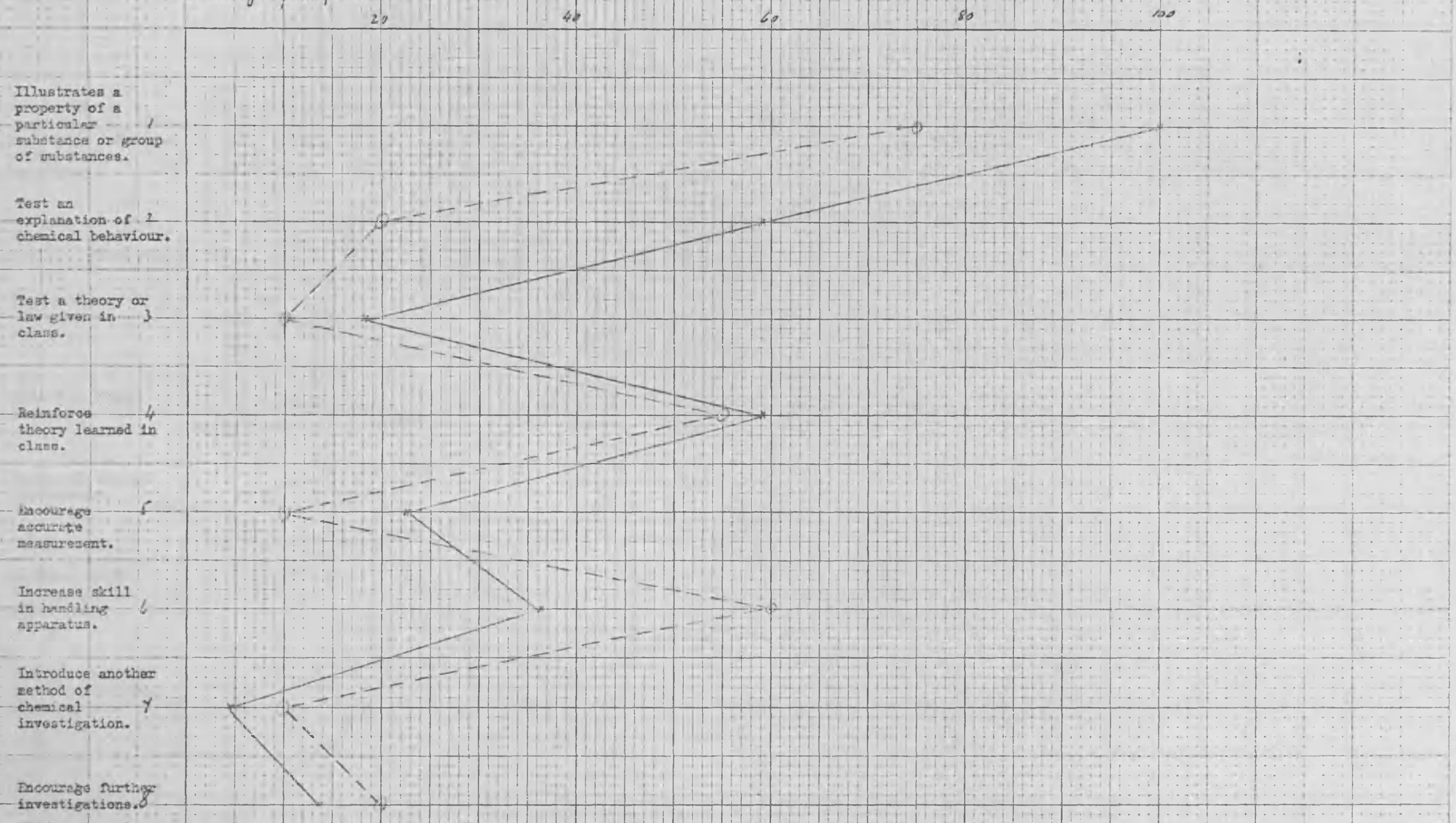
Oxidation states of vanadium   Responses. Pupils 34
Teachers 20.



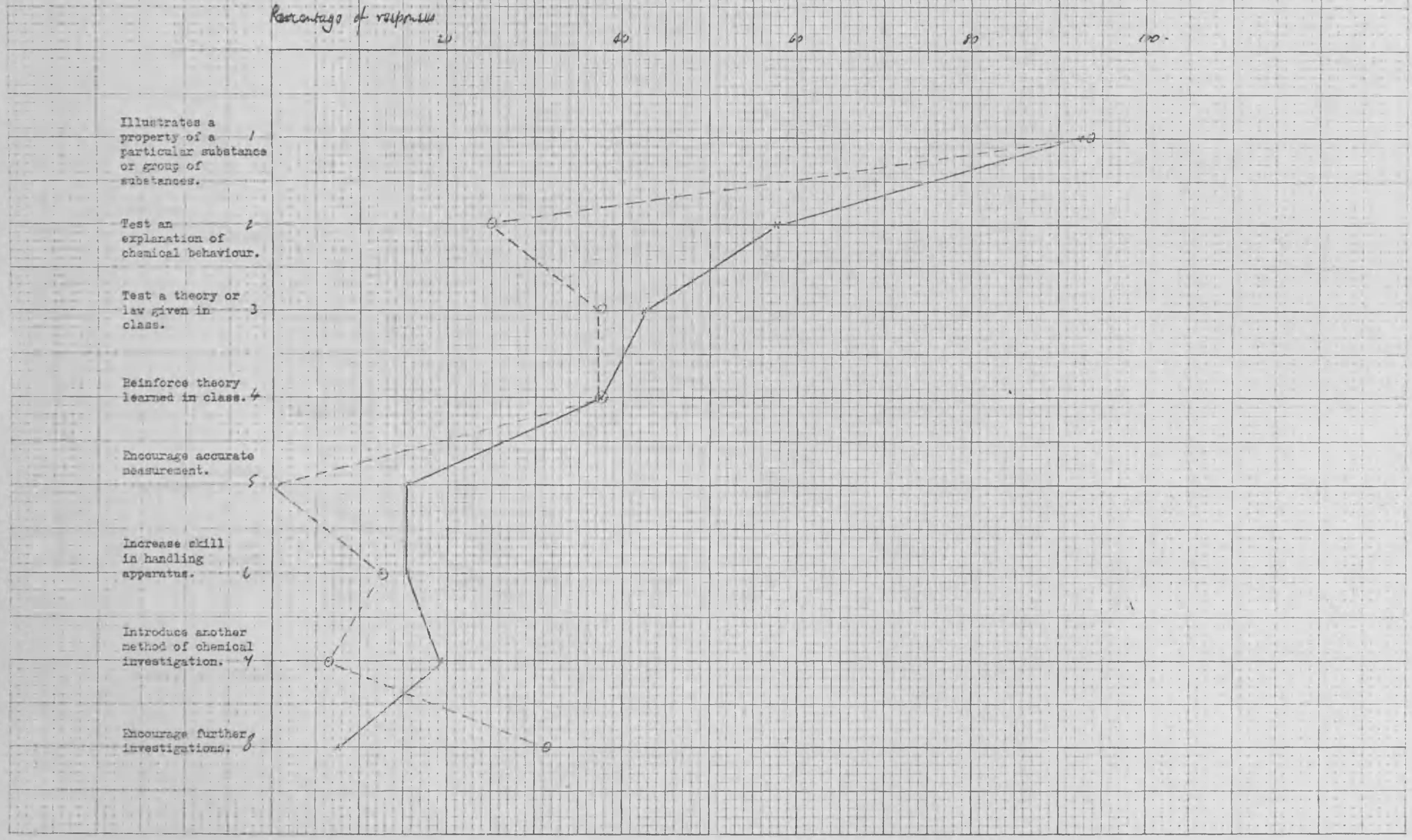
Preparation of benzoic acid
using a Grignard reaction.

Responses Pupils 22.
Teachers 20.

Percentage of responses.

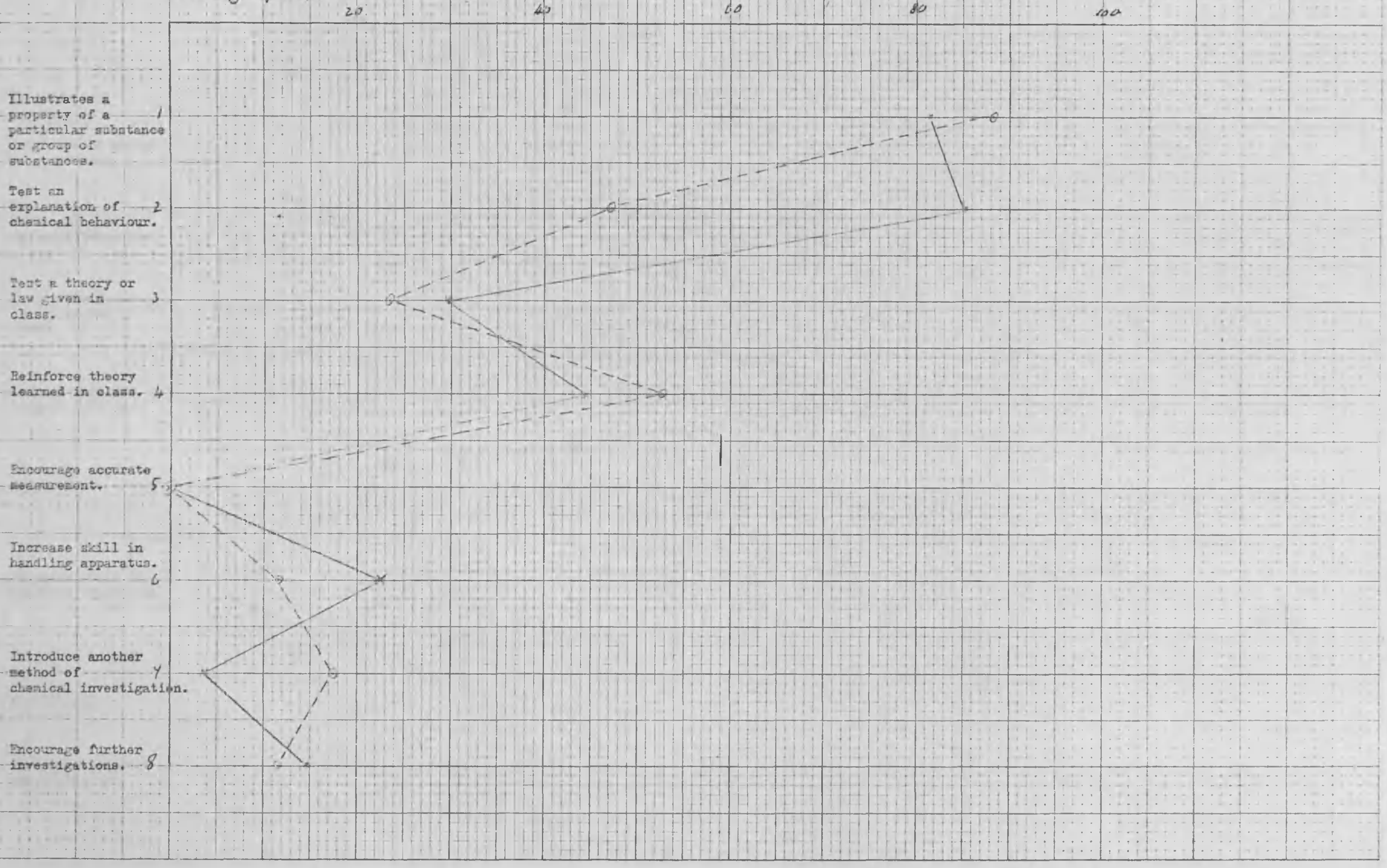


Preparation of Tutton salts. Responses Pupils. 26
Teachers. 14.

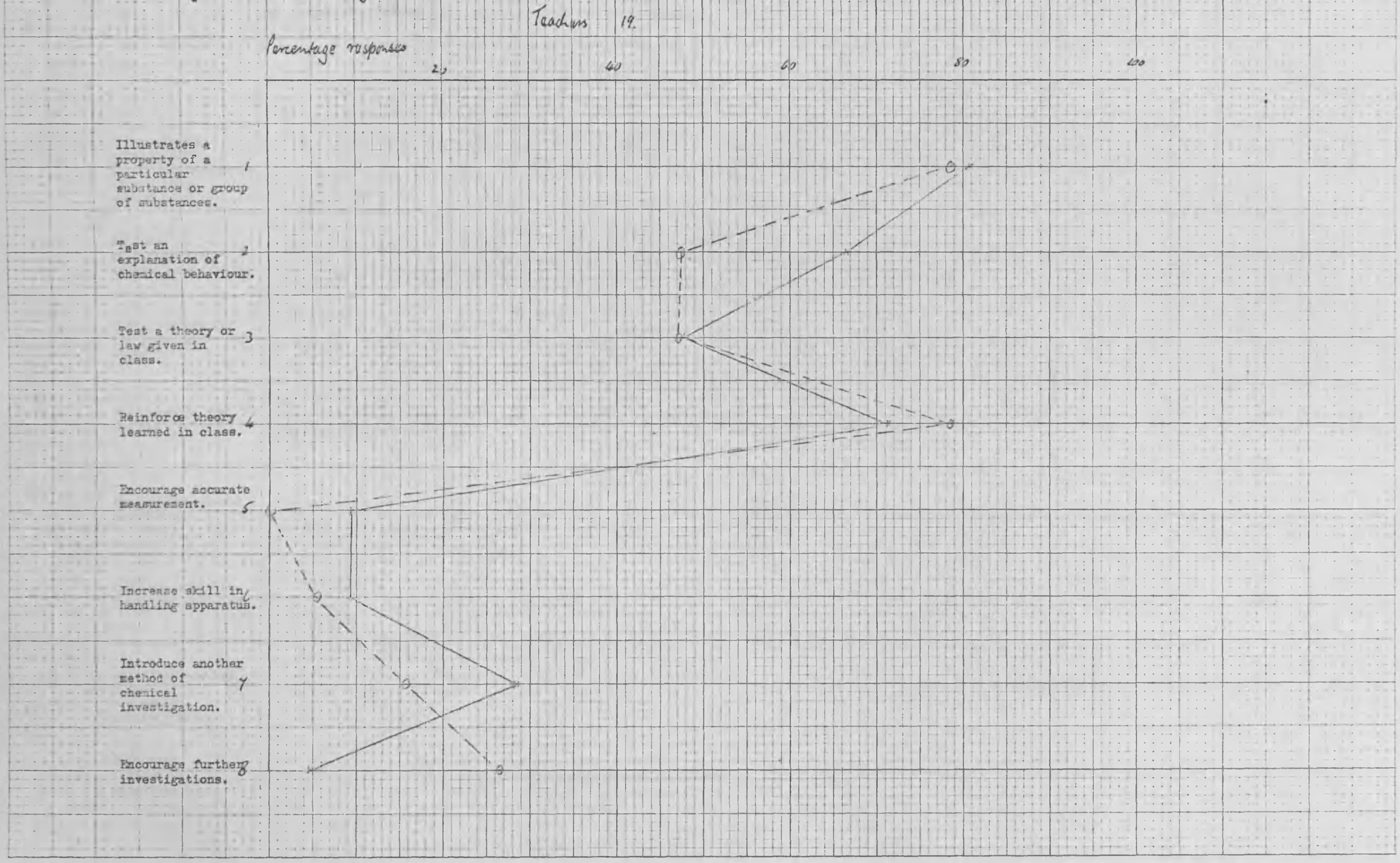


Reaction of an alkene and a halogen in U.V. light.
Percentage of responses.

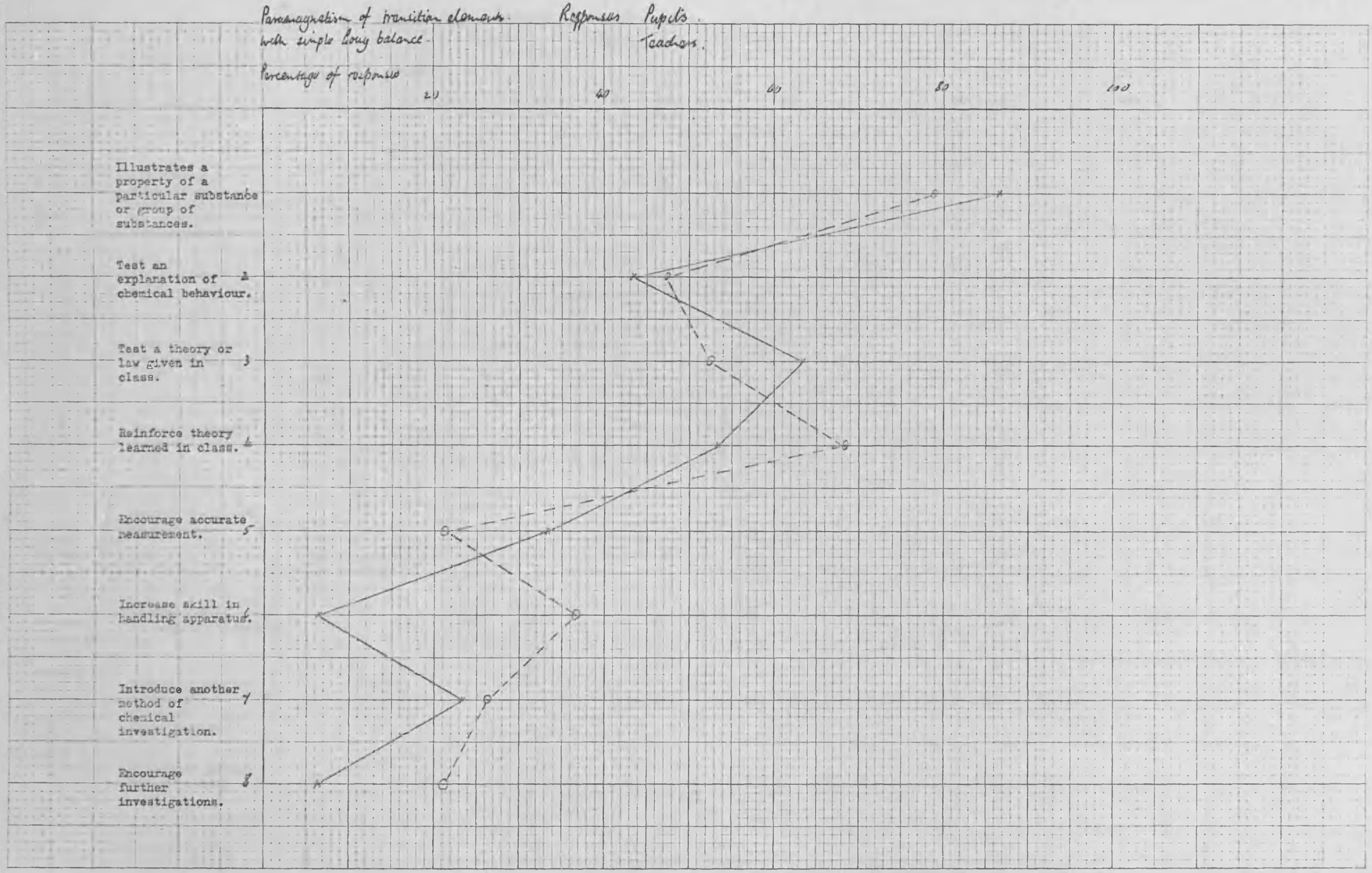
Responses Pupils 27
Teachers. 17.



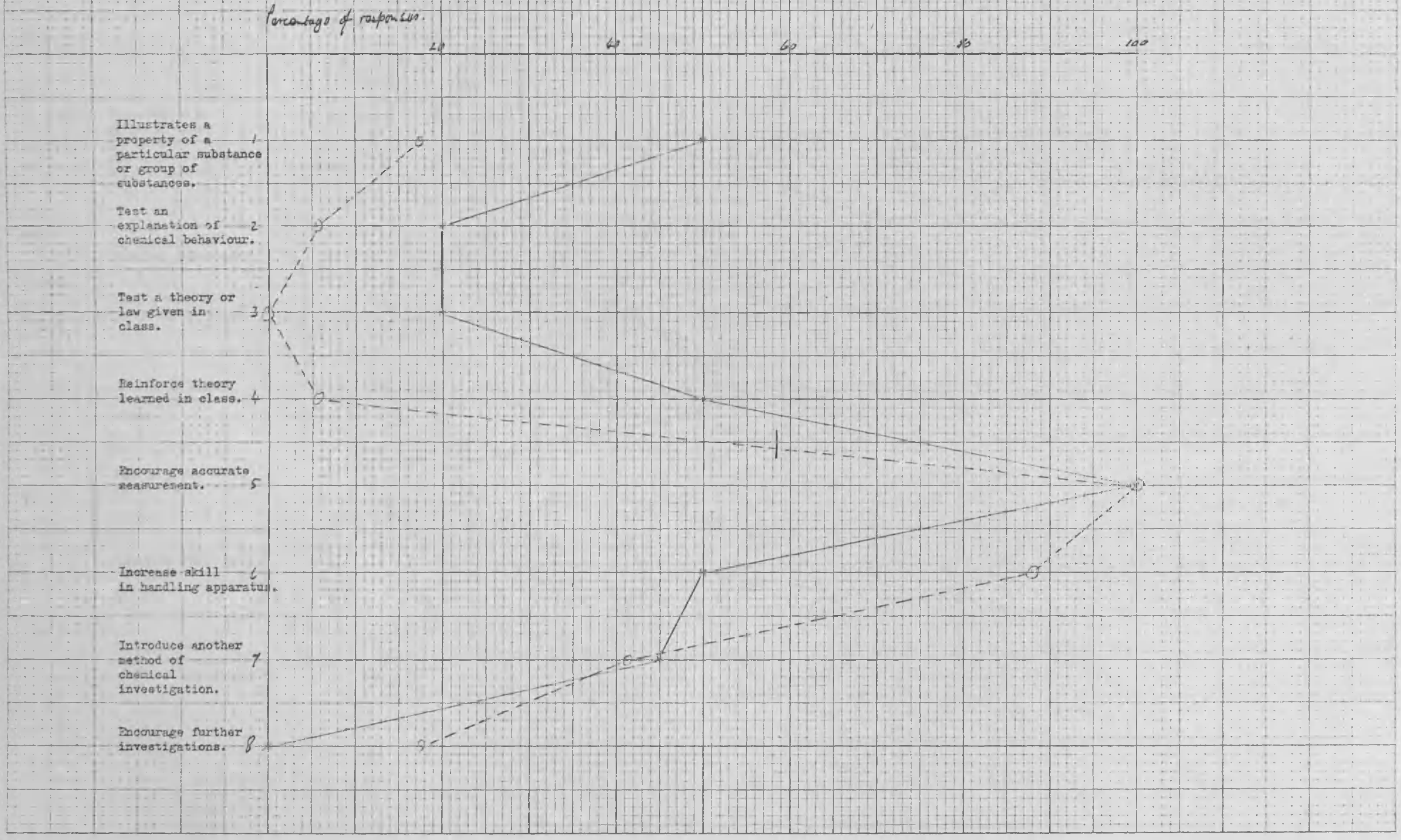
Ligands and colour change.



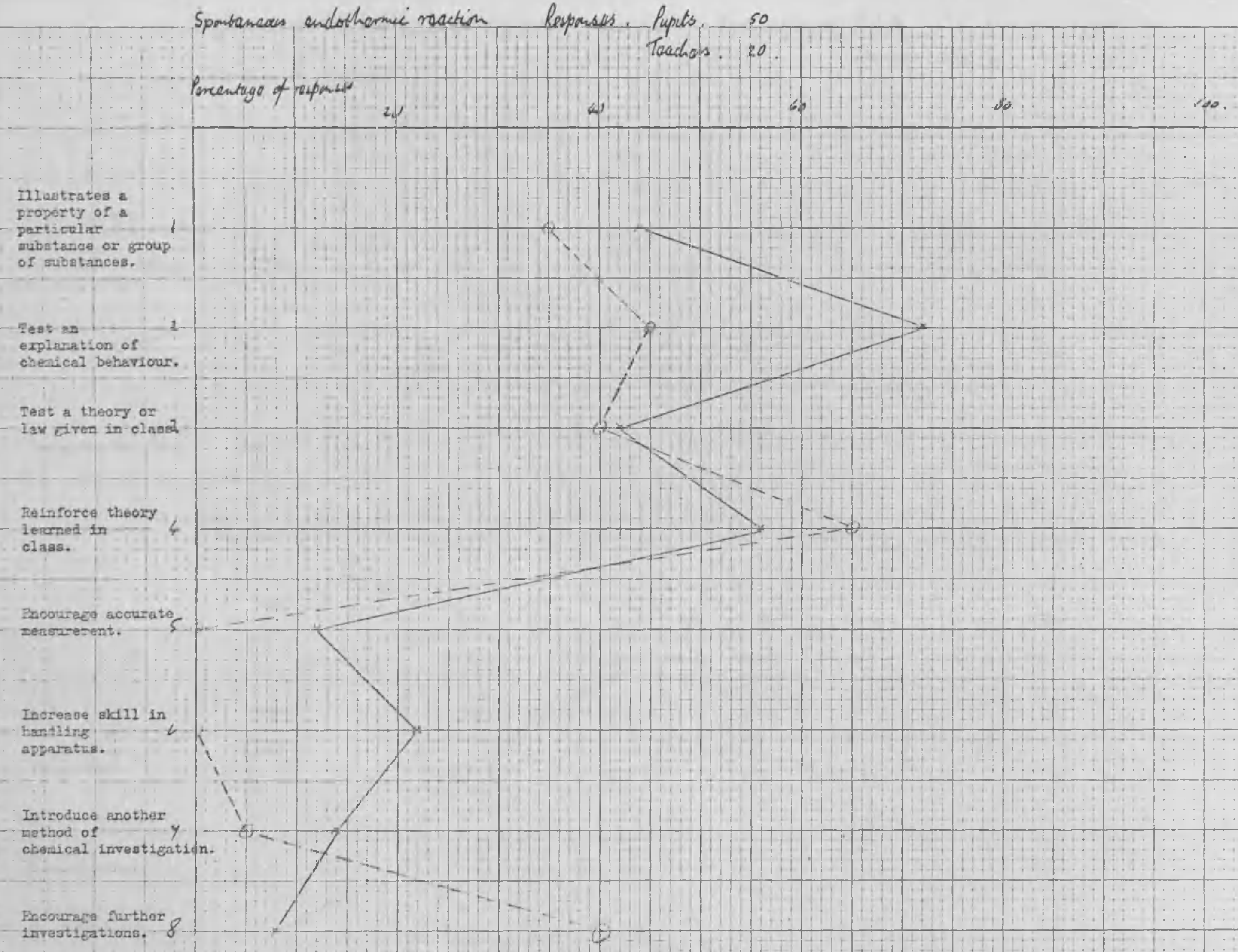
Paramagnetism of transition elements with simple Gouy balance.

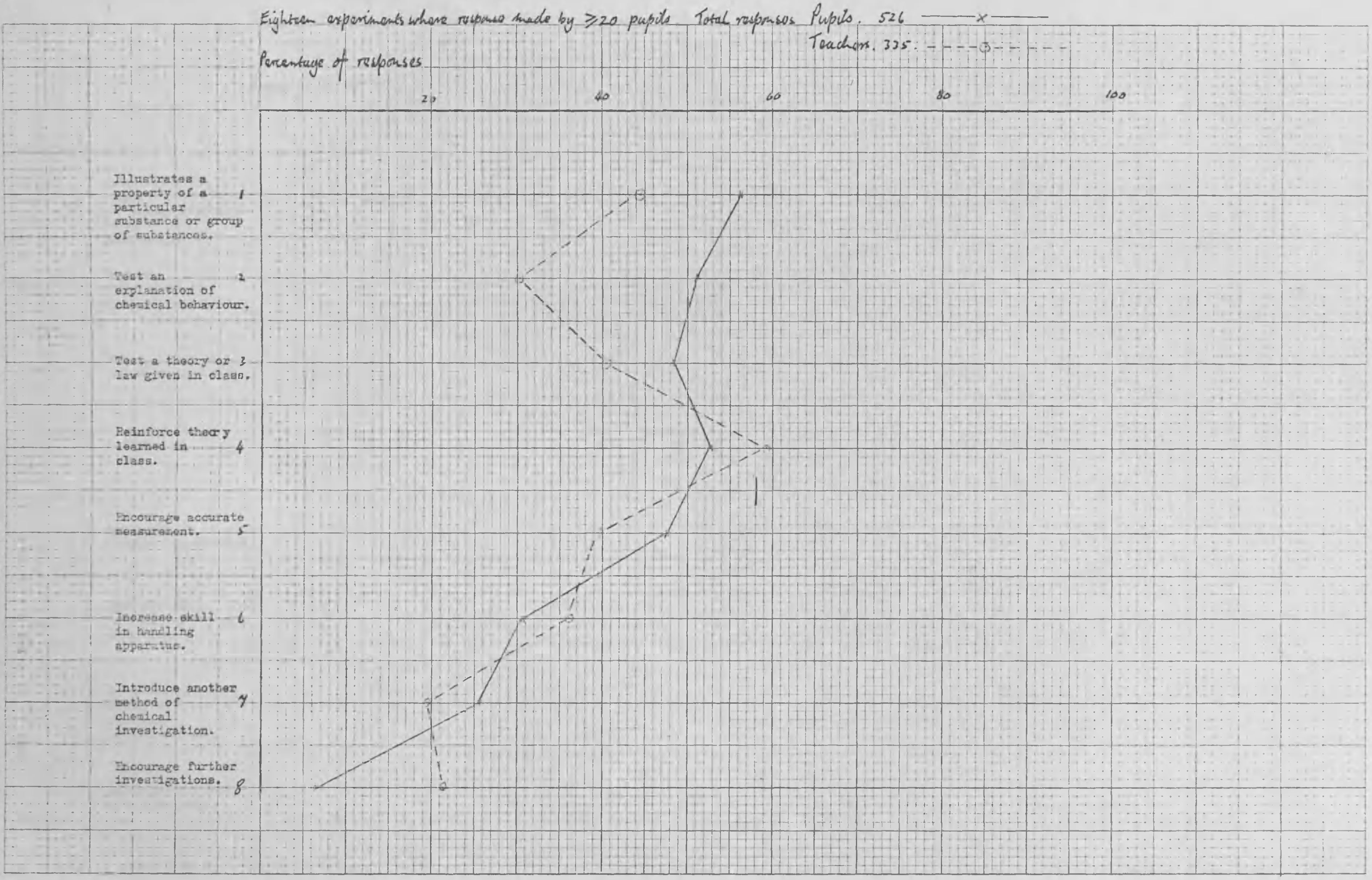


Ignition of $BaCl_2 2H_2O$ Responses. Pupils. 20
Teachers 17.

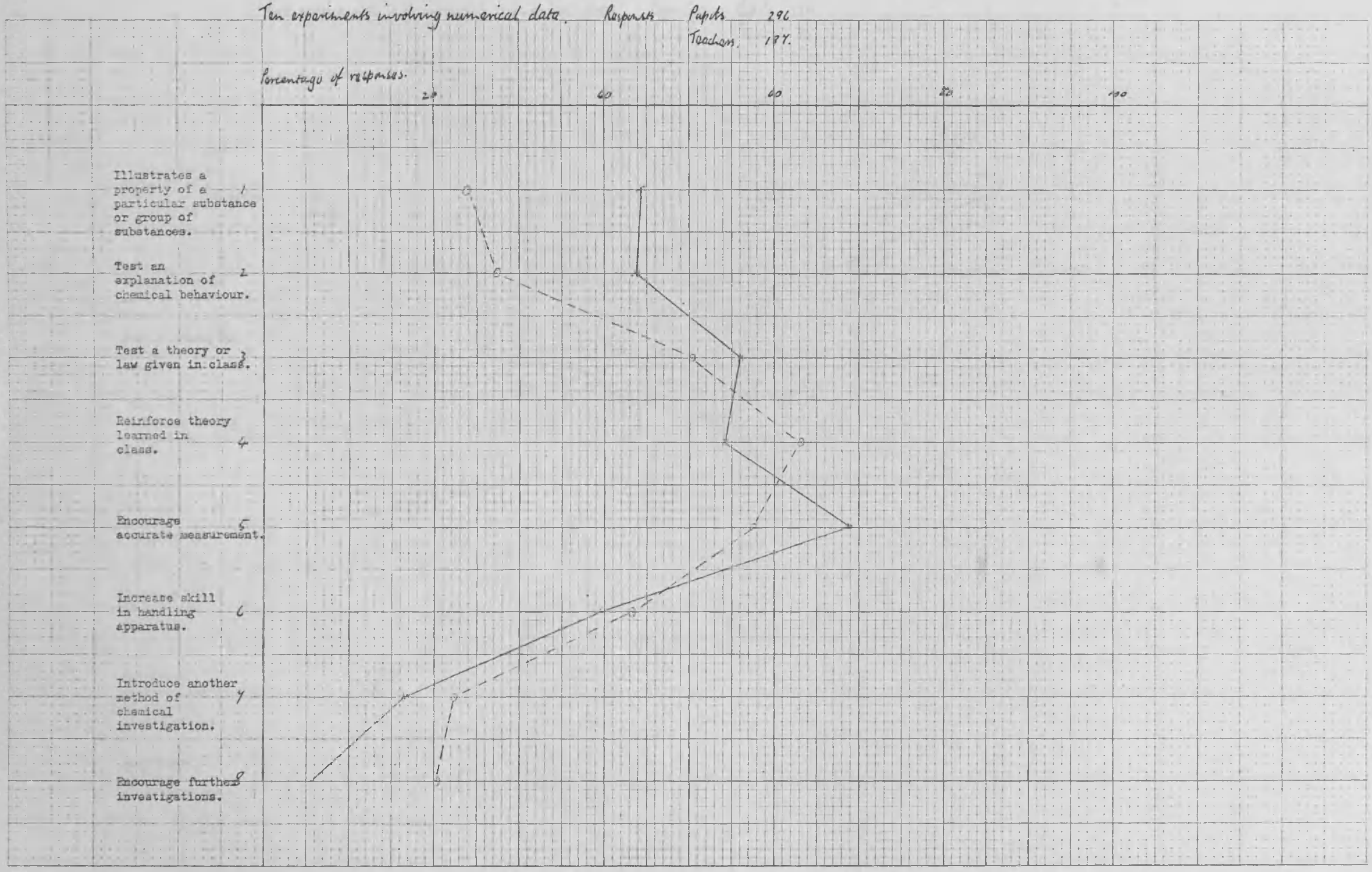


A3 - 24

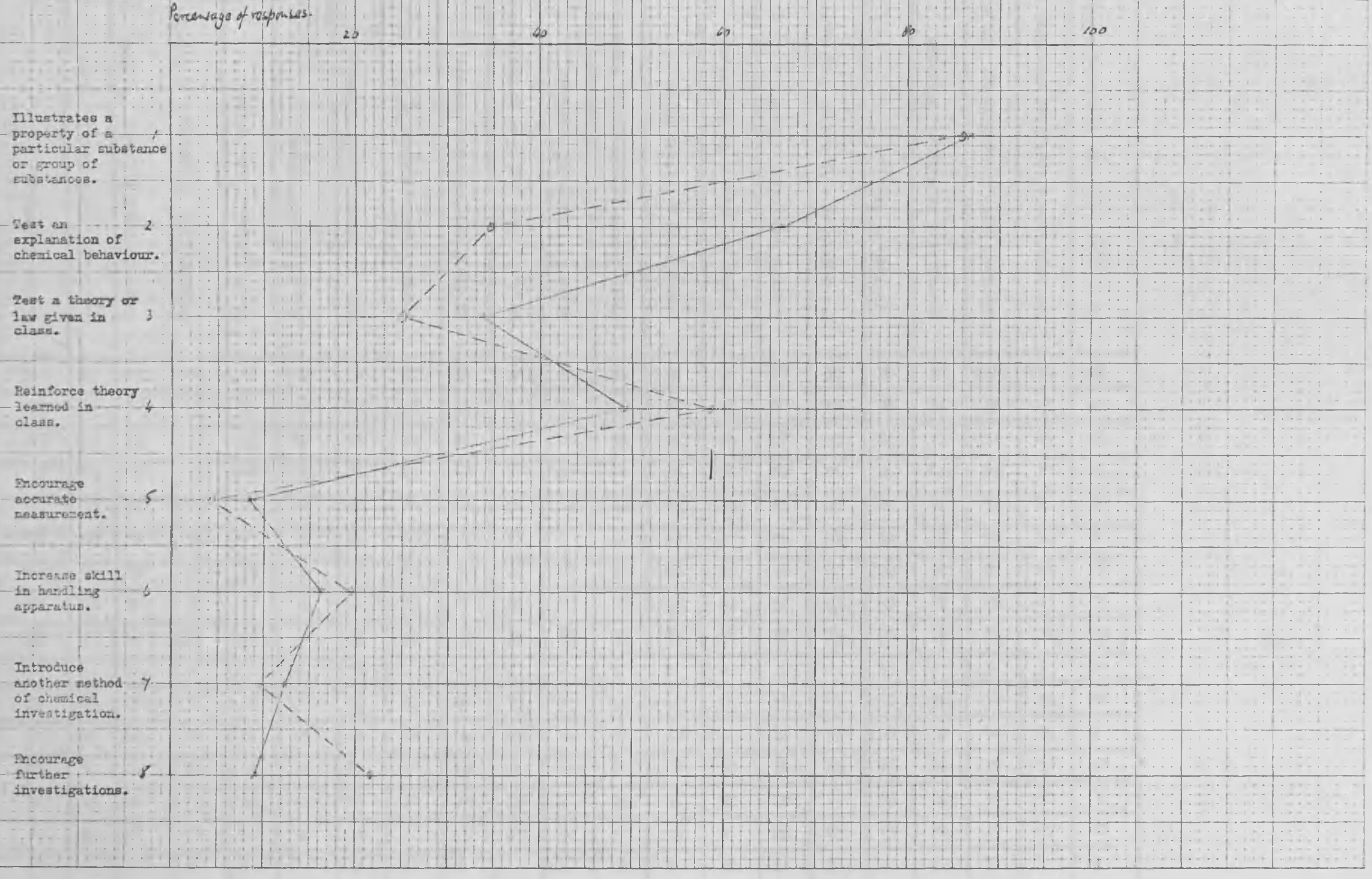

Spontaneous endothermic reaction
Responses. Pupils. 50
Teachers. 20.
Percentage of responses
20
40
60
80
100.
Illustrates a property of a particular substance or group of substances. 1
Test an explanation of chemical behaviour. 2
Test a theory or law given in class. 3
Reinforce theory learned in class. 4
Encourage accurate measurement. 5
Increase skill in handling apparatus. 6
Introduce another method of chemical investigation. 7
Encourage further investigations. 8



Eighteen experiments where response made by ≥20 pupils


Ten experiments involving numerical data.
Responses
Pupils 296
Teachers 177.
Percentage of responses.
20
40
60
80
100
Illustrates a property of a particular substance or group of substances. 1
Test an explanation of chemical behaviour. 2
Test a theory or law given in class. 3
Reinforce theory learned in class. 4
Encourage accurate measurement. 5
Increase skill in handling apparatus. 6
Introduce another method of chemical investigation. 7
Encourage further investigations. 8

Five experiments not involving numerical data   Responses   Pupils 130
Teachers 92.



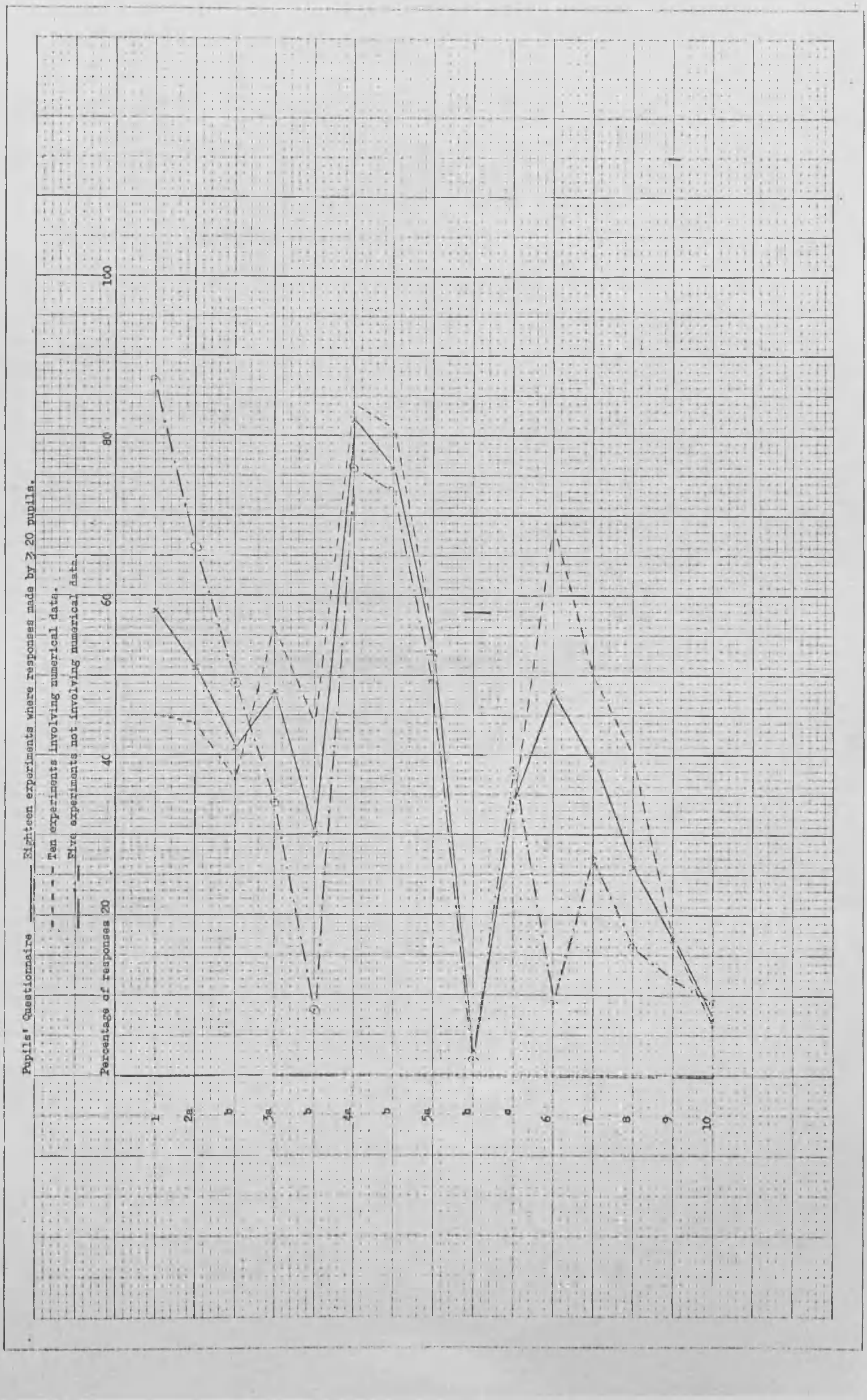
	Responses.	1	2a	b	3a	b	4a	b	5a	b	c	6	7	8	9	10
Iodine Coulometer.	31	36	55	32	13	10	77	77	58	-	29	71	81	32	39	10
Comparison of ΔG and ΔH Al/HCl	20	20	25	20	70	40	90	80	35	-	45	85	30	45	10	-
Comparison of ΔG and ΔH Cu/$AgNO_3$	19	37	68	68	58	58	84	74	63	5	26	63	26	26	21	-
Decomposition Temperature of $NaHCO_3$	33	61	33	33	49	42	91	91	46	-	36	76	64	49	24	3
Verification of Hess's Law	42	5	45	41	98	93	95	91	67	-	29	67	43	45	5	5
Partition coefficient	33	67	67	58	46	30	64	70	58	6	27	58	49	61	12	3
Heat of combustion of alcohols	34	77	18	15	62	44	97	94	38	12	35	79	68	59	21	15
Transition temperature Na_2SO_4 $10H_2O$	28	43	43	25	71	32	93	75	61	-	32	66	57	29	7	7
pH acid/base titration curves	34	56	47	47	29	35	74	77	68	-	24	59	21	21	15	9
Ka for a weak acid from pH measurement	22	41	41	27	64	27	68	68	36	5	55	73	46	18	14	-
Oxidation states of Vanadium	34	82	62	53	32	9	77	71	53	-	41	-	15	3	9	6
Prep. of Benzoic acid using Grignard reagent	22	100	59	46	18	-	77	77	59	5	32	23	59	36	5	14
Preparation of Tutton salts	26	92	58	35	42	15	69	62	23	8	65	15	23	15	19	8
Alkene and halogen in U.V. light	27	82	85	56	30	-	74	63	44	-	26	-	30	22	4	15
Ligands and colour change	21	81	67	57	48	14	86	52	71	-	19	10	14	10	29	5
Paramagnetism with simple Gouy balance	30	87	43	33	63	23	77	60	53	-	47	33	20	7	23	7
Ignition of $BaCl_2.2H_2O$	20	50	20	20	20	20	100	95	50	5	30	100	40	50	45	-
Spontaneous endothermic reaction	50	44	72	62	42	18	80	76	56	2	26	12	20	22	14	8
Eighteen expts. responses by 20 pupils	526	58	51	41	48	30	82	76	53	3	34	48	39	31	17	7
Ten experiments involving numerical data	296	45	44	37	56	44	84	81	54	3	33	69	50	40	17	6
Five experiments not involving numerical data	130	87	66	49	34	8	76	73	49	2	38	9	27	16	12	9

	Iodine Coulometer r = 0.57			Comparison of ΔG and ΔH Al/HCl r = 0.78			Comparison of ΔG and ΔH Cu/AgNO$_3$ r = 0.62			Decomposition Temperature at NaHCO$_3$ r = 0.39			Verification of Hess's Law r = 0.99			Partition Coefficient r = 0.53			Heat of Combustion of Alcohols. r = 0.50		
	P	T	Z	P	T	Z	P	T	Z	P	T	Z	P	T	Z	P	T	Z	P	T	Z
R	31	19		20	13		19	18		33	19		42	22		33	16		34	22	
1	36	32	0.28	20	23		37	17		61	16	3.20	5	5		67	25	2.78	77	55	1.72
2	55	42	0.09	25	23		68	22	2.87	33	16	1.35	45	36	0.68	67	31	2.34	18	23	
3	13	11		70	62	0.50	58	61	-0.2	49	68	-1.42	98	96	0.47	46	63	-1.13	62	18	3.11
4	58	37	1.46	35	69	-1.90	63	83	-1.34	46	68	-1.64	67	68	-0.12	58	63	-0.33	38	73	-2.52
5	71	58	0.95	85	77	0.58	63	67	-0.22	76	37	2.79	67	68	-0.12	58	44	0.92	79	50	2.30
6	32	47	-1.08	45	31	0.83	26	44	-1.13	49	53	-0.29	45	55	-0.72	61	38	1.54	59	41	1.31
7	39	79	-2.77	10	0		21	11		24	11		5	5		12	6		21	5	
8	10	21		0	31		0	17		3	16		5	14		3	19		17	23	

	Transition Temperature $Na_2SO_4 \cdot 10H_2O$ r = 0.81			pH Acid/base Titration Curves r = 0.22			Finding Ka for a weak acid from pH measurement r = 0.61			Oxidation states of Vanadium r = 0.88			Preparation of Benzoic Acid using a Grignard Reagent. r = 0.78			Preparation of Tutton Salts r = 0.84		
	P	T	Z	P	T	Z	P	T	Z	P	T	Z	P	T	Z	P	T	Z
R	28	16		34	22		22	20		34	20		22	20		26	16	
1	43	25	1.19	56	27	2.04	41	15	1.85	82	95	1.94	100	75	2.5	92	94	-0.19
2	43	25	1.19	47	27	1.52	41	25	1.06	62	35	1.91	59	20	2.61	58	25	2.04
3	71	69	0.18	29	18	0.93	64	50	0.91	32	10		18	10		42	38	0.31
4	61	44	1.06	68	50	1.35	36	75	-2.57	53	65	-0.86	59	55	0.27	23	38	1.00
5	64	44	1.32	59	59	-0.02	73	75	-0.16	0	10		23	10		15	0	
6	29	31	-0.19	21	55	-2.61	18	30		3	5		36	60	-1.57	15	13	
7	7	19		15	46	-2.57	14	35		9	0		5	10		19	6	
8	7	25		9	27		0	15		6	20		14	20		8	31	

	Reaction of an Alkene and a Halogen in U.V. Light r = 6.87			Ligands and Colour Change r = 0.91			Paramagnetism with simple Gouy Balance r = 0.85			Ignition of $BaCl_2 \cdot 2H_2O$ r = 0.73			Spontaneous Endothermic Reaction r = 0.69			Eighteen Experiments Response ⁄/ 20 pupils r = 0.79		
	P	T	Z	P	T	Z	P	T	Z	P	T	Z	P	T	Z	P	T	Z
R	27	17		21	19		30	19		20	17		50	20		526	335	
1	82	88	-0.59	81	79	0.16	87	79	0.73	50	18	2.02	44	35	0.69	56	45	3.31
2	85	47	2.72	67	47	1.21	43	47	-0.28	20	6		72	45	2.08	51	36	5.91
3	30	24		48	47	0.01	63	53	0.76	20	0		42	40	0.15	48	40	2.29
4	44	53	-0.57	71	79	-0.54	53	68	-1.08	50	6	2.94	56	65	-0.69	53	59	1.86
5	0	0		10	0		33	21	0.94	100	100	0	12	0		48	40	2.29
6	22	12		10	5		7	37		50	88	-2.45	22	0		31	36	1.61
7	4	16		29	16		23	26		45	41	0.09	14	5		17	20	1.11
8	15	12		5	26		7	21		0	18		8	40		7	21	6.30

	Ten experiments involving numerical data r = 0.79			Five Experiments not involving numerical data r = 0.89		
	P	T	Z	P	T	Z
R	296	187		130	92	
1	45	24	4.56	87	86	0.21
2	44	27	3.69	66	35	4.62
3	56	50	1.26	34	25	1.4
4	54	63	1.96	49	59	1.4
5	69	58	2.47	9	4	1.24
6	40	43	0.74	16	20	0.65
7	17	23	1.59	12	10	0.61
8	6	20	4.92	9	22	2.6


Pupils' Questionnaire —— Eighteen experiments where responses made by ≥ 20 pupils.
– – – Ten experiments involving numerical data.
—·— Five experiments not involving numerical data.
Percentage of responses
20
40
60
80
100
1
2a
b
3a
b
4a
b
5a
b
c
6
7
8
9
10

CHAPTER 4.

FURTHER INVESTIGATIONS.

FURTHER ENQUIRIES

In April 1972 questionnaires were sent to eighteen schools. Geographically the schools were distributed throughout Scotland from the Shetlands to the Lowlands industrial belt, and included selective and comprehensive schools. Questionnaires were sent to each teacher and each pupil involved in Sixth Year Studies Chemistry. Copies of the questionnaires are in the appendix pp. A4-1 to A4-9. The areas of enquiry were:-

Teachers' Questionnaire.

Availability of data books.

Integration of theory and practical work.

Difficulties found in allocating practical work.

Pupils' Questionnaire.

Use of data books.

Overall success of practical work in achieving objectives.

Number of experiments performed.

Preliminary enquiry to see if skills acquired through practical work could be assessed by pencil and paper tests.

Availability and use of Data Books.

It would be expected that in a sixth year course pupils would be using data books to check results of experiments, to predict possible reactions and as an aid in devising experiments in project work. This is implied in the syllabus for Sixth Year Studies Chemistry[4].

The availability of data books was established from the teachers' questionnaire. There were 26 responses to the question:-

Is each pupil provided with a data book?	Yes	62%
	No	38%
Is a data book provided in the laboratory?	Yes	100%

An indication of the use of the data books was obtained from the pupils' questionnaire. There were 126 responses to the question.

During your practical work you have consulted a data book:-

Frequently	Infrequently	Very Rarely
30%	48%	22%

It would seem that, at least in this group of teachers, a data book for each student is not considered a necessity and that although all students have access to data books in the laboratory they are certainly not extensively used.

If pupils are to acquire facility in using data books it may well be that some experiments will have to be constructed so that data books must be used for the completion of the experiments.

Integration of Theory and Practical Work.

In the April 1971 questionnaire (2 - 1) teachers were asked how they organised their practical work. Because of the small amount of practical work being done it was thought that the findings might not represent a very accurate picture. To test the validity of the findings a similar question was put in the 1972 questionnaire (A4 - 2) together with two supplementary questions.

The following is a comparison of the responses to the repeated question. The results are expressed as a percentage of the total responses in each year.

Practical work is organised as follows:-

	April 1971	April 1972
Total responses	126	27
Closely integrated with theory	68%	93%
Working through prescribed experiments in any order	24%	4%
Any other methods	9%	4%

Although the total of the responses in April 1972 is small the differences are statistically significant. The increase in the response to 'closely integrated with theory' could be due to the sample being biased. The 1971 responses were taken from all the schools. The 1972 responses were taken from co-operative schools with possibly a 'better' approach to practical work.

To try to establish what the teachers understood by 'closely integrated with theory' two supplementary questions were asked in 1972 with the following results:-

(a) Before starting the theory of a topic, pupils carry out an experiment which generates discussion (total responses 27)

	Percentage of responses	
Frequently	11%	
Infrequently	37%	
Rarely	37%	52%
Never	15%	

In this sense practical work is not really integrated with theory by a large number of schools when 52% rarely or never use experiments to generate discussion.

(b) During the teaching of a topic pupils carry out experiments to verify facts before proceeding with the rest of the topic (total responses 27).

	Percentage of responses
Frequently	63%
Infrequently	23%
Rarely	12%
Never	2%

In this sense practical work is more closely integrated with theory, but from the evidence of the answers to questions (a) and (b) it would appear that practical work is not as closely integrated with theory as the 93% of the responses in 1972 would indicate. If questions (a) and (b) had been asked in 1971 and the same relationship had prevailed it would seem that 67.5% of schools closely integrating practical with theory would be an optimistic figure.

It would appear that in something like 50% of schools practical work is not treated as an integral part of the course.

Difficulties found in Allocating Practical Work.

In the April 1972 questionnaire the teachers were asked to indicate where they had difficulty in allocating practical work in the following manner:-

'The main syllabus topics are listed below. Against each place a tick in the appropriate box to indicate how difficult you found it to allocate practical work to your pupils.

Where you have indicated difficult or very difficult insert in the right hand box (A) if the difficulty was due to lack of apparatus or (E.D.) if due to lack of experimental details.'

The results are summarised in the following table.

		Percentage of responses			Responses	
	Responses	Very Difficult	Difficult	Easy	Apparatus	Exp. Details
Thermodynamics	21		24%	76%	1	4
Volumetric work including redox	23		5%	95%	1	
Spectroscopy	23	39%	48%	13%	17	2
Atomic structure (orbitals)	20	50%	35%	15%	5	9
Molecular shape	20	30%	40%	30%	6	11
Organic	20	5%	15%	80%	1	3
Rest of Group IV	21		19%	81%		3
Solution chemistry	23		22%	78%	2	3
Transition elements	20		10%	90%	1	1

Because of the small sample size the above results may not be identical with results obtained from all of the teachers, but they do indicate where difficulties lie.

Some of the results are as expected. It is difficult to find experiments in the 'traditional' sense which can be used for spectroscopy, atomic structure and molecular shape. In the case of spectroscopy, lack of apparatus was overwhelmingly put forward as the cause of difficulty.

It could well be that teachers are looking for experiments that are too sophisticated requiring elaborate apparatus, whereas a simpler approach could provide what was required. With atomic structure and molecular shape all that could be attempted would be the use of 3cm wave apparatus and model building.

With thermodynamics, organic chemistry and group IV chemistry the problem would appear to be lack of knowledge of suitable experiments. The only direct solution would be the provision of details of tested experiments.

In the case of solution chemistry both lack of apparatus and details of experiments appear as problems. The non-available apparatus would probably be pH meters. This should be only a temporary problem as robust pH meters are available from several manufacturers in the £30 - £35 price range. Even without this there are suitable experiments which could be carried out using short range pH paper. Again this is a matter of transmitting knowledge of these experiments to teachers. As described in chapter 2, experiments have been devised and tested. It is hoped that details will be communicated to teachers in due course.

Number of Experiments Performed.

It was hoped to check on the reliability of the findings from the 1971 questionnaire on the average number of experiments being used by pupils (2 - 9). The pupils were asked 'How many experiments, excluding projects, have you carried out this year?'

The results were collated and compared with the findings from 1971.

No. of Experiments	Pupils' statement of No. of expts. carried out in 1972.		Teachers' estimate of avge. No. of expts. carried out per pupil 1971.		No. of expts. used per school in 1971 (2 - 7)	
Responses	127		118		130	
	No. of pupils	%	No. of schools	%	No. of schools	%
<10	0	0	14	12	10	8
11 - 15	3	2	21	18	18	13
16 - 20	19	15	27	23	22	17
21 - 25	24	19	15	13	29	22
26 - 30	51	40	21	18	28	22
31 - 35	9	7	10	9	20	15
36+	24	19	10	9	3	2

No conclusions could be drawn as too many assumptions would have to be made about sample sizes. The teachers' estimates in 1971 were from 118 teachers in 118 schools. The pupils' statements were from 130 pupils in 18 schools. We have to assume that the number of experiments carried out is either a function of the school or of the pupil. If we assume the former we have to compare a sample size of 18 with a sample size of 118. If we assume the latter, we then have to compare a sample size of 130 with an estimated sample size of the number of pupils taking Sixth Year Studies Chemistry in 1971, i.e. approximately 1100 (A2 - 43).

Conclusions based on these assumptions would not have enough weight to influence the validity or reliability of the 1971 findings.

Overall Success of Practical Work in Achieving Objectives.

To establish an overall picture of what the practical work had achieved the objectives, as on the questionnaire on individual experiments (A3 - 3) were listed. The pupils were asked to list wehther the course was very successful, successful or not successful in achieving these objectives.

Another objective was added which would not have been appropriate with individual experiments, i.e. increasing enjoyment of the study of chemistry.

Practical work on this occasion also includes the project so that by comparing these results with the pupils'reactions to the eighteen experiments, on which information had been collated, some of the influence of the project might be noted.

The total number of pupil responses was 127 and the results were expressed as percentages of the total responses.

	Very Successful	Successful	Not Successful
Illustrating properties of substances	14%	81%	7%
Testing explanations of chemical behaviour	21%	67%	12%
Testing theories or Laws given in class	20%	55%	26%
Reinforcing theories given in class	23%	59%	18%
Encouraging accurate measurement	37%	41%	24%
Increasing skills in handling apparatus	38%	48%	13%
Introducing a variety of methods of chemical investigation	27%	56%	15%
Encouraging further investigation	14%	43%	44%
Increasing enjoyment of the study of chemistry	32%	53%	15%

The percentage responses to 'very successful' and 'successful' were added and the totals were compared with the composite of positive returns on the eighteen experiments.

	Very successful + successful. (Includes project) 127 responses.	Eighteen Experiments. (Excludes project) 526 responses.
Illustrating properties of substances	95%	56%
Testing explanations of chemical behaviour	87%	51%
Testing theories or Laws given in class	75%	48%
Reinforcing theories given in class	82%	53%
Encouraging accurate measurement	78%	48%
Increasing skills in handling apparatus	87%	31%
Introducing a variety of methods of chemical investigation	83%	*17%
Encouraging further investigation	56%	7%
Increasing enjoyment of the study of chemistry	85%	

*The actual statement on the questionnaire was:-

'I learned a new method of chemical investigation during this experiment'.

The relative differences in the size of the percentage returns makes direct comparison difficult but trends can be seen when the data is presented graphically.


Percentage of Responses
x______x Sum of successful and very successful.
o - - - - o Composite of 18 experiments
100
80
60
40
20
1
2
3
4
5
6
7
8
9

For the first five objectives there is a good parallel 'fit' between the graphs and this reinforces the assumption made in chapter 3, 3 - 7 that the composite of the eighteen experiments gave a reasonable cross-section of the course practical work.

There is a divergence with objectives 6 (increasing skills in handling apparatus) and 7 (introducing a variety of methods of chemical investigation). It seems reasonable to believe that the increased response on these objectives is due to the influence of the project.

There does not however seem to be much difference in the comparative response to objective 8 (encouraging further investigation). Pupils still rate it low in achievement as an objective. It was rated not successful by 44% of the pupils in the April 1972 questionnaire. No further objective was rated not successful by greater than 27% of the pupils.

On a happier note 85% of the pupils thought carrying out practical work increased their enjoyment of the study of chemistry. Only three other objectives were rated higher. It is not possible to decide how much of this success is due to course practical work and how much to project, but the high response is encouraging.

Feasibility of Assessing Practical Skills by Pencil and Paper Test.

In was decided to take advantage of the fact that questionnaires were being sent to schools and make a preliminary investigation of the feasibility of assessing some of the practical skills by pencil and paper tests. At present practical work is assessed by a visiting examiner (usually another teacher of Sixth Year Studies Chemistry). This method is receiving some criticism because of difficulties of standardisation and expense. It would also appear from the findings in chapter 2 of the amount of practical work being done in schools, that some examiners may not be realistically assessing practical work.

A short objective type examination paper was constructed (A4-4 to A4-9) which included questions on:-

choice of apparatus;

choice of method;

interpretation of practical instructions;

interpretation of a graph;

choice of apparatus to carry out a task safely;

degree of accuracy expected in a calculation from experimental data.

These were arbitrarily chosen to reflect potential skills, i.e. they could not be fully attempted without some laboratory contact. When the tasks were returned they were marked and a rank order was produced for each school. The teachers were also asked to make out a rank order (without marks), and to return this along with the external examiner's rank order (again without marks).

Rank correlations were then made with the exam rank order, the teacher's rank order and the examiner's rank order.

Not all the returns from the schools were useable. There was evidence of collusion from two schools. Another school submitted flippant answers. Some schools had classes which were too small to obtain a meaningful rank order. Three schools did not return the questionnaires. Some schools did not include the examiner's rank order so only the teacher versus test rank order correlation has been included.

School	No. of pupils.	Teacher versus test rank order correlation.
1	13	+0.57
2	5	+0.05
3	4	+0.35
4	8	+0.14
5	5	+0.36
6	14	+0.43
7	14	+0.06
8	5	+0.6
9	9	+0.43

Where an examiner's rank order was available it was either the same as the teacher's or ~~very~~ similar to it confirming that the practical mark is an agreed one.

Very few of the teacher versus test rank order correlations were high, but they were all positive. This indicates that it might be worthwhile continuing the investigation with a better constructed test.

Discussion.

The findings of this chapter confirm to some extent the findings of chapter 3 and of previous surveys[15,16,17] in showing a difference between stated aims and actual achievements. Data books are provided in the laboratory and they are not used frequently by pupils. A large number of teachers say they closely integrate theory and practical work and yet their manner of using experiments does not confirm this statement.

The difficulties of allocating practical work agree with the findings of chapter 2, and indicate a lack of awareness among teachers as to what is required and what is possible with limited apparatus.

The pupils' rating of the overall success of the practical work in achieving the objectives listed in chapter 3 agree closely with the findings from chapter 3. What differences there are in the responses to 'increasing skill in handling apparatus' and 'introducing a variety of methods of chemical investigation' could readily be attributed to the effect of the project.

The fact that pupils rate 'increasing enjoyment of the study of chemistry' highly as an objective for practical work is justification for doing practical work. Anything which improves the motivation of pupils must receive consideration.

The results from the pencil and paper tests on practical skills are at least promising. If suitable test items can be devised this might help the standardisation of practical marks. Teachers observe their pupils throughout the year and therefore have more information than anyone else on which to establish an order of merit. Their orders of merit are, therefore, probably very reliable. What they cannot do is to place their pupils in the national scale. With the results of pencil and paper tests it should be possible to place the pupils on the national scale.

Some teachers might teach directly for the pencil and paper test without doing the practical work. As long as the practical work is not badly neglected there could still be some benefits. What was learned by the pupils would be used in later practical work.

University of Glasgow
Research in Chemical Education April 1972

Questionnaire for teachers of Sixth Year Studies, Chemistry.

Thank you for your assistance with this project. Your reply will contribute towards the future revision of the course.

It is important that pupils' and teachers' questionnaires from the same school can be related to each other. If you wish to retain annonymity the following procedure could be adopted. Enter a three digit number e.g. 592 as a code for the school. Enter the code on both the teachers' and pupils' questionnaires and omit the teacher's name etc. In any case all views will be expressed annonymously on publication.

Please tick the appropriate box(es) throughout and insert the required numbers.

NAME .... **SCHOOL** ....

1. Number of years teaching S.Y.S. ☐

2. Of the S.Y.S. syllabus you have taught
   all ☐
   part ☐

3. Number of periods allocating to S.Y.S. per week is ☐

   These periods are allocated as follows:-
   (e.g. 2 x 3 periods and 2 x 1).

4. For how many periods are the pupils in contact with a teacher? ☐

5. How is the time allocated between practical ☐
   (Exclude project work) and theory ☐

6. In your experience your total allocation is
   adequate ☐
   too much ☐
   too little ☐

7. Do you have a sixth year laboratory
   yes ☐
   no ☐

8. You regard your laboratory accommodation for S.Y.S. as
   generous ☐
   adequate ☐
   barely adequate ☐
   totally inadequate ☐

9. (a) Is each pupil provided with a data book?
   Yes ☐
   No ☐

(b) Is a data book available in the laboratory?
   Yes ☐
   No ☐

(c) The average number of experiments done by each pupil during the session (including project) is ☐

(d) Practical work is organised as follows.

Closely integrated with theory ☐

Working through prescribed experiments in any order ☐

Any other method (please specify) ☐

(e) Before starting the theory of a topic, pupils carry out an experiment which <u>generates</u> discussion
   Frequently ☐
   Infrequently ☐
   Rarely ☐
   Never ☐

(f) During the teaching of a topic pupils carry out experiments to <u>verify</u> facts before proceeding with the rest of the topic
   Frequently ☐
   Infrequently ☐
   Rarely ☐
   Never ☐

10. The main syllabus topics are listed below. Against each place a tick in the appropriate box to indicate how difficult you found it to allocate practical work to your pupils. Where you have indicated difficult or very difficult, insert in the extreme right hand box (A) if the difficulty was due to lack of apparatus or (E.D.) if due to lack of experimental details.

	Very Difficult	Difficult	Easy	
Thermodynamics				
Volumetric work (Including redox)				
Spectroscopy				
Atomic structure (orbitals)				
Molecular shape				
Organic				
Rest of Group IV				
Solution Chemistry				
Transition elements				

11 Please list your candidates in order of merit with regard to practical work (excluding project). Rank order only, without marks.

Your order of merit

Examiner's order of merit

University of Glasgow

Research in Chemical Education April 1972

Questionnaire for Pupils

NAME .... SCHOOL ....

This is a serious survey the results of which will be taken into account in shaping the future S.Y.S. course.

Please answer by ticking the appropriate box or inserting a number.

1. How many experiments, excluding projects, have you carried out this year

2. The following are some objectives in practical chemistry. Please indicate how successful you think your practical work was in achieving these objectives.

	Very Successful	Successful	Not Successful
Illustrating properties of substances			
Testing explanations of chemical behaviour			
Testing theories or laws given in class			
Reinforcing theories given in class			
Encouraging accurate measurement			
Increasing skills in handling apparatus			
Introducing a variety of methods of chemical investigation			
Encouraging further investigation			
Increasing enjoyment of the study of chemistry			

3. During your practical work have you consulted a data book

Frequently	Infrequently	Very rarely
☐	☐	☐

4. There now follows an exercise to determine if the skills learned in practical work can be assessed in a written test form. Please answer where appropriate. The results of this will not be taken down and held in evidence against you.

(a) Here is a set of instructions for an experiment. Read this carefully and then answer the questions.

"Rate of reaction of halogenation of acetone".

The reaction between a halogen and aqueous acetone is acid catalysed

$$I_2 + CH_3COCH_3 + H^+ \rightarrow CH_3COCH_2I + 2H^+ + I^-$$

The influence of iodine concentration on the rate of reaction can be studied if concentrations of acetone and acid catalyst remain constant during the reaction. This is achieved by using a large excess of acetone and acid in the initial reaction mixture.

Mix 25 ml. of M aqueous acetone with 25 ml. of M sulphuric acid, and note the time when 50 ml. of 0.02 M iodine is added with good shaking.

Withdraw a 10 ml. portion and stop the reaction in the sample by running it into 10 ml. of 0.5 M sodium bicarbonate. Note the precise time at which the sample is released into the bicarbonate.

Titrate the iodine present with 0.01 M sodium thiosulphate using a starch indicator (about 1 ml.) added near the end point.

Withdraw further 10 ml. samples about every seven minutes, and treat them similarly, always noting the precise time at which the sample is run into the sodium bicarbonate.

Plot a graph of titration against time.

(1) Which apparatus would you use to measure the 25 ml. portions of aqueous acetone?

Pipette ☐
Burette ☐
Measuring Cylinder ☐

(11) Which apparatus would you use to withdraw the 10 ml. portions?

(111) Withdrawing 10 ml. portions seems a clumsy method of determining how far the reaction has proceeded. Why is the progress of the reaction not followed by?

(a) Measuring change in pH with a pH meter.

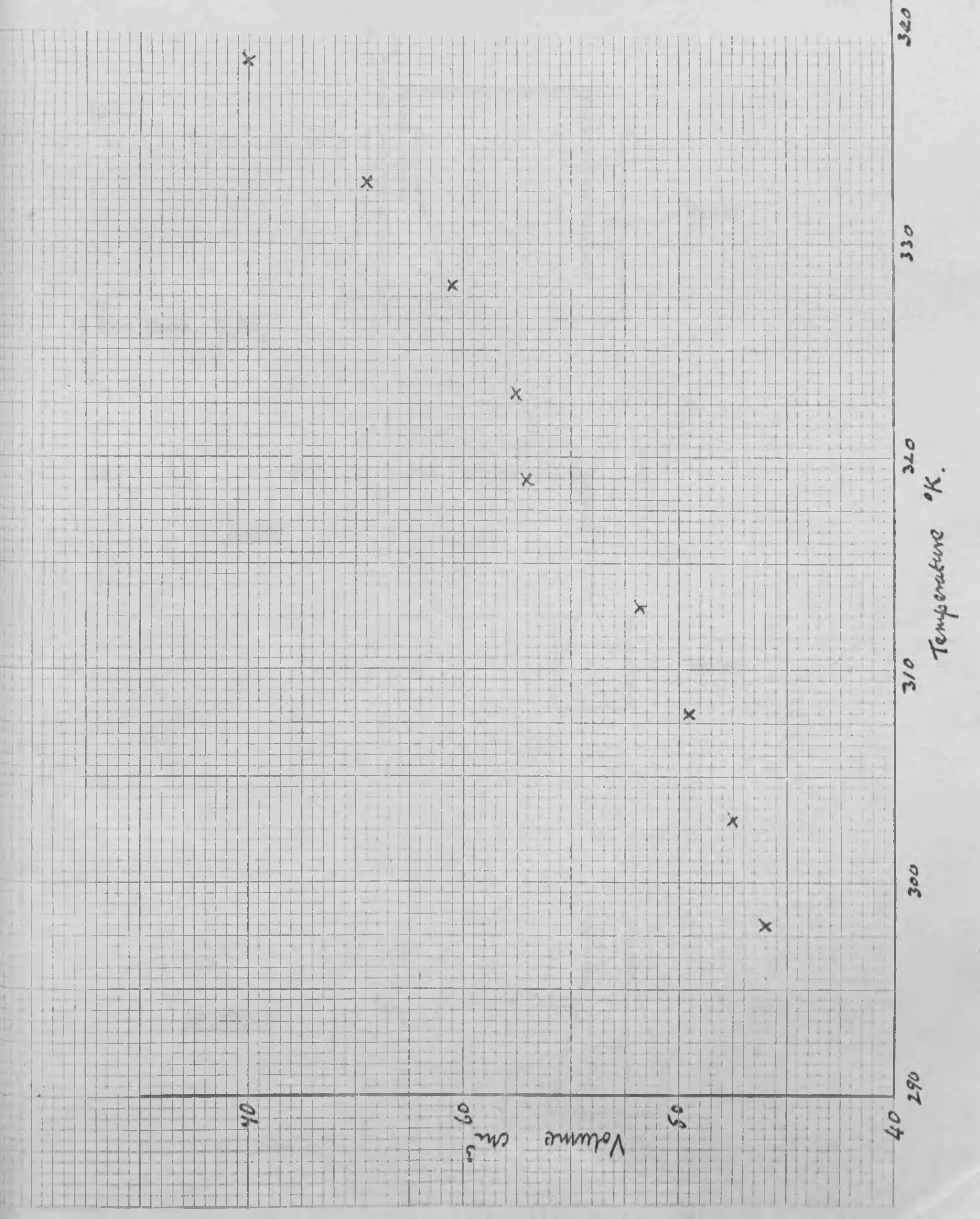
(b) Measuring change in conductivity.

(iV) Indicate with a tick which, if any, of the following solutions used in the experiment require to be made up accurately to volumetric analysis standards

M aqueous acetone ☐
M sulphuric acid ☐
0.02 M iodine ☐
0.5 M soldium bicarbonate ☐
0.01M sodium thiosulphate ☐

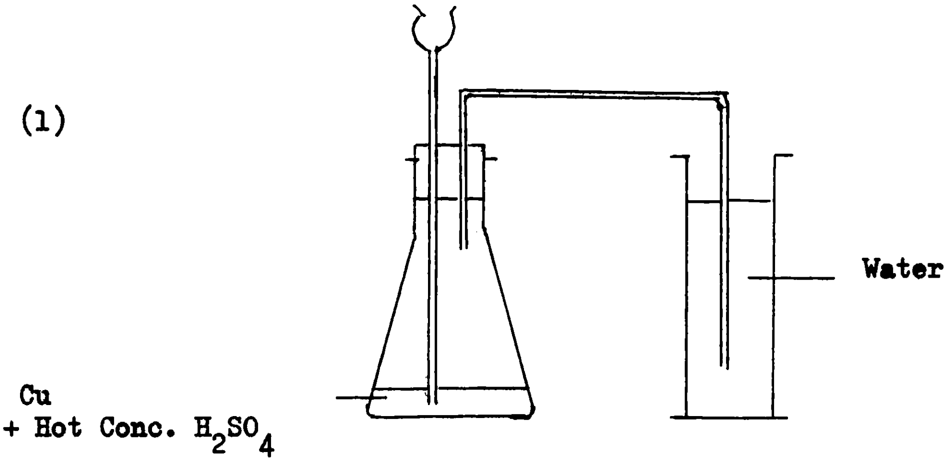
Questionnaire for Pupils

4 (b) Draw what you consider to be the most appropriate graph to fit the points on the accompanying sheet of graph paper.

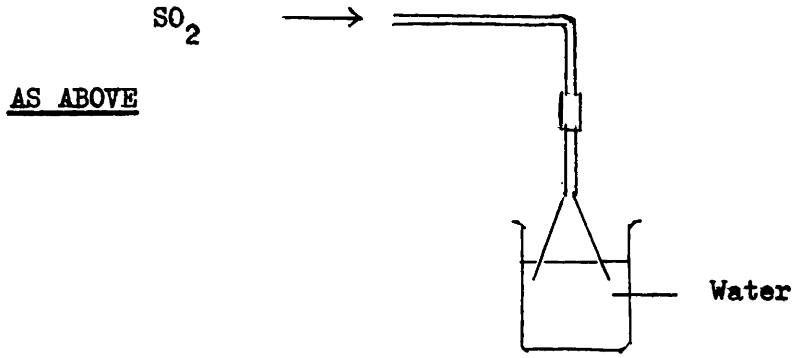


4 (c) Sulphur dioxide can be produced by the reaction between copper turnings and hot concentrated sulphuric acid. The diagram illustrates three possible methods of dissolving the sulphur dioxide in water. Indicate the advantages and disadvantages of each method.

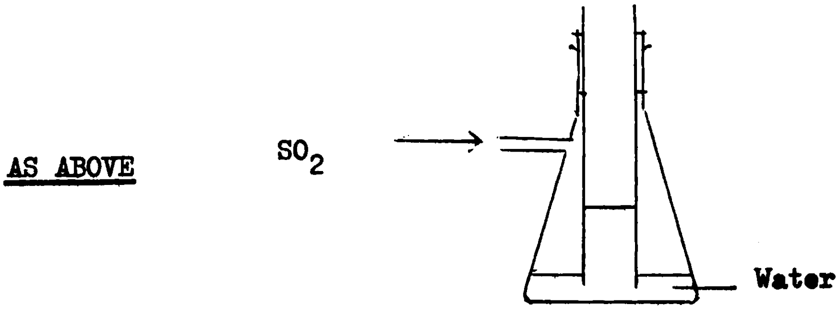
(1)



(2)



(3)



4 (d) In an experiment to find Avogadro's number the following measurements were taken:-

Vol. of H_2 liberated = 50 ml. (to nearest ml.)

Current = 0.50 amp (to nearest 0.05 amp)

Time = ,15 mins. (to nearest 10 secs.)

On the basis of these results alone, which value for Avogadro's number would be the <u>most</u> accurate that you would be justified in submitting as the answer? (no calculation is required)

A 6×10^{23} ☐

B 6.0×10^{23} ☐

C 6.2×10^{23} ☐

D 6.25×10^{23} ☐

CHAPTER 5.

CONCLUSIONS.

CONCLUSIONS AND FURTHER INVESTIGATIONS

From consideration of the examiners' reports on Sixth Year Studies Chemistry (2-2, 2-3) it appears that parts of the course are being badly taught. During this investigation it has been found that a considerable number of schools do only a small amount of practical work (2,7).

Both the poor teaching of sections of the course and the small amounts of practical work being done, occur within what the original planners considered to be an adequate allocation of time. In spite of this pupils who take Sixth Year Studies Chemistry subsequently perform better at university than their contemporaries.[3, 21] This is one advantage in taking Sixth Year Studies Chemistry, but the reasons for this advantage are difficult to locate.

The reasons could be a combination of the following:-

(a) Although the course planners set out not to anticipate the content of first year university courses, some of it must inevitably be included. This could give students who have taken Sixth Year Studies Chemistry an easier introduction to university work. If however too much of the first year university course is anticipated some students become lazy because they already know the work and do not have to study.

(b) Some topics in chemistry which used to be taught only at university level are introduced at a less sophisticated level in Sixth Year Studies Chemistry to small groups of pupils. This could be an advantage for further study.

(c) The extra year at school before entering university may by itself be an advantage as a time for maturing and consolidating previous knowledge. Motivation may also be better because the pupils have had time to think about their future. The report by D.E. Hoare[21], however indicates that the extra year is of benefit only if some chemistry is studied during that time.

(d) The project within Sixth Year Studies Chemistry may have increased maturity and self-reliance, and interested the pupils in further study of chemistry.

(e) From the poor teaching of some parts of the course and the small amount of practical work done in some schools, it could be inferred that a number of pupils were often left to their own devices. This in itself may make them more self reliant.

(f) Sixth Year Studies Chemistry also provides more scope for independent study both in project and course work than does the 'O' and 'H' grade courses. This should help the formation of study habits more appropriate to students than to pupils.

It may not be easily possible to find which of these is the most important, but general improvements can be made in the course. The Scottish Certificate of Education Edamination Board have already taken steps to ensure that a greater amount of practical work is done in Sixth Year Studies Chemistry by insisting on a minimum number of experiments being completed and written up before a mark for course practical work is given. Information on experiments suitable for schools may soon be circulated. Both these actions should help to improve the teaching of Sixth Year Studies Chemistry but they do not get down to the fundamental problem of what practical work does.

The general procedure for producing chemistry curricula seems to be to decide on the theory content and then to pick 'suitable' practical work. In view of the amount of time allocated for practical work in Sixth Year Studies Chemistry (5/8 of the 100 hours for course work) fairly arbitrary decisions as to what practical work should be included does not seem logical. Decisions have to be made as to just what are the objectives of practical work within a course.

Practical work then has to be selected which will achieve these objectives and that practical work has to be assessed to see if it does achieve the objectives.

The most important objectives of practical work in Sixth Year Studies Chemistry in the opinion of the pupils were:-

Illustrating a property of a particular substance or group of substances;

Testing an explanation of chemical behaviour;

Increasing enjoyment of the study of chemistry;

Testing a theory or Law given in class;

Reinforcing theory learned in class;

Encouraging accurate measurement;

Increasing skill in handling apparatus.

The teachers agreed with this with some differences in rank order.

Assessing the Achievement of Objectives of Practical Work.

This is probably best done by questionnaire. Apart from selecting appropriate questions the following are some of the difficulties involved in using questionnaires.

(a) For the results to be statistically significant a large number of responses from pupils in a variety of types and locations of schools must be obtained.

(b) To allow for questionnaires which are not returned, the number of pupils involved has to be greater than might otherwise be thought necessary. (In the investigation of objectives achieved by particular experiments, 841 questionnaires were returned by approximately 100 pupils. This meant that there were insufficient returns on some experiments for any meaningful conclusions to be drawn)

(c) Collating the information from large numbers of questionnaires is time consuming and tedious. Results could be obtained faster by:-

(i) Collecting the information directly on computer cards

or

(ii) Planning the questionnaire for easy transfer of the information to punched cards.

(d) The questionnaires have to be made as simple and easy to complete as possible to encourage more pupils to complete them.

Improving the Achievement of Objectives of Practical Work.

It is very unlikely that any experiment will achieve all its objectives, but a high degree of success should be looked for. It appears that for psychological reasons (3 - 20) and from pupils' statements (4 - 11) that there are objectives of practical work not tied to particular experiments, i.e. providing time for internal ordering of new knowledge and increasing enjoyment of the study of chemistry. There may then be a case for retaining some experiments even though they may not have a high rate of success in achieving specific objectives. There are however some actions which could be taken to improve the success rate in achieving objectives.

Experiments involving numerical data produced more differences between expected and achieved objectives than those not involving numerical data. This arose at least in part through the pupils seeing the behaviour of substances rather than the concepts. This can be avoided by using familiar substances to test theories or laws.

Where a particular unfamiliar substance must be used the pupils should be familiarised with its properties beforehand. It is possible that at 'O', 'H' and Sixth Year Studies levels an unnecessarily large variety of chemicals are being used to put across a limited number of ideas. It should be possible to devise a scheme of work which would cover the syllabus requirements of 'O', 'H' and Sixth Year Studies levels using a minimum number of different chemicals. With fewer varieties of trees the pupils might become more conscious of the wood.

The mathematics involved in the manipulation of numerical data is a constantly recurring problem in chemistry. This is at present under investigation by Miss K. Urquhart at Glasgow University.

Teachers tended to think they were integrating theory and practical work better than was shown to be the case (4 - 4).

If the practical work was an integral part of the course (i.e. experiments were used to arouse interest, to start discussions or to substantiate theories where appropriate throughout the course), more objectives might be achieved. This would also help in that the pupils would have a better idea of what the objectives are, and where the pupils know what the objectives are there is a much better chance of their being achieved (3 - 19).

As well as stating the objectives to the pupils before an experiment, structuring the instructions should help in achieving the objectives. With structuring ~~stureturing~~, the objectives could be made more obvious and the pupils would be less likely to be simply following a recipe. Structured practical instructions are being prepared (A2 - 47) and they could be tried out in a group of schools. Their effect on objective achievement could then be assessed against a control group or the present findings.

Part of the structuring of practical instructions could involve pupils having to consult data books to obtain sufficient information to carry out the experiment. This situation does not happen frequently at present (4 - 2)

Projects and Course Practical Work.

When the success of the total practical work, including project, in achieving the objectives listed (4 - 8) is compared with that of the course practical work, it is difficult to state whether the differences are significant or not. There appears to be a greater achievement of 'increasing skill in handling apparatus' and 'introducing another method of chemical investigation'. It is possible that there is also an improvement in 'encouraging further investigation'. If these differences are significant then they are probably due to the project.

It is very difficult to measure what a project actually does for pupils. All the assessments are subjective but there seems to be general agreement that most pupils become more mature and self-confident through carrying out projects. It could well be that all the objectives of practical work could be achieved solely through a project.

Areas of Weakness found in Examinations in Sixth Year Studies Chemistry

The areas of weakness shown up in the examiners' reports (2 - 2, 2 - 3) were principally in:-

Organic chemistry;
Anything involving calculations;
Transition elements;
Group IV chemistry;
Dynamic equilibrium;
Theory of buffer solutions.

The causes of most of these weaknesses are being investigated at Glasgow University. In the case of the transition elements a possible cause could be the initial study of a new topic at too sophisticated a level. This could be investigated by taking the transition element topic and teaching it in two different ways. The topic content could be divided into three different parts of increasing sophistication and taught with intervals of two or three weeks between.
The topic could also be taught in the normal fashion, i.e. in as many consecutive lessons as necessary to cover the topic. Comparison of the trial groups might then show if periods of internally structuring information helped the pupils in understanding difficult topics.

Assessment of Practical Skills by Pencil and Paper Tests.

The preliminary investigation into assessing practical skills through pencil and paper tests did not give conclusive results, but they are encouraging enought to warrant further investigation. If a set of objective test items was devised and pretested the results would be more meaningful. The conditions under which the testing was carried out would have to be clearly specified. During the investigation there was strong evidence of collusion in several cases. Those returns were of course not used in drawing any conclusions.
If this type of testing became widely used, there is the possibility that some of the skills would be taught outwith the practical work, e.g. significance of data, limits of accuracy, interpretation of data, safety precautions. This need not invalidate the method of testing. It is better to have thse skills taught by any means rather than not taught at all. In any case it is very likely that the pupils would utilise these skills in subsequent practical work.

Practical Work as a Means of Aiding the Enjoyment of the Study of Chemistry.

Pupils rated 'increasing the enjoyment of the study of chemistry' very highly as an achieved objective of practical work (4 - 11) This alone provides justification for the inclusion of practical work in a chemistry course, but should not give grounds for complacency. Routine laboratory work can induce boredom. A balance must be struck in making the experiments thought provoking enough to make them interesting but not so difficult that the pupils lose sight of the objectives. Again the use of structured practical instructions might help.

REFERENCES

1. 'Alternative Chemistry Syllabuses Ordinary and Higher Grades'. Scottish Education Department - Circular 512. October, 1962.
2. Proposed 'A' Grade Syllabus in Chemistry - Advisory Committee on Education, 1962.
3. Scottish Certificate of Education - Special Committee on Post-Higher Edamination - Memorandum to Subject Panels, EB/E/65/2, 1965.
4. 'Certificate of Sixth Year Studies - Chemistry Syllabus' Scottish Certificate of Education Examination Board, 1968.
5. 'Certificate of Sixth Year Studies Examination in Chemistry, 1970. Notes for guidance in Project Assessment'.
6. Sixth Year Studies Chemistry, 1971. Examiners Report. Scottish Certificate of Education Examination Board.
7. A.H. Johnstone and J. McGuire. National Curriculum Development Centre. Bulletin No. 1, 1972. P33 et seq.
8. 'Theory and Practical Work in School Science; Some International Comparisons of Achievement':- Publisher - John Wiley. Not yet published.
9. 'Certificate of Sixth Year Studies - Chemistry. Memorandum for the guidance of teachers planning this new course'. Scottish Education Department, 1969.
10. Scottish Certificate of Education Examination Board. Chemistry, Ordinary and Higher Grades. Syllabuses and notes.
11. Priest, R.H. School Science Review, 1972, 187 Vol. 54, 323.
12. Chemistry: An experimental ~~manual~~ science, laboratory manual. Editor L.E. Malm. Publisher W.H. Freeman.
13. 'Certificate of Sixth Year Studies - Chemistry Syllabus'. Scottish Certificate of Education Examination Board, 1973.
14. Kerr, J.F., Practical Work in School Science (Leicester University Press 1963).

15. Buckley, J.G. and Kempa, R.F., 'Practical work in sixth-form chemistry courses - an enquiry'. School Science Review, 1971, 182, 53, 24.

16. West, R.W., 'Objectives for practical work in school chemistry'. School Science Review, 1972, 186, 54, 148.

17. 'Nuffield Advanced Science - Chemistry'. Penguin 1970.

18. 'Nuffield Advanced Science - Physical Science'. Penguin 1973.

19. McCallum, M.A. 'Student Views of Practical Work - The result of a project on Student attitudes'. Paper presented at Symposium on the Role and Nature of Experimental Work in Chemistry Courses. Nottingham, September, 1972.

20. Russell, R.W. Former Professor of Clinical Neurology, Oxford. 'Learning, that cobweb of the brain'. The Times, June 2nd, 1971.

21. Hoare, D.E. 'Performance of Sixth Year Study Students (Chemistry) at University'. A Report. April, 1973.

ACKNOWLEDGEMENTS

No investigation of this type can take place without the co-operation of a large number of people too numerous to mention by name, but whose assistance I should like to acknowledge. Among these are the pupils and teachers who completed questionnaires and the headmasters and directors of education who gave permission for the teachers and pupils to be approached.

I wish to acknowledge the constructive criticisms offered by Professor D.W.A. Sharp and the guidance and encouragement given by Dr. A.H. Johnstone.

Thanks are also due to Dr. J.G. Sime for assistance with computer analysis, and to Miss K.D. Urquhart for assistance with statistical analysis.

I should also like to thank Dr. A. McAuley and Dr. G. Webb who made the periods of course work at Glasgow University interesting, profitable and enjoyable.

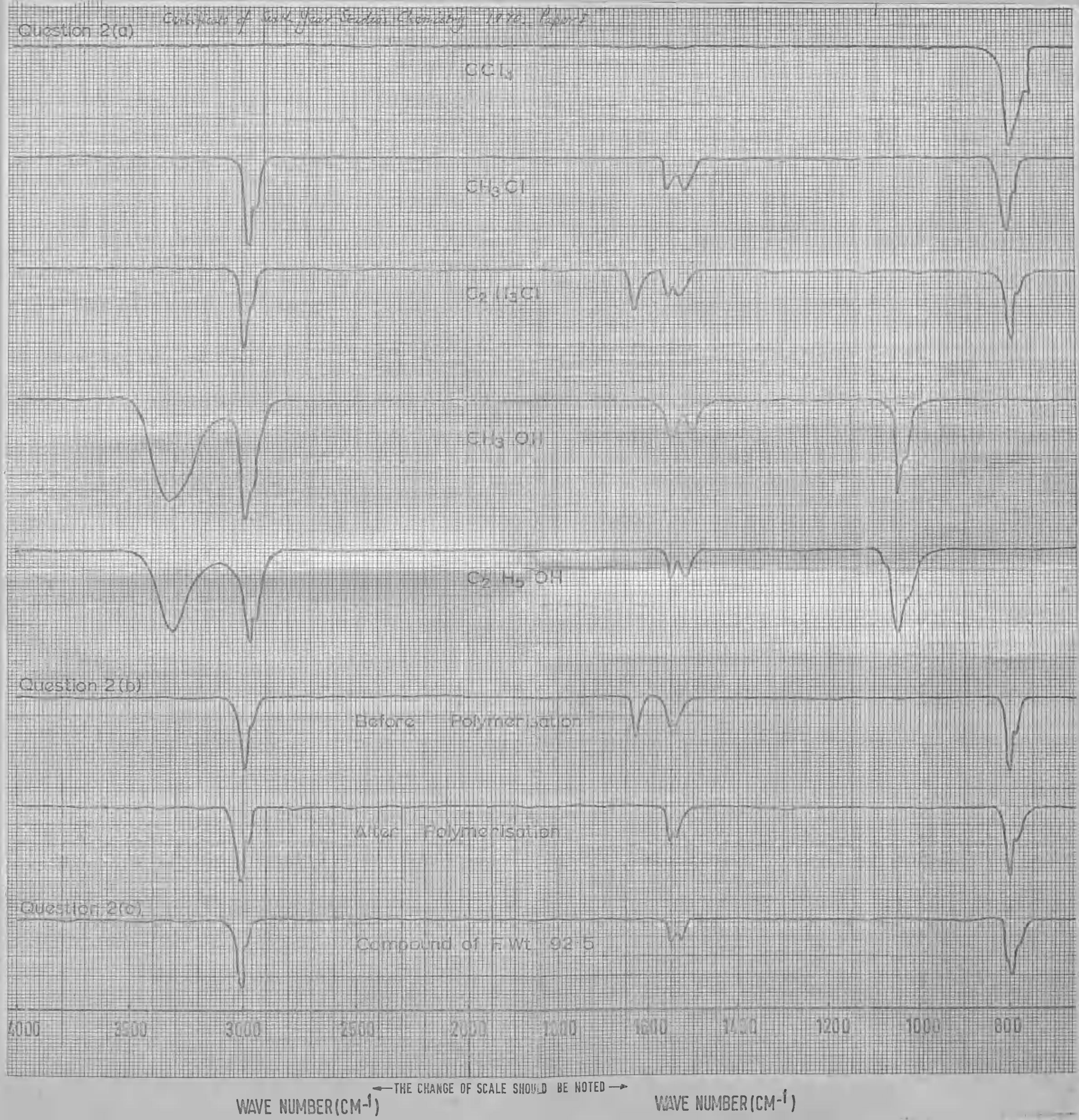
I thank the Scottish Certificate of Education Examination Board for their permission to reproduce examination papers.

The assessment of experiments by the 1971 - 1972 class of post-graduate chemists at Notre Dame College of Education must also be acknowledged. They were very thorough and their comments were very useful.

I wish to thank the Governors of Notre Dame College of Education for their support, and the Principal of Notre Dame College of Education for permission to use College facilities during this research.

J. McGuire.
24th April, 1973.

Certificate of Sixth Year Studies Chemistry 1970. Paper I



University of Glasgow Research in Chemical Education

Sixth Year Studies in Chemistry

After you have completed each experiment, please fill in a copy of this form and give it to your class teacher. The object of this is to provide a clear picture of how useful and successful the practical work of S.Y.S. is. On the basis of your comments, future modifications will be made.

Please fill in the form independently and frankly.

NAME: SCHOOL:

TITLE OF EXPERIMENT:

Please indicate with a tick where you think the question refers to the experiment you have just completed.

1. This experiment illustrated a property of a particular substance or group of substances ☐

2.(a) An explanation of chemical behaviour was tested in this experiment. ☐

(b) From the results of the experiment I was convinced that the explanation was correct. ☐

3.(a) This experiment tested a theory or Law given in class ☐

(b) The numerical results obtained from this experiment convinced me of the truth of the Law. ☐

4.(a) I was aware of the aim of the experiment throughout the experiment. ☐

(b) I was aware of the reason for carrying out each stage of the experiment during the experiment. ☐

5. Carrying out this experiment

(a) Helped me to understand the theory ☐

(b) Confused me. ☐

(c) Made no difference to my understanding. ☐

6. This experiment made me aware of the need for accurate measurement. ☐

7. During the experiment other problems became apparent. ☐

8. Carrying out this experiment increased my skill in handling apparatus. ☐

9. I learned a new method of chemical investigation during this experiment. ☐

10. Carrying out this experiment interested me in making further investigations. ☐

Thank you.

University of Glasgow Research in Chemical Education

Sixth Year Studies in Chemistry

Please indicate with a tick the statements which you think apply to each experiment completed by your pupils

NAME: SCHOOL:

TITLE OF EXPERIMENT:

This experiment was intended to

1. Illustrate a property of a particular substance or group of substances. ☐
2. Test an explanation of chemical behaviour. ☐
3. Test a theory or Law given in class ☐
4. Reinforce theory learned in class ☐
5. Encourage accurate measurement. ☐
6. Increase skill in handling apparatus. ☐
7. Introduce another method of chemical investigation. ☐
8. Encourage further investigations. ☐

Thank you.