

# CHEMISTRY IN NEW ZEALAND

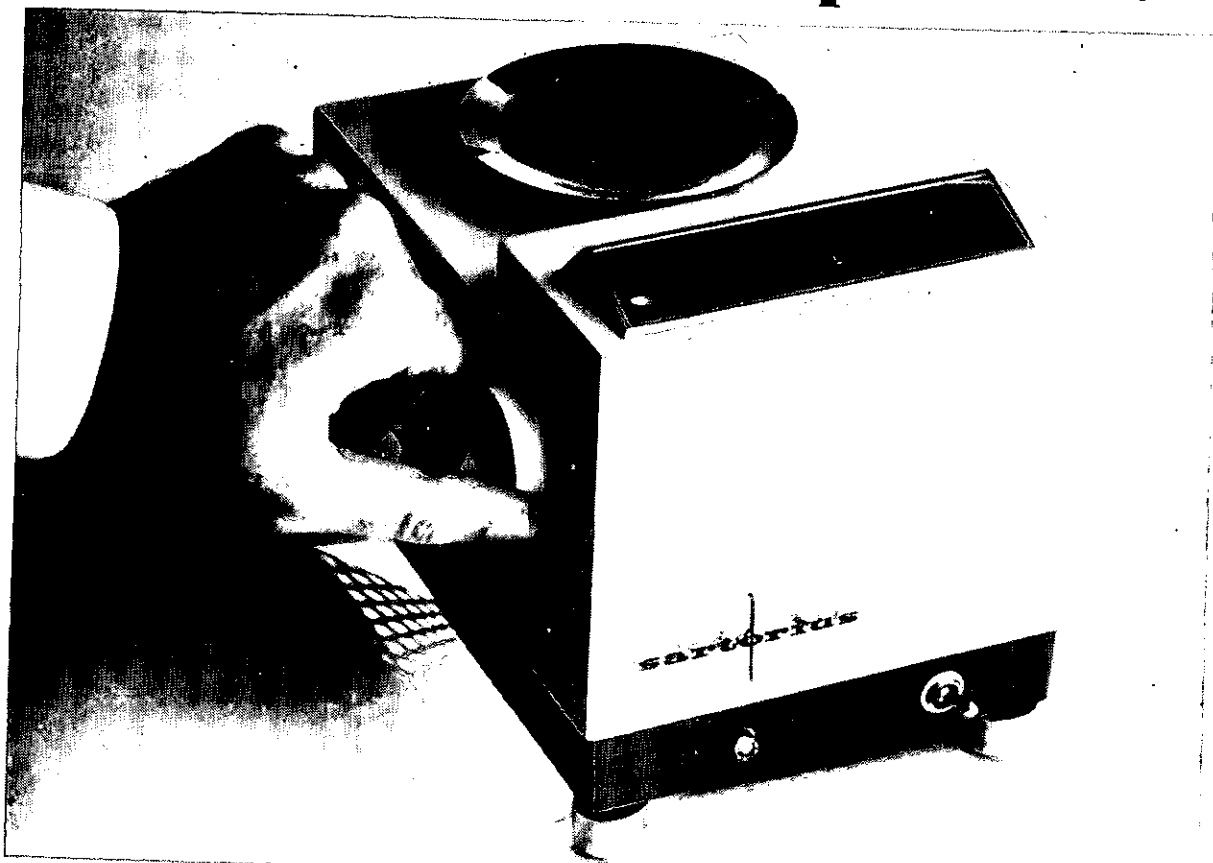
JOURNAL OF  
THE NEW ZEALAND  
INSTITUTE  
OF CHEMISTRY



CONFERENCE ISSUE

Vol. 34, No. 4, August, 1970

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# CHEMISTRY IN NEW ZEALAND

## Journal of The New Zealand Institute of Chemistry

Vol. 34, No. 4. August 1970

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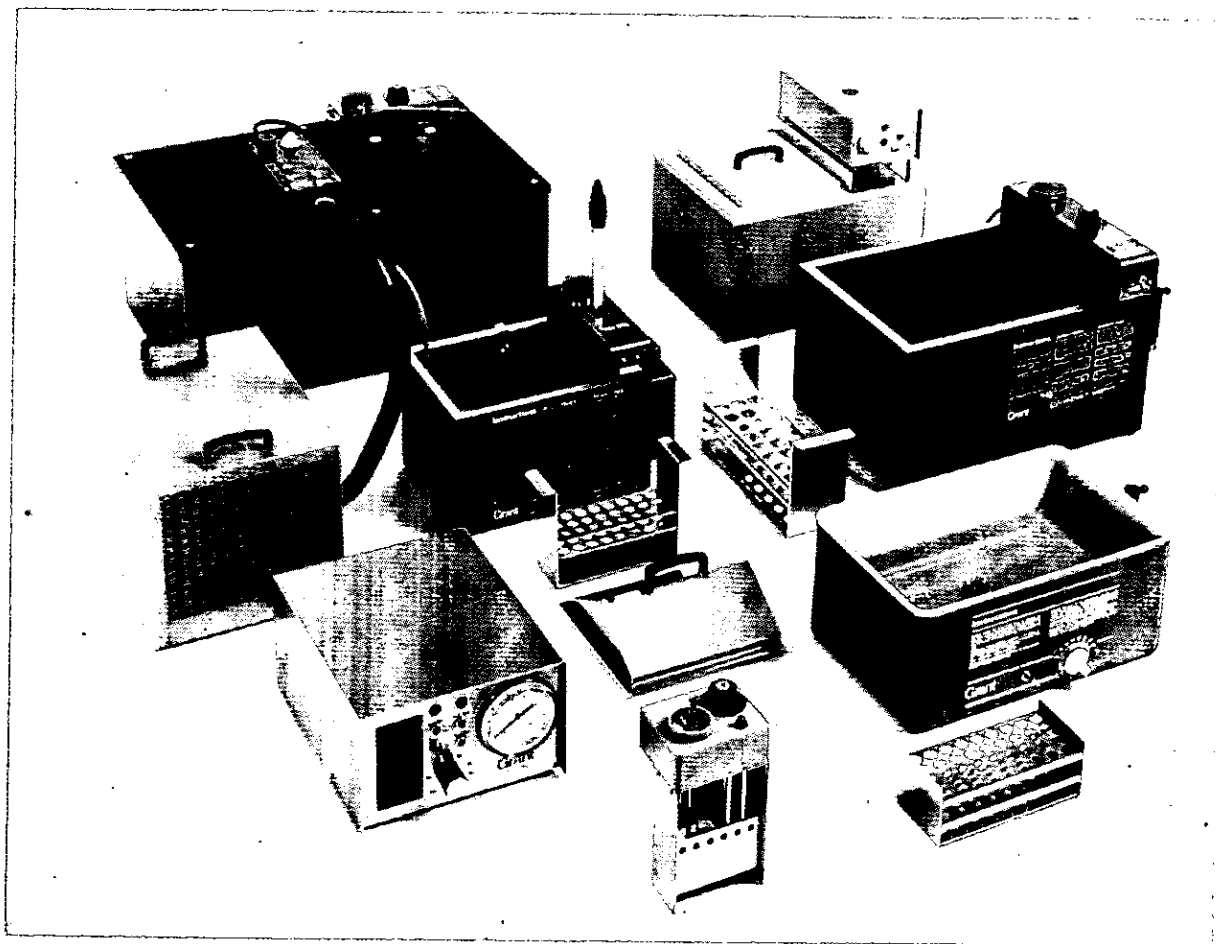
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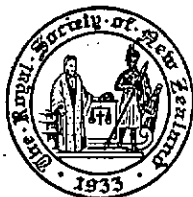
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# Newsletter

THE ROYAL SOCIETY OF NEW ZEALAND

No. 9 AUTUMN 1970

## NEW FELLOWS OF THE ROYAL SOCIETY

Mr. B. G. Barratt-Boyes  
Dr. L. Corkill  
Professor P. B. D. de la Mare  
Dr. M. P. Hartshorn  
Professor B. G. Wybourne.

## OFFICERS ELECTED MAY 1970

*President:* Dr. R. W. Willett  
*Honorary Treasurer:* Professor I. J. Cunningham  
*International Secretary:* Professor G. A. Knox  
*Home Secretary:* Dr. N. H. Taylor.

## ROYAL SOCIETY AWARDS

Hector Medal: Professor B. G. Wybourne, of the University of Canterbury, for his contributions to knowledge in the field of atomic physics.  
E. R. Cooper Medal: Mr. C. R. James, of Chemistry Division D.S.I.R., for his paper "Second Generation Geothermal Power", N.Z. Eng. 23 (6) 1968.

## MEMBER BODIES COMMITTEE APPOINTMENTS

*Vice-Chairman:* Dr. F. B. Shorland  
*Member Bodies' Councillors:* Dr. R. B. M. Miller, Mr. C. Toebes.

## QUEEN HONOURS A FELLOW OF THE ROYAL SOCIETY

Professor J. C. Beaglehole, F.R.S.N.Z., received the Order of Merit from the Queen during her recent visit to New Zealand.

## **SECONDARY SCHOOL AWARDS**

Medal: David John Brooks (Waipu District High School)—Project: "An investigation into the possibility of nitrogen fixation in *Coprosma*". Vacation work in Plant Diseases Division, D.S.I.R. Now studying for B.Sc. at Auckland. Member Body: Auckland Institute.

Certificate: Robert Jim Knappstein (Rutherford High School)—Project: "A study of esterification using acid as a catalyst". Vacation work in Chemistry Department, Victoria University. Now studying for B.Sc. at Auckland. Member Body: N.Z. Institute of Chemistry.

## **ASSOCIATE EDITORS NEEDED FOR TRANSACTIONS**

Mr. B. G. Hamlin has asked to be relieved of his duties through pressure of other work, and Professor W. C. Clark will be going overseas on sabbatical leave later this year. This means there are vacancies in both the Botanical and Zoological fields. Anyone willing to assist please contact the Editor of the Transactions, P.O. Box 196, Wellington.

## **COOK BICENTENARY EXPEDITION**

A general account and the scientific reports of the thirteen projects undertaken on this expedition will be published as Bulletin 8 of the Royal Society of New Zealand.

## **PROFESSOR N. L. EDSON**

We record with regret the death of Professor N. L. Edson, F.R.S.N.Z., on 12 May 1970 at Auckland. Professor Edson recently retired from the Chair of Biochemistry at Otago University.

## **CONFERENCES**

New Zealand Psychological Society: Conference at the University of Otago, Dunedin, 14-18 August 1970.

New Zealand Ecological Society: Conference at Lincoln, 27-29 August 1970.

New Zealand Weed and Pest Control Society at Palmerston North, 11-13 August 1970.

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## NEW ZEALAND FERTILISER MANUFACTURERS' RESEARCH ASSOCIATION (INC.)

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### APPOINTMENTS FOR GRADUATES IN CHEMISTRY

The New Zealand Fertiliser Manufacturers' Research Association wishes to add 2 chemists under 30 years of age to its present team of 9 graduate and 10 technical staff. Consideration will be given to applicants, female as well as male, who expect to complete their degree studies in 1970.

The New Zealand Fertiliser Manufacturers' Research Association has well equipped laboratories at Otara, South Auckland and serves the 6 companies which in 12 works throughout the country currently manufacture about 2 million tons of fertiliser per annum. The industry is growing and its Research Association's annual expenditure is now approximately \$120,000 with increases of 10% p.a. budgeted for the 1970/72 triennium.

The work of the appointees will initially be in analytical chemistry using X-ray fluorescence and diffraction and atomic absorption and other instrumental techniques as well as classical chemical methods. The need is for outward-looking graduates interested in, and with capacity for, co-operation with staff at Otara and in the fertiliser companies and in government and university laboratories. The work involves projects on raw materials, manufacturing processes and agronomic research. An excellent library with interloan privileges is maintained.

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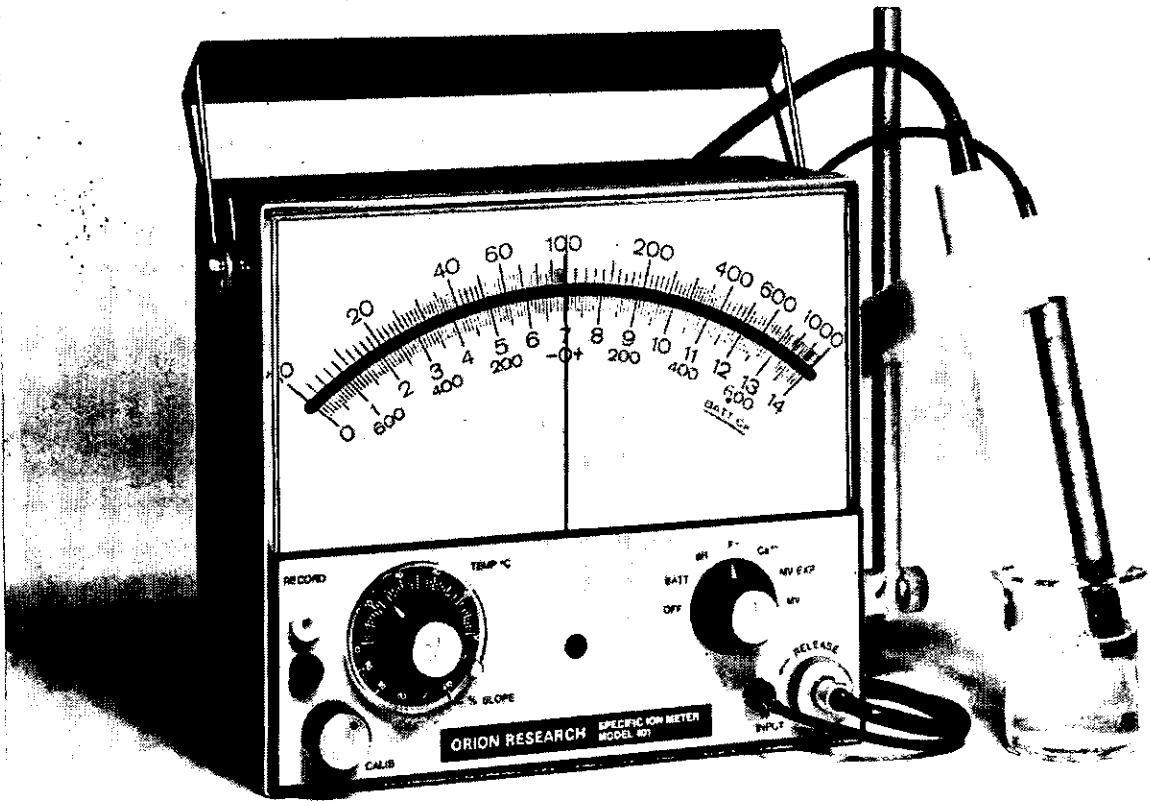
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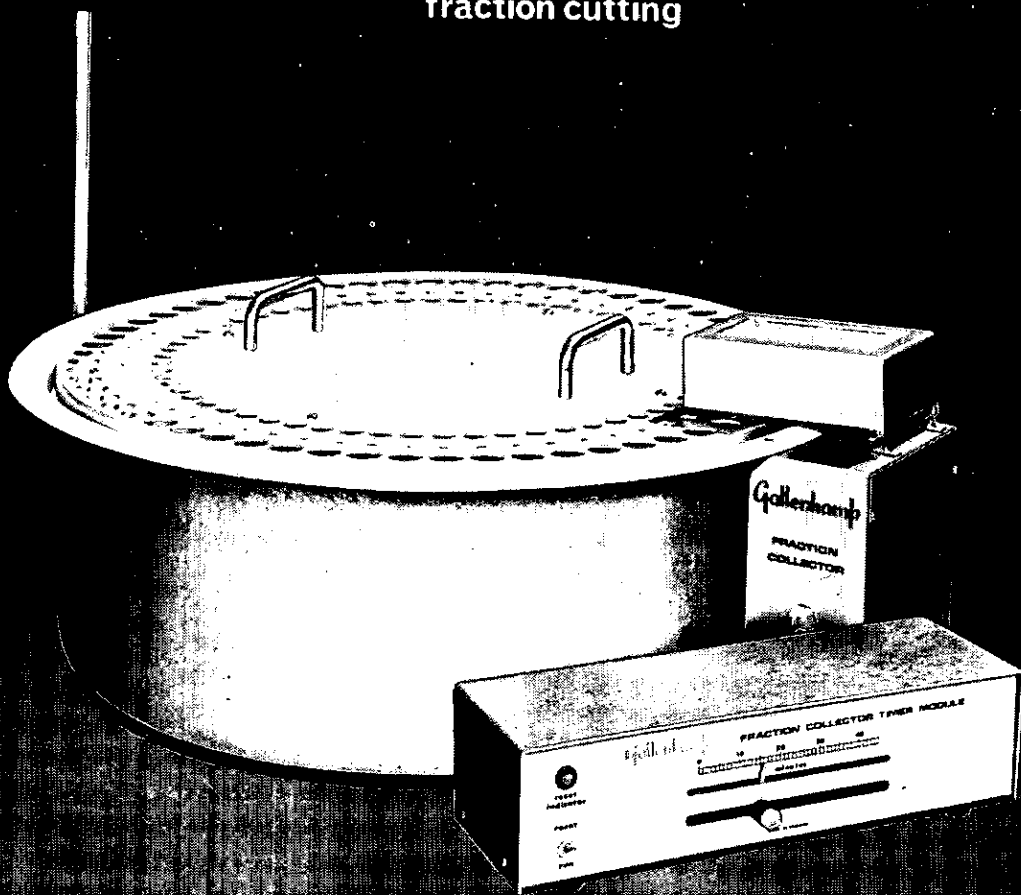
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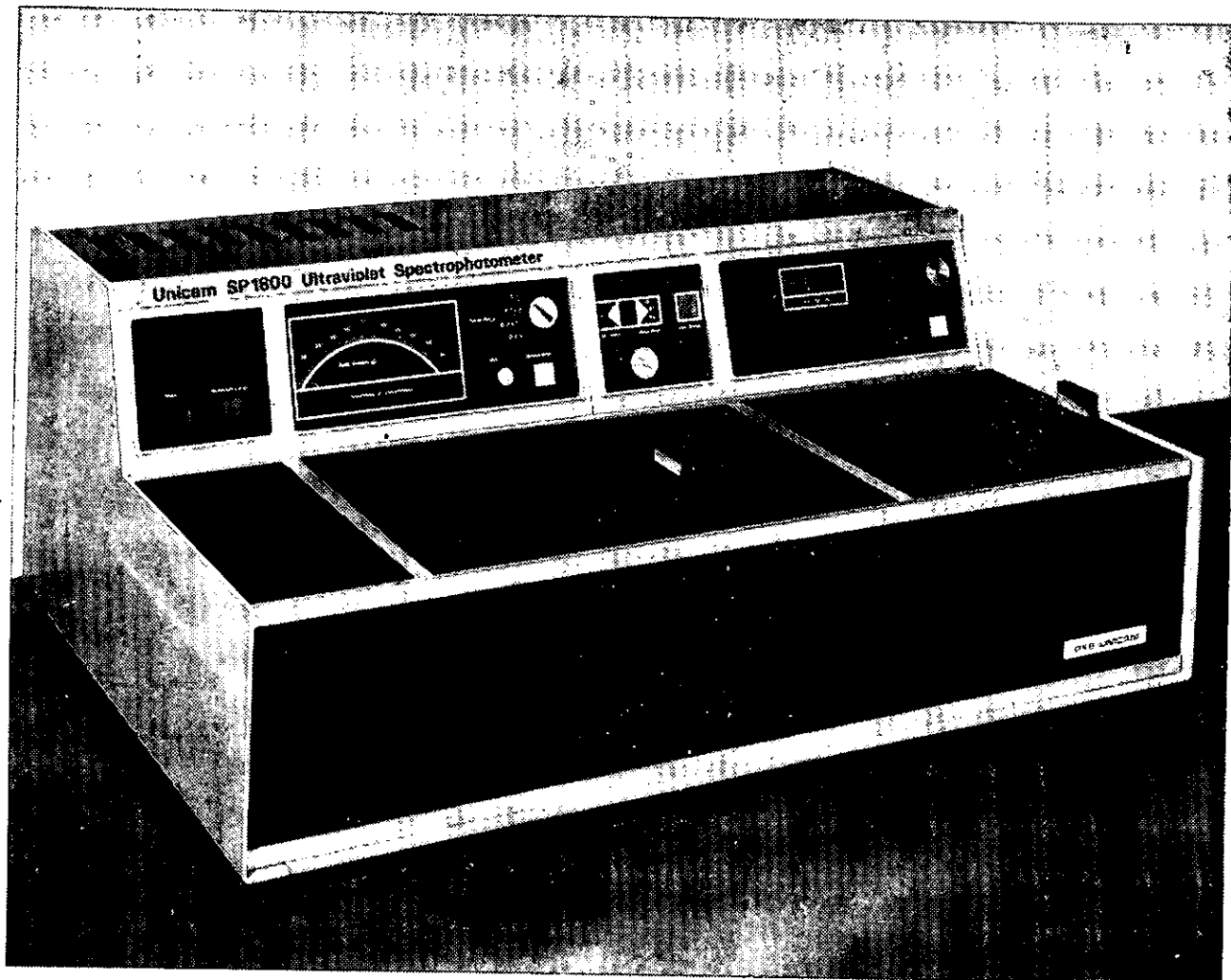
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Clin. Sci. 1962 (Vol. 22) — 1969 (Vol. 37).

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## WELCOME TO MASSEY AREA FOR THE 1970 CONFERENCE

Very considerable changes in scientific enterprises have taken place in the Massey area of Palmerston North in the seven years since the last Institute Conference was held here. The New Zealand Dairy Research Institute which formerly shared premises with the Department of Agricultural Biochemistry at Massey Agricultural College is now accommodated in its own attractive buildings. The former Plant Chemistry Division of the D.S.I.R. has been expanded to become the Division of Applied Biochemistry. In the same period Massey College has been transformed into Massey University with six faculties including three Applied Science Faculties and a Science Faculty. Numerous university buildings have been erected, one of which, the Science Building, is shown on the front cover and will be the venue for the 1970 Conference.

Members of the Manawatu Branch are pleased to have this opportunity of entertaining Conference delegates, and of showing to them the many new scientific facilities in the area. We extend to you all a very warm welcome.

The Conference itself will have some novel features in that most of the sessions have been organised by specialist groups. In addition to these the Conference Committee has arranged a symposium on "Chemical Aspects of Environmental Pollution", for which Dr. E. C. Potter of C.S.I.R.O. in Sydney has been invited as Conference Guest Lecturer. The Committee also has taken advantage of the presence in New Zealand of Dr. M. Spiro of Imperial College, London, and has invited him to deliver a lecture to the whole Conference. The Electrochemistry Group has arranged for an additional invited lecture to be given by Professor B. J. Welch of the University of New South Wales. The Easterfield Medal Address and the Institute Presidential Address will provide other official occasions when all delegates will meet together. Naturally a full social programme has been arranged also!

The Conference Committee wishes you all a most enjoyable Conference.

Conference Chairman.  
G. N. Malcolm,

---

### THE NEW ZEALAND INSTITUTE OF CHEMISTRY

## Notice of Meeting

ANNUAL GENERAL MEETING

to be held at Massey University  
Monday, August 24th, 1970, at 7.30 p.m.

Agenda:—

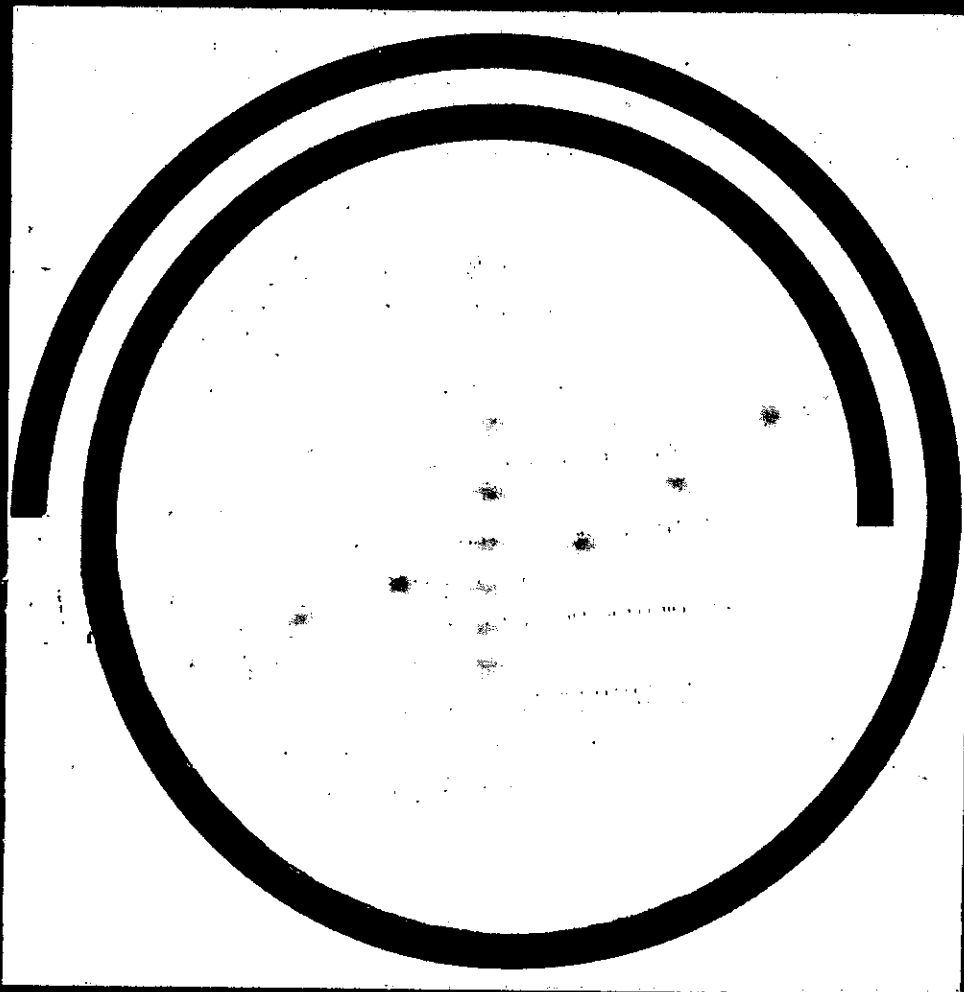
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Minutes of last A.G.M.  
Chairman's Remarks.  
Adoption of Annual Report and Balance Sheet.  
General.

E. HARVEY, Secretary.

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## CHEMISTRY AND BIOCHEMISTRY AT MASSEY UNIVERSITY

By PROFESSOR R. D. BATT

Department of Chemistry and Biochemistry, Massey University

With the occupation of the new Science Building during 1969 the first phase in the housing of the Science Faculty at Massey University was completed. Planning and progress reports on the building programme at the University have appeared in earlier issues of the Journal. The first, published in April 1963, was intended to provide information for members of the Institute of Chemistry who were planning to attend their 1963 Conference in Palmerston North. At this time the institution was called Massey University College of Manawatu and justification documents were being prepared for future science buildings. The Institute Conference that year was memorable in many respects. For the future University it was an important occasion for discussions with visitors including Professor Ralph of the University of New South Wales and the Professors of Chemistry from other New Zealand Universities, on the way in which Massey science might be developed.

By October 1965 when the second report appeared, specific reference could be made to the "Massey University of Manawatu Building Projects". Working drawings were being prepared by the Government Architect for the Science Block and it was anticipated that a start would be made on construction in the immediate future. The four storey building had a gross area of 101,000 sq. feet and the report stated that:

"this will provide badly needed space for the Science departments which are at present cramped in the main building and in other quarters around the campus".

By this date, regulations for the new science degrees had been approved and the University policy of placing emphasis on the biological sciences in the first instance was re-

flected in the prescriptions for the advanced science subjects which were to be taught for the first time in 1966. Reference was made to the introduction of two new subjects which would replace the traditional teaching of first year botany, zoology and organic chemistry for all pure and applied science degree courses.

"To be known as Cell Biology and Multicellular Biology, the former will deal with the individual cell as the building block of living matter, while the latter will cover the aggregation of cells into multicellular organisms."

During the detailed drawing phase for the new Science Building, B.Sc. classes started in the existing buildings at Massey. By the time the new building contract went to tender it was clear that science classes would greatly exceed projections, and that at the most only one discipline other than chemistry and biochemistry would be housed in the completed building. The construction of the building was started at the beginning of 1967 and the first tower was occupied in November 1968. All three towers and their connecting links were handed over by May 1969. One floor of one tower is occupied by part of the Department of Microbiology and Genetics; the rest of the building is occupied by the Department of Chemistry and Biochemistry.

### Growth of the Department of Chemistry and Biochemistry

The present department had its beginnings in the Department of Agricultural Biochemistry which was established at Massey Agricultural College in 1940 with the appointment of Dr. C. R. Barnicoat as the only staff member. In 1946 Dr. W. A. McGillivray joined the staff of the department and until

1959 these two biochemists formed the continuum for biochemistry teaching at the College. By 1959 the staff included four lecturers and a demonstrator and in that year Dr. Barnicoat resigned to take up his appointment as Director of the Cawthron Institute and Dr. McGillivray joined the staff of the N.Z. Dairy Research Institute to become, later, Director of that Institute. Dr. Barnicoat was President of the N.Z. Institute of Chemistry in 1957-58; Dr. McGillivray will hold this office for 1970-71.

The Massey department was the first Biochemistry Department to be established in New Zealand. In an article written by Professor N. L. Edson on "The teaching of Biochemistry" published in the *Journal* in 1956, the following reference was made to the Massey department:

"The one centre which possesses advantages, unique in this country, for the development of teaching in biochemistry is Palmerston North. The nucleus of a full-scale department of biochemistry exists in Massey Agricultural College hard by the Dairy Research Institute and the Plant Chemistry Laboratory of the Grasslands Division, D.S.I.R. If the College Department of Agricultural Biochemistry were strengthened and linked with the full resources of the other institutions, it would be possible for the College to give an excellent training in general theoretical biochemistry and to offer special instruction in applied biochemistry directly relevant to agriculture and the food industry."

The Department of Biochemistry at the Otago Medical School had been created as quite independent from Physiology in 1949. Professor Edson, in looking forward to the need for further expansion of biochemistry teaching in New Zealand, stated:

"The next logical step to develop the teaching of biochemistry in New Zealand is the extension of educational facilities at Massey College, possibly in conjunction with similar expansion in microbiology and other subjects. The institution of undergraduate teaching for the B.Sc. degree is

probably the best way of securing an effective school. Postgraduate teaching and research in branches of applied biochemistry related to the agricultural problems of New Zealand have been conducted in the College ever since its foundation; but it is likely that the full potential of the educational resources available in Palmerston North will not be utilized until Massey College possesses a department of general biochemistry."

In 1958, the Department of Agricultural Biochemistry started to teach first year Chemistry as a science unit under the regulations for Victoria University. By 1963 the name of the department was changed to Chemistry and Biochemistry and the staff started to increase rapidly in numbers. In 1970 the staff includes three professors (Biochemistry, Physical Chemistry and Mass Spectrometry), four readers, five senior lecturers, nine lecturers and four junior lecturers. The technical staff number 17 including an electronic engineer, a glassblower and a storeman. The scope of the teaching programmes in the department are indicated by the following figures for 1970 enrolments in the various courses offered by the department:

1st year courses:

Chemistry Intermediate	427
Cell Biology (part responsibility)	441

2nd year B.Sc. courses:

Chemistry	57
Biochemistry	120

3rd year B.Sc. courses:

Chemistry	20
Biochemistry	22

Masterate	11
Ph.D.	10

Chemistry and Biochemistry courses in second and third year for the applied faculties	202
---	-----

Elementary Chemistry for Diploma courses	85
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### Special features of the Chemistry and Biochemistry courses at Massey University

In 1964 the Massey Council agreed that science programmes in the University:

“should not necessarily develop along the lines of the other New Zealand universities. In fact, it would be preferable to specialise first in aspects of science training of importance to New Zealand which are inadequately covered elsewhere.”

From discussions on where such areas of inadequate tertiary science education exist in New Zealand, the need was recognised for the introduction of science courses with special emphasis on macromolecules (in view of the major dependence of the New Zealand economy on such compounds, particularly proteins).

Over 90 percent of New Zealand's overseas earnings are derived from biological macromolecules — proteins, polysaccharides and complex lipids; over 70 percent of these earnings are derived from proteins. In the report of a protein symposium held at the N.Z. Dairy Research Institute in October 1967 it was stated that:

“at present, the output of the N.Z. universities of people trained in protein chemistry was negligible. If advances are to be made in the development and utilisation of protein products such people are needed.”

Subsequently, in a report of the Tenth Technical Conference of the Meat Industry Research Institute, the need was stressed for the development of macromolecule training courses in the universities, and more recently, an editorial in the N.Z. Journal of Dairy Technology, in making reference to the need for biologically-oriented scientists, mentioned specifically training in the macromolecule sciences.

It seems clear that at least one University department should specialise in undergraduate and graduate courses which placed particular emphasis on macromolecules and especially proteins. To provide effective courses it is essential that academic chemists

and biochemists work closely together. These views have led to the establishment of a theme for Massey Chemistry and Biochemistry in the macromolecule sciences. The provision of a new building and an equipment grant have contributed considerably to the introduction of the courses with special orientations to macromolecule chemistry.

Facilities for the isolation and purification of macromolecules from biological materials have been installed and plans are being implemented to prepare proteins in crystalline form and in a high degree of purity for work on tertiary structures, conformational changes, kinetics of enzyme catalysed reactions and the thermodynamics of macromolecular chemical changes. Fundamental work on sequencing problems using high resolution mass spectrometry is being pursued concurrently with the more traditional methods used in sequence studies. Much of the work introduced at the graduate and research level demands collaborative effort and the contributions from a range of special disciplines on a macromolecule problem are possible with the type of integration effected in Chemistry and Biochemistry in the Massey department.

Although protein chemistry and biochemistry are aspects of the departmental activities which are being specifically developed, a number of other fields of chemical and biochemical research have been developed and are being extended. In the general field of metabolism, work is proceeding with plant, animal and microbial systems including both *in vivo* and *in vitro* studies. Several members of the department are working on the toxin produced by *Dothistroma pini* which is the causative agent of red band needle blight of pines. An investigation into the relationship between structure and function of the enzyme phosphofructokinase has been initiated and work is centred at present on the preparation of crystals for X-ray crystallographic analysis. Both NMR spectroscopy and mass-spectrometry are being applied to macromolecule studies, in addition to contributing to other research projects in organic and physical chemistry. One group has developed excel-

lent facilities for elemental analyses using techniques including emission spectrography, atomic fluorescence and atomic absorption spectroscopy. The work is related especially to problems in geochemistry with particular reference to the uptake of elements by plants as a guide to prospecting for mineral deposits.

It is often claimed that chemists and biochemists should work together more closely. The opportunities to do this have been provided in the combined department of Chemistry and Biochemistry at Massey University. Although it is premature to judge fully the merits of the association, it is clear that there are many advantages in such a collaboration.

## Obituary

Mr. Eric D. Pain, a member of the Wellington branch since 1945, and an Associate since 1935, died suddenly at the age of 64.

He started his career as a part-time student in the Westfield Freezing Works in Auckland; during the war he was engaged in the laboratory work of plywood and other product manufacture at the Fletcher organisation. After the war he came to Wellington to work for the well known public analyst, H. W. Lawrence & Son in Johnsonville, working with the "& Son", Mr. G. A. Lawrence. It was during this time that he met with an accident involving fractures of both arms and both legs and was in hospital for over a year. In the following years his remarkable efforts to regain normal walking and working ability were an example to all who knew him.

Some 10 years at Wellington Technical College followed, and around 10 years ago he decided to move to the Correspondence School.

As well as his strong interest in the teaching of chemistry and other sciences, he was well known, especially in Wellington's northern suburbs, as a lay preacher, and he will be greatly missed for his cheerfulness, helpfulness and generosity by a great number of friends and pupils. His wife and two children survive him.

C. L. H. Stonyer.

## THE P. W. ROBERTSON CLUB

The inaugural meeting of the P. W. Robertson Club, constituting the Old Members' Society of the Department of Chemistry of Victoria University, was held in the Student Union Building on Tuesday, July 7th, following a sherry party and dinner. There was an attendance of some 40 graduates including staff members of the Department of Chemistry and academic staff of the Robertson era in other Departments.

In opening the meeting, Professor J. F. Duncan, Head of the Department of Chemistry, said that the replies to the circular describing the proposal to form an Old Members' Society indicated enthusiastic support. Letters of apology from distinguished contemporaries of Professor Robertson highlighting his achievements and his personality were read. The interim Chairman, Dr. F. B. Shorland, with supporting comments by Professor P. B. D. de la Mare, Head of the Chemistry Department of Auckland University, outlined Professor Robertson's achievements which had involved not only a substantial contribution to our understanding of the mechanism of organic chemical reactions but also the production of works of high literary merit. In his first book entitled "A Souls Progress" published in 1920 and in later publications he displayed a deep insight into a number of foreign cultures and literatures which was assisted by his linguistic abilities, meriting the conclusion that few New Zealand writers have attained such an intimate knowledge of the non-British world while remaining so truly British. His scholastic attainments included Dux, Wellington College 1900, M.A. first class honours in Chemistry 1905, M.Sc. 1906, many scholarships including the first Rhodes Scholarship from Victoria University College, M.A. first class in natural sciences Oxford, and Ph.D. Leip-

zig. He was successively Professor, Rangoon College, Burma 1909-11, Lecturer, Imperial College of Science, London 1911-19, and finally Professor, Victoria University College where he remained until he retired in 1949. He returned to London as Professor Emeritus and died on May 7th, 1969.

His continued interest in science and art is demonstrated by a treatise on "Colour Words and Colour Vision" which appeared in 1967.

The meeting, after unanimously agreeing to form the Old Members' Society and to adopt the name of The P. W. Robertson Club, elected the interim committee comprising Professor N. F. Curtis, Mr. W. E. Dasant, Professor J. F. Duncan, Mr. W. Freitag, Dr. A. T. Rafter, O.B.E., and Dr. F. B. Shorland, O.B.E. (Chairman) to hold office for the ensuing year. After the meeting the members proceeded to the Easterfield Building where the guest speaker, Professor I. A. Gordon, unveiled a portrait of the late Professor Robertson. Professor Gordon, as a personal friend and member of staff during the Robertson era, delightfully referred to the close relationships between the Departments and to his interest in Robertson's literary work. He treasured in particular Robertson's book "Life and Beauty", now a rarity, which the author had presented to him. In New Zealand New Writing with which Professor Gordon had been associated, Robertson had contributed a short story entitled "Odyssey on Wellington Harbour" which was one of the finest examples of New Zealand prose. Professor Gordon also paid a tribute to Professor Robertson's likeable qualities and to his extraordinary understanding of foreign cultures including their languages and their literatures.

## CONFERENCE 1970



**DR. E. C. POTTER**

**Conference Guest Lecturer**

Until 1968 Edmund Potter lived and worked in England, in which year he joined the CSIRO Division of Mineral Chemistry in Sydney. He took his B.Sc. (Special Chemistry) with honours in 1944 from the University of London and studied electrochemical kinetics at Imperial College, becoming Ph.D. in 1950. Before this, wartime work in food preservation and canning technology nur-

tured his interest in basic industrial research and initiated the attachment to metallic corrosion science he maintains today.

After a year studying diffusion at the Paint Research Station he joined the Central Electricity Generating Board in 1951 to set up a team seeking advances in power station chemistry, including the vexed question of metal/water interactions during steam generation. For his work in this field he was awarded the Beilby Memorial Award in 1958 by the Royal Institute of Chemistry, of which he is a Fellow. In 1964 he was appointed Deputy Director of the Water Research Association at a time of notable expansion of research into all aspects of water supply and quality.

Having been invited to Australia twice before, he moved to CSIRO two years ago to enlarge his experience of environmental quality, concentrating upon particulates from coal combustion. Aside from research interests, he accumulated twelve years of varied honorary duties for the Society of Chemical Industry before leaving England, and has done much scientific writing, including a textbook on electrochemistry and extensive review work. He has visited New Zealand on two previous occasions: in 1963 as a corrosion specialist and in 1969 to examine Auckland's green-water problem.

**DR. MICHAEL SPIRO**

**Conference Guest Lecturer**

Michael Spiro, Mellor Visiting Professor at Otago for the latter half of 1970, is very pleased to have the opportunity of being in New Zealand again. He left St. Andrew's College, Christchurch in 1946 with a University Junior Scholarship and entered Canterbury University College where he was awarded the Institute of Chemistry Prize, a University Senior Scholarship and graduated M.Sc. with First Class Honours under the



guidance of Professor H. N. Parton. Then followed several years of continent jumping. An 1851 Exhibition Scholarship allowed him to join R. P. Bell's group in Oxford. In 1953, with a D.Phil. degree and a Post-doctoral Fellowship of the National Research Council of Canada, he carried out research in Professor A. R. Gordon's laboratory at Toronto University. From 1956 to 1960 he was Lecturer in Physical Chemistry at the University

of Melbourne. Since then he has been on the staff of Prof. R. M. Barrer's department at the Imperial College of Science and Technology in London where for the last 5 years he has been Reader in Physical Chemistry. Dr. Spiro's main research interests are transference numbers in aqueous and non-aqueous solvents and the heterogeneous catalysis of solution reactions. It is on the latter subject that he will talk to this year's Conference.

## Abstracts of Papers

### ANALYTICAL SECTION

#### THE DECOMPOSITION AND ANALYSIS OF CHROME SPINEL — A SURVEY OF SOME PUBLISHED TECHNIQUES

K. A. Rodgers

*Geology Department, University of Auckland*

Investigation of published procedures for the decomposition and subsequent analysis of chromite and chrome ores show some to be unnecessarily complicated and time consuming. Others fail to yield consistent and reproducible results. Decomposition is rapidly and effectively accomplished using the peroxide frit technique of Rafter. Chromium may then be removed and determined volumetrically allowing the rest of the analysis to proceed along conventional silicate lines. Fe(II) is determined by oxidimetry following digestion with a mixture of phosphoric and sulphuric acids in the presence of ceric sulphate.

#### GAS CHROMATOGRAPHIC ANALYSIS OF 17-OXOSTEROIDS

Mary G. Metcalf

*Medical Unit, Princess Margaret Hospital*

The major 17-oxosteroids in urine are androsterone (A), aetiocholanolone (E), dehydroepiandrosterone (DHA), 11 $\beta$ OH-A, 11 $\beta$ OH-E and 11-oxo-E. They are metabolites of adrenal and gonadal steroids, and may be used to identify the causes of virilization in women and of infertility in both men and women. 17-oxosteroids are excreted as glucuronides and sulphates. In 0.5N-HCl at 100° their rates of decomposition relative to the rates of hydrolysis of their conjugates were found to be:

Steroid	Excreted as	% Decomposition/Min		% Hydrolysis/Min	
		Free Steroid	Glucuronide	Sulphate	
A	90% glucuronide	0.2	12.5	0.9	
E	75-85% glucuronide	<0.1	6.3	0.7	
DHA	sulphate	1.0	—	7.7	
11 $\beta$ OH-A	glucuronide	2.8	—	—	
11 $\beta$ OH-E	glucuronide	1.8	—	—	
11-oxo-E	glucuronide	<0.1	4.3	—	

Using this information rapid gas chromatographic assays for A + E, E and DHA in urine have been developed. Twenty samples may be prepared for injection within 2 hours (A and E) or 4 hours (DHA) compared with the 11 to 144 hours of current procedures.

#### ACCELERATED AMINO ACID ANALYSIS

P. D. Pearce

*Applied Biochemistry Division, D.S.I.R.*

The Beckman/Spinco 120 C Amino Acid Analyser uses the Spackman, Stein and Moore method of separating amino acids on columns of sulphonated styrene with citrate buffers. In analysing physiological fluids the basic amino acids are separated first on an intermediate length (23 cm) column, followed by the separation of the acidic and neutral amino acid on a long (56 cm) column. This procedure takes nearly 12 hours.

The column effluent is mixed with ninhydrin and passes through a reaction coil to the colorimeter system. This consists of three cuvettes; two 6 mm cuvettes operating at 570  $\mu$  and 440  $\mu$ , and a 2 mm cuvette operating at 570  $\mu$ . In general, this last cuvette is not used when calculating amino acid compositions. By replacing this 2 mm cuvette with a 6 mm cuvette, installing a second reaction coil and rearranging the flow system of column effluents, both the basic and the acidic and neutral analyses can be done simultaneously. With these modifications the time required for an amino acid analysis is reduced to 6 hours, leaving enough time to regenerate the columns and start a second analysis the same day. This effectively doubles the rate of analysis.

## THE ANALYTICAL CHEMISTRY OF URANIUM

N. E. Whitehead

*Chemistry and Biochemistry Department,  
Massey University*

Current methods of analysis for uranium are reviewed, including colorimetric, fluorescent, and radioassay. The fluorescence assay involves the purification of the sample by a solvent extraction system and fusion of the sample with a flux containing sodium fluoride. The cooled pellet is irradiated with ultraviolet light and the resulting fluorescence measured in a specially designed attachment, utilising the electronics of an atomic-absorption spectrophotometer. The influence of such factors as heating time is described. The radioactive assay depends on the measurement of emitted gamma rays at 295 keV and 186 keV. It is rapid but not as sensitive as the fluorescence method.

## SOME CRITICAL PARAMETERS AFFECTING THE APPLICATION OF BEER'S LAW IN AA SPECTROPHOTOMETRY

R. L. Goguel

*Chemistry Division, D.S.I.R.*

The flame as a spectrophotometric cell for the determination of atoms lacks clear definition of its dimensions. If the flame rises from a long slot, as usually applied for premixed high temperature flames, the density of atom population changes in all directions that have a component vertical to the slot.

Commercial spectrophotometers are usually designed to sample a very narrow zone of the flame which equally attenuates all the portions of the light beam, and Beer's law is obeyed provided that the flame is sampled by the light of one resonance line only.

Elements which remain incompletely atomized throughout the flame produce maximum atom population in a very narrow portion of the inter-conal zone. For these cases normal apertures are too wide and strong deviations from Beer's law are obtained.

Among the various methods used for straightening calibration curves priority is given to those which improve the flame as a spectrophotometric cell rather than reduce the aperture of the spectrophotometer or apply corrections with the help of sophisticated readout electronics. The control of the temperature of the burner slot and/or the use of separated flames are most effective for the purpose.

Changes in the curvature of calibration curves connected with changes in the concentration of solid and acid content in the sample solution will also be discussed.

## DETERMINATION OF IRON AND ALUMINIUM IN TAMM'S SOIL EXTRACTS BY HIGH TEMPERATURE FLAME EMISSION

P. L. Searle

*Soil Bureau, D.S.I.R.*

Iron and aluminium extracted from soil by oxalate solution are important as a measure of the non-crystalline forms of these elements and as a guide to the stage of weathering useful in soil classification.

Measurements of iron and aluminium in oxalate extracts were previously made using colorimetric and titrimetric techniques but these have now largely been superseded by atomic absorption (A.A.). Recently however, new atomic absorption instruments with high quality optical and burner systems have introduced the possibility of using flame emission (F.E.) methods. This technique, especially with the advent of high temperature flames, offers superior detection limits for a number of elements, particularly aluminium.

This paper describes the use of a nitrous oxide/acetylene flame for the F.E. determination of iron and aluminium in oxalate extracts and compares the results obtained with those from other methods of measurement. Results for both iron and aluminium are more conveniently obtained by F.E. and agree closely with those determined by A.A.

## THIN-LAYER CHROMATOGRAPHY AS A PURIFICATION STEP IN THE IDENTIFICATION OF DRUGS BY ULTRAVIOLET SPECTROSCOPY

R. J. Norris

*Chemistry Division, D.S.I.R.*

The purification and identification of microgram quantities of drugs is a constant problem to the toxicologist, particularly so when investigating tissue extracts which may contain traces of protein and fat in addition to metabolic products. A potential solution to this problem is the use of thin layer chromatography as a purification step followed by removal of the drug from the plate for spectroscopic or gas-liquid chromatographic identification. The principal difficulties in executing such a scheme are the presence of extractable impurities in the thin layer and the presence in an eluate from a plate of small particles of adsorbent, both of which interfere in subsequent identification of a drug.

A systematic approach to this problem has been made and the above difficulties overcome by the use of foil-backed TLC sheets, and the choice of suitable elution solvents and methods of separating adsorbent particles. The results achieved in typical toxicological investigations have indicated the applicability of this technique to many of the problems encountered in this work.

## BIOCHEMICAL SECTION

### THE APPLICATION OF NITROUS ACID DEAMINATION TO THE NUTRITIONAL EVALUATION OF LEAF PROTEIN PREPARATIONS

R. M. Allison

*Applied Biochemistry Division,  
D.S.I.R., Lincoln*

The value of leaf protein concentrates as supplements to cereal diets has been established in feeding experiments with chicks, rats and pigs. Their value for man in countries where protein malnutrition is prevalent has also been demonstrated. It has been pointed out that this critical evaluation of leaf proteins requires measurements of Biological Value (BV) and True Digestibility (TD) to be compared with amino-acid analyses.

The present paper describes the application of nitrous acid deamination of the epsilon amino-group of lysine in intact protein and correlates the data obtained for deaminatable lysine with the nutritive value (BV x TD) of a range of leaf protein concentrates. Significant generalisations on the effect blocking deaminations by quinone-amine reactions on nutritive value are drawn.

### SOME FACTORS INVOLVED IN DEOXYRIBONUCLEASE ACTIVITY

R. C. Lawrence and Audrey W. Jarvis

*N.Z. Dairy Research Institute, Palmerston North*

A sensitive assay for deoxyribonucleases using a thin layer gel-diffusion technique will be described. The addition of sodium chloride to the medium had no effect on the activity of pancreatic deoxyribonuclease (DNase I), either with native DNA or denatured DNA as substrate. The activity of staphylococcal deoxyribonucleases however was greatly increased as the sodium chloride concentration increased up to about 0.5 M using denatured DNA, whereas the reverse was true using native DNA. The effect of substrate concentration, pH and divalent ions will be discussed in light of the known stabilizing effects of high ionic strength on the double-stranded structure and on the re-association of single strands of DNA.

### THE REACTION MECHANISM OF L-LACTATE OXIDASE (DECARBOXYLATING)

P. A. Sullivan

*Biochemistry Department, University of Otago*

The flavoprotein, L-lactate oxidase (decarboxylating) (E.C. 1.1.3.2) is an internal monooxygenase:

it catalyzes the overall oxidative decarboxylation of L-lactate to acetate and CO<sub>2</sub>.

Stopped-flow studies on the enzyme obtained from *Mycobacterium smegmatis* have shown that the reduction of the enzyme proceeds via an intermediate which exhibits absorbance beyond 500 mμ. The analysis of these results together with other studies are consistent with a reaction mechanism in which the long wavelength intermediate reacts directly with molecular oxygen. The fully reduced flavin is not involved in the catalytic cycle. This mechanism will be discussed together with some properties of the enzyme.

### SOLVATED ELECTRONS AND THE MECHANISATION OF DENATURATION OF PROTEINS BY ULTRAVIOLET LIGHT

T. R. Hopkins

*Department of Biochemistry, University of Otago*

Ultraviolet light is absorbed by tyrosine and tryptophan residues in proteins which transfer the absorbed energy to cystine which results in reductive cleavage of disulfide bonds. Examining the fate of excited-state energy in indole by fluorescence lifetime and quantum yield measurements. Walker *et al.*<sup>1</sup> showed that u.v. irradiated indole groups formed complexes with polar molecules (exciplexes) and that de-excitation of the exciplex occurred by the usual temperature-independent processes and by a strongly temperature-dependent, non-radiative process.

Using the specific electron scavenger N<sub>2</sub>O, we have found that the temperature-dependent, radiationless deactivation process of indole exciplexes is electron ejection into the solvent. Quantum yields of electron ejection from indole and the temperature dependency agree well with values estimated from the above fluorescence quenching study. Quantum yields are 0.3-0.4 at physiological temperatures.

It is now possible to give a fairly complete picture of the consequences of excitation of tryptophan and tyrosine groups in protein solutions at room temperature. Because the exciplex emission band does not overlap the ground state absorption band, resonance transfer will favour the funneling of electronic quanta from excited tyrosine and excited tryptophan located in hydrophobic areas of the protein to tryptophan residues able to rapidly form exciplexes. Biological activity will be lost if the solvated electrons produced by exciplex decay react with nearby susceptible bonds (-S-S-, -C-S, etc.) or, in the presence of O<sub>2</sub>, initiate oxidative attack. (Supported in part by PHS 1-F2-AM25717-02 and AEC AT (11-1)-894).

<sup>1</sup> M. S. Walker, T. W. Bedhar and R. Lumry, *Molecular Luminescence*, Ed. E. C. Lim, W. A. Benjamin, Inc., New York (1969).

### THE ROLE OF CYSTEINE IN THE CATALYTIC MECHANISM OF PYRUVATE CARBOXYLASE

J. Nielsen and D. B. Keech

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and University of Adelaide*

Pyruvate carboxylase, isolated from sheep kidneys, can be inhibited by reaction with N-ethylmaleimide (NEM). This inhibition was shown to be due to reaction between the inhibitor and a cysteine residue. Pyruvate,  $\text{HCO}_3^-$  and ATP could not protect the enzyme from inactivation by NEM. Acetyl-CoA and related compounds (ADP and 2' (3') AMP, but not acetyl pantetheine) afforded partial protection only. This protection appears to indicate that the nucleotide portion of acetyl-CoA binds to the enzyme close by the essential thiol group. An analysis of the dependence of the degree of protection on acetyl-CoA concentration yielded results consistent with the hypothesis that at least two molecules of acetyl-CoA can bind to each molecule of enzyme. Reaction of the enzyme with NEM decreased the rate of the  $\text{CO}_2$ -fixation reaction whether or not acetyl-CoA was present in the enzymic activity assays. NEM specifically reduced the rate of the ATP- $\text{P}_i$  exchange catalyzed by the enzyme without altering the rate of the ATP-ADP or pyruvate-oxaloacetate exchanges. A comparison of the kinetic constants of native and chemically modified enzyme samples showed that the  $V_{\text{max}}$  for bicarbonate remained unaltered while the apparent  $K_m$  increased upon modification.

It is concluded that the essential thiol group of pyruvate carboxylase is involved in a binding of  $\text{HCO}_3^-$  to the enzyme, preliminary to the formation of E-biotin  $\sim \text{CO}_2$ .

### RELATIONSHIPS BETWEEN AUXIN AND METABOLISM OF PROTEIN AND RNA IN PLANTS

Pauline Penny

*Massey University*

The short term kinetics of the effect of the plant growth hormone indolyl-3-acetic acid (IAA) on the growth rate of light grown lupin hypocotyl segments have been studied. There is a latent phase of 19 minutes before an IAA induced increase in growth rate occurs. Using  $^{32}\text{P}$  or  $^{14}\text{C}$ -uracil, RNA synthesis can be detected within 40 minutes of IAA addition, but it can be detected in a 40 minute incorporation period 5 hours after IAA addition. Kinetic experiments with cycloheximide indicate that protein synthesis is not necessary for the initial action of IAA. The incorporation of  $^{14}\text{C}$ -amino acids during short time periods has been studied. A model for the mechanism of action of the hormone will be discussed.

### CHANGES IN PATTERNS OF PHOTO- SYNTHETIC CARBON ASSIMILATION DURING COLD STRESS OF TROPICAL GRASSES

A. O. Taylor

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Palmerston North*

Photosynthesis of  $\text{C}_4$  pathway plants drops 75 percent if the temperature is reduced from 25° to 10°. Light, water,  $\text{CO}_2$  and ATP do not appear to be limiting. Starch disappears rapidly from the leaf so a slowdown in translocation or starch utilization is not responsible.

The flow of photoassimilated  $^{14}\text{CO}_2$  into alcohol soluble compounds was investigated at 25° and 10°, and at 25° after varying lengths of time at 10°. At 10° the proportionate labelling of malate doubles and radiocarbon flow into Calvin Cycle products such as sucrose is reduced. Total malate in *Sorghum* and *Paspalum* is low (10 to 20 percent of that in ryegrass) and does not alter significantly in concentration until secondary stress lesions occur. If the leaf temperature is raised after periods at 10° the proportion of radiocarbon (5 minute labelling and 5 minute chase) in alanine rapidly increases, mainly at the expense of sucrose (*Sorghum*, *Paspalum*) or aspartic acid (*Amaranthus*); total alanine also increases.

The results may be consistent with an initial temperature effect on the low Calvin Cycle potential of these plants followed by a reduction in pyruvate-synthase activation. The biochemical pattern of subsequent stress lesions in the tropical grasses will also be discussed.

### CELLULAR ASPECTS OF $\text{CO}_2$ EXCHANGE PROCESSES IN PLANTS

John H. Troughton

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D.S.I.R., Lower Hutt*

Regulation of the rate of carbon dioxide exchange in leaves resides, directly or indirectly, in the cellular events, although these events can be modified by the environment. The contribution that the cellular processes of carboxylation, liquid phase transport of  $\text{CO}_2$  and photorespiration make to the overall exchange of the leaf can be estimated by accounting for the gaseous phase diffusion of  $\text{CO}_2$  up to the cell wall. These gaseous phase components may be avoided by passing air through rather than over the leaf or estimated from the equation

$$NP = \frac{2(c - R_{R_1})}{r + r_l + 2r_x}$$

where NP is the rate of  $\text{CO}_2$  exchange,  $r$ ,  $r_l$ ,  $r_x$  and  $r_x$  are the boundary layer, leaf, intracellular and excitation resistances respectively,  $c$  is the  $\text{CO}_2$

concentration,  $R$  is the rate of respiration and  $r_R$  is a resistance dependent on the sites of photosynthesis and respiration within the leaf. When this equation is used in conjunction with light response curves the rate constant for the cellular events can be determined.

### PATTERNS OF NUCLEIC ACID SYNTHESIS DURING DEDIFFERENTIATION OF SOME PLANT CELLS

K. L. Giles

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After the isolation of a leaf from the gametophore of the moss *Funaria hygrometrica*, the cells of the leaf undergo dedifferentiation prior to the formation of secondary protonemata and the regeneration of new gametophores. During this period of dedifferentiation many of the chloroplasts within the cells divide, and in those cells forming protonemata the products of division move into the growing filament. Studies have been made of the roles of chloroplast and nuclear metabolism during chloroplast division. Changes in the nucleic acids have been followed especially closely using radio-active precursors of DNA and RNA synthesis and inhibitors of nucleic acid and protein synthesis.

Very shortly after isolation of the leaf DNA replication occurs in both the nucleus and chloroplasts. DNA replication is biphasic and during the non-replicative phase there is a period of RNA synthesis in nuclei and chloroplasts. The chloroplast RNA appears to code for enzymes responsible for an increase in structural lipids, and is translated on chloroplast ribosomes. The RNA of nuclear origin causes a marked rise in cytoplasmic protein synthesis. The enzymes responsible for chloroplast DNA replication are nuclear in origin.

### GALACTOLIPID BIOSYNTHESIS BY SPINACH CHLOROPLASTS

T. R. Eccleshall and J. C. Hawke

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The chloroplasts of plant cells contain most of the cellular monogalactosyl diglyceride (MGDG). These lipids usually contain highly unsaturated fatty acids, with six double bonds per molecule. The biosynthesis of MGDG is from UDP-D-galactose and 1,2-diacyl-*sn*-glycerol. When acetone-powder preparations of spinach chloroplasts were incubated with chemically-synthesized *rac*-1,2-diacyl glycerols and UDP-D-galactose-<sup>14</sup>C there appears to be no specificity with respect to the fatty acyl moieties of the diglycerides at lower diglyceride/acetone powder ratios (w/w). This non-specificity of the enzyme involved has been confirmed by incubating chloroplasts with UDP-

D-galactose-<sup>14</sup>C and fractionating the MGDG molecules according to their unsaturation. Since MGDG normally contains only  $\alpha$ -linolenic acid as the fatty acyl moiety, pathways for the formation of these MGDG molecules will be discussed. The implication is that the desaturation of the fatty acids occurs after the formation of the MGDG molecule.

### A NOVEL EXAMPLE OF THE OXIDATIC REACTION CATALYSED BY PLANT PEROXIDASE

J. M. Wilson and E. Wong

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Palmerston North*

Many organic molecules are dehydrated in reactions catalysed by plant peroxidase enzymes. These reactions may be classified as peroxidatic or oxidatic when the hydrogen acceptor is hydrogen peroxide or molecular oxygen respectively. Oxidation of aromatic compounds by oxygen addition (hydroxylation) can also occur in reactions coupled to the oxidatic reaction. We have found that 2', 4', 4-trihydroxychalcone (representing a class of compound believed to be intermediates in the biosynthesis of other classes of flavonoid plant products), in the presence of molecular oxygen and hydrogen peroxide, undergoes a simultaneous dehydrogenation and oxygenation reaction catalysed by a peroxidase enzyme preparation either from garbanzo bean (*Cicer arietinum*) or commercial horse-radish peroxidase.

The main products are novel flavonoid-type compounds, some of which are isomeric with 4', 7-dihydroxyflavonal. Quantitatively minor products include hydrated aurone isomers and the dihydroflavonol, garbanzol. The reaction requires stoichiometric amounts of oxygen and consumes catalytic quantities of hydrogen peroxide. Increased reaction rates are observed as hydrogen peroxide concentration is increased to stoichiometric levels. The effects on this system of a selection of activators and inhibitors of the oxidatic reaction catalysed by peroxidase have been determined.

A scheme has been devised to rationalize this new reaction in terms of free-radical mechanisms accepted for previously recorded examples of the peroxidase-oxidase reaction.

### ENZYMES OF THE DEVELOPING WHEAT GRAIN

Peter Meredith

*Wheat Research Institute, Christchurch*

The grain is predominantly a storage organ in which we are able to observe the synthesis and deposition of starch and protein as nutritional stores for subsequent germination and growth of the embryo. Serial harvestings of immature stages

of several varieties of wheat have been made and grains analysed for the deposition of starch and protein, the concentrations of possible precursors and the rise and fall of appropriate enzymic activities. Existing text-book theories of development and synthesis are not all acceptable in explaining the observations.

### THE ROLE OF $\beta$ -CYANOALANINE IN ASPARAGINE BIOSYNTHESIS

Lupin  $\beta$ -cyanoalanine synthase occurs mainly in cotyledon and stem mitochondria. During growth at 25°C in the dark, it reaches a maximal level after five days, a stage when major changes occur in the plant and asparagine synthesis is rapid. However, ability to assimilate HCN is maximal after three to four days, before asparagine accumulation begins.

Of the labelled substances supplied, aspartate and fumarate are more effective asparagine precursors than are possible precursors of cyanide and  $\beta$ -cyanoalanine. The 4-carbon skeleton is retained but with some equilibration that suggests there are multiple pools of aspartate.

It is concluded that the  $\beta$ -cyanoalanine pathway does not contribute significantly to asparagine biosynthesis in lupins.

### THE MONOSACCHARIDE COMPOSITION OF THE EXTRACELLULAR POLYSACCHARIDES OF RHIZOBIA

R. W. Bailey

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Palmerston North

Most *Rhizobia* produce in mannitol cultures large amounts of extracellular polysaccharides. These polymers produced by the two main classes of *Rhizobia*, acid- and non-acid-producers, have been isolated and their monosaccharide-components identified. Polysaccharides from the acid-producing strains consistently contain glucose (main component), galactose and uronic acids together with traces of mannose but no other sugars. The polymers from the non-acid producing strains show a much wider variation in monosaccharide composition. Uronic acids, glucose, galactose and mannose may be absent or present in large amounts while fucose and rhamnose are occasionally present. In addition to these compounds several as yet unidentified monosaccharides have been detected on chromatograms of the hydrolysates of these polysaccharides. One of these possible sugars has the properties of a 6-methyl pentose, while the other two behave as neutral hexoses or mono-methyl hexoses. The properties and possible identities of these sugars will be discussed.

### CYTOKININS AND GROWTH OF SPIRODELA

P. J. A. McCombs

Department of Cell Biology,  
University of Auckland

Growth of *Spirodela* on glucose medium ceases within two days of transfer into darkness. Kinetin satisfies the non-photosynthetic red-light requirement for growth. Radiosotope studies show that precursor incorporation into protein and nucleic acid continues in non-growing axenic cultures. The specific activity of tRNA relative to rRNA following short term P<sup>32</sup> labelling is higher in non-growing than in growing *Spirodela*. Following venom diesterase digestion of tRNA most of the radioactivity is associated with 5'-AMP. The possibility that cytokinin controls growth by modifying tRNA end-group turnover is discussed.

### CYTOKININ BINDING TO RIBOSOMES

M. V. Berridge and R. K. Ralph

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University of Auckland

and D. S. Letham\*

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The synthetic cytokinins kinetin and 6-benzylaminopurine exhibit equilibrium type binding to purified chinese cabbage leaf ribosomes. At 2.3 x 10<sup>-5</sup>M and 4° one molecule of kinetin and 1.35 molecules of 6-benzylaminopurine are bound per ribosome. Adenine and adenine derivatives that are inactive as cytokinins showed much less affinity for ribosomes. Pretreatment of ribosomes with 0.5M NH<sub>4</sub>Cl or -Triton-X100 did not reduce the extent of cytokinin binding. Binding was temperature, magnesium and concentration dependent, and appeared to be to the 83S ribosome species. A positive correlation between the extent of binding and the biological effect of various cytokinin analogues was demonstrated. We have not been able to demonstrate an effect of cytokinins on *in vitro* 68S ribosome-requiring protein synthesizing systems from chinese cabbage. These results are discussed in terms of cytokinin control of growth processes at the level of the ribosomes.

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## STUDIES OF REOVIRUS RNA TRANSCRIPTASE

R. M. Reynolds

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Reovirus, a spherical animal virus, contains a fragmented genome of 10 segments of double-stranded RNA. In addition, the virus particle contains one or several molecules of an RNA transcriptase. When the virus enters a cell the transcriptase functions by producing viral messenger RNA, thus initiating the infectious cycle.

The transcriptase of purified virus particles may be activated *in vitro* by chymotrypsin digestion or by heat treatment. Both these methods produce viral "cores" which contain double-stranded nucleic acid enclosed by the inner coat protein capsomeres. Cores, incubated with the four ribonucleoside triphosphates, at pH 8.5 proceed to synthesise large amounts of RNA.

Conditions for *in vitro* transcriptase activity have been investigated. The concentration of magnesium ion and of nucleoside triphosphate is particularly critical for optimum activity. Provided that exogenous nuclease activity is inhibited, the product corresponds in size and sequence to the viral messenger RNA's synthesised *in vivo*. The manner by which the enzyme initiates the synthesis of RNA chains has been examined, using <sup>3</sup>H-labelled substrates to measure chain growth, and substrates labelled with <sup>32</sup>P in the  $\gamma$ -position to measure chain initiation. Though extensive chain growth occurs, little <sup>32</sup>P-incorporation into termini has been observed. Possible explanations for this finding are discussed.

## CHANGES IN ACTIVITY OF TWO FORMS OF RAT HEPATIC PYRUVATE KINASE DURING DEVELOPMENT

N. C. Middleton

*Ruakura Animal Research Station*

Two forms of rat hepatic pyruvate kinase have been distinguished on the bases of kinetic, chromatographic, electrophoretic and immunological criteria. The properties of the two forms, designated type L and type M, were compared with those of pyruvate kinase from rat muscle. The chromatographic and electrophoretic properties of the type M hepatic enzyme are similar to those of the enzyme from muscle but there are some kinetic and immunological differences between them. In contrast, the properties of type L hepatic pyruvate kinase were markedly different from those of the enzyme from muscle.

The activity profiles of the type L and type M hepatic enzymes have been determined during the developmental period of the rat by utilizing the different kinetic properties of the two forms. The

high activity of the type M enzyme in the early foetal rat decreased in late gestation and immediately after birth to reach a low level which remains essentially constant for the remainder of the development period. The activity of the type L enzyme, however, was low in the foetal and early neonatal liver but increased markedly at the onset of weaning to approach adult values about 30 days after birth.

The possible rate of the two forms of hepatic pyruvate kinase in the control of glycolysis and gluconeogenesis will be discussed.

## CONTROL OF GLYCOGEN SYNTHESIS IN SKELETAL MUSCLE

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The rate-limiting reaction in the synthesis of glycogen from glucose in skeletal muscle appears to be that catalysed by glycogen synthetase. Glycogen synthetase exists in two forms, an active (I) form and a less active (D) form. The I form can be converted to the D form by an ATP-dependent kinase and the D to I by a specific phosphatase.

Skeletal muscle preparations were found to convert the D form of glycogen synthetase to the I form. This reaction was stimulated about 20-fold by ATP and Mg<sup>2+</sup>; ATP alone was inhibitory and cyclic 3',5'-AMP was without effect. The increase in synthetase I activity was paralleled by the release of P<sup>32</sup> from glycogen synthetase previously labelled with ATP<sup>32</sup>. Evidence will be presented that this enzyme is not identical with the described synthetase phosphatase. It is likely that there is more than one phosphatase acting on glycogen synthetase or that the phosphatase exists in two or more forms. The role of the ATP-dependent phosphatase in the hormonal control of glycogen synthesis is as yet uncertain.

## THE MOVEMENT OF SOLUTES THROUGH MEMBRANES

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About 10 litres of water a day cross the gut wall to the blood. The construction of a computer programme to simulate calcium metabolism in man has raised the question of the extent to which this flow of water drags along dissolved substances with it. It would be naive to suppose that all dissolved substances are carried along completely with the flow of water, but equally naive to suppose that solutes permeate the wall independently of this flow.

Application of the principle of linearity of combinations of flows and forces, pioneered by Onsager and developed by Kedem and Katchalsky for the case of simultaneous flows through membranes,

leads to the conclusion that solvent drag is likely to override diffusion as the mode of transfer of solutes.

The result is

$$J_s = aJ_1C_0 + b \frac{C_0 - C}{x} (y/(cy-1))$$

where  $y = aJ_1/bx$ ,  $J_2$  is the flow of solute, and  $J_1$  the flow of solvent. The concentration of the solution entering the membrane of thickness  $x$  is  $C_0$ , and that leaving it is  $C$ .  $a$  and  $b$  are constants whose values are decided by the relative friction of solute, solvent, and membrane taken in pairs. The first term describes solvent drag, the second diffusion.

## THIOL LEVELS IN PREKERATIN TISSUES

### I. Weatherall

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Keratinized tissues such as wool are characterized by a high cystine content. Studies on the incorporation of cystine and of protein biosynthesis in the prekeratin tissue have been facilitated by recently developed methods for obtaining wool roots. The isolation of wool root tissue has been coupled with studies directed towards determining the integrity of the preparations.

Experiments have been carried out on the extraction of proteins from wool roots and wool root cells and comparisons made with fully keratinized wool in order to determine if the methods employed result in the isolation of proteins characteristic of wool and of the prekeratin tissue *in vivo*.

The thiol and disulphide levels in wool roots have been measured and the results related to similar measurements made on the soluble proteins of wool roots. Measurements have been made on the thiol and disulphide levels in different regions of the wool follicle and in wool root cells. The soluble proteins have been similarly characterized. Tentative conclusions have been reached on the thiol levels in prekeratin tissue in relation to the process of keratinization.

## THE ROLE OF LIPIDS IN THE ACTIVITY OF SOME MICROSOMAL ENZYMES

P. D. Jones

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Evidence will be presented to show that two microsomal enzyme systems, the DPNH-cytochrome c reductase and the stearyl-CoA desaturase, require lipids for their activity.

The DPNH-cytochrome c, but not the TPNH-cytochrome c reductase activity of microsomes was reduced approximately 80 percent by extraction of

the microsomes with 10 percent aqueous acetone. Addition of two different phospholipids, phosphatidylcholine and lysophosphatidylcholine, when solubilized together, completely restored the DPNH-cytochrome c reductase activity to acetone-extracted microsomes. Micelles containing from 40 to 70 percent of phosphatidylcholine by weight, when added to acetone-extracted microsomes, stimulated the DPNH-cytochrome c reductase activity to levels which were 3 to 4 times higher than that of the original microsomes. Micelles formed from the synthetic phospholipid,  $\gamma$ -oleyl- $\beta$ -butyrylphosphatidylcholine were able to restore over 85 percent of the original DPNH-cytochrome c reductase activity to acetone-extracted microsomes, presumably because this phospholipid forms micelles having the same or closely related physicochemical characteristics to those micelles formed by mixtures of phosphatidylcholine and lysophosphatidylcholine.

The stearyl-CoA desaturase activity of microsomes was reduced to extremely low levels by extraction of microsomes with 10 percent aqueous acetone. Micelles prepared from a mixture of microsomal phospholipids, triglycerides and free fatty acids restored the original desaturase activity when added to acetone-extracted microsomes. If phosphatidylcholine was substituted for the microsomal phospholipids in these micelles, 60 percent of the original desaturase activity was restored.

The similarities between the lipid requirements of the DPNH-cytochrome c reductase and the stearyl-CoA desaturase activities of microsomes will be shown to support the suggestion that the two enzyme systems share a common electron transfer pathway or carrier, cytochrome b<sub>5</sub>.

## BIOCHEMICAL PROBLEMS RELATING TO THE TREATMENT OF LEUKAEMIA WITH CYTOSINE ARABINOSIDE

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The drug cytosine arabinoside, an analogue of deoxycytidine is used in the treatment of acute leukaemia. However, the drug is successful in a clinical sense in only 10-25 percent of patients. If biochemical studies could elucidate the reasons for success or failure of the drug on different leukaemic cells, then this would enable drug treatment to be confined to the proportion of patients with favourable drug sensitivity.

The first factor studied was the rate of drug degradation. Cytosine arabinoside is deaminated by serum and liver enzymes. Cultured cells were used to devise a biological assay system for serum levels of cytosine arabinoside. High rates of degradation of drug were observed in two patients who failed to respond. However, lower rates of degradation

did not necessarily imply that treatment would be successful.

The drug is phosphorylated intracellularly by the enzyme deoxycytidine kinase. Phosphorylation is necessary for cytotoxic activity. A partial correlation was observed between the activity of deoxycytidine kinase in leukaemic cells and the success of the drug.

The aim of anti-leukaemic drugs is to be selectively toxic to leukaemic rather than normal cells. The role of enzymes and cell kinetics in this process will be discussed.

## ELECTROCHEMISTRY GROUP

### Electrochemistry Invited Address

#### MOLTEN SALT ELECTRO-TECHNOLOGY

B. J. Welch

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Molten salt electrochemical processing has become firmly established for electrowinning of metals such as aluminium, sodium and magnesium. Attempts to utilize the inherent technological advantages of molten salt systems (i.e. conductivity, faster electrode kinetics, and better thermodynamic energy efficiencies) for other electrowinning and electrical energy conversion systems have been less successful. This has usually been due to secondary or side reactions occurring between the electrolyte and electrode products. Side reactions also present problems in existing processes involving molten salt electrochemical technology.

In reviewing problems associated with both established (particularly aluminium) and technologically attractive molten salt processes, considerable emphasis will be given to the roles of the undesirable side reactions on process economics. Results of fundamental studies aimed at understanding selected reactions will also be presented.

### Physical Chemistry of Electrolytes

#### THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTANCE OF SOME ALKYLAMMONIUM FLUOROBORATES

G. D. Coster and J. W. Tomlinson

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Victoria University of Wellington*

Over the past decade, the shortcomings attached to a simple description of the temperature variation of molten electrolyte transport properties in terms of transition state theory have become increasingly apparent. Attention has been focussed especially on the non-Arrhenius character of the isobaric behaviour and on the pressure dependence.

These form respectively the themes of the researches described in this and the subsequent paper.

Most previous research relates to electrolytes with monatomic or simple polyatomic ions, e.g.  $M^+$ ,  $Cl^-$ ,  $NO_3^-$  and the alkylammonium fluoroborates were chosen specifically because their larger size emphasises the two effects referred to above.

The conductances and densities of tetra n-pentyl, hexyl, heptyl and octyl-ammonium tetrafluoroborates have been examined over ranges of temperature of about 100K from the melting points ( $\sim 100^\circ C$ ). These results, together with those of other workers for the propyl and butyl salts, are examined comparatively in the light of current theories.

#### THE PRESSURE AND TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTANCE OF (n-HEXYL)<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup>

R. J. Speedy and A. F. M. Barton

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The electrical conductance of (n-hexyl)<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> has been examined over a temperature range of about 100K above the melting point and from 1 to 1000 bar. Using an estimated compressibility, it is shown that the isothermal volume dependence is small and nearly independent of temperature whereas the isochoric temperature dependence is larger and decreases with increasing temperature.

The implications of these and other observations are discussed in the light of current theory.

#### ASSOCIATION CONSTANTS FOR ELECTROLYTE EQUILIBRIA FROM DIFFERENT EXPERIMENTAL METHODS

Chan Chee Yan and M. H. Panckhurst

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The theoretical possibility that different experimental methods may give different values for association constants for electrolyte equilibria has been recognised for some time. In many cases the experimental situation has been complicated because there has been no agreement about association constants obtained from the *same* experimental approach used in different laboratories. This disagreement, when the same method has been used, has often been said to arise from different assumptions about the activity coefficients of "free" ions.

In this paper we report precise solubility and spectrophotometric determinations of association constants for equilibria involving TlCl and TlBr in aqueous solution. The activity coefficient assumptions for both free ions and uncharged molecules will be discussed together with the effect on the

conclusions of the presence of small amounts of higher complexes. It will be shown that there is no substantial evidence for different association constants arising from the two types of measurements considered.

#### DETERMINATION OF CATION ACTIVITIES IN RAW SKIM BOVINE MILK

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and R. D. Reeves

*Massey University, Palmerston North*

Milk is a complex electrolyte mixture. The principle cations present and their approximate total molar concentrations and molar activities respectively are: Sodium (0.02, 0.015), Potassium (0.04, 0.03), Magnesium (0.005, 0.0003) and Calcium (0.03, 0.008). These cations, particularly the divalent cations, are important in determining many of the properties of milk. Methods available for measuring cation activities are briefly surveyed and a cation exchange resin method is described. This method involves equilibration of a large quantity of milk with a small quantity of resin and subsequent determination of the individual cation loadings on the resin by flame photometry. Calibration of the resin is achieved by equilibrium with solutions containing ions at known activities.

Results for milk are presented for the 1968/69 dairying season. There are relatively large changes in the cation activities in the milk during the season and the electrolyte composition of the milk tends to become more like that of blood as the season progresses.

#### THE THERMODYNAMICS OF ELECTROLYTE EQUILIBRIA IN MIXED SOLVENTS

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The behaviour of equilibrium constants in solvents of variable composition is discussed with particular reference to systems in which water is one component of the solvent. Theories which attempt to correlate changes in the equilibrium constant with variations in dielectric constant, water concentration and water activity are considered.

#### Electrode Processes

##### APPLICATION OF THE ROTATING DISC ELECTRODE TO THE STUDY OF HOMOGENEOUS REACTIONS IN LIQUID SOLUTIONS

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The time independent hydrodynamics of the rotating disc system provide a steady-state method of investigating rapid homogeneous reactions in liquid solution.

Generally, electroactive products of the homogeneous reaction taking place in the diffusion layer are oxidised or reduced at the disc electrode at a rate that is transport controlled. The magnitude of the disc current is related to the rate of the homogeneous reaction. A similar situation obtains at the rotating ring-disc electrode, but, in this case, the reactant is generated at the disc at a constant rate, and consumed at the ring electrode which is maintained at a constant potential.

An alternative approach to the application of the rotating disc electrode to rapid homogeneous redox processes, is to pass small, reactant-generating currents so that the electrode potential is determined by the Nernst equation. The concentration of reactant at the electrode surface depends upon the relative magnitudes of the generating current and the rate of the homogeneous reaction. Analysis of the current, potential data immediately yields the order of the reaction with respect to the reactant, and by comparison with the electrode potentials obtained in the absence of homogeneous kinetics, the magnitude of the rate constant can be obtained.

##### THE MERCURY(I) PHOSPHATE ELECTRODE

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The importance of phosphates in solution in biology, water chemistry and agricultural science is well known and it would be of considerable advantage to have available an electrode reversible to phosphate ion, particularly at low concentration. However, in spite of the rapid recent development of specific ion electrode systems no reliable phosphate ion electrode has yet been described, though a number of possible electrode systems have been studied.

This work is briefly reviewed and research on mercury(I) phosphate electrodes is described. Two electrode systems have been investigated involving  $\text{Hg}_2\text{PO}_4$  and  $\text{Hg}_2\text{HPO}_4$ , which are stable at low and high phosphoric acid concentrations respectively.

## THE AMPEROMETRIC DETERMINATION OF CYANURATE USING MERCURIC ION

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Mercuric ion reacts quantitatively with cyanurate ion to form the very insoluble salt  $\text{Hg}^{2+}(\text{C}_3\text{O}_3\text{N}_3)^{2-}$  in neutral solution and this has been made the basis of a very precise determination of cyanurate by amperometric titration with mercuric ion. The titration may be made in the range 5-100 p.p.m. or stronger using a phosphate buffer at pH 8 and an electrode system consisting of a conditioned copper-amalgam electrode and the S.C.E., no external potential being applied.

If a clean, freshly amalgamated electrode or a stirred mercury pool is used erratic results are obtained. The electrode commences by being negative to the S.C.E. and the end-point is very sluggish, pH sensitive and is overshot. However, if the freshly amalgamated electrode is treated with mercuric ion in a phosphate buffer of pH 8, then there is initially no current and the electrode has the same potential as the S.C.E. When mercuric ion is present in the solution just after the endpoint, the electrode becomes positive and a rapid increase of current occurs, the endpoints being precise and reproducible.

In this paper discussion will be presented on this electrode behaviour and the uses of this titration, especially its application to the estimation of cyanurate in swimming pools.

## THE EFFECT OF HYDROGEN DISCHARGE KINETICS ON THE POTENTIALS OF SOME ACTIVE METALS

W. B. Earl

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It has been shown using high-speed measurements on freshly formed reactive metal electrodes that the changes in anode process kinetics up to and at the peak are the cause of subsequent decay to the mixed potential. The rate of this decay is, however, then controlled by the discharge kinetics of hydrogen. On electrodes which facilitate this cathodic process, the peak potential can also become a mixed potential and the whole potential is moved positively with control now entirely by the cathodic process.

## CYCLIC VOLTAMMETRY AT COPPER SURFACES

P. C. A. Bailey and G. A. Wright

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The anodic oxidation and cathodic reduction of a polycrystalline copper surface in buffered electrolyte solutions (pH 8.0 to 14.0) have been studied by the potential sweep method. Current has been

recorded as a function of potential. By studying the area beneath the current peaks to determine charge passed, the nucleation of oxide films, their growth to a thickness of about 100 Angstroms and their removal by reduction has been studied. Current peaks have been assigned to the formation and reduction of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  [or  $\text{Cu}(\text{OH})_2$ ] with the appearance of  $\text{Cu}_2\text{O}_3$  at higher pH values.

## INORGANIC SECTION

### TRIACIDO COMPLEXES OF Co(III) AND Cr(III) WITH TRIDENTATE POLYAMINE LIGANDS

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In an attempt to determine the influence of chelate ring size on the stereochemistry adopted by octahedral Co(III) and Cr(III) polyamine complexes, the compounds  $\text{M}(\text{dien})\text{X}_3$  ( $\text{M} = \text{Co}, \text{Cr}$ ),  $\text{Co}(2,3\text{-tri})\text{X}_3$  and  $\text{Co}(\text{dpt})\text{X}_3$  have been prepared. ( $\text{dien} = 2,2\text{-tri} = [\text{NH}_2(\text{CH}_2)_2]_2\text{NH}$ ,  $2,3\text{-tri} = \text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ ,  $\text{dpt} = 3,3\text{-tri} = [\text{NH}_2(\text{CH}_2)_3]_2\text{NH}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{NO}_2, \text{NCS}, \text{N}_3$ ).

These non-electrolytes can theoretically exist in two geometric forms with the tridentate ligands *cis* (facial) or *trans* (peripheral). All the above Co(III) complexes have the *trans* configuration and only with Cr(dien)Cl<sub>3</sub> were two isomers, green (*cis*) and violet (*trans*), isolated.

Hydrolysis products of the halogenotriamine complexes in acid solution have also been investigated using ion-exchange chromatography to separate the complex cations formed. Isomerisation of the *trans*-Co(A<sub>3</sub>)(OH<sub>2</sub>)<sub>3</sub><sup>3+</sup> ions to the *cis* isomers occurs for A<sub>3</sub> = dien and 2,3-tri, but with the *trans*-Cr(dien)(OH<sub>2</sub>)<sub>3</sub><sup>3+</sup> and *trans*-Co(dpt)<sub>3</sub>(OH<sub>2</sub>)<sub>3</sub><sup>3+</sup> ions, metal-nitrogen bond rupture takes place. From this and other evidence it appears that six-membered chelate rings prefer the *trans* configuration.

### SALT EFFECTS IN THE RACEMISATION OF THE TRISOXALATOCHROMIUM(III) ANION

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Arguments based on the Debye-Huckel Theory have long been used to rationalise the effects of added electrolytes on ionic reaction rates in aqueous solution. The concept of constant ionic strength and the use of large amounts of added inert electrolyte have become accepted as standard procedures for studying such reactions.

Using an "ionic strength" approach an attempt has been made to explain the observed kinetic behaviour of the racemisation of the trisoxalatochromium(III) anion in aqueous solution in the presence of the rate accelerating species  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ .

The failure of such an approach was compensated for by the success of an interpretation based on the postulate of the addition of the metal ions to form ion-pairs with substrate and other anions in a series of pre-equilibria, this being followed by a rate determining racemisation of the various trisoxalato species.

Using such an approach the observed racemisation rates of the trisoxalatochromium(III) anion in the presence of various  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  salts have been systematised in the presence of sodium perchlorate and without it.

### NITROSYL COMPLEXES AND SOME REACTIONS OF THE NITROSYL LIGAND

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Preparation of the new dinitrosyls of ruthenium and osmium,  $\text{Ru}(\text{NO})_2\text{L}_2$  and  $\text{Os}(\text{NO})_2\text{L}_2$ , ( $\text{L} = \text{PPh}_3$ ), which involves a ligand combination reaction between nitrite and carbon monoxide will be described.  $\text{Ru}(\text{NO})_2\text{L}_2$  reacts with oxygen to give as final product the oxygen complex  $\text{Ru}(\text{O}_2)(\text{NO})_2(\text{NO})\text{L}_2$ . Oxidation in the presence of strong acids produces the dinitrosyl cation  $[\text{Ru}(\text{OH})(\text{NO})_2\text{L}_2]^+$  in which it is believed both linear and bent nitrosyl groups are present. Oxygen and chloride ion bring about oxidation of one nitrosyl ligand in this cation, producing  $\text{RuCl}_2(\text{NO})_2(\text{NO})\text{L}_2$ . Several reactions involving modification of the nitrosyl ligand by hydride addition will also be described.  $\text{Ir}(\text{NO})\text{L}_3$  reacts with three moles of  $\text{HCl}$  to give  $\text{IrCl}_3(\text{NH}_2\text{OH})\text{L}_2$ , involving co-ordinated hydroxylamine;  $\text{Os}(\text{NO})_2\text{L}_2$  with two moles of  $\text{HCl}$  to give  $\text{OsCl}_2(\text{NHOH})(\text{NO})\text{L}_2$ , involving co-ordinated hydroxylamido radical; and  $\text{OsCl}(\text{CO})(\text{NO})\text{L}_2$  reacts with one mole of  $\text{HCl}$  giving  $\text{OsCl}_2(\text{CO})(\text{HNO})\text{L}_2$  believed to contain co-ordinated nitroxyl. Thus all three reduction products of  $\text{NO}$  have been obtained, complexed to a metal.

### U.V. SPECTRAL AND OTHER STUDIES ON A SERIES OF TRICARBONYL $\omega$ -PHENYL-POLYENAL IRON COMPOUNDS

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The change in reactivity which organic dienes undergo on co-ordination to transition metal ions can be related to the interaction of the metal with

the  $\pi$  and  $\pi^*$  molecular orbitals of the diene. Therefore in an attempt to elucidate the nature of the electronic distribution in such systems a series of  $\omega$ -phenylpolyenal iron tricarbonyl compounds and their 2,4-dinitrophenylhydrazone derivatives has been investigated. The reaction of the polyenals with tri-iron dodecarbonyl affords isomeric mixtures of compounds of the general stoichiometry  $[\text{Ph}(\text{CH}=\text{CH})_n\text{CHO}]_2\text{Fe}(\text{CO})_3$ ;  $n = 2-5$ . The location of the coordinated  $\text{Fe}(\text{CO})_3$  moiety in the polyene chain was determined from the n.m.r and i.r spectra, and, as predicted by theory, the major product is the complex in which the iron is bonded to the butadiene fragment adjacent to the aldehyde function. The ultraviolet spectra of the free polyenals,  $\text{Ph}(\text{CH}=\text{CH})_n\text{CHO}$ , show absorption maxima, assignable to the  $\pi \rightarrow \pi^*$  transition, which move to longer wavelengths and increase in intensity as  $n$  increases. The spectra of the complexes show maxima at shorter wavelengths showing some loss of conjugation has occurred. Moreover the spectra of the 2,4-dinitrophenylhydrazone derivatives confirm that the  $\text{Fe}(\text{CO})_3$  group considerably interrupts the transmission of conjugative effects along the polyene chain.

### GERMYL DERIVATIVES OF METAL CARBONYLS

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Germypentacarbonylmanganese,  $\text{GeH}_3\text{Mn}(\text{CO})_5$ , and analogous rhenium and cobalt derivatives have been prepared from  $\text{GeH}_3\text{Br}$  and the carbonylanion. These molecules are simpler than the other known germanium hydride-transition metal species like  $\text{H}_2\text{Ge}(\text{Mn}(\text{CO})_5)_2$  or  $\text{H}_2\text{Ge}(\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2)_2$ —and spectroscopic studies yield more detailed information.

The vibrational spectra will be discussed: characteristic features include  $\delta\text{GeH}_3$  at  $800\text{cm}^{-1}$  and the Ge-M stretch at  $219\text{cm}^{-1}$  ( $\text{GeMn}$ ),  $224\text{cm}^{-1}$  ( $\text{Ge-Co}$ ) or  $209\text{cm}^{-1}$  ( $\text{Ge-Re}$ ). The derivative  $\text{GeH}_3\text{GeH}_2\text{Mn}(\text{CO})_5$  shows metal-metal modes at  $273$  and  $265\text{cm}^{-1}$ , indicating interaction between  $\nu\text{GeGe}$  and  $\nu\text{GeMn}$ .

The mass spectra show successive loss of  $\text{CO}$  and rearrangement of  $\text{H}$  on to the metal. Loss of  $\text{H}$  from  $\text{GeH}_3$  and of  $\text{O}$  from  $\text{CO}$  are minor processes. Ions retaining  $\text{Ge}$  and the transition metal carry more than half the ion current in all species.

Preliminary studies of reactions demonstrate substitution of  $\text{H}$  on  $\text{Ge}$  and displacement of  $\text{CO}$  as well as cleavage of the Ge-metal bond.

### IONISATION POTENTIALS OF $\text{Me}_3\text{M}$ RADICALS ( $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ and $\text{Pb}$ ) FROM MASS SPECTROMETRIC MEASUREMENTS

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The ionisation potentials of the radicals  $\text{Me}_3\text{M}$  have been found from a series of ionisation and appearance potential measurements on compounds of the type  $\text{Me}_3\text{MM}'\text{Me}_3$  and  $\text{Me}_3\text{M}$ , where  $\text{M}$  and  $\text{M}'$  are the Group 1VB elements  $\text{C}, \text{Si}, \text{Ge}, \text{Sn}$  and  $\text{Pb}$ . In order to check the consistency of the values obtained, the ionisation potentials of the  $\text{Me}_3\text{M}$  radicals were calculated by three different methods, using the appearance potential data and independently determined thermochemical results. The first calculation was based on the known bond dissociation energy of  $\text{Me}_3\text{C}-\text{CMe}_3$ . The second used the kinetically determined silicon-silicon bond dissociation energy in  $\text{Me}_3\text{Si}-\text{SiMe}_3$ . The third was based on the known heats of formation of  $\text{Me}_3\text{Sn}$  and  $\text{Me}_3\text{Sn}_2$ .

In this work all ionisation and appearance potentials were determined mass spectrometrically using an A.E.I. MS 9 instrument, and the ionisation efficiency curves were interpreted by the Lossing semi-log plot method. The averaged values of the radical ionisation potentials were used to calculate the metal-metal and metal-carbon bond dissociation energies in  $\text{Me}_3\text{M}-\text{MMe}_3$  and  $\text{Me}_3\text{M}-\text{Me}$  respectively.

The bond dissociation energies of transition metal-Group 1VB metal bonds in compounds of the type  $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{M}-\text{M}'\text{Me}_3$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{M}' = \text{Ge}$  or  $\text{Sn}$ ) have also been found using the ionisation potentials of  $\text{Me}_3\text{Ge}\cdot$  and  $\text{Me}_3\text{Sn}\cdot$ .

These results will be discussed with particular reference to the accuracy of thermochemical data derived from mass spectrometric measurements.

### STRAIN ENERGY MINIMISATION: A METHOD OF PREDICTING MOLECULAR GEOMETRIES OF COORDINATION COMPLEXES

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A strain energy minimisation procedure has been used to predict stable conformations and distorted geometries in some strained metal complexes. In brief, a Urey-Bradley type molecular force field is adopted and the molecule under study is subjected to an energy minimisation procedure starting from some assumed initial geometry. The atomic coordinates are co-operatively shifted under the constraints of the force field until a minimum energy configuration is achieved. In general, the minimised molecular geometries are found to be in good agreement with the observed geometries from crys-

tal structure analyses. Further, the minimised energies provide a useful guide to the expected order of relative stabilities within an isomeric series.

A brief description of the method will be given, followed by examples of successful application of this technique to polyamine metal complexes.

## ORGANIC SECTION

### THE PRINS REACTION WITH CYCLOPENTENE AND CYCLOPENTADIENE

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The condensation of formaldehyde with five membered cyclic olefins has been investigated as a possible route to analogues of 2-deoxyribose. The diol obtained from cyclopentene has been identified by comparison with the reduction product from ethyl cyclopentanone-2-carboxylate. Two other products of the reaction have been isolated and characterised. The reaction with cyclopentadiene leads to the isolation of an isomeric diol.

### A HAMMETT EQUATION STUDY OF THE DEHYDROCHLORINATION OF DDT, PROMOTED BY CHLORIDE IONS IN ACETONE

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Although classical reaction conditions for dehydrohalogenation of alkyl halides to olefins require that a strong base be used, it has been found that DDT and ring-substituted analogues:  $(p\text{-RC}_6\text{H}_4)_2\text{CHCCl}_2$  are dehydrochlorinated to form the corresponding DDE compounds:  $(p\text{-RC}_6\text{H}_4)_2\text{C}=\text{CCl}_2$ , when treated with  $n\text{-Bu}_4\text{NCl}$  in acetone containing 2,4,6-collidine.

Such halide-promoted eliminations have previously been observed only when secondary and tertiary alkyl halides are involved, and DDT is thus the most "acidic" substrate known that undergoes this reaction. A Hammett plot of  $\log k$  for each substituted DDT v.s.  $2\sigma$  is approximately linear, and the Hammett rho parameter is 1.31, indicating that the  $\beta$ -carbon atom bears negative charge in the transition state, although not as much as in the ethoxide-promoted reaction where rho is 2.3. It is also found that  $\text{DDD}:(p\text{-ClC}_6\text{H}_4)_2\text{CHCHCl}_2$  is much less reactive than DDT.

The implications of these results will be discussed in terms of the controversy between the classical E2H mechanism and the recently proposed E2C mechanism (involving elimination via nucleophilic attack at the  $\alpha$ -carbon as well as the  $\beta$ -proton) of Parker and Winstein.

The question of additivity of substituent effects in benzhydryl-type compounds will be discussed, and a method whereby the linearity of somewhat deviant Hammett plots may be improved will be described.

### DIENE INTERMEDIATES IN AROMATIC NITRATION

Dr. G. J. Wright

*Chemistry Department, University of Canterbury*

Methylbenzenes react with nitric acid in acetic anhydride to give aryl nitro and aryl acetoxy products. Work carried out recently has shown that the acetoxylation reaction proceeds through 1,4-diene intermediates. The results of this work will be described.

### A NOVEL ETHANO BRIDGED SYSTEM

Dr. K. E. Richards

*Chemistry Department, University of Canterbury*

A novel condensation of two molecules of methyl-ene-anthrone gives an ethano bridged product with unusual stereochemistry. The mode of formation and the reactions of the product will be discussed.

### STEREOCHEMISTRY OF ADDITION OF CHLORINE ACETATE TO UNSATURATED SYSTEMS

M. J. Rosser and M. A. Wilson

*Chemistry Department, University of Auckland*

The reaction of chlorine acetate with a number of unsaturated systems has been studied and the results of these studies suggest that the mechanism of addition is markedly different from that for the addition of chlorine. Reaction through a cyclic transition state is postulated as a possible explanation of the observed results.

### ACID-CATALYSED ACETYLENE-ALLENE ISOMERISATIONS IN DIPOLAR APROTIC SOLVENTS

M. D. Carr

*Chemistry Department, University of Waikato*

Isomerisations in the hexyne-hexadiene system promoted by solutions of  $\text{HF}\cdot\text{BF}_3$  in sulpholane will be discussed and the carbonium ion intermediates postulated in these isomerisations will be discussed. Experimental evidence, favouring the formation of vinyl carbonium ions rather than allyl carbonium ions, will be presented.

### THE REARRANGEMENT OF N-BROMO- $\alpha$ -HALOGENAMIDES AND N-BROMOPERHALOGENOAMIDES

W. P. Judd and B. E. Swedlund

*Chemistry Department, University of Auckland*

Previous investigators of the rearrangement concluded that the conjugate base of the N-halogeno-

amide rearranged intramolecularly via a cyclic four-membered transition state to give an alkyl halide and cyanate ion. This mechanism is incompatible with evidence presented. The rearrangements of N-bromoperfluorobutyramide and N-bromo- $\alpha$ -chloroisobutyramide in alkaline solution were not first order reactions. In neutral aqueous solution the N-halogenoamide conjugate bases did not rearrange. However, in the presence of an excess of hydroxide ion the N-halogenoamide rearranged readily. The rearrangement was catalysed by hydroxide ion and ammonia and inhibited by many reagents including oxygen, hypobromite, iodide, cupric hydroxide, silver oxide, and amides of carboxylic and sulphonic acids. Possible rearrangement mechanisms are discussed. The effects of small proportions of the inhibitors showed that the rearrangement was a chain reaction. Two probable steps in the chain reaction are the addition of hydroxide ion to the N-halogenoamide conjugate base to give a dianionic intermediate and heterolysis of the nitrogen-bromine bond in this intermediate to give a nitrene.

### THE CLEMMENSEN REDUCTION OF 1,4-DIKETONES

D. R. Crump and B. R. Davis

*Chemistry Department, University of Auckland*

The reduction of 1,4-diketones with amalgamated zinc and hydrochloric acid may take a variety of courses depending on the structure of the diketone. Thus the major products may be either monohydric alcohols with unchanged carbon skeletons, cyclobutane-1, 2-diols, the products of 2,3-bond cleavage, or merely the products of normal conversion of carbonyl to methylene. The structural features necessary for these various pathways will be discussed.

### PHYSICAL CHEMISTRY SECTION THERMODYNAMIC OF MACROMOLECULE SOLUTIONS

G. N. Malcolm and S. P. Koh

*Massey University*

In the original quasi-lattice theory for liquid mixtures it was assumed that it was only the configurational properties which changed on mixing a system of two pure liquids to form a system of one liquid solution. Other properties of the molecules such as their free volumes and the thermal motions of their molecules were supposed to be the same before and after mixing. This theory was eventually unable to account for experimentally observed phenomena in non-polar polymer systems such as negative heats of mixing, volume changes on mixing and lower critical solution temperatures. This has led to a reconsideration of the possible effect

on thermodynamic mixing functions of changes in the non-configurational properties of the pure components. Some, but not all of these effects are easy to understand qualitatively. For example, in the mixing of two liquids with considerably different densities the free volume per molecule of one component will increase and that of the other component will decrease. These changes need not balance one another, and will be accompanied by both energy and entropy changes.

The properties of the two pure components and of the solution can be represented by equations of state for the three liquids. Theories which seek to take account of the effect of differences in these properties on the mixing functions have been called equation of state theories. According to these theories, equation-of-state contributions to the mixing functions should be greater, the greater the disparity between the characteristics of the pure components. These differences are especially large for macromolecule solutions, which therefore afford examples of special interest.

Solutions of polymethylsiloxane in carbon tetrachloride and in chloroform have been studied by measuring the full range of thermodynamic mixing properties. The results are compared with the predictions of the equation of state theory of Flory.

#### DETERMINATION OF THE STRUCTURE OF PROTEIN HYDRATION SHELLS BY NUCLEAR MAGNETIC RELAXATION

J. H. Buckingham, D. F. S. Natusch  
and R. H. Newman  
*D.S.I.R., Gracefield*

Spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) nuclear relaxation times can provide detailed information about molecular motion. In particular, relaxation measurements provide considerable insight into any ordering or structuring processes which influence normal Brownian motion in fluids. The fullest information is obtainable when both  $T_1$  and  $T_2$  are measured as a function of n.m.r. frequency, and the effects of temperature, concentration, pH and ionic strength determined. We have performed such measurements for the water protons in solutions of bovine serum albumin (B.S.A.) using n.m.r. frequencies in the range 2.5 MHz to 60 MHz. The degree of hydration and the strength of the protein-water interactions have been calculated.

The present work indicates that this technique may have important biological applications. In particular, it is possible to correlate the degree of hydration with the persistence of foams generated from solutions of B.S.A.

#### VISCOSITIES OF BINARY LIQUID MIXTURES

J. M. Shah\* and M. V. Pandya  
*Department of Chemical Engineering,  
University of Canterbury*

Viscosities of aniline and dimethyl aniline solutions have been determined over the entire range of composition in carbon tetrachloride, benzene, toluene, chlorobenzene, nitrobenzene and bromobenzene solvents at 25 and 45°C. The excess molar Gibbs free energy of activation  $\Delta^*G^E$ , for flow, and excess viscosity  $\eta^E$  are evaluated for all the twelve systems. Comparison of these excess properties for aniline solutions with those of dimethyl aniline solutions clearly supports the N-H...N bond in aniline. Temperature coefficients of  $\eta^E$  of aniline solutions are decreasing in magnitude, much more rapidly than that of dimethyl aniline solutions. The solvent effect, in terms of viscous interaction energy, is in the following order—  
carbontetrachloride  $\approx$  benzene < toluene < chlorobenzene < nitrobenzene  $\approx$  bromobenzene. This solvent order is in accord with different interactions among different sites on molecules in solutions.

\*R.N.J. College, Bombay-77, India.

#### THERMODYNAMIC PROPERTIES OF GASEOUS MIXTURES

P. J. McElroy, N. F. Judd and A. G. Williamson  
*Department of Chemical Engineering,  
University of Canterbury*

The equation of state for a binary gaseous mixture at low pressures can be written in the form  
 $PV = RT + B_m P$

where  $B_m = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}$

and  $B_{ij}$  represents the virial coefficients for interaction between molecules of type  $i$  and type  $j$ . The relation between  $B_{12}$  and  $B_{11}$  and  $B_{22}$  is of interest in the examination of combining rules for determining the intermolecular potential between unlike species.

A direct measure of the difference between  $B_{12}$  and the arithmetic mean of  $B_{11}$  and  $B_{22}$  can be obtained from the volume of mixing of gases. The temperature coefficient of this difference can be obtained from the enthalpy of mixing of the gases.

Experimental methods for measuring these quantities are described. Results obtained for mixtures of cyclohexane and benzene at 358K are compared with data derived from PVT measurements on the mixtures.

These data are discussed in terms of various combining rules.

### THE FORCE FIELD AND NORMAL COORDINATES OF SPIROPENTANE

G. R. Burns, D. McGavin and H. Wong

*Chemistry Department,  
Victoria University of Wellington*

A study of the gas phase vibrational spectrum at room temperature and the solid state vibrational spectrum at 77K has enabled us to assign wave-numbers to most of the fundamentals of the  $D_{2d}$  molecule, spiro-pentane. Using the new assignments we will report the General Harmonic Force Field that we have obtained.

### LASER RAMAN SPECTRA AND STRUCTURES OF SOME METAL HALIDE SYSTEMS

M. J. Taylor

*Chemistry Department, University of Auckland*

Observation of Raman spectra provides a direct means of structure determination in metal-halide phase systems which has been applied particularly to colourless compounds of Group II and III metals. For experimental reasons most previous work has been on melt phases, but with the advent of lasers as radiation sources and improved monochromators as crystalline solid phases can be successfully explored.

An investigation by laser Raman spectroscopy of the gallium-chlorine system will be described. This can be related directly to a recent revision of the phase diagram and gives structural evidence of new compounds  $Ga_2Cl_6$  and  $Ga_3Cl_7$  in addition to known compounds  $GaCl_2$  and  $GaCl_3$ . In these compounds gallium appears in oxidation states (I) and (II) as well as (III).

These results will be put in context by relating them to knowledge of compounds of aluminium and indium and to the semiconductor material gallium(II) sulphide.

### TETRAMER FORMATION IN TETRAGONAL TRANSITION METAL ION COMPLEXES OF GLYCYL-L-HISTIDINE

P. J. Morris

*Department of Chemistry,  
University of Waikato*

The well characterized complex of Cu(II) with glycyl-L-histidine consists of a tridentate ligand bound to Cu(II) by amino, ionized amide, and one of two imidazole nitrogen donors. The Ni(II) and Pd(II) complexes possess a similar structure. The 1:1 complexes of all three metal ions undergo an ionization at about pH 9.6. Significant blue shifts in the absorption spectra accompany this ionization, suggesting that a nitrogen donor rather than hydroxide ion replaces water in the fourth

coordination position about the transition metal ion. Ionization at an unbound imidazole nitrogen permits it to coordinate at the fourth position of a metal ion chelated by another ligand molecule. Quantitative spectrophotometric analysis of the yellow Ni(II) complex indicates that the structure formed after ionization is tetramer,  $(ML)_4^{4-}$ . Space-filling molecular models show that a unique tetramer is the smallest polymer which permits four nitrogen donors about each metal ion and no un-coordinated nitrogen atoms.

## ENVIRONMENTAL POLLUTION

### DISCUSSION

#### SOME CHEMICAL ASPECTS OF WATER POLLUTION

L. Wilkinson

*Chemistry Division, D.S.I.R., Christchurch*

This paper briefly reviews the contribution of chemists, with particular reference to New Zealand, to the assessment of water quality and to the treatment of wastes.

The assessment of quality involves analytical chemistry concerned with three major areas of enquiry—the inter-relation of putrescible material and the oxygen regime of flowing and impounded waters; the status and persistence of chemicals toxic to man, animals and aquatic life; and the study of nutrient substances which stimulate excessive growth of objectionable plants in impounded waters and estuaries. The inter-actions of putrescible material, toxic chemicals and nutrients in the water environment are briefly discussed.

For economic reasons control of pollution has in the past depended on adequate dilution of the wastes in the receiving waters or on physical and biological methods of treatment. Purely chemical methods of treatment had been confined mainly to the removal of toxic chemicals from certain classes of wastes and there had been little regard given to the removal of nutrients. The rapid increase in growth of cities and of industrial and agricultural activity together with the consequent explosive demand for clean safe water for multi-purpose uses, now necessitates more advanced treatment processes which are likely to involve physico-chemical principles. Further technological advances will require increased effort by chemists in the study of physico-chemical methods of separation of colloids and solutes from the water phase and in the development of more exotic methods of analyses.

## THE REGISTRY

The following were elected on 11.5.1970:

### Honorary Fellow

Council unanimously resolved that Professor L. H. Briggs be elected as an Honorary Fellow of the Institute.

### Fellow

HARTMAN, Leopold, Dip.Chem.Eng.(Lwow), D.Sc.(N.Z.), University of Campinas, Brazil (Professor of Food Chemistry).

### Associates

BLUNT, John William, B.Sc.(Hons.), Ph.D. (Cantua), Chemistry Dept., University of Canterbury (Lecturer).

COMPSTON, Ronald David, B.Sc., BALM Paints (N.Z.) Ltd., Auckland (Technical Officer).

DOWNS, Mrs. Lesley Frances, B.Sc., Westlake Girls' H.S., Milford, Auckland (Assistant Mistress).

GALLOWAY, David John, M.Sc.(Otago), Applied Biochemistry Division, D.S.I.R., Palmerston North (Scientist).

HUNT, James Robinson, B.Sc., A.R.A.C.I., Comalco Industries, Auckland (Marketing and Development Manager).

RODGERS, Kerry Anthony, M.Sc.(Auck.), Geology Dept., Auckland University (Lecturer in Geochemistry).

ROSSER, Maxwell John, M.Sc. (Monash), A.R.I.C.I., Chemistry Dept., Auckland University (Junior Lecturer).

SHANKS, George Frederick, B.Sc.(Hons.), Ph.D. (Tasmania), A.R.I.C.I., Central Institute of Technology, Petone (Tutor in Pharmacology).

SIMPSON, James, B.Sc.(Hons.), Ph.D., Chemistry Dept., Otago University (Lecturer).

SMART, Deanne William, B.Sc., Fletcher Timber Co., Taupo (Plant Chemist, Particle Board Factory).

TOWLER, Charles, B.Sc.(Hons.)(Edin.), Dairy Research Institute, Palmerston North (Research Officer).

### Graduate Members

BOWLES, John Cameron, B.Sc., Chemistry Dept., Auckland University (Ph.D. Student).

DAVEY, Kalvyn Frederick, B.Sc., Ivan Watkins-Dow Ltd., New Plymouth (Production Supervisor).

FAED, Ellen Margaret, M.Sc.(Auck.), Applied Biochemistry Division, D.S.I.R., Palmerston North (Scientist).

HAY, Douglas Miller, B.Sc., B.E.(Chem.), N.Z.P.A.C.R.A., Lower Hutt (Research Engineer).

PAPPS, Murray Douglas, B.Sc.(Hons.)(Cantuar.), Unilever N.Z. Ltd., Petone (Production Manager).

REED, Christopher Alan, M.Sc.(Auck.), Chemistry Dept., Auckland University (Ph.D. Student).

STRANGE, Judy Robin, B.Sc., Contract Manufacturers and Packers Ltd., Auckland (Chief Chemist).

SUTHERLAND, Bruce Leslie Sinclair, B.Sc. (Hons.)(Cantuar.), Chemistry Dept., Canterbury University (Ph.D. Student).

TREBILCOCK, Murray John, M.Sc.(Auck.), c/o Rosyth Hostel, Tokoroa (Pulp Mill Chemist, N.Z. Forest Products).

WADDINGHAM, Donald Markham, B.Sc., BALM Paints N.Z. Ltd., Auckland (Group Leader, Automotive Section Technical Lab.).

WHITCHER, Helen Pippa, B.Sc., Shell Oil N.Z. Ltd., Petone (Industrial Chemist).

WILSON, Michael Amos, B.Sc., Chemistry Dept., Auckland University (Junior Lecturer).

### Resignations

Miss A. P. COOKE, R. HODGES, K. H. KHOO, J. K. MARTIN, J. K. SCOTT.

### Deaths

The following deaths were noted with regret:  
Mrs. K. BROWN, C. L. CARTER, F. G. CAUGHLEY, S. R. J. COTTON.

W. BOUSTRIDGE was deleted from the List of Members.

**THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)**  
**INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30th APRIL, 1970**

1969	EXPENDITURE	\$	\$	INCOME	\$
	<i>Administration Expenses</i>			Subscriptions—Annual	6883.58
	Printing, Stationery, Postages, Tolls, etc.			Proportion Compound Subscriptions	—
1005	Salary, Registrar	1361.39		<i>Interest Received</i>	
628	Travelling Expenses	675.00		Bank of New Zealand	92.33
1008	Branch Expense Allowances	577.43		Local Body Stock	180.64
440	Honoraria (Less Proportion charged to Journal)	380.00			
200	Audit Fees	320.00			
127	Donation—S.A.N.Z.	105.00			
50	Depreciation	50.00			
23	Royal Society of New Zealand—Donation	22.50			
100	Membership Fee	20.00			
20					
(3601)	Cost of Journal	3159.27	3511.32		
3617	Less Revenue from Advertising	2014.83			
2367			1144.44		
(1250)	Prize—Conference Student	25.00			
25	"Careers in Chemistry" Publication	401.44			
1000	"List of Members" Publications	67.59 <i>cr</i>			
557			358.85		
59	Excess of Income over Expenditure for Year	2141.94			
(1641)			\$7156.55		
152			\$6644		
			\$7156.55		

**OVERSEAS VISITORS TRAVELLING FUND**

\$		\$
407	Balance 30/4/69	33.36
	Travelling Expenses Paid during Year	193.90
		34
		\$407
		\$227.26
		\$
	Balance 30/4/69	142.69
	Conference Profit	84.37
	Balance 30/4/70	\$227.26



## BRANCH NOTES

### AUCKLAND

#### *Branch Meetings*

The May meeting took the form of a symposium on Environmental Pollution in conjunction with the New Zealand Water Conference 1970. Four speakers addressed an audience of over 150 and a lively discussion took place.

On June 24th Professor R. C. Cambie gave an address on "The Utilization of New Zealand Natural Products". Professor Cambie was presented with the Research Medal of the N.Z. Association of Scientists by Dr. A. H. Kirton, the President of that Association.

#### *Aakronite Decoratives Ltd.*

This company was formed in 1969 by Mr. L. R. Darroch, B.Sc., ANZIC, who is Managing Director and principal shareholder. Mr. Darroch has developed a new process for producing synthetic stone based on a polyester plus mineral composition. A variety of decorative finishes can be obtained, resembling the translucent natural gemstones such as jade, greenstone and onyx. The firm manufactures synthetic stone for the local market and will be entering the export field soon.

#### *New Zealand Fertiliser Manufacturers' Research Association*

A member of the scientific staff, Mr. J. E. Rouse, N.Z.Cert.Sci., ANZIC, has been granted study leave to the Department of Chemical Physics, University of Surrey, where he has been accepted as a candidate for the M.Sc. degree in Crystallography for the academic year beginning in October.

#### *Student Chemical Society*

The Society has completed a very successful first year. Activities have included regular scientific meetings, tours, annual dinner, social functions and the preparation of an annual review for publication.

At the AGM recently Mr. G. T. Burstein was elected President and Miss J. Rainey Secretary.

#### *University of Auckland*

Professor A. L. Odell has returned from short leave at the University of Wisconsin where he worked on the chemistry of hot atoms produced in a nuclear reactor. Professor Odell has been appointed to the Liaison Committee between Auckland Technical Institute and the University.

Dr. M. J. Taylor has returned from study leave at the Universities of York and Kent where he studied molecular structure by laser raman spectroscopy.

### WAIKATO

The Deputy Director of the Meat Industry Research Institute, Dr. B. B. Marsh, has been awarded the Distinguished Meats Research Award presented by the American Meat Research Association. In a lecture to the Branch this year Dr. Marsh described some of his research at the University of Wisconsin on the problem of watery pork.

Two lectures on the theme "Chemistry in Action" were given by Branch members to sixth form students. The lectures, which were enthusiastically received by large audiences, were "Radioactivity—Friend or Foe" by Dr. D. E. Wright of Ruakura Agriculture Research Centre and "Geothermal Chemistry" by Mr. W. A. J. Mahon, D.S.I.R., Wairakei.

At the June meeting of the Branch, Dr. A. F. Wilson, Superintendent of N.Z. Forest Products, Kinleith, gave a lecture on "Technical Work in the Forest Products Industry."

### WELLINGTON

Wellington Branch members with news items suitable for inclusion are asked to bring them to the attention of the following persons:

Chemistry Division: Dr. T. D. R. Manning.  
Institute of Nuclear Sciences: Dr. H. C. Sutton.

Soil Bureau: Dr. K. R. Tate.

Biochemistry Dept., V.U.W.: Dr. H. D. Ellerton.

Chemistry Dept., V.U.W.: Dr. A. F. M. Barton.

In April a most informative lecture entitled "E.S.R. and ENDOR" was delivered by Mr. M. A. Collins of the Physics and Engineering Division, D.S.I.R.

In May Professor J. F. Duncan of Victoria University gave a lecture entitled "Chemistry and National Development". This interesting lecture gave a large audience an insight into the activities of the National Development Council.

There have been a number of recent staff arrivals at Chemistry Division:

Miss L. Clarkson, B.Sc., a former teacher, has joined the forensic section.

Mr. R. Newman, B.Sc.(Hons.), a recent graduate from Canterbury University, is working in the N.M.R. section.

Mr. J. Lewin, B.Sc.(Hons.), a bursary student who completed his degree at Canterbury University last year, is working in the toxicology section.

Miss C. Chapman, B.Sc., and Mr. M. A. Pitt, M.Sc., recent graduates from Victoria University, have joined the food section of the laboratory.

Dr. I. Maxwell, a recent graduate of Australian National University, has returned to Chemistry Division and is working in the X-ray crystallography section.

Dr. W. Passl, who until recently worked for a pharmaceutical firm in his native Austria, has joined the drugs section of the food laboratory.

Dr. T. Seward, a recent D.Phil. graduate from the University of Manchester where he worked in the field of hydrothermal chemistry with Professor Fyfe, is now with the geo-thermal section.

Dr. John P. M. Bailey has recently returned to Chemistry Division after 3½ years overseas

on study leave. He spent three years at the Mathematical Institute, University of Oxford, studying for his doctorate in the field of theoretical and computational chemistry under the supervision of Professor C. A. Coulson, F.R.S. A further six months were spent at the I.B.M. Research Laboratory, San Jose, California, working with Dr. E. Clementi on the use of large high-speed computers for molecular orbital calculations.

#### *Institute of Nuclear Sciences*

We are pleased to report that Dr. T. A. Rafter has recovered successfully from the operation on his hip which was performed in May. He now has considerably improved freedom of movement.

Mr. P. J. Mathew was awarded his Ph.D. in June for his studies in Nuclear Physics. After a short visit to India he has returned to New Zealand and taken up an appointment at Victoria University, where he will work in co-operation with the Institute. Dr. Mathew is the third to be awarded Ph.D. for experimental work carried out at the Institute; Drs. C. H. Hendy and I. Devereaux received their degrees last year.

Dr. C. H. Hendy has been awarded a Junior Fulbright travel grant to America where he will take up a Research Fellowship for two years at the Lamont Geological Observatory at Columbia University.

Dr. C. B. Taylor attended the second Water Conference organised by the N.Z. Royal Society at Auckland University in May.

A symposium on Vulcanology organised by the N.Z. Royal Society in June was attended by Drs. C. J. Adams and G. L. Lyon.

#### *Soil Bureau*

Miss M. Vause, who was until recently in the Physical Chemistry Section, is now working at the Dental Research Unit.

#### *Chemistry Department, Victoria University*

Dr. R. J. Ferrier, D.Sc., has been appointed to the Chair of Organic Chemistry in this department and will arrive towards the end

of the year. Dr. Ferrier is at present Reader in Organic Chemistry at Birkbeck College, London. He has been post-doctoral N.A.T.O. Fellow at the University of California, and a Visiting Lecturer at the University of Ife in Nigeria. His research interests are primarily in carbohydrate chemistry, in which he has obtained an international reputation. He has lectured in Sweden, Denmark, extensively in North America, and at several international conferences, including the Gordon Research Conference on the Chemistry of Carbohydrates in U.S.A. An invited paper was presented at a Symposium on "Unsaturated Carbohydrates" at the 1968 American Chemical Society meeting. He has visited the Institute of Organic Chemistry in Moscow for the purpose of collaborating in a programme on mass spectrometry of carbohydrates derivatives, and has undertaken a five-week lecture tour of Indian institutes and universities.

Dr. J. T. Craig, Senior Lecturer in Organic Chemistry, has returned from refresher leave which he has spent at the University of Melbourne, where he worked with Dr. Q. N. Porter in the field of polynuclear heterocyclic compounds. Dr. Craig also visited Monash University and gave seminars on the current work on polycyclic aromatic chemistry at Victoria University.

At a farewell party in the Chemistry Department on Friday 12th June a presentation was made to Dr. M. F. M. Coleman, who has taken up a position at the Wellington Polytechnic. Dr. Coleman, a graduate of Auckland and Melbourne Universities, has held a Post-doctoral Fellowship in the Chemistry Department, and has carried out research in the fields of ceramics and mineral extraction.

A Chemistry Department student, Mr. Bruce L. Dickson, has been awarded the New Zealand Honorary Memorial Ramsey Fellowship. This important British scholarship does not provide finance, but is an award of high standing on which we congratulate Mr. Dickson.

Dr. Margaret L. Bailey (who is Mr. Bruce Dickson's sister) has returned to a Post-

Doctoral Fellowship in the Chemistry Department. While overseas with her husband, Dr. John Bailey, she obtained a doctorate in the field of theoretical biochemistry, working with Professor C. A. Coulson F.R.S. at Oxford. Later, during her stay in California, she worked with Professor I. Tinoco, Jr., in the Biophysical Chemistry Department of the University of California, Berkeley, doing calculations on the circular dichroism spectra of polynucleotides.

#### *Biochemistry Department*

Professor J. N. Smith returned to Wellington recently after 5 months' sabbatical leave. Professor Smith spent most of his time in the London area and was able to visit colleagues at several universities there. He was particularly interested in research being done at Queen Elizabeth College on the isolation of pure enzymes for therapeutic purposes; one such carbohydrase enzyme is known to be lacking in the brain of sub-normal children, and purification could lead to a better understanding of its function. Professor Smith was also able to observe the "Open University" in action, in which lectures are presented by television. The biochemistry lectures for the open University were housed at Queen Elizabeth College.

Dr. Peter D. Jones joined the faculty of the Biochemistry Department at the Victoria University of Wellington in December of 1969. After graduating from Victoria University with an M.Sc. degree in Biochemistry in 1963, Dr. Jones was awarded a Fulbright Travel Grant and went to Duke University in Durham, North Carolina, where he obtained his Ph.D. degree in Biochemistry under the direction of Professor Salih J. Wakil, internationally known for his work on the biosynthesis of fatty acids. This was followed by 18 months post-doctoral research in Professor Donald J. Hanahan's laboratory at the University of Arizona in Tucson, Arizona. Dr. Jones is primarily interested in the metabolism of fatty acids and lipids, lipid-requiring enzymes and enzyme systems, the interaction of lipids with proteins, the structure of biological membranes, the physical characteris-

tics of lipid micelles, and microsomal electron transfer processes.

#### *Teachers' Course*

On the 3rd and 4th of July the V.U.W. Departments of University Extension and Chemistry organised a Chemistry Refresher Course for VIth and VIIth Form teachers which covered some of the basic principles of chemistry and indicated how these might be presented to senior post-primary students. Mr. P. Culliford of the Secondary School Inspectorate opened the course, and the teachers were welcomed by Mr. W. E. Dasent, who is an Honorary Lecturer in Chemistry, Bursar, and Assistant to the Vice-Chancellor. Speakers were Dr. G. R. Burns, Professor N. F. Curtis, Dr. B. Halton and Professor W. E. Harvey. It is hoped that the course will become an annual event.

#### *V.U.W. Chemistry Society*

At a panel discussion held on the 8th July at Victoria University on the B.Sc. as a qualification for life, the subjects of vocational training, relevance to practical aspects, specialisation, and the attitude to life of graduates were considered by Professor Tomlinson and Dr. Sinn of the Chemistry Department, and Dr. Newport, a general practitioner. Professor Duncan was in the chair.

### **MANAWATU**

#### *Massey University*

Dr Sylvia Rumball, a lecturer in the Department of Chemistry and Biochemistry, has been granted leave of absence and with her baby son she will accompany her husband to Cornell University. While she is there she will be working with Professor Scheraga on the theoretical calculation of protein tertiary structure from a knowledge of the primary sequence.

Dr Malcolm Chick has been appointed a Senior Lecturer in the Department of Chemistry and Biochemistry. He is interested in biogenesis and has recently been working with Professor Birch at the Australian National University, Canberra.

Dr A. M. Brodie has been appointed a Lecturer in the Department of Chemistry and Biochemistry. He graduated Ph.D. from Canterbury University in 1968 and has spent some time with Professor J. Lewis at University College, London.

Dr M. Hardman, also a Canterbury University graduate, has been appointed Lecturer in the Department of Chemistry and Biochemistry. He has been studying the kinetics of ester hydrolysis at University College, London, and his current interest is in the field of enzyme kinetics.

Professor R. Hodges has been granted \$44,000 for the purchase and installation of an electronic Data Acquisition System which will enhance the usefulness of the mass spectrometer very considerably. For example, the elemental compositions of substances being studied will be routinely available.

#### *N.Z. Dairy Research Institute*

Mr D. W. King, Chief Engineer of the Institute, has recently returned from a mission on behalf of the World Bank to examine the feasibility of establishing a dairy industry in South Korea.

Professor T. A. Nickerson and his wife have recently departed from the Chemistry Department of the N.Z.D.R.I. Professor Nickerson had spent a year here studying flavour adsorption on to lactose, and methods of isolating the enzyme  $\beta$ -galactosidase (lactase) from a yeast.

Professor J. Sherbon will be visiting the Chemistry Department of the N.Z.D.R.I. for a year, and during this time he will be studying some of the physical properties of butterfats.

Dr Akira Akashi from the University of Kyushu, Fukuoto, has been visiting the Microbiology Department of the N.Z.D.R.I. where he has been working on the effect of lysozyme on micro-organisms.

#### *D.S.I.R.*

Dr D. I. H. Jones has been given a Sir Arthur Stapledon Award to work at the Applied Biochemistry Division during the

next year. He is the Chief Plant Chemist at the Aberystwyth Plant Breeding Station in Wales and will be studying the nutritive value of pasture species during his stay.

## CANTERBURY

### University

Dr. G. A. Rodley has returned to the Chemistry Department from sabbatical leave which he spent in teaching and research with Professor Harry B. Gray at the California Institute of Technology.

Dr. W. G. Mumme of the Mineral Chemistry Division, C.S.I.R.O., Melbourne, spent six weeks in the department recently furthering his studies of the structure of minerals using the departments X-ray crystallography equipment.

Professor J. Vaughan is at present overseas on an Erskine Fellowship visiting Australia, Canada, and the United Kingdom.

A six lecture course in Chemical Process Technology has been given in the latter part of the second term. The course, which is a preliminary to a new B.Sc. unit, is intended to give chemists a background to some of the principles underlying the operation of chemical processes on a commercial scale. In addition to lectures from the staff of the Department of Chemical Engineering, further lectures were given by Dr. D. K. Sewell (Ivon Watkins-Dow), Dr. B. Fergus (N.Z. Forest Products) and Mr. E. Beauland (Chemistry Division, D.S.I.R.) on certain aspects of industrial chemical processing.

A very successful refresher course on "Separation and Purification of Chemical Compounds" was run by the Departments of Chemistry and Extension Studies during the May vacation. Approximately twenty-five chemists attended the course and they were about equally divided between industry and school teaching. Subjects covered included distillation, electrophoresis, column and thin layer chromatography, and ion exchange.

### Personal

Messrs. G. M. Moir and G. J. E. Hunter have transferred to Christchurch from New Plymouth and Nelson respectively on their retirement.

Mrs. C. C. Winterbourn has returned to New Zealand from Canada and will be resident in Christchurch.

Mr. J. A. Peters, lately secretary of the Waikato branch, has transferred from Rukura A.R.S. to the Forest and Range Experiment Station of the N.Z. Forest Service, Rangiora, as biochemist and toxicologist.

## BOOK REVIEWS

*Solubilization by Surface-Active Agents*, by P. H. Elworthy, A. T. Florence and C. B. Macfarlane. Published by Chapman and Hall, Great Britain, 1968, 335 pages. Price U.K. 63/-.

The authors of this book are all lecturers in pharmaceutical chemistry at the University of Strathclyde, Scotland. Their book is largely concerned with the effects that surface-active agents in solution have on the solubility of added substances, with particular emphasis on applications in chemistry and the biological sciences. It is essentially a practical book which surveys the literature on surfactants and their applications over the past decade. The authors claim that the book was written with both final-year and post-graduate students of pharmaceutical and colloidal chemistry in mind, as well as workers in industry.

The pattern of the book follows the traditional layout of most specialist titles. The first two chapters survey the theory of surfactants and the remaining five chapters deal with their numerous applications. Chapters one and two give an up-to-date account of the phenomenon of micellization and the theories of solubilization, along with the many experimental techniques of studying the latter. The remaining five chapters discuss a diverse range of topics, including the solubilization of pharmaceutical preparations and drugs, cosmetics, insecticides and many naturally occurring substances such as lipids, steroids and carcinogens. The final chapter is devoted to some chemical and industrial applications including polymerization, detergency and analytical procedures. Each chapter is accompanied by many illustrations and diagrams, most of which are reproduced from the original journals. The average number of references

is one hundred and fifty per chapter and the reviewer might be excused for thinking that the co-authors were competing to compile large bibliographies. An appendix of chemical structures and trade names of surfactants is also listed and the index is very satisfactory.

Overall, the authors have succeeded in their aim to produce a comprehensive monograph on the subject of solubilization. The questionable readability and terse style of presentation would deter most students from reading beyond the first few chapters, but teachers of pharmaceutical chemistry would find the book valuable. It should also be of value as a reference source to workers in quality control laboratories dealing with organic and pharmaceutical materials.

L. H. BOULTON.

## SIXTH FORM CHEMISTRY BULLETINS

*Sixth Form Chemistry Bulletins.* Published by the Department of Education, Christchurch, with the co-operation of the New Zealand Institute of Chemistry. No. 1: "Le Chatelier's Principle"—G. N. Malcolm and H. N. Parton. No. 2: "Lewis Structures"—A. H. Wooff.

A Council sub-committee with Professor J. Vaughan as chairman was appointed some eighteen months ago to consider ways of producing short, authoritative bulletins which would be useful in the teaching of University Entrance, Bursary and Scholarship chemistry. Numbers 1 and 2 have now been published and distributed to all New Zealand secondary schools. Sufficient scripts are in hand or promised to maintain a steady production of about four bulletins per year. The number of copies that can be produced is not large but costs are minimal, and through the Department of Education distribution system the bulletins reach all schools including the very small ones unlikely to be reached by conventional publication methods.

This has been an excellent example of Institute-Department of Education co-operation and the success of the venture has been in no small measure due to Mr. R. U. Roy of the Secondary School Inspectorate, Christchurch.

Other publications for schools published by or with the assistance of the Institute are:

- (1) "Chemistry in Action—1969". This has been published by the Canterbury Branch and contains lectures by Philippa M. Wiggins, R. R. Brooks and J. F. Duncan. It is the third in a series which have been generously sponsored by Messrs. Watson Victor Limited. It has been distributed to all New Zealand secondary schools.
- (2) "Molecular Architecture" by W. E. Dasent, J. Vaughan and G. J. Wright. This is being published by the School Publications Branch of the Department of Education and is a companion volume to "Atoms, Bonds and Polymers" by W. E. Dasent, G. N. Malcolm and M. H. Panckhurst which appeared in 1965.

## BOOKS RECEIVED

The following books are available for review. A member wishing to review a particular book should write to The Editor, P.O. Box 250, Wellington.

Reviews should be completed and sent to the Editor within three months of receiving the book. Reviewer keeps the book.

*Basic Principles of Ligan Field Theory* by H. L. Schläfer and G. Gliemann, published by Wiley Interscience, a division of J. Wiley and Sons. 1969. A\$18.95.

*Halides of the First Row Transition Metals* by R. Colton and J. H. Canterford, published by Wiley Interscience, a division of John Wiley and Sons. 1969. A\$21.25.

*Fundamental Aspects of Inorganic Chemistry* by B. Chiswell and D. W. James, published by John Wiley and Sons, 1969. A\$4.95.

*General and Inorganic Chemistry* by Gunnar Hägg, published by John Wiley and Sons, 1969. A\$24.15.

*The Computation of Chemical Equilibria* by F. van Zeggeren and S. H. Storey, published by Cambridge University Press 1970. U.K. £2.50.

*Thermochemical Kinetics: Methods for the Estimation of Thermodynamical Data and Rate Parameters* by Sidney W. Benson, published by John Wiley and Sons, 1968. A\$10.45.

*Steroid Reaction Mechanisms* by D. N. Kirk and M. P. Hartshorn, published by Elsevier Publishing Company, 1968. U.K. 200/-.

*Mass Spectrometry and Ion-molecule Reactions* by P. F. Knewstubb, published by Cambridge University Press, 1969. U.K. £2.

## IUPAC NEWS

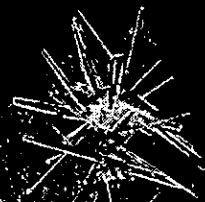
### N.Z. National Committee for Chemistry

Information has been received from IUPAC on forthcoming international chemistry symposia as follows:

1. Symposium on Non-aqueous Electrochemistry—Paris, France—8-10th July, 1970.
2. VIIth Microsymposium on Macromolecules: Polyvinyl Chloride, Its Formation and Properties—Prague, Czechoslovakia—7th-10th September, 1970.
3. International Congress on Industrial Waste Water—Stockholm, Sweden—2nd-6th November, 1970.
4. Vth International Conference on Organometallic Chemistry—Moscow, U.S.S.R.—16th-21st August, 1971.
5. International Symposium on Chemical Education — Sao Paulo, Brazil — 30th August-3rd September, 1971.
6. Symposium on Man-made Polymers in Papermaking—Helsinki, Finland—5th-8th August, 1972.

C. J. Wilkins, Hon. Secretary.

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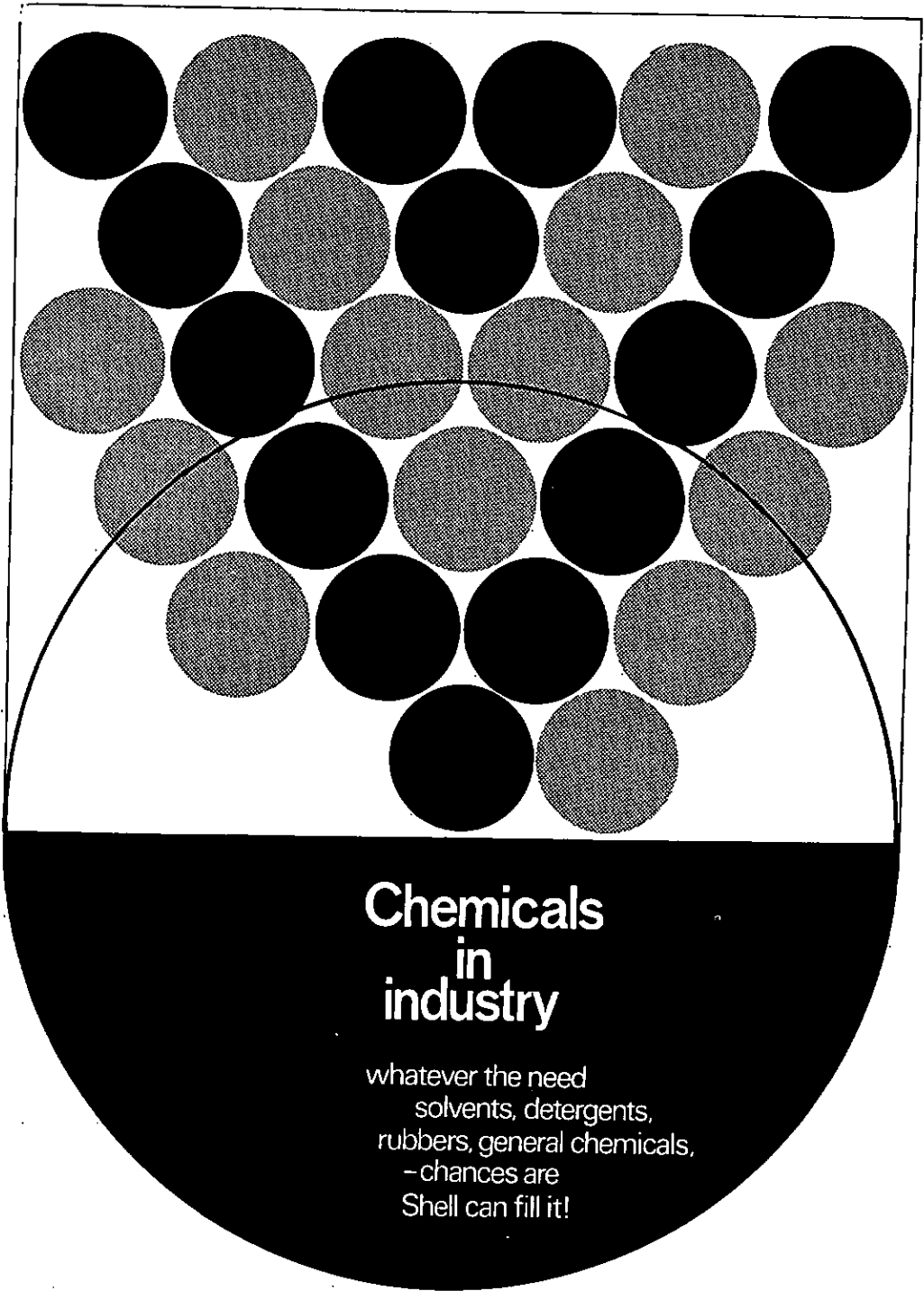
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<b>52839</b>	<b>ELVIRA</b>	<b>66853</b>	<b>DIOXITOL</b>
<b>53164</b>	<b>KEREX</b>	<b>66854</b>	<b>TRIOXITOL</b>
<b>53773</b>	<b>DELAK</b>	<b>67314</b>	<b>OXILUBE</b>
<b>54625</b>	<b>SHELL device</b>	<b>67806</b>	<b>GRAMEVIN</b>
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<b>58747</b>	<b>DOBANE</b>	<b>70690</b>	<b>DOBANIC</b>
<b>59128</b>	<b>PHOSDRIN</b>	<b>72050</b>	<b>BIDRIN</b>
<b>59130</b>	<b>NEMAGON</b>	<b>72707</b>	<b>CARADATE</b>
<b>59329</b>	<b>NITRA-SHELL</b>	<b>72708</b>	<b>CARADOL</b>
<b>59330</b>	<b>VIANOL</b>	<b>72709</b>	<b>GARDONA</b>
<b>59598</b>	<b>CARINA</b>	<b>72711</b>	<b>BIRLANE</b>
<b>59602</b>	<b>CARINEX</b>	<b>74536</b>	<b>PLANAVIN</b>
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<b>79202</b>	<b>VEOVA</b>	<b>76162</b>	<b>VERTHION</b>
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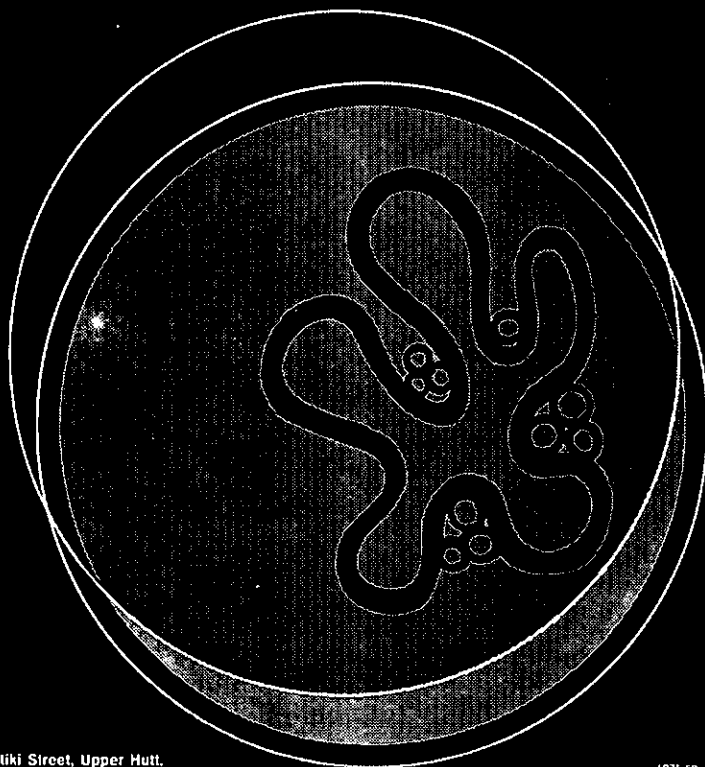
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## **INTERNATIONAL UNIONS NEWS**

Arising from a resolution passed at the Symposium on Recent Crustal Movements held in Wellington in February, the International Unions concerned have set up a sub-commission for the study of recent crustal movements and associated seismicity in the circum-Pacific region. Professor H. W. Wellman is convener.

### **International Meetings**

12th Pacific Science Congress, Canberra, Australia, 18 August-3 September.  
42nd ANZAAS Congress, Port Moresby, Papua, New Guinea, 17-21 August 1970.

### **Representation at International Meetings**

Fifteen scientists, six of whom received financial support from the Royal Society, represented New Zealand at overseas meetings of eight international scientific unions during recent months.

### **Appointment**

Dr. F. B. Shorland has been appointed by the International Union of Nutritional Science to be a member of the Committee on Schools of Food Science and Technology of the Commission on Nutrition Education and Training.

## **OTAGO BRANCH CENTENARY BOOKLET**

To mark the completion of its first one hundred years the Otago Branch of the Royal Society (previously the Otago Institute) organised a number of review addresses. These are to be published as a booklet of about 36 pages to be offered for sale to all members of Member Bodies of the Royal Society at a cost of about 50-75 cents depending on the demand for the booklet.

At this stage it would be very helpful if some indication of demand could be gauged. Those who would like a copy (on the understanding that it would cost not more than 75 cents) please send their order (no money at this stage) to

Mr. K. R. Dawber,  
(Hon. Secretary, Otago Branch of the Royal Society),  
Physics Department,  
University of Otago,  
P.O. Box 56, Dunedin.

Contents will include A History of the Otago Branch, and edited versions of the following addresses:

Professor J. N. Dodd, "One Hundred Years of Physics"

Professor R. F. H. Freeman, "One Hundred Years of Biology"

Professor D. S. Coombs, "One Hundred Years of Earth Sciences"

Professor C. F. H. Higham, "One Hundred Years of Anthropology"

Professor J. B. Mackie, "Navigation from Cook to the Present Day"

Professor W. Davidson, "Mathematics in Science; a Hundred Years of Achievement".

The booklets should be ready for mailing during August.

## **BIOLOGICAL SCIENCE TEXTBOOK**

The 6th form students' textbook *Biological Science. Processes and Patterns of Life*, Chairman and Supervising Editor Professor Knox, published by the N.Z. Department of Education, approaches biology largely through New Zealand ecology and examples. In its 764 pages there is an enormous amount of information, well written and illustrated, which could be both useful and interesting to those Royal Society members who are amateur scientists.

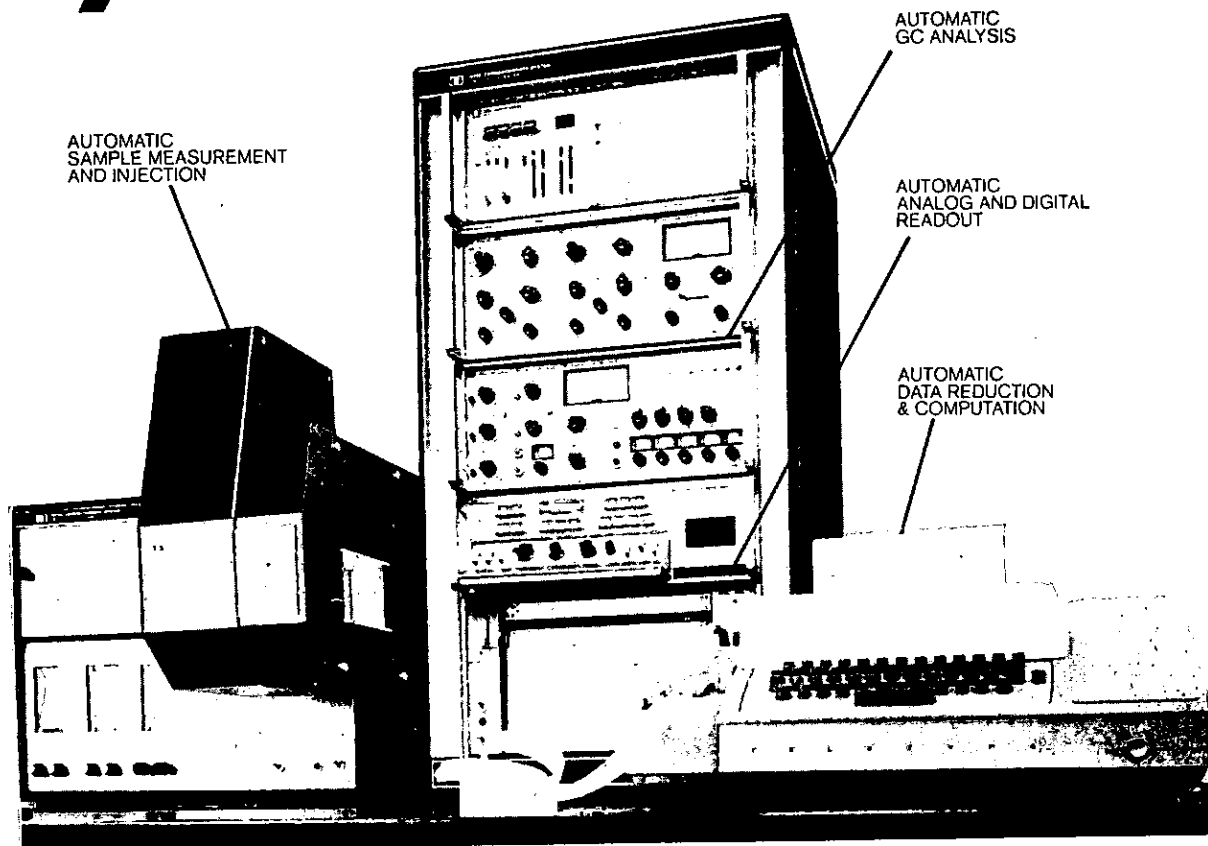
So much information in so many pages has inevitably resulted in a heavy book, too large to hold comfortably. The lay-out is rather cramped, the binding good and the cover attractive. At \$9 it is good value. It would probably serve its purpose better if it were published in separate sections as paperbacks—more easily handled by the reader and more easily brought up to date.

This Newsletter has been compiled for your information and interest by members of the Member Bodies' Committee. Suggestions for later numbers will be welcome; please send to the General Secretary, Royal Society of New Zealand, Box 196, Wellington.

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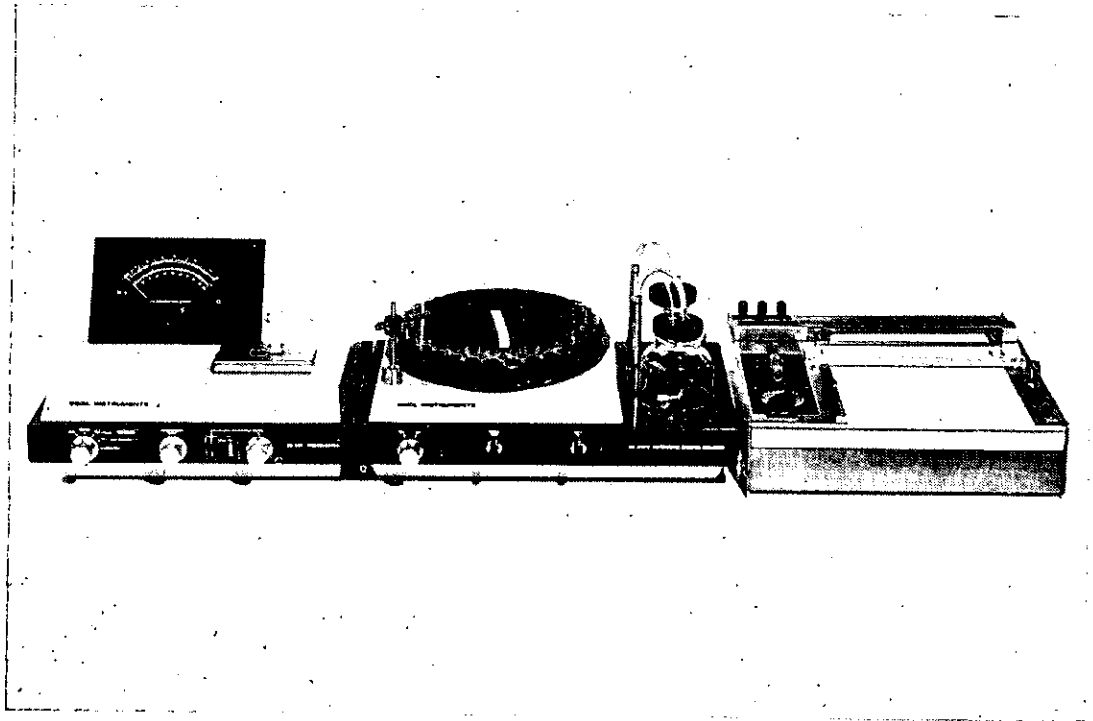
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the outlines, and weigh them.



the sauce while the maître himself uses the

For example, we heard about English realtors who weigh their pieces of property on a Mettler.

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Star French cooks use a Mettler balance as a double. They determine the 48 ingredients of a «Sauce à la mode du maître» accurately to 1/100 g and then let

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