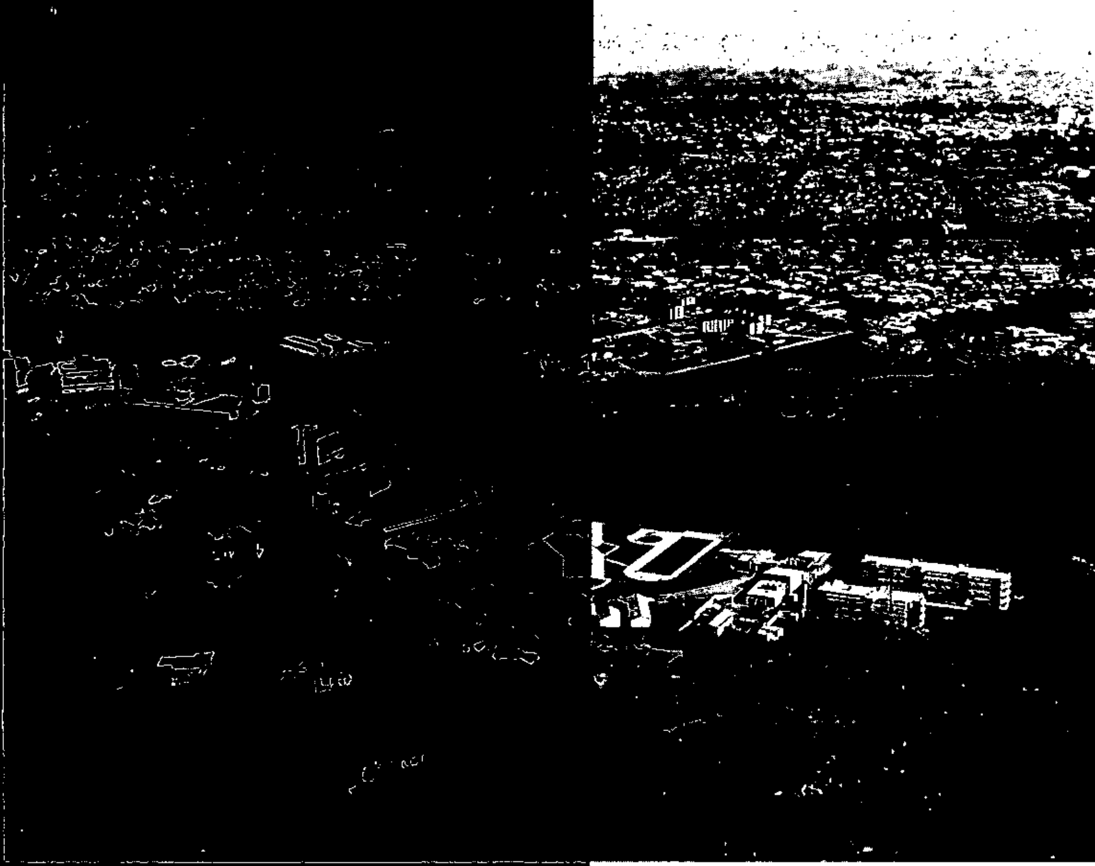
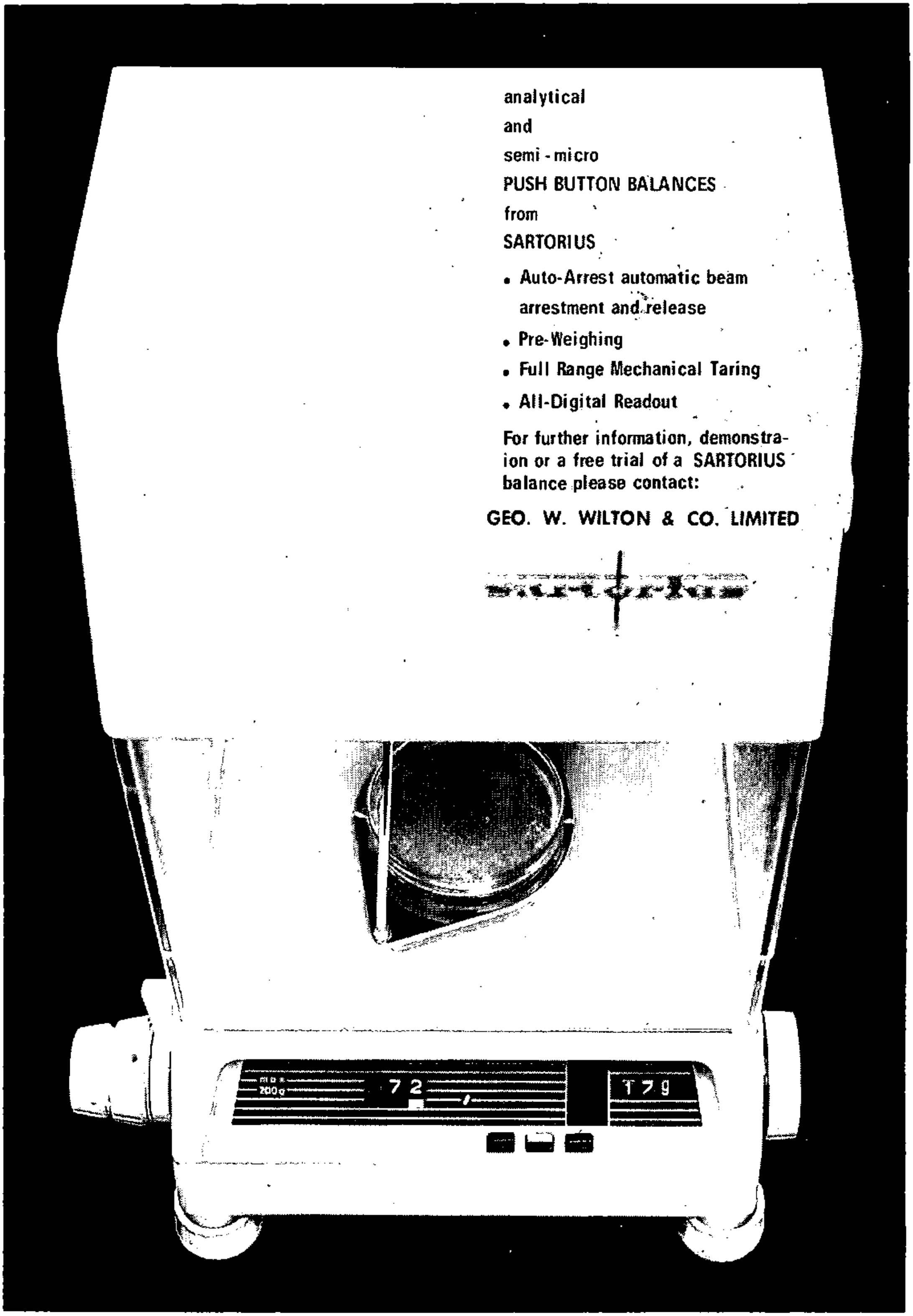
CHEMISTRY IN NEW ZEALAND

JOURNAL OF
THE NEW ZEALAND
INSTITUTE
OF CHEMISTRY



CONFERENCE ISSUE

Vol. 35, No. 4, August, 1971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CHEMISTRY IN NEW ZEALAND

Journal of
The New Zealand
Institute of Chemistry

Vol. 35, No. 4 August 1971

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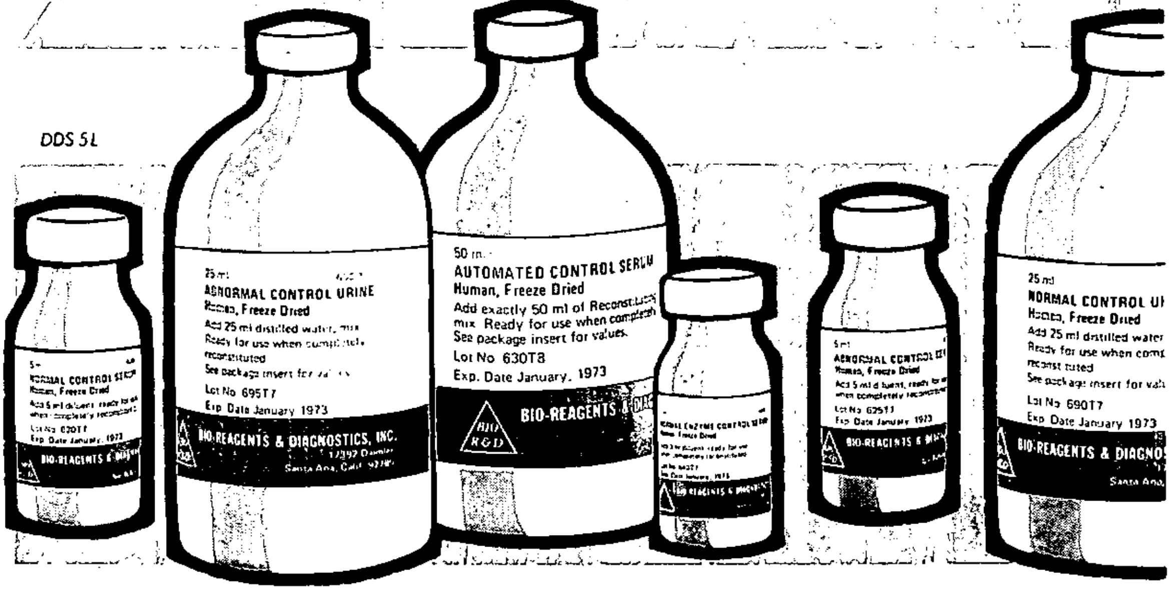

GENERAL DESCRIPTION AND USE.

All Bio – R & D control products are of human origin carefully processed and freeze-dried (lyophilized) for maximum stability during shipment and storage. Reconstitution must be with distilled or de-ionized water except for the Automated Control Serum where a special reconstituting fluid accompanies the serum. After reconstitution, the stability of the various constituents of the controls is the same as if in a laboratory specimen.

Assays have been performed by at least three reference clinical laboratories. Methods of assay and assay results are supplied in the form of a direction insert in each package. After reconstitution, the control products are to be tested in the same manner as unknown specimens. If results obtained are the same as the direction insert values (within normal limits of variation), test procedures are considered "in control", and thus, specimen values may be reported with confidence. Significantly different values from those reported in the direction insert indicate "out of control" conditions exist, and immediate efforts to discover the source of difference are necessary to produce reportable results.

NORMAL CONTROL SERUM, HUMAN, DRIED. (Catalogue No. 620) 6 x 5 mls

Serum derived from healthy humans containing all constituents usually found in serum at "normal" concentrations.

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Human serum carefully processed and freeze-dried so as to preserve the most delicate enzymes normally found in serum. Assayed by the reference laboratories using a variety of methods and reported in various popular enzyme units.

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ELEVATED BILIRUBIN CONTROL SERUM, HUMAN, DRIED. (Catalogue No. 660) 6 x 3 mls.

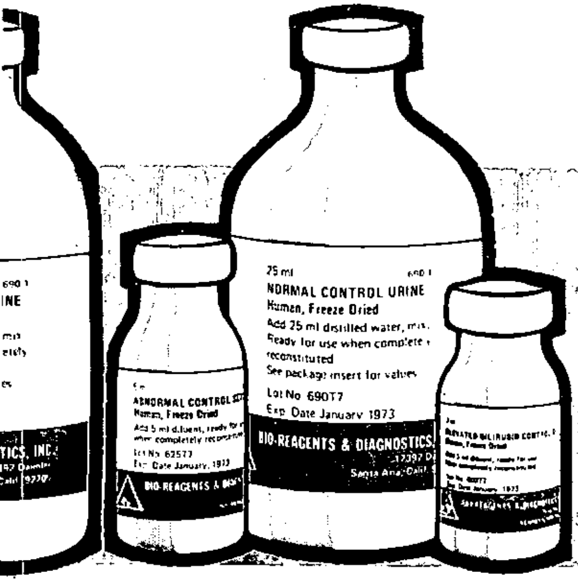
Human serum processed in same manner as all other Bio – R & D control products. Supplemented with bilirubin meeting nationally – established criteria of purity. Therefore, may be used as a secondary reference as well as a control serum.

NORMAL CONTROL URINE, HUMAN, DRIED. (Catalogue No. 690) 4 x 25 mls.

Urine derived from healthy humans and containing constituents usually found in urine specimens in "normal" concentrations including hormones associated with pregnancy. Processed in the same manner as all other Bio – R & D control products. Designed specifically for the control of assay procedures using urine as the specimen.

ABNORMAL CONTROL URINE, HUMAN, DRIED. (Catalogue No. 695) 4 x 25 mls.

Human urine similar to NORMAL CONTROL URINE except constituents are present in concentrations usually considered abnormal. In addition, assays are supplied for some constituents which would not normally occur in measurable amounts in urine.



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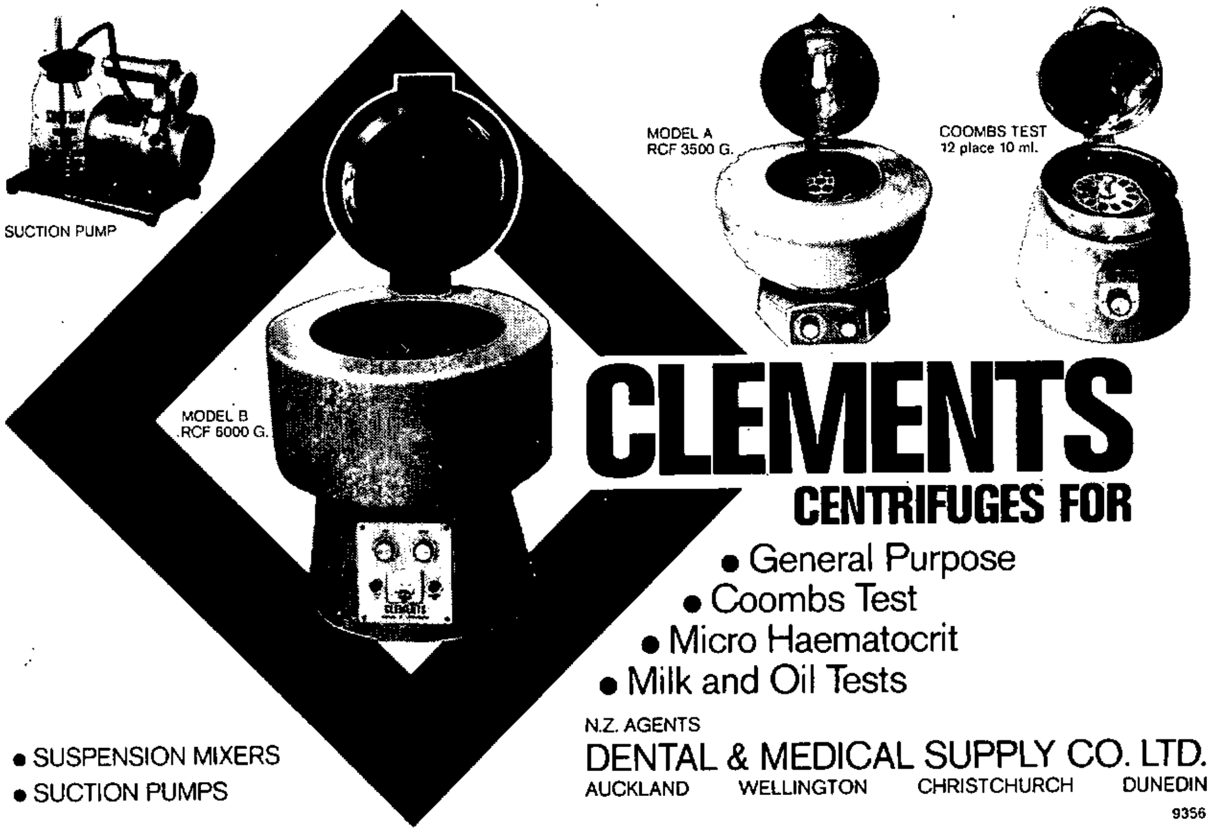


BIOCHEMISTRY DEPARTMENT

WELLINGTON HOSPITAL BOARD

The Biochemistry Department, Wellington Hospital, has a vacancy for an experienced laboratory worker to take charge of the section of routine service biochemistry. Duties will include the supervision of existing automated equipment and the progressive introduction of further automation to increase the service capacity. Plans to significantly increase the degree of automation within the Department are in preparation. This position would suit either a grade technologist or a science graduate with experience in a clinical chemistry laboratory. Provision could be made for the tuition of a suitable applicant in basic automated techniques if necessary.

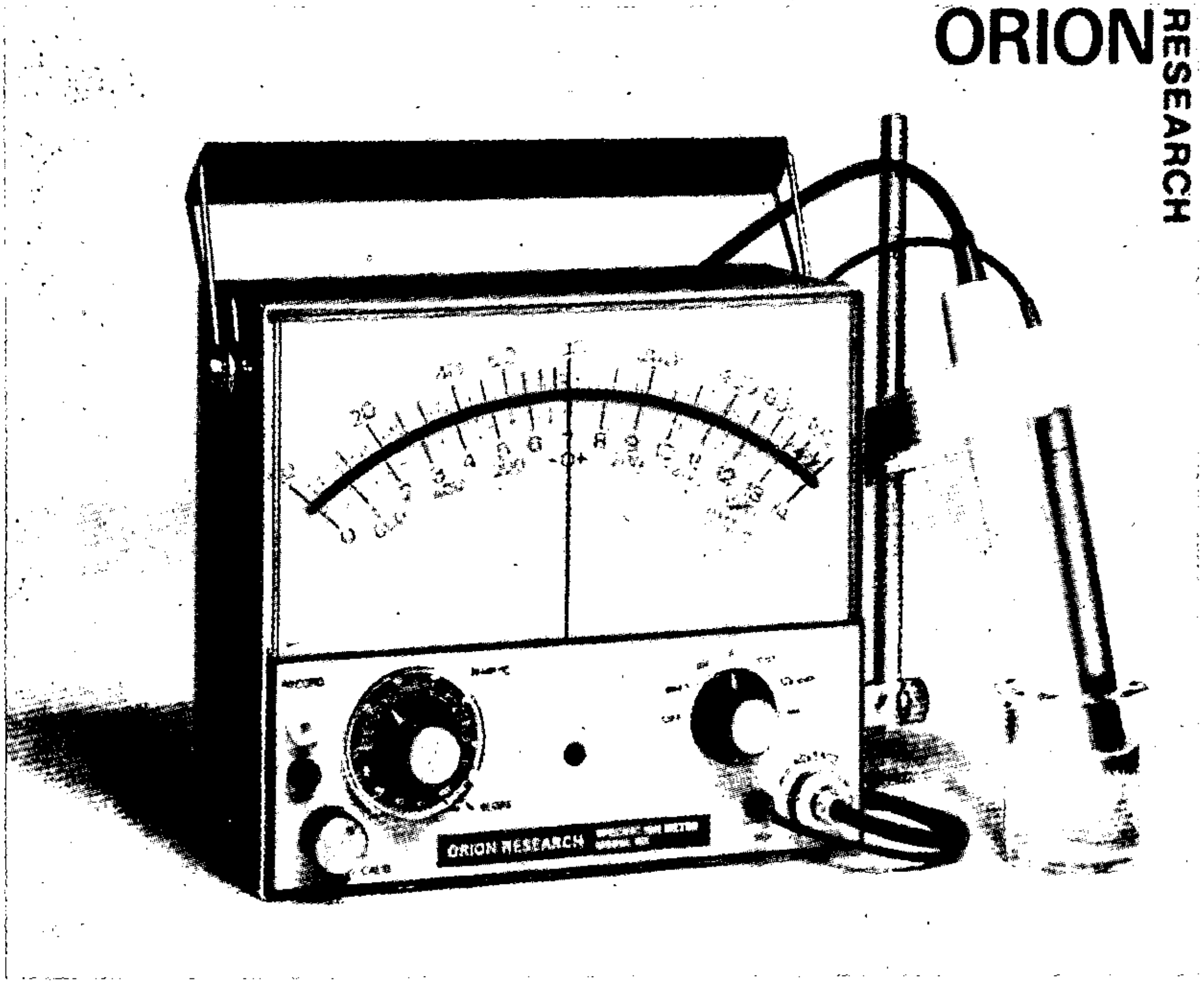
The post is currently classified as a maximum Grade 2 of Scale 3 Hospital Laboratory Workers Regulation (maximum salary $5046). Present plans for expansion will increase responsibility leading to its being regraded to at least Grade 3 (maximum salary $5557).

In addition, a technologist reaching maximum grading for the post may achieve higher grading on the basis of personal merit.

Commencing salary will be commensurate with qualifications and experience and will be determined by the Laboratory Officers' Salaries Grading Committee.

Enquiries regarding this post would be welcomed by the Director of Laboratory Services, Wellington Hospital.

Application giving full particulars of age, qualifications and experience, together with references, should reach the Secretary, Wellington Hospital Board, P.O. Box 10245, Wellington, by 9.00 a.m., Thursday, 30th September, 1971.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ORION RESEARCH

CONFERENCE 1971

Welcome to Hamilton

To ask one person thrice in thirteen years to write an introduction to a Hamilton conference is to invite retrospection. Time has brought considerable changes. Hamilton, population 43,000 and sixth largest city in 1958, now claims, with 75,000, to be (*pace* Dunedin) the fourth. Lacking a University venue, we met in 1951 and 1958, like the Institute's first conference in 1935, in the Girls' High School. In 1964 we moved to the new University of the Waikato and now for the first time we meet there in (the familiar atmosphere of) a Science Department.

The 1951 Conference Committee, all concerned with the soil-grass-animal complex, purposely moulded a programme with an agricultural chemistry bias. Conference 1958 had sessions related to local interests in agriculture, forestry and coal. By 1964 the editorial noted that the programme had "no flavour peculiar to the Conference District and little to mark it as a conference of chemists working in New Zealand." This year we can choose from over ninety submitted papers in five divisions based not on application but on "subdisciplines" of chemistry. Most of the titles reveal little relevance to industry or primary products, although four-letter words like soil, milk and wool do occur (and blood and guts, drugs, pollution and sex (insects) are in the background of others). A proportion of the papers come from the Universities and most report a basic approach to their subject.

There will be four Guest Speakers this year. Dr. B. Johnson, in New Zealand as Mellor Lecturer comes from Cambridge. J. B. Mellor, who in "Modern Inorganic Chemistry" invoked Occam's Razor in his discussion of the valency of nickel in carbonyls, would have appreciated Dr. Johnson's subject, organo-metallic complexes in organic synthesis. Dr. B. J. Ralph, Head of the School of Biological Technology, University of New South Wales, will speak of Unisearch, an organisation which seeks to aid by research "the application of science to industry and commerce." His message may be timely when, in the year of EEC negotiations, we need more than ever to diversify in products and markets. Dr. M. C. Probine, Director of the Physics and Engineering Laboratory, will send our thoughts in the same direction. Professor F. L. Warren, visiting Fellow at Ruakura from the CSIR National Products Research Laboratory, University of Capetown, discussing differences in chemical structure that influence relations between plants and insects, and between sexes, may point the way to better pest control.

Waikato is the name of a passable brew as well as of the river which (through intricate chemical processes of course) provides the water for it; and sophisticated expansion of the local wine industry now requires a chemist in oenology at Ruakura. The organoleptic analysis of beer and wine, with proteins bovine, ovine and avian, will not be the only chemical savour at the two social functions, for there will be the usual spontaneous discussions between old and new friends with common interests in chemistry. These alone are of sufficient professional value to justify a Conference. Wherever chemistry is discussed, at a plenary session or at the bar, let there be full exchange of information, for only thus can chemistry and knowledge and human welfare, be advanced.

N. T. Clare

NEW ZEALAND INSTITUTE OF CHEMISTRY MEMBERSHIP BY EXAMINATION

In 1969 Council decided to phase out admission to professional membership of the Institute by examination and gave notice that this means of entry would end in 1974. In the June 1971 issue of Chemistry in New Zealand, the Auckland Branch presents a case for retaining this means of entry and the following comments are offered by the Canterbury Branch Committee..

At the Council meeting in August 1970 it was established as a *principle* that a candidate for entry by examination (rule 9.2.4) who had passed Chemistry III, theory *and* practical, at a New Zealand University would be exempted the N.Z.I.C. examination. (A pass in Chemistry III theory is required by N.Z.I.C. regulations. The Institute then examines the candidate by a four-day practical exam). This decision was subsequently suspended at the May meeting and the question of entry by examination is again being intensively studied.

The basic standard of admission to professional status in the Institute is a university degree which includes Chemistry III or Biochemistry III (Rule 9.2.1.). Alternative standards for entry are the possession of "equivalent" qualifications (e.g. B.E. (Chem).); membership of a sister Institute; by examination; or by "having training, knowledge and experience *fully* equivalent to that required by 9.2.1."

The decision to replace N.Z.I.C. examinations by university stage III Chemistry is a consequence of the general feeling that the N.Z.I.C. is too small a body to set its own examinations. The extension of this to full exemption of any N.Z.I.C. examination is an invitingly logical step but the consequences are considerable and should be carefully considered. Such consideration leads the Canterbury Branch Committee to the conclusion that the 1969 decision to abolish this method of entry was correct.

The consequences of the automatic acceptance of Chemistry III theory and practical need to be examined separately. The general debate about entry by examination is a separate issue. It is possible, notwithstanding point 8 of the Auckland Branch article, to take Chemistry III having passed only Chemistry I and II and Math I. Hence an N.Z.I.C. candidate could be admitted on the basis of 4 units, i.e. half a degree. Further, it is possible to get a variety of special exemptions to study at University and it is quite possible that a candidate for N.Z.I.C. could have passed Chem. I, II and III only. For this reason, taking rule 9.2.1. as the basic standard, Canterbury Branch is strongly opposed to the *automatic* granting of professional status to a candidate who has passed Chemistry III, theory and practical. Such candidates should be considered under rule 9.3 and be required to show that they have achieved a standard of training and experience *"fully equivalent"* to 9.2.1. This leads us to the inevitable conclusion that this is the best way of admitting the present candidates for entry by examination. They can still take Chemistry III and then apply for consideration under 9.3 and submit themselves to professional interview as is done for entry to the New Zealand Institute of Engineers.

In support of this argument we offer the following comments on the points raised in the Auckland article.

1. Rule 9.3 makes no mention of age.
2. It is not the N.Z.I.C.'s place to "help applicants in their careers" and to lower entry standards for this reason would be gross irresponsibility on the part of the Institute.
3. The members referred to might very well have been admitted under 9.3.

4. No mention of N.Z.C.S. is made in the rules. A pass in Chemistry III does not require N.Z.C.S. plus Chemistry II. If however, an N.Z.C.S. plus Chemistry III is to be recognised as equivalent to a B.Sc. then entry could be by 9.2.2, but this would need a conscious decision of Council and the Membership Committee after a thorough examination of the standards. It is of relevance that the present N.Z.C.S. generally only enables a student transferring to University to be granted at most three Stage I units so that N.Z.C.S. plus Chemistry III equates to 5 units for B.Sc.
5. The people who have attained membership under rule 9.2.4 could well have been expected to be admitted to membership under rule 9.3 since no entry rule is made to be an easy or substandard route to membership.
6. The State Services Commission recognises associate membership as a professional qualification and hence the standard of membership must be seen to be consistent with that recognition. The Institute does require the same standard of qualification as for all professional societies.
7. The N.Z.I.C. entry standards, a Pass Degree, are in fact, lower than those of the R.I.C. or the South African Institute. Relativity with overseas bodies is not of prime importance in this debate.
8. Each candidate for membership not holding a degree, or its equivalent, must be examined on his own merits. The data in the Auckland memorandum are not factual.
9. *Automatic* membership must not be available to applicants who do not obviously come within the category of the primary route of entry (rule 9.2.1). Each special case must be dealt with on merit.

Canterbury Branch Committee

Membership of the Institute by Examination

In conjunction with the article on this subject published in the June issue of the *Journal* (*Chem. N.Z.*, 35(3), p.90, 1971), a survey of opinion of Auckland Branch members was carried out. Each member was asked to reply to the following proposition:

"I think that rule 9.2.4 of N.Z. Institute fo Chemistry permitting entry to Associate Membership by examination should be retained/abolished (delete whichever you disagree with)."

The result of the survey are as follows:

Status of Member	Total Membership	Received Replies	For Retention	For Abolition
Fellows	41	26	25	1
Associates	201	108	100	8
Grad. mbrs.	26	7	7	0
Local mbrs.	21	2	1	1
Overall	289	143	133	10

The response was overwhelmingly in favour of retention of the examination route to membership; 93% of the replies being in favour of the status quo.

Auckland Branch Committee

CONFERENCE . . . . HAMILTON, AUGUST 23-27, 1971

ABSTRACT OF PAPERS

ELECTROCHEMISTRY SECTION

WATER STRUCTURE AS A DETERMINANT OF ION DISTRIBUTION IN LIVING CELLS

Philippa M. Wiggins
Department of Medicine, University of Auckland

Most living cells are bathed by a solution containing Na^+, K^+, Ca^{++}, Mg^{++}, Cl^-, HCO_3^-, $H_2PO_4^-$, HPO_4^{--}, SO_4^{--}, H_3O^+ and OH^- ions. Of all these ions only those which are negatively hydrated (K^+, Cl^-, HCO_3^-, $H_2PO_4^-$ and HPO_4^{--}) are present in most cells in concentrations as high as those predicted for a simple equilibrium distribution. The positively hydrated ions (Na^+ Ca^{++}, Mg^{++}, SO_4^{--}, H_3O^+, and OH^-) are all relatively excluded. It is suggested that the intrinsic hydrogen-bonded structure of water is enhanced by stabilisation at protein surfaces inside cells, and that this has the effect of making cell water a poorer solvent for positively hydrated ions than is bulk phase water.

A model for cell water has been found in the pore water of a silica gel. This water, with presumably enhanced hydrogen-bonding resulting from its proximity to the hydrogen-bonding surface of the gel, relatively excludes Na^+, Ca^{++}, Mg^{++} and H_3O^+ but has normal solvent properties for K^+ and Cl^-. Moreover its selectivity for K^+ relative to Na^+ changes with the degree of ionisation of the surface.

The conditions under which this mechanism of ion distribution might operate in living tissue is discussed in the light of these experimental results.

PASSIVE FILMS ON METALS

G. T. Burnstein and D. E. Williams*
Department of Chemistry, University of Auckland

When a metal is made the anode in an electrolytic cell with a suitable electrolyte, an insoluble film will grow on the surface. Such films may protect the metal from further attack, such as those that form on nickel, cupro-nickel alloys and stainless steel. In other cases the film may be non-protective, such as the films of rust that form on iron. The mechanisms by which these films grow and conduct electricity are of interest. Electrochemical measurements are being used to study these mechanisms in the case of films on bismuth metal. Films of Bi_2O_3, BiOCl, BiOBr and BiOl have been investigated and films of $BiPO_4$ and Bi^2S^3 are also of interest. Both ionic migration and electronic conduction can occur and can be described theoretically.

IN SEARCH OF A PHOSPHATE SENSITIVE ELECTRODE

R. B. Williamson
Department of Chemistry, University of Auckland

One of the most important developments in analytical potentiometry has been the appearance and use of ion selective electrodes, of which the most well known and useful is the glass electrode. These electrodes are available for a variety of ions, but no practical sensor has been reported for phosphate ions. Insoluble inorganic phosphates were examined in a membrane form for response to changes in phosphate activity, as in recent years there have been several reports of this occurring. $BiPO_4$, $BiPO_4$ doped with Ca^{2+}, $(UO_2)_3(PO_4)_2$, UO_2HPO_4, La_3O_4, Ag_3PO_4/Ag_2S were examined, and were all found to be cation responsive. This behaviour was examined more closely with $BiPO_4$ using different cations, and it was found that the potential response could be reasonably predicted by the equation,
$E = E^\circ + (nRT/F) \ln (a_1^{1/n} + K_{12}^{1/n} a_2^{1/n})$,
where K_{12} is the selectivity constant for hydrogen ions (a_2) over sodium ions (a_1).

THE CUBIC LAW OF CUPROUS OXIDE FILM GROWTH IN ALKALINE SOLUTIONS

P. C. A. Bailey
Department of Chemistry, University of Auckland

A potentiostatic method was used to study the nucleation and growth of cuprous oxide on polycrystalline copper surfaces in borate and sodium hydroxide solutions. The charge passed during growth was measured by integrating the current density versus time curves measured at each applied potential. The following growth law was found to hold,

$$x^3 = 3kt + x_o^3$$

where x is the thickness of the oxide film, k is a constant t is time and x_o is a constant representing film thickness at t = O. The slope 3k varied monotonically with increasing applied potential.

Copper samples were allowed to form films for various time intervals without the influence of applied potentials. These films were then cathodically reduced using a potential sweep technique. It was found that oxygenated solutions were needed to promote oxide growth and this growth again followed a cubic rate law. The addition of benzotriazole to the above aerated solution inhibited the growth of oxide, decreasing k threefold.

A mechanism for the growth process is proposed based on the Cabrera-Mott model for ionic migration through films.

$$H_2O(aq) \rightleftharpoons O^{2-}(ads) + 2H^+(aq)$$

The presence of adsorbed oxide ions at the oxide surface promotes the formation of cation vacancies. The transport of ions through the oxide film is by way of inward migration of these vacancies to the metal-oxide interface.

THE ANODIC DISSOLUTION OF NICKEL IN ACIDIC IODIDE SOLUTIONS

G. T. Burstein
Chemistry Department, University of Auckland

The anodic dissolution kinetics of nickel in aqueous acidic iodide solution have been determined

$$Ni \rightarrow Ni^{2+}(_{aq}) + 2e^-.$$

A potentiostatic sweep technique was used, in which the potential was varied as a linear function of time, and the current density recorded. Current density curves were plotted, and these were analysed in terms of the Tafel equation.

$$E = a + b \log i.$$

Results showed that at iodide concentrations of less than 10^{-2}M, the reaction was independent of iodide concentration. Above 10^{-2}M I^- the reaction was accelerated by iodide, and became independent of pH. All experiments were done at constant ionic strength, with perchloric acid and sodium perchlorate being used as base electrolytes. The surface of the metal became polished after anodic dissolution in pure perchlorate solution, whereas in iodide solution the surface became deeply pitted.

The results are explained in terms of a mechanism involving two consecutive electron transfers. The intermediate postulated is NiI adsorbed on the metal surface to a fairly high coverage. This adsorption is explained in terms of the Frumkin isotherm, which considers not only interactions between adsorbate and adsorbant, but also long range interactions between adsorbed molecules themselves.

THE ELECTROCHEMICAL REDUCTION OF NITROUS OXIDE

J. R. Duncan* and G. A. Wright
Department of Chemistry, University of Auckland

Nitrous oxide has been used extensively as a scavenger for hydrated electrons in photoemission experiments. The depression of hydrogen gas yields in electrolysis reactions by the introduction of N_2O has been adduced as evidence that hydrated electrons are involved as intermediates. It has been claimed in support of this that N_2O is not electroreducible at mercury, and no full study of the electrochemistry of aqueous N_2O has been reported previously.

We find that N_2O may be reduced at high cathodic potentials at both mercury and platinum electrodes. Although complete polargrams have not been obtained, the transfer coefficient, α, and the exchange current density, i_o, have been determined.

(a) At mercury, $\alpha = 0.23$, and $i_o = 10^{-15}$ A cm^{-2}. The rate determining step for N_2O reduction at the mercury electrode appears to be:
$N_2O(ads) + e^-(Hg) \rightarrow N_2 + O^-(ads)$

(b) At platinum $\alpha = 0.5$, and $i_o = 10^{-0.5}$ A cm $_2$. The slow step in the reduction on platinum is probably the reaction with adsorbed hydrogen atoms:
$N_2O + H\ (ads) \rightarrow N_2 + OH\ (ads).$

ELECTROCHEMICAL PHASE DIAGRAMS FOR BISMUTH

A. A. Stanley and G. A. Wright*
Department of Chemistry, University of Auckland.

The bismuth electrode has been chosen as a model system for studying the anodic dissolution and passivation of metals. But before much progress can be made on understanding the kinetics of these processes it is necessary to have an accurate knowledge of the thermodynamics of the solid phases and dissolved species that may be formed.

Electrochemical phase diagrams were first introduced by Pourbaix, who mapped the stability regions of the compounds of an element, as a function of electrode potential and pH. The original Pourbaix diagram for bismuth was based on partly erroneous data, and included several compounds (Bi_2H_4, Bi_2O_4, Bi_4O_7, BiO^+) which are now known to be non-existent.

We have investigated the higher oxides of bismuth and find that only one compound exists, $Bi_2O_5(s) + 10H^+ + 4e^- = 2Bi_3^+ + 5H_2O$, $E^\circ =$ 1050 mV. Combining this result with recently determined solubility products, stability constants and standard electrode potentials of bismuth compounds, it has been possible to construct a revised phase diagram which is in accord with the experimental facts. In the presence of halide ions, new solid compounds and complexes are formed, and phase diagrams have been constructed for the fluoride (BiF_3, Bi_2OF_4, $BiOF$, BiF_6^-), chloride ($BiOCl$, $BiCl_6^{3-}$), bromide ($BiOBr$, $BiBr_6^{3-}$), and iodide (BiI_3, $BiOI$, BiI_6^{3-}) systems.

These phase diagrams can be used to interpret the behaviour of bismuth electrodes under various conditions. For example anodic films of either BiI_3 or $BiOI$ will grow on bismuth depending on the pH, but only $BiOI$ forms a tightly adherent, protective layer. At high electrode potentials, $Bi^{3+}(aq)$ is oxidised to Bi_2O_5 which forms a deposit on the platinum anode, and decomposition of this compound appears to be associated with ozone evolution.

THE KINETICS OF THE ANODIC DISSOLUTION OF BISMUTH METAL IN HALIDE SOLUTIONS

P. T. Wilson
University of Auckland
(Student paper)

A potentiostatic sweep technique was used to study the kinetics of the anodic dissolution of bismuth in halide solutions. A rotating disc electrode, constructed from a pure bismuth rod, was used in order to have well defined diffusion conditions. Halide ions, iodide, bromide, and chloride accelerate the dissolution process relative to the rate in perchloric acid. In this investigation, the current density was measured as a function of potential and halide ion concentration (bromide and iodide) at constant ionic strength, the indifferent electrolyte being perchloric acid. Mass transfer of the halide ion to the metal surface was shown to be partially limiting, because of the formation of bismuth halide complexes. The concentration of halide ion at the metal surface was calculated assuming a linear concentration gradient.

The tafel slope and halide order have been calculated from the experimental results. For bromide solutions the tafel slope depends on bromide ion concentration, varying from 20-30 mV. The bromide order varies from 5-2.5. For iodide solutions the tafel slope was 70 mV, and an iodide order lying in the range 3-1 was observed. A mechanistic interpretation of the results has been postulated.

CONDUCTANCES OF SOLUTIONS APPROACHING THE CRITICAL POINT

S. K. Fellows* and J. W. Tomlinson
Chemistry Division, DSIR, and Chemistry Department, Victoria University of Wellington.

The results of measurements of the conductivity of KCl and $CaCl_2$ solutions, to 350°C and to high concentration, are presented. These are used to calculate the equivalent conductance, which is seen to pass through a maximum as the temperature is raised, for any one solution. The maximum is attributed to the opposing effects of increasing thermal energy and increasing ion association. The extent of association can be related to the critical temperatures of the solutions, and has been tentatively calculated. The temperature of maximum equivalent conductance T_{max} varies with solution composition in a way which can also be related to the critical temperatures.

The isothermal composition dependence of equivalent conductance approaches the Onsager limiting law, in very dilute solutions, up to the highest temperatures used. However, above very low concentrations the composition dependence predicted by a quasi-lattice or cell model gives a much better representation of the data. In the region of the maximum equivalent conductance it appears that results plotted at constant T/T_{max} are more meaningful than isothermal correlations.

TRANSPORT PROCESSES IN FUSED ZINC CHLORIDE + 2-AMINOETHANOL HYDROCHLORIDE MIXTURES

A. J. Easteal* and C. B. Kelly
Chemistry Department, University of Auckland

The binary fused salt system $ZnCl_2$ + pyridinium chloride (PyHCl) has been established in previous work as a close analogy to—but experimentally more tractable than—the technologically important $BeF_2 + LiF$ and $SiO + Na_2O$ systems. Substitution of 2-aminoethanol hydrochloride (RCl) for PyHCl yields mixtures which have substantially lower liquidus temperatures than those of corresponding $ZnCl_2$ + PyHCl mixtures, and which are glass-forming over a much wider composition range (ca, 10 - 100 mole % $ZnCl_2$).

Electrical conductance and shear viscosity data (for temperature ranges extending above and below the liquidus temperatures of the $ZnCl_2$ + RCl mixtures) show non-Arrhenius temperature dependences. The data for each melt can be represented with good precision by 3-parameter functions of 1/T derived from a free volume theory of transport processes in liquids.

The composition variation of the transport parameters suggests that tetrachlorozincate and hexachlorozincate ions may be important kinetic entities in these melts.

DIRECT POTENTIOMETRIC MEASUREMENT OF HYDROGEN ION CONCENTRATIONS IN SODIUM CHLORIDE SOLUTIONS OF FIXED IONIC STRENGTH

G. R. Hedwig and H. K. J. Powell
University of Canterbury

The calibration of the cell glass electrode // H^+ (aq)/calomel electrode as a $[H^+]$ probe in the pH range 2.0 to 10.3 and at $I = 0.04, 0.10, 0.15$ and 0.20 M (NaCl) is described. Calibration is effected against dilute HCl solutions and the buffer solutions ethylenediamine / ethylenediammoniumchloride and sodium acetate/acetic acid, all of known $[H^+]$. Plots of pH′ (measured pH) against $p[H^+]$ are colinear for the three systems and coincident, within experimental error, for each ionic strength. The relationship $pH' = 0.995p[H^+] + 0.088$ was observed. From this calibration, $[H^+]$ can be accurately determined from pH′ for NaCl solutions at these ionic strengths.

In contrast, calibration against standard buffers and conversion of pH′ to $p[H^+]$ by use of the Davies equation for mean ionic activity coefficients involves significant assumptions concerning residual liquid junction potentials and activity coefficients. The two approaches are shown to give quite different results for $[H^+]$ measurements.

The described method of calibration is applied to the determination of the protonation constants for 1,5,8,12-tetraazadodecane.

SOME ASPECTS OF THE APPLICATION OF ION SELECTIVE ELECTRODES TO SOIL ANALYSIS

F. G. Thomas

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Sixteen elements or ions are commonly analysed in soils for studies on plant nutrition. They are considered in three groups for their amenability to analysis by ion selective electrodes—

Group 1: Methods generally in common use or free of complications
nitrate, potassium, chlorine, sodium, calcium, hydrogen.

Group 2: Worthwhile results should accrue from further research
ammonium, magnesium, sulphur, copper, molybdenum, boron.

Group 3: No application is readily apparent
phosphate, iron, manganese, zinc, cobalt.

A brief discussion is given of each member of Groups 1 and 2, with particular emphasis on the use of the nitrate electrode in the analysis of Eastern Australian soils.

THE APPLICATION OF IRREVERSIBLE THERMODYNAMICS TO ELECTROLYTE SOLUTIONS

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When the thermodynamics of irreversible processes is applied to isothermal transport processes in electrolyte solutions, expressions for the conductance, diffusion coefficient, cell and Hittorf transference numbers can be derived in terms of general phenomenological transport coefficients l_{ij}. These l_{ij} are more fundamental than the common transport coefficients for special cases, such as the equivalent conductance of diffusion coefficient, which turns out to be combinations of the l_{ij}. The cross coefficients $l_{ij}, i \neq j$, are especially important and directly represent the ionic interactions.

A fundamental principle of irreversible thermodynamics is the symmetry relation $l_{ij} = l_{ji}$, known as the Onsager reciprocal relation. A comparison of cell and Hittorf ttransference numbers provides a direct test of the validity of the Onsager relations for electromechanical systems with transference. This paper reports transference numbers obtained from emf measurements of the concentration cell

$Ag \mid AgCl \mid CdCl_2(m_1) \vdots CdCl_2(m_2) \mid AgCl \mid Ag$

and a Hittorf apparatus for concentrated aqueous solutions of cadmium chloride where ion association is appreciable and the l_{ij}, $i = j$, are significantly larger than for strong electrolytes.

PHYSICAL CHEMISTRY SECTION

PREDICTIONS OF VOLUME CHANGES OF MIXING FROM EQUATIONS OF STATE

I. D. Watson and W. Tam
Massey University

Until recently, the most successful models used to explain the behaviour of liquid mixtures were based on the assumption that the mixing process took place with no volume change. This, of course, excluded the prediction of volume change. However, there has now been significant progress made in our understanding of the behaviour of pure liquid, and in our treatment of unlike interactions in liquid mixtures. This has made it possible to predict volume changes on mixing using equations of state for fluids. The success and limitation of this approach will be outlined and discussed.

OXIDATION KINETICS OF SPENT BREWING GRAIN

by I. K. Walker
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Spent malted barley grains from which beer has been brewed can provide a nutritious stock food, but they are prone to spontaneous ignition if stored dry. The kinetics of exothermic gaseous oxidation are thus of commercial importance.

Oxidation of the oil in spent brewing grain displays a marked period of induction during which the reaction rate slowly rises to a maximum. Thereafter, the rate falls, as is normal for chemical reactions of order greater than zero. This period of induction exhibits a marked temperature coefficient.

Conventional kinetic theories express reaction rate in terms of concentration of reactants or of reaction products. However, it it not known what components of the seed oil are reacting with oxygen. Since the reaction is exothermic, the cumulative release of heat has been considered as a reaction product; the measured reaction rates are therefore expressed in terms of heat generated. By conventional calorimetry reaction rates of two samples have been measured over a limited range of temperatures, times and partial pressures of oxygen. An empirical equation can then be written to express reaction rate in terms of temperature and oxygen partial pressure. This equation can be transformed to relate further these parameters to elapsed time.

THE DISSOLUTION RATES OF POLYCRYSTALLINE SAMPLES OF THE GYPSUM and ORTHORHOMBIC FORMS OF CALCIUM

A. F. M. Barton and N. M. Wilde
Victoria University of Wellington

The dissolution rates in water of gypsum and orthorhombic calcium sulphate (anhydrite) were studied at 25° using a rotating disc of the polycrystalline materials, and the kinetics were followed by means of a calcium ion selective electrode. Over the rotation speed range studied, the gypsum dissolution rate was observed to be transport controlled, and the dissolution of anhydrite was a process of a type intermediate between transport and chemical control. The dissolution rate of anhydrite was found to be considerably greater than previously reported, the rate of anhydrite prepared at 400°C being approximately 50% of that of gypsum. At the low convection rates applicable in soils it is likely that both gypsum and anhydrite as fertilisers would dissolve at transport controlled rates, with the anhydrite dissolution rate being rather greater than the gypsum rate.

LABORATORY INVESTIGATIONS INTO THE SULPHUR DIOXIDE CORROSION OF ALUMINIUM

D. J. Spedding
University of Auckland

The adsorption of sulphur dioxide at atmospheric concentrations by aluminium has been investigated using sulphur-35 sulphur dioxide. The apparatus used enabled the kinetics of the process to be followed.

The results showed a strong dependence on atmospheric humidity for the adsorption process, with greatest uptake occurring at very high humidity. A desorption was found when the partial pressure of sulphur dioxide was reduced to zero. This was also humidity dependent.

The implications of these results in the sulphur dioxide corrosion of aluminium will be discussed

CATALYSIS OF THE REACTION BETWEEN BROMATE AND IODIDE IONS

A. F. M. Barton, Boon-Hian Loo, and J. W. L. Martin
Victoria University of Wellington

Ammonium molybdate has frequently been used to catalyse the analytically important reaction between bromate and iodide in acidic aqueous solution, but little has been known of the kinetics or mechanism of the catalysis process.

$$BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O$$

The effects of Mo (*VI*) and similar oxy-ions have been investigated by means of a rotating disc electrode system for iodine determination. The molybdate-catalysed reaction in the pH region 2 to 3 follows the rate law

$$-d[BrO_3^-]/dt = k_o[H^+]^2[I^-]\,[BrO_3^-] + k'[H^+]\,[I^-]\,[BrO_3^-]\,[Mo(VI)]$$

At 25° and ionic strength 1.00 mol l^{-1} the 'uncatalyzed' term has the usual form[1] and a rate constant $k_o = 50.3\ l^3\ mol^{-3}\ s^{-1}$, and the catalysis term has the form previously observed for catalysis by carboxylates[1] with a rate constant almost a thousand times greater than k_o, $k' = 3.4 \times 10^4\ l^3\ mol^{-3}\ s^{-1}$.

[1] A. F. M. Barton and G. A. Wright, *J. Chem. Soc. (A)*, 1747 (1968).

INFRARED AND RAMAN STUDIES OF STRUCTURE AND BONDING IN SOME COMPLEXES OF THE HALOGENS AND THE HALIDES

by G. A. Bowmaker and M. J. Taylor
University of Auckland

Multicentre bonding has often been postulated to account for the stability of a wide range of halogen and halide complexes. Certain consequences for the vibrational properties of such molecules follow from the delocalized bonding postulate, so a study of their vibrational spectra is of particular interest.

The bis-amine halogen (I) cations, and the dihalo copper(I) anions are examples of systems for which simple 3-centre bonding schemes have been proposed in the past. The i.r. and Raman spectra of a number of compounds containing such ions have been measured, and the results used to obtain information about the structure and bonding in the ions.

ADSORPTION OF ALKYLAMMONIUM CATIONS BY POROUS CRYSTALS. COMPARISON BETWEEN MONTMORILLONITE AND SYNTHETIC NEAR-FAUJASITE

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The adsorption of various alkylammonium cations from aqueous solution by sodium saturated montmorillonite and synthetic zeolites (Linde Sieves) X and Y has been studied. In both instances, adsorption occurs through an exchange reaction between the sodium ions on the clay or zeolite and the organic ions in solution. All of the exchangeable sodium ions in the montmorillonite crystal are accessible and can be replaced by the organic cations, whereas for the zeolites no complete replacement of the sodium ions, initially present, is effected. This is interpreted in terms of structural and steric factors as well as the relative affinity of the cations for the surface.

For montmorillonite, the affinity of the alkylammonium ions increases in a regular manner with an increase in molecular weight (and polarizability) of the cations. This is ascribed to the adsorption energy as the size of the cation becomes larger. For the zeolites, on the other hand, both the affinity and the upper limit to exchange decrease with an increase in ionic size. Further, the maximum extent of exchange is dependent on the affinity of the organic ion and the nature of inorganic ion which it replaces. This indicates that the exchangeable ions occupying different sites in the zeolite crystal are in mutual equilibrium which is influenced by the nature of the replacing ion and that of the ion initially present.

THE HIGH SPIN-LOW SPIN CROSSOVER IN IRON (III) COMPLEXES

L. W. N. Brown and E. Sinn
Victoria University of Wellington

When the $^6A_1$ (high spin) and $^2T_2$ (low spin) states of Fe(III) are separated by an energy difference of the order of kT, anomalous magnetic and spectroscopic properties may be observed. In this case, ferric dithiocarbamates and ferric monothio-β-diketones are studied using measurements both in solution and in the solid state. The data is interpreted in terms of a mathematical model of the "crossover" system, which covers the temperature dependence of the magnetic susceptibility, N.M.R. and Mossbauer spectra. A computer is used to correlate the observed results with the model.

The N.M.R. spectra of the ferric dithiocarbamates are further complicated by hindered rotation of the alkyl substituents on the ligand nitrogen atoms. This is best observed in the analogous Cobalt (III) complexes.

E.S.R. and X-ray data have also been obtained and the results for the monothio-β-diketones have been analysed to obtain information, regarding the degree of distortion in the $^2T_2$ state, as well as calculating the eigenvalues for the low spin Hamiltonian.

Spectral observations show that the rate of exchange between high and low spin forms is comparatively slow for ferric monothio-β-diketones, whereas the dithiocarbamates exchange at a much faster rate and only the weighted mean is observed, rather than the contributions from the individual spin isomers.

A THEORETICAL INVESTIGATION OF MAGNETIC EXCHANGE INTERACTION IN BINUCLEAR SYSTEMS

H. Wong and E. Sinn
Victoria University of Wellington

Magnetic exchange interactions in polynuclear complexes have hitherto been treated by the 'spin only, method. The 'spin only' model has enjoyed considerable success in explaining the apparently anomalous magnetic properties of certain polynuclear complexes. The model is, however, inadequate for the *general* case in that it ignores any degree of orbital degeneracy.

A model is proposed for binuclear complexes which allows for the effects of spin orbit coupling, site distortion and orbital contribution. The results of attempts to correlate experimental results with the model proposed will be presented.

PREDICTION OF STRUCTURE FROM MAGNETIC INTERACTIONS AND VICE-VERSA

E. Sinn
Victoria University of Wellington

Magnetic properties (magnetic susceptibilities, NMR, C.D., ESR, etc.) have long been used to predict the structures of unknown monomeric paramagnetic (and diamagnetic) metal complexes. Conversely, the structures of such complexes, as determined by single crystal X-ray studies, have been used to predict their magnetic exchange properties. As all paramagnetic complexes exhibit magnetic exchange interactions, it should in principle be possible to predict these interactions from the strctures in much the same way, or to predict the structures from the observed interactions.

Polynuclear complexes often exhibit quite strong ferro- or antiferromagnetic exchange interactions, and a good understanding of the phenomenon is gained by a systematic study of polynuclears of gradually increasing complexity. Using a specific series of polynuclear complexes as examples, success and difficulties are outlined in the prediction of structure from magnetic properties and vice versa.

FREQUENCY DISPERSION OF IMPEDANCE IN MOLTEN ELECTROLYTES

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Some errors in impedance measurements in electrolytes are more fundamental than those due to inadequate purity, equipment or technique. Frequency dispersion of impedance is of this type.

Variation of electrical impedance is a phenomenon which has not been fully explained theoretically nor predicted fully for a particular electrolyte and cell system.

The impedance of molton Cd/CdI_2 mixtures has been examined at 400°C over a large frequency range in cells of both high and low cell constant. The low cell constant tends to accent the effect to be studied.

The measured impedances are analysed in terms of simple RC networks with some frequency dependent components. The models used include theoretically determined equivalent circuits for faradic impedance and the electrical double layer.

The variation with $\omega^{-\frac{1}{2}}$ of several impedance components are considered in some detail, as are the variations of the frequency dispersion of impedance with changes in melt composition and cell constant.

ACID CATALYSED HYDROLYSIS REACTIONS

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University of Auckland

The rate laws describing acid catalysed reactions for attack at a single centre are of many forms. Sometimes the rate equation includes a term of proton concentration, at other times an acidity function term, and activity of water may or may not be included. These variations reflect in part the complexities of the rate-acidity profiles. As the acidity increases the rate may

a) continually increase,
b) continually decrease,
c) exhibit a maximum at intermediate acidity, or
d) exhibit a maximum at intermediate acidity followed by a local minimum at higher acidity.

During our studies on the hydrolysis of various substrates we have observed all these variations. Thus, for example, the rate acidity profiles for the hydrolysis of benzonitrile, sucrose and glycyl tyrosine are of type (a); ureas are of type (b); most amides are of type (c); and a number of substituted acetanilides are of type (d).

FREE-RADICAL REDUCTIONS OF ARENEDIAZONIUM IONS IN AQUEOUS SOLUTIONS

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University of Auckland

^{60}Co γ-Radiation has been used to initiate the free radical reduction reactions

$ArN_2^+ + RH_2 \rightarrow ArH + R + N_2 + H^+$
where RH_2 is the two electron reducing agent methanol, ethanol, i-propanol, formate or hypophosphorous acid. Studies of $G(-ArN_2^+)$ (the number of molecules of ArN_2^+ destroyed per 100 ev of radiation absorbed) as a function of $[ArN_2^+]$, $[RH_2]$, dose rate and added scavengers yield much information on the mechanisms.

The propogating steps of the chain reaction are

$$Ar\cdot + RH_2 \rightarrow ArH + \cdot RH$$
$$\cdot RH + ArN_2^+ \rightarrow Ar\cdot + R^+N_2 + H^+$$

The importance of various terminating reactions varies with each of the reducing agents studied.

THE USE OF F-CENTRES IN CRYSTALLINE SOLIDS AS CATALYSTS IN THE EXCHANGE REACTION OF TRITIUM GAS AND HYDROCARBON

B. J. Cowell, M. Matthews and A. L. O'Dell
University of Auckland

SELF-DIFFUSION STUDIES OF GEL HYDRATION AND THE OBSTRUCTION EFFECT

A. G. Langdon
University of Waikato

By modifying the capillary method a moderately rapid and quite accurate means of measuring trace diffusion coefficients in chemically equilibrated gels has been obtained. At various gel compositions and total salt concentration, trace diffusion coefficients have been obtained for the anions chloride and iodide. The dependence on gel composition is linear and independent of electrolyte concentration below 0.1 molar. Trace cation diffusion coefficients for sodium showed a similar behaviour over the concentration range 0.05 to 0.5 molar. The results are adequately accounted for in terms of a model picturing the gel as a collection of randomly oriented and heavily hydrated needles.

ORGANIC SECTION

STEREOCHEMISTRY IN CARBOHYDRATE CHEMISTRY

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An assessment will be given of current understanding of the molecular shapes of carbohydrates and their derivatives, and of the various factors upon which these shapes depend. Attention will be devoted mainly to the stereochemistry of monomeric cyclic and acyclic species, but reference will be made to the influence of molecular shape on the properties of macromolecules. Small stereochemical changes can have dramatic influences on such properties, as is illustrated by starch and cellulose whose first-order structures differ primarily in stereo-chemical detail.

THE MASS SPECTROMETRY OF HEX-2 AND HEX-3-ENOPYRANOSYL DERIVATIVES

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The mass spectra of a series of hex-2-enopyranoside derivatives indicated that fragmentation of members of this class occurs by two general paths:

(i) by loss of the substitutes attached to C-1, C-4 and C-6, giving a series of cyclic ions related to pyran, and
(ii) by retrodienic cleavage.

Recognition of the ions produced by this latter method can provide means for allocating the positions of double bonds in unsaturated carbohydrates; but since allylic rearrangements can, in some circumstances, precede fragmentations, care has to be taken in interpreting the spectra.

A HIGH MOLECULAR WEIGHT FLAVONOID — POLYSACCHARIDE COMPOUND FROM *MONOCLEA FORSTERI* (HEPATICAE)

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The association of lignin with polysaccharides in higher plants appears most likely to be due to chemical bonding. However, the nature of this lignin-carbohydrate bond has proven exceedingly difficult to elucidate, largely due to the size and complexity of the parent molecules.

The current isolation from *Monoclea forsteri* of the first known members of the phenol-polysaccharide group of compounds has provided a model, the study of which might yield, by analogy, an insight into the nature of the lignin-carbohydrate bond. This paper describes the isolation and partial structure determination of this natural product.

The compound is shown to be a flavone-polysaccharide, molecular weight about 4200, in which a 6- or 8- substituted 5, 7, 3', 4' – pentaoxygenated flavone is chemically bound to a water-soluble poly-saccharide (possibly of the hemicellulose type) containing about 20 sugars per flavonoid unit. This is the first reported isolation from natural sources of a compound of the phenol-polysaccharide type.

DITERPENOIDS AS OPTICALLY-ACTIVE RELAYS FOR SYNTHESIS

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The ideal in a total synthesis is to start with materials derivable from petroleum or coal tar, combine and manipulate them until the required compound is formed, and then if chiral centres have been produced, resolve the product into its enantiomers. Frequently, when there is a paucity of material (yields are cumulative!) a racemic intermediate in a synthesis can be resolved and its optically active form can be derived from natural sources. The latter is then used to continue the full synthesis. The application of intermediates derived from podocarpic acid for this purpose will be discussed.

IDENTIFICATION OF PHENOL AS THE SEX ATTRACTANT OF THE GRASS GRUB BEETLE, *COSTELYTRA ZEALANDICA (WHITE)* AND ITS POTENTIAL USE AS A CONTROL AGENT

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The laboratory bioassay method used in the sex attractant studies on the grass grub beetle is described. The sex attractant can be extracted from female abdomens with diethyl ether; various preliminary concentration techniques were studied to establish a method of isolating the sex attractant. The behaviour of active ethereal extracts when partitioned against water and aqueous buffers (as well as in thin layer and paper chromatography) was consistent with that of a phenolic compound. The active component, phenol, was isolated from 1500 female beetles by preparative gas chromatography and identified by mass spectroscopy.

The female grass grub beetle uses phenol as a sex stimulant as well as a sex attractant. The time of production of phenol in the female beetle in relation to mating activity is also discussed. The possible ways of using phenol in the field and its potential use as a control agent for grass grub infestations are considered, together with some of the problems involved in finding suitable dispensers to control the extent and rate of volatilisation of phenol.

THE SEX-PHEROMONE OF THE FALSE CODLING MOTH

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The false codling moth, *Cryptophlebia leucotreta* Meyr (formerly *Argyroploce leucotreta* Meyr), a pest in the citrus plantations in Southern Africa, has been shown to have *cis*-dodec-7-en-1-yl acetate as the female sex pheromone. The breeding of 1,700,000 moths, isolation of the pherome by g.l.c., associated biological tests and analyses are described. The structure is elucidated by microhydrolysis; chain length by retention time in g.l.c. and mass spectrometry; and confirmed by synthesis.

INSECT HORMONES FROM PLANTS

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Many plants, particularly podocarpaceae, contain phytoecdysones which intiate moulting in insects. The distribution of these compounds in the New Zealand flora has been established using the house-fly ligature bioassay. Plants giving positive results are being systematically extracted and fractionated to isolate new and known compounds with moulting hormone activity. In particularly, the bark from the tree *Dacridium intermedium* contains a remarkably high concentration of ecdysterone (ca 1%) together with smaller amounts of several 5β-hydroxy ecdysones. The isolation, chemistry and biological implications of these steroids will be discussed.

SOME REARRANGEMENTS OF 5α-OXYGENATED-9β-CHOLESTANES

J. M. Coxon, M. P. Hartshorn and C. N. Muir
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Rearrangements of some 5α-acetoxy-9α-cholestane derivatives with BF_3-Ac_2O, and some 4,5-, and 5,6-epoxy-9α-cholestane derivatives with BF_3-Et_2O in benzene give products in which backbone rearrangement has occurred in the trans-anti-trans-anti-trans skeleton of the steroid. These rearrangements are considered to proceed by a stepwise mechanism involving a series of intermediate carbonium ions, but little supporting evidence is available.

We now report results of the rearrangements of 5α-oxygenated-9β-cholestane derivatives; in one of these reactions partial backbone rearrangement involved the *trans-syn-cis* system of the 9β-cholestane skeleton. This provides support for a stepwise mechanism.

CYCLOPROPYL CARBINYL REARRANGEMENTS IN NATURAL PRODUCT SYNTHESIS

R. A. J. Smith
University of Otago

Rearrangements of certain oxycyclopropyl carbinyl cations have been found to proceed in an unexpected but predictable manner. Utilisation of these reactions provides a facile synthesis of compounds, not readily obtainable by other methods, which are useful in terpenoid synthesis.

SYNTHESIS OF MODEL COMPOUNDS FOR DOTHISTROMIN

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(Student paper)

Dothistromin (a toxic metabolite of the fungus *Dothistrome pini*) contains the furo(2,3-b)benzofuran ring system, and is thus structurally related to a number of other fungal metabolites including the aflatoxins. The synthesis of several hydroxy furo(2,3-b)benzofurans which duplicate the hydroxylation pattern present in this part of the dothistromin molecule has been undertaken to facilitate study of various aspects of the behaviour of the metabolite. Introduction of a hydroxy group at the tetiary benzylic position of a furo(2,3-b)benzofuran was one of the maor problems of the synthesis. The nature of the site makes hydroxylation of the intact molecule difficult. The main line of attack has been to elaborate a branched chain contained the necessary functional groups, followed by the cyclisation to the required ring system. Formation of the benzylic hydroxyl group in this way has been the more successful. Efficient and flexible synthesis of such model compounds will, it is hoped, provide material for spectroscopic (particularly mass spectrometry) and chemical study of the behaviour of the furo(2,3-b)benzofuran ring system. Furthermore, total synthesis of dothistromin would appear to, depend upon the availability of such compounds.

ANCHIMERIC ASSISTANCE BY AN AZIRIDINE RING

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The stereoelectronic requirement for cyclopropyl participation in the tricyclo $[3,2,1,0^{2,4}]$ octane series is well documented [1,2]. Dramatic anchimeric assistance to solvolysis of the 8-tosyl and 8-brosyl ester derivatives is observed only when the substitute is *anti* to an *endo*-cyclopropane ring[1]. This enhancement is reasonably ascribed to cyclopropyl sigma electron participation involving the *tris*-homocyclopropenyl cation. In like manner, decarbonylation of a series of 8-keto derivatives is enhanced only when the fused cyclopropane ring is *endo*[2].

The present investigation is directed towards a study of the related thermal and photochemical behaviour of 3-azatricyclo $[3,2,1,0^{2,4}]$ octanes in order to demonstrate analogous participation by a fused aziridine ring.

1. J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.* (1969), *91*, 3020.
2. B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup and M. E. Brennan, *J. Amer. Chem. Soc.* (1967), *89*, 5964.

PYROLYTIC CLEAVAGE OF THE CYCLOBUTANE RING IN PINANE DERIVATIVES

J. M. Coxon, R. P. Garland and M. P. Hartshorn
University of Canterbury

The thermal cleavage of the cyclobutane ring of pinanes results in formation of dienes and monocyclic olefins. The latter compounds must necessarily result from 1,4-diradical intermediates while the formation of dienes may result from a concerted thermal cyclorevision, or via 1,4-diradical intermediates. The dienes so produced undergo a series of rearrangements and cyclisation reactions which for hydroxy-pinanes often result in formation of aldehydes.

7,7-DICHLOROBENZOCYCLOPROPENES

Brian Halton* and Paul J. Milsom
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Although benzocyclopropene and several of its derivatives have been synthesised, the only hitherto known *gem*-dihalo compound with 7,7-difluorobenzocyclopropene, prepared by dehydrobromination of 1,6-dibromo-7,7-difluorobicyclo [4,1,0] hept-3-ene. The *gem*-dichloro compounds, having more labile carbon-halogen bonds, might be expected to undergo either facile solvolysis to afford benzocyclopropenones by analogy with 1,2-di-aryl-3,3-dichlorocyclopropenes, or solvolytic ring cleavage to give acids or esters by analogy with tetrachloro-and 1-aryltrichlorocyclopropenes. The first synthesis of a *gem*-dichlorobenzocyclopropene and some of its solvolysis reactions wil be reported.

^{13}C LABELLING AS AN AID IN DETERMINATION OF ION STRUCTURE IN MASS SPECTROMETRY

P. D. Woodgate
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Bond-forming processes leading to skeletal rearrangement are widespread in mass spectrometry. Formulation of the structures of fragment ions is complicated by such rearrangements, and valid mechanistic fragmentation schemes must involve isotopic labelling experiments. Skeletal rearrangement in the electron-impact induced decomposition of phenyl azide has been investigated using phenyl azide-1-^{13}C. The $[M\text{-}HCN]^{+\cdot}$ and $[M\text{-}C_2H_2]^{+\cdot}$ fragments are shown to arise partially from rearranged molecular ions. Similarly, phenyl-1-^{13}C *n*-butyl ether has been used to determine the nature of the $[C_6H_6O]^{+\cdot}$ ion in the spectrum of phenyl alkyl ethers. In this case, no loss of ring position identity occurs prior to fragmentation, and $[C_6H_6O]^{+\cdot}$ is therefore "phenol-like".

NEGATIVE ION MASS SPECTROMETRY

Peter C. Rankin
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A study of the negative ion mass spectra of a number of complex organic molecules (pesticides) and long chain aldehydes and alcohols was undertaken to determine what structural information this technique would yield. The simplicity of the negative ion spectra was a characteristic feature. For long chain aldehydes and alcohols the most prominent negative ion was the P-H ion. This fact enabled identification of the long chain aldehyde and alcohol compounds in a fourteen component mixture. The simplicity of the negative ion spectra of the pesticides studied suggested a possible application to the identification of carbamate pesticides.

PROTODECARBOXYLATION OF SOME AROMATIC CARBOXYLIC ACIDS

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Protodecarboxylation reactions may be represented in general by the following equation:

$$ArCOOH + H^+ \longrightarrow ArH + CO_2 + H^+$$

The 2,4-, 2,6- and 2,4,6- methoxybenzoic acids undergo protodecarboxylation in moderately concentrated mineral acids according to a first order rate law, with rate maxima in 7M, 8.5M (both at 50°C) and 5M (10°C) perchloric acid respectively. Elucidation of a mechanism is complicated by the fact that the carboxylic acid behaves as a base, leading to the formation of the conjugate acid, $ArCO_2H_2^+$. The decline in rates at higher solvent acidities is attributed, at least in part, to oxocarbonium ion formation.

$$AcCO_2H_2^+ \rightleftharpoons ArC^+O + H_2O$$

In contrast, decarboxylation of the corresponding hydroxy benzoic acids occurs in dilute mineral acids where only the parent acid (ArCOOH) and anion ($ArCOO^-$) exist. Rate profiles in each case follow ionisation curves, and constant decarboxylation rates mark complete formation of the undissociated acid, ArCOOH. No evidence is found for the formation of the conjugate acids $ArCO_2H_2^+$ in concentrated mineral acids.

The protodecarboxylation of both of these groups of aromatic carboxylic acids will be discussed, and reasons suggested to account for the anomalous behaviour of the hydroxybenzoic acids.

INTERMEDIATES IN THE CHLORINATION OF OLEFINIC SUBSTANCES BY MOLECULAR CHLORINE AND CHLORINE ACETATE

M. A. Wilson
University of Auckland

Chlorination by both molecular chlorine and chlorine acetate appear to go *via* carbonium ion and chloronium ion intermediates. However, the stereochemical course of additions of chlorine acetate to some *para*-substituted methyl cinnamates appears to be markedly less stereo-selective than the corresponding reactions initiated by electrophilic chlorine. It appears that different intermediates are involved for these two reagents. The nature of these intermediates is discussed.

MECHANISTIC VARIATIONS IN THE BROMINATION AND CHLORINATION OF SOME ALKYL PHENOLS, PHENYL ETHERS AND PHENYL ESTERS

B. N. B. Hannan
University of Auckland

The bromination and chlorination of various alkyl phenols, phenyl ethers and phenyl esters have been studied, and products of substitution and functional group rearrangement have been identified. Addition-elimination sequences in the formation of products of aromatic substitution have been observed in some cases.

The dependence of the mechanistic pathway on the structure of the aromatic substrate, the solvent, the concentration of reactants and the presence of added electrolytes will be discussed.

DITERPENE SYNTHESIS

P. K. Grant and L. N. Nixon
Otago University

The stereospecific synthesis of an isomeric series of 1,2-disubstituted A-nor diterpenes from a six ring precursor will be discussed.

INORGANIC SECTION

METAL ION COMPLEXES OF SOME TETRA-AZA MACROCYCLIC LIGANDS

D. F. Cook
Victoria University of Wellington

The reaction between diaminoethane and benzylidene acetone to yield 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene has been recently reported. Only one of the two possible isomeric forms has been isolated (tentatively assigned as the *meso* form).

Reduction of this isomer with sodium borohydride in methanol yields three isomeric tetraazacyclotetradecanes due to the formation of two further chiral carbon atoms. The types of metal ion complex formed and their stereochemistry will be discussed.

THE CO-ORDINATION CHEMISTRY OF THE CYCLIC TETRA-AMINE 3-3-DIMETHYL-1,5,8,11-TETRA-AZACYCLOTRIDECANE

N. F. Curtis
Victoria University of Wellington

The co-ordination compounds of the thirteen membered cyclic tetra-amine 3-3-dimethyl-1,5,8,11-tetra-azacyclotridecane with nickel(II) and cobalt (III) will be described and compared with those of twelve and fourteen membered analogues. Complexes are formed with the amine in both 'planar' and 'folded' co-ordination. Compounds with the amine in three of the five possible configurations arising from the four chiral co-ordinated secondary amino groups have been isolated, and evidence (stereochemical, X-ray structural, and p.m.r.) for the identity of these configurations will be discussed.

DIPEPTIDE COMPLEXES OF COBALT(II) AND COBALT(III)

P. J. Morris
University of Waikato

Cobalt(II) ion promotes ionisation of amide hydrogens near pH 10 in dipeptides to yield 2:1 complexes with 4 nitrogen and two carboxylate oxygen donors. Complexes of 18 dipeptides yield 4 d-d transitions at 1250, 1000, 610 and 480nm. The first and third bands are assigned to the low spin and the second and fourth to the high spin components of octahedral complexes. Magnetic susceptibility and extensive titration results are consistent with the high spin-low spin equilibrium. Large side chains in the carboxyl terminal residue provide steric inhibition to amide hydrogen ionisation and oxygenation of the cobalt(II) complexes. Side chains in both residues of the dipeptide usually yield the same sign for the circular dichroism of the 2:1 cobalt(II) and cobalt(III) complexes. In both kinds of complexes, the magnitude of the CD consists of independent and additive contributions from each amino acid residue.

THE COORDINATION OF OXYGEN BY COBALT(II) COMPLEXES IN SOLUTION: A THERMOCHEMICAL STUDY

H. K. J. Powell
University of Canterbury

Ammonia, polyamine, aminoacid and many related cobalt(II) complexes are known to react as reversible oxygen carriers and simulate the iron (II) and copper(I) species which store and transport oxygen in biological systems. The role of cobalt(II) as a model is enhanced by the observation that cobalt(II) substituted hemoglobin (coboglobin) has an O_2 affinity very similar to that of hemoglobin. Much is being learnt from the simple cobalt(II) analogues: the 1:1 adducts, $CoL_n:O_2$ are paramagnetic and ESR studies have probed the atomic and electronic structure of the metal-oxygen link. X-ray structural analyses have been reported for two 2:1 adducts $(CoL_n)_2O_2$.

INTRAMOLECULAR METAL-CARBON BOND FORMATION IN SOME TRIARYL PHOSPHITE COMPLEXES OF THE PLATINUM METALS

By E. W. Ainscough and S. D. Robinson
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Recent interest in the activation and cleavage of aryl C-H bonds in transition metal complexes has prompted this report of the most extensive series of such reactions disclosed to date. Iridium, platinum, palladium and osmium triphenyl phosphite complexes in high boiling point solvents undergo reactions leading to formation of products containing intramolecular metal-carbon bonds.

We find, for example, that $[IrHCl_2(C_8H_{12})]$ reacts with $P(OPh)_3$ in boiling benzene to give $IrHCl_2[P(OPh)_3]_3$(A) (*ca* 70% yield) and $IrHCl[P(OPh)_2(OC_6H_4)][P(OPh)_3]_2$ (B) (*ca.* 30% yield): the latter complex is assigned a metal to ortho carbon bonded structure on infra-red, n.m.r. and X-ray evidence. The formation of complex (B) is thought to involve loss of HCl from $[IrHCl_2(C_8H_{21})]_2$ followed by stubstitution to give $IrCl[P(OPh)_3]_3$ which undergoes an intra molecular oxidative addition reaction involving cleavage of an ortho C-H bond to yield the required product. Other reactions leading to inserted iridium compounds will be discussed.

Platinum (II), osmium (II) and (IV), and to a lesser extent palladium (II) phosphite complexes, undergo a similar series of reactions. The influence of chelate ring size on the course of these reactions will be discussed.

ALLOPHANE—STRUCTURE AND USES

N. B. Milestone
University of Waikato
(Student paper)

Allophane, an amorphous alumino silicate clay derived from weathering of volcanic ash, forms the major part of the clay fraction of the volcanic ash soils of the North Island. A large part of the agricultural production in New Zealand is carried out on these soils which are rare in the world and are not used for intensive agriculture.

This paper describes attempts to elucidate the structure of allophane, and its possible uses in industry.

CHEMICAL EXPLOITATION OF WAVE FUNCTIONS

R. L. Griffiths
University of Canterbury
(Student paper)

For small molecules, accurate numerical wavefunctions (to the Hartree-Fock limit and beyond) can now be calculated. Properties such as dipole and quadrupole moments, polarizability, vibrational constants and transition probabilities can be obtained theoretically with an accuracy approaching that of experiment. With the continuing advances in computers, the same molecular orbital methods will become increasingly useful for larger systems. The theory has been developed sufficiently to permit calculation of molecular geometries and potential energy surfaces for some reactions. Energy, however, should never be used as the sole criterion of the quality of a wavefunction; the wavefunction contains much more information. Ways of extracting this information and expressing it more clearly are discussed. Charge transfer and hybridization can be determined from the Mulliken population analysis. Charge and spin densities, localization of orbitals and bond energy analyses can all be used to solve chemical problems. Some simple applications are described.

0-18 EXCHANGE STUDIES ON THE TRISOXALATOCOBALT(III) ANION

A. L. Odell and D. B. Rands
University of Auckland

The rate of acid catalysed exchange of oxygen atoms between solvent water and the trisoxalato complex of cobalt(III) has been investigated. Carbonyl oxygens have been shown to exchange at a greater rate than carbonyl oxygens at lower temperatures (e.g. 17°C, 28°C). At higher temperatures (55°C) carbonyl and carboxyl oxygens become kinetically equivalent with respect to exchange. These results suggest two different mechanisms of exchange for the two types of oxygen, the rate determining step in the carboxyl oxygen exchange process being the anation of the bisoxalatodiaquo cobalt(III) ion. The significance of this finding in relation to the racemisation of the trisoxalatocobaltiate anion is discussed.

ROUTES TO HALOPOLYGERMANES

K. M. Mackay
University of Waikato

By following the ^1H n.m.r. spectrum, it has been shown that Ge_2H_6 undergoes hydrogen-halogen exchange with a variety of covalent halides.
For example,

$$Ge_2H_6 + SnCl_4 \rightarrow Ge_2H_5Cl + SnHCl_3$$
$$Ge_2H_5Cl + SnCl_4 \rightarrow 1:2\ Ge_2H_4Cl_2$$

Preliminary experiments indicate that Ge_3H_8 and Ge_4H_{10} react similarly.

As well as indicating polygermane substitution patterns, the experiments also gave evidence for the transient existence of hitherto-unknown hydrides like $PHCl_2$: both these aspects will be discussed.

APPLICATIONS OF ^{1}H NMR IN THE DETERMINATION OF THE STEREOCHEMISTRY OF HYDRIDOPHOSPHINE COMPLEXES OF OSMIUM

K. R. Grundy and K. R. Laing
University of Auckland

A number of hydride complexes of Osmium have been prepared and these have proved to be very amenable to ^{1}H n.m.r. studies. The spectra show well-defined hydride signals (τ = 14.0 — 24.0) with the correct integrated ratios, as well as the signals due to the attendant ligands, triphenylphosphine, p-tolyl isocyanide and acetonitrile. The hydride signals show multiplet structure interpretable in terms of ^{1}H — ^{31}P splitting. The measured coupling constants J_{cis} (10 — 30 Hz) and J_{trans} (50 — 90 Hz) lie in the expected ranges.

A rough correlation exists between the observed τ values and the osmium-hydrogen stretching frequency in the infrared. A consideration of the ^{1}H n.m.r. and I.R. spectra of a complex can sometimes provide an unambiguous assignment of its stereochemistry.

BIOCHEMISTRY SECTION

TEMPERATURE EFFECTS ON THE LEVEL AND ACTIVITY OF PHOTOSYNTHETIC ENZYMES IN SOME TROPICAL GRASSES

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When many agronomically important tropical grasses (maize, *Sorghum*) are exposed to chilling temperatures of 8 to 12 C under bright sunlight, their CO_2 assimilation rate drops instantaneously and then continues to fall more slowly in a time-temperature-light dependent process that ultimately results in leaf necrosis.

Some key mitochondrial and photosynthetic enzymes undergo a sharp increase in activation energy at these temperatures, and the level of the light activated, C_4-pathway photosynthetic enzymes pyruvate Pi-dikinase and NADP-malate dehydrogenase falls rapidly. Differing rates of incorporation of $^{14}CO_2$ into some photosynthetic products seem explicable in terms of these changes in enzyme activity.

Comparable enzymes in a number of tropical grass species of several genera are not affected to the same extent by low temperature stress. The importance of these enzyme characters in a breeding programme aimed at incorporating low temperature tolerance into *Sorghum* and maize will be discussed.

GROWTH LIMITING PROTEINS IN RELATION TO AUXIN-INDUCED ELONGATION IN LUPIN HYPOCOTYLS

Pauline Penny
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It was shown previously that in lupin hypocotyl segments protein synthesis is not required for the initial action of auxin, but that it becomes necessary within minutes of auxin addition. The role of protein synthesis in auxin-induced cell elongation was studied further, using cycloheximide. The effect of cycloheximide on protein synthesis was complete in nine minutes. Experiments adding cycloheximide at various times before and after indolyl-3-acetic acid will be reported. These experiments allowed estimates to be made of the relative amounts of growth limiting protein(s) (GLP) and of a first order rate constant for the apparent turnover of GLP. Progress that has been made to identify the GLP will be reported.

METABOLISM OF PARTS OF FRENCH BEAN SEEDS DURING EARLY GERMINATION

D. M. Collins and A. T. Wilson
University of Waikato

The metabolism of the embryonic axis and cotyledons of French beans (*Phaseolus vulgaris*) has been investigated using tritiated water (because protons from water enter into many biochemical reactions). The presence or absence of label in a metabolite gives an indication of the metabolism occurring.

The metabolism of the two parts shows similar, but not identical, increasingly complex labelling with time. Amino acid metabolism occurs even at five minutes. Alanine is labelled before γ-aminobutyric acid in the embryonic axis; the reverse is true for cotyledons. For both parts citrate is also labelled at five minutes, but labelling of other compounds indicates that the Kreb's cycle is probably not functioning before thirty minutes. Sucrose is labelled at three hours for the embryonic axis and at six hours for the cotyledons.

One of the supposed functions of cotyledons in growing seedlings is to manufacture sucrose for translocation to the embryonic axis. This cannot be the case in the first six hours of French bean germination.

EFFECT OF THE CURING SYSTEM ON THE MICROBIOLOGICAL DETERIORATION OF VULCANIZED NATURAL RUBBER

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The influence of the curing system on the rate of microbiological deterioration of vulcanized natural rubber by waterborne micro-organisms was investigated. The criteria for the measurement of the rate of deterioration were the respiratory activities of micro-organisms growing on the surface of strips of vulcanized natural rubber suspended in a water bath. Visual inspection of the rubber surface, measurements of the loss in tensile properties and increase in hardness of the rubber confirmed the extent of the deterioration.

The choice of curing system determines the nature and density of the cross-links, resistance to oxidative ageing and the physical properties of the valucanized natural rubber.

Vulcanized natural rubber containing carbon-carbon crosslinks was most susceptible to microbiological deterioration. The presence of curing agent and accelerator residues with microbiocidal-activity in the extra-network material of sulphur cross linked rubber had the most marked effect on the relative resistance of vulcanized natural rubber to microbiological attack.

LACTIC ACID METABOLISM IN THE MYCOBACTERIA

D. G. S. Clark, P. A. Sullivan and G. W. Emerson
University of Otago

The only established lactate oxidoreductase in mycobacteria is the mixed function lactate oxidas[1,2] which with L-lactic acid ——→ acetic acid + carbon dioxide.

Purified lactate oxidase has no significant activity with electron acceptors other than molecular oxygen.

The presence of additional oxidoreductases or lactate oxidising systems was indicated by the following observations:

1. Crude cell-free extracts of mycobacteria catalyse the oxidation of lactic acid with .dyes such as DCIP and methylene blue electron acceptors[1,3].
2. The ability of the mycobacteria to grow on synthetic media which contained lactic acid as the sole source of carbon[1]. There is no known pathway for the net conversion of two carbon compounds into three or four carbon intermediates in this organism[4].
3. The accumulation of radioactive acetic acid and lactic acid when these organisms were incubated with [U-^{14}C] glucose in the presence of sodium arsenite[5].
4. The labelling pattern in cell glucose following the incubation of these organisms with specifically labelled lactic acid in the presence and absence of sodium arsenite[5].

Liew[6] isolated a ferricyanide-linked D-lactate dehydrogenase from *Mycobacteria smegmatis.* Further growth studies by Clark[5] showed that these bacteria could be maintained on synthetic media which contained either D-lactic acid or L-lactic acid as the only source of carbon. Preliminary evidence for a dye-linked L-lactate dehydrogenase has since been found in the same organism.

The lactate oxidoreductases in different strains of mycobacteria will be discussed.

1. Edson, N. L. (1951) Bact. Rev. *15,* 147.
2. Sullivan, P. A. (1968) Biochem. J. *110,* 363.
3. Cousins, F. B. (1956) Biochem. J. *64,* 297.
4. Morrison (1959) Ph.D. thesis. University of N.Z.
5. Clark (1971) Ph.D. thesis (in preparation).
6. Liew, V. (1970) Part III report.

THE INITIAL STEPS OF GLYCEROL METABOLISM IN *MYCOBACTERIUM SMEGNATIS.*

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Cell-free extracts of mycobacteria have been shown to contain enzymes which would provide two parallel routes for the entry of glycerol into the Embden-Meyerhof pathway—

(1) glycerol → glycerol phosphate → dihydroxyacetone phosphate
(2) glycerol → dihydroxyacetone → dihydroxyacetonephosphate

The two pathways may be distinguished by the labelling pattern produced in triose phosphate derivatives when L-[1^{14}C] or L[3-^{4}ʃ^{1}C] glycerol is metabolised, since pathway (2) includes a symmetrical intermediate while (1) does not .

In the present studies L-[3-^{14}C] glycerol was synthesised from D-[1-^{14}C]- glucose by a yeast fermentation at high pH in the present of bisulphite. The labelling was verified by periodic oxidation.

The labelling pattern in glucose from two strains of *M. smegmatis* following incubation with L-[3-^{14}] glucose will be discussed.

BIOSYNTHESIS OF PREKERATIN IN THE WOOL ROOT

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Wool Research Organization, Christchurch

Polyribosomes, nucleic acids and S-carboxymethylated proteins from wool roots have been extracted and characterised.

Two groups of polyribosomes are evident: a polydisperse group of light polysomes which sediments in eight discrete bands, and a homogenous group of heavy polysomes which sediments as a single band, on sucrose density-gradient centrifugation. The two groups have been separated and their role in prekeratin biosynthesis is being determinued by cell-free system analysis. Improvements to the 'classic' method of isolating transfer RNA/

enzyme preparations has led to enhanced incorporation of amino acids into proteins of high specific activity which have been characterised by gel electrophoresis.

CASEIN PROTEOLYSIS IN CHEESE AND IN SOLUTION

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New Zealand Dairy Research Institute

There are three sources of proteolytic enzymes in cheese: (i) those that come from the milk, (ii) those that are synthesized by the starter bacteria, and (ii) those introduced into the milk (as rennet) to set it. These latter enzymes are the principal proteolytic agents acting in the cheese, and during the 6-8 month maturing period of the cheese, they extensively degrade α_{s1} but not β-casein. When solutions of casein at neutral pH are hydrolysed using rennets, the β-casein is hydrolysed as rapidly as the other caseins.

It has been found that rennin, the major enzyme in calf-vell rennet, hydrolyses three bonds in β-casein. The rate of hydrolysis of these bonds is inhibited in the presence of other solutes such as sucrose or NaCl in the solution, whereas the hydrolysis of some rennin-sensitive bonds in α_{s1}-casein is not affected to the same extent. Thus the inhibition of β-casein proteolysis in cheese seems to be closely related to the lowered water activity ($aw = 0.96$) in cheese as compared with aqueous solution ($aw > .99$). The role of the relative importance of enzyme and substrate conformational change with water activity are not yet apparent.

UNSTABLE HAEMOGLOBINS AND ASSOCIATED HAEMOLYTIC ANAEMIA

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Christchurch Hospital

Over 120 molecular variants of human haemoglobin are now known. Although many of these abnormal haemoglobins function normally, others give rise to haemolytic anaemias of varying severity. These are the unstable haemoglobins; they are less stable and precipitate more readily than normal haemoglobin. *In vivo* this instability is shown by the presence in the red cells of Heinz Bodies, microscopic particles which appear to be membrane bound and which consist of precipitated haemoglobin. In general in the unstable haemoglobins, the amino acid substitution is localized in the haem pocket of the globin, and there is no change in charge. Interactions between haem and globin play a major role in determining the secondary and tertiary structure of haemoglobin, and minor modifications to this region markedly influence the stability of the molecule. Haemolytic anaemia associated with Heinz Body formation also occurs in red cells which contain normal haemoglobin subjected to highly oxidizing conditions (such as in certain enzyme deficiency diseases, or after administration of oxidative drugs). Under conditions which normally promote Heinz Body formation within the red cell, unstable or normal haemoglobins precipitate from solution into Heinz Body-like particles. Studies on normal haemoglobin and haemoglobins Sydney ($\beta 67$ val → ala) and Christchurch ($\beta 71$ phe→ser) have shown that this precipitation is accompanied by oxidation of two haemoglobin sulfhydryl groups. These studies are being used to gain greater understanding of the mechanism whereby the intracellular oxidative precipitation of haemoglobin directly, or indirectly, brings about destruction of the red cell.

DRUGS FROM NEW ZEALAND PLANTS

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University of Otago

Although most modern drugs are purely synthetic, the "sieving" of natural products for pharmacological activity has occasionally proved worthwhile. This task has become much easier during the last decade or two because of technical advances in chemistry, pharmacology and cognate subjects. Even so, a comprehensive pharmacological study of natural products peculiar to New Zealand would be beyond our present resources. From a purely financial viewpoint, research along these lines would be unlikely to give a good return, since the odds against finding a new, marketable drug have become very great. One must remember, however, that little medical research would be carried out if financial gain were the chief motive. The chief consideration should be how best to employ limited resources. To illustrate general difficulties in this field, reference will be made to work on pharmacologically active constituents of such plants as the giant stinging nettle, karaka and tutu.

THERMOSTABILITY OF 6-PHOSPHOGLUCONATE DEHYDROGENASE FROM THERMOPHILIC FUNGI

Hugh M. Miller
University of Otago
(Student paper)

Comparative studies have been carried out on macromolecular systems from thermophilic and mesophilic fungi in an attempt to define the factors which determine the upper temperature of life of an organism. Although thermophily in eucaryotic organisms has not been investigated, thermophilic bacteria have been the subject of extensive investigation. This paper describes the properties of 6-phosphogluconate dehydrogenase from the thermophile *Penicillium duponti* and the mesophile *Penicillium notatum*. The thermophilic enzyme has been found to be more heat stable than the enzyme from the mesophile. Furthermore, the thermophilic enzyme has been found to be more resistant to inactivation by urea, acetamide and sodium dodecyl sulphate. Arrhenius curves for both enzymes have been found to be discontinuous, with breaks apparently related to the lower temperature limits of each organism.

THE CRYSTAL STRUCTURAL OF INSULIN AND ITS RELATION TO BIOLOGICAL ACTIVITY

D. C. Hodgkin, E. N. Baker and others
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The crystal structure of pig insulin has been determined by X-ray crystallographic methods. The asymmetric unit within the crystal contains two insulin monomers related by an approximate two-fold axis. Combined with the crystallographic three-fold axis, this gives a hexameric structure. Two zinc atoms, situated along the three-fold axis, are co-ordinated to each hexamer of insulin.

The A and B chains of each insulin monomer are held together by two disulphide bonds and by hydrophobic interactions between sidechains. The two monomers in the asymmetric unit are in turn held together by a combination of hydrophobic interactions and hydrogen bonds. Comparison of this structure with the known amino acid sequences of insulin from difference species suggests that such a dimer represents a stable structure for all species. Although no active site on the molecule can be recognised, many chemical and physical observations are explained by the crystal structure and some further speculations on the mode of action of insulin can be made.

VIRAL RNA POLYMERASE: ELECTRON MICROSCOPY OF REOVIRUS REACTION CORES

Susan Gillies, S. Bullivant and A. R. Bellamy
University of Auckland

Reovirus is an icosahedral virus commonly found associated with mild upper respiratory infections in man. The virus contains double-stranded RNA enclosed in a two-layered protein shell. Virus cores (virus particles in which the outer layer of protein has been artificially removed) are known to contain an RNA polymerase. This enzyme activity is usually studied by the incorporation of radioactive ribonucleoside triphosphates into the acid precipitable product of the enzyme. Certain aspects of the mechanism of the enzyme cannot be investigated readily by such isotopic methods. We have used the Kleinschmidt surface spreading technique and electron microscopy to observe reovirus cores that have synthesised messenger RNA.

Electron microscopy indicates that some viral cores probably synthesise all ten possible messenger RNA molecules *in vitro*. Messenger molecules appear to arise from a different position on the surface of the core, implying that a number of different enzymic sites are present in each viral core.

EFFECTS OF A VIRUS INFECTION ON THE PATH OF CARBON FIXATION IN PHOTOSYNTHESIS

J. R. Bedbrook and R. E. F. Matthews
University of Auckland

Turnip yellow mosaic virus (TYMV) is a small icosahedral virus containing RNA, which infects various species in the Cruciferae. It is usually studied in Chinese cabbage (*Brassica pekinensis*, Rupr.). Previous work has shown that the cytological and biochemical changes brought about by infection in this host are largely confined to the chloroplasts. These changes include: a reduction in chlorophyll content; a reduction in Fraction I protein; rounding up and clumping of the chloroplasts; and the formation of numerous small vesicles near the periphery of the chloroplasts.

In healthy Chinese cabbage we have now shown, using short term labelling periods with $^{14}CO_2$, in the light, that the first labelled compound to be detected is phosphoglyceric acid (PGA). The tissue has a relatively low concentration of the enzyme phosphoenol pyruvate carboxylase. Thus Chinese cabbage appears to be a classical C3 or Calvin cycle plant. In parallel labelling experiments with virus-infected tissue, malic and aspartic acids contain a higher percentage of the radioactivity than PGA. From an early stage of infection, phosphoenol pyruvate carboxylase activity is raised 20-100% above that of healthy tissue. We suggest that in TYMV-infected tissue the C4 (Hatch-Slack) pathway of carbon fixation may be operating as well as the C3 pathway.

THE PHOTOSENSITIZED REDUCTION OF NUCLEIC ACIDS BY INDOLYL-3-ACETIC ACID

A. E. Reeve and T. R. Hopkins
University of Otago

Anaerobic aqueous solutions of indolyl-3-acetic acid (IAA) were irradiated with 275-295 nm ultraviolet light in the present of nucleic acid-derived bases. While no reaction was observed with purines, the pyrimidines lost their characteristic 260 nm absorption during irradiation. When the excited fluorescent state of IAA was quenched by KNO_3 the photo-reaction was also inhibited. This observation, along with the demonstration of a direct correlation between quantum yields of electron ejection for a series of indole compounds[1] and the quantum yields of pyrimidine photo-product, suggests a mechanism involving electron transfer to ground state pyrimidine upon collision with excited state IAA.

The photoproducts of u.v. irradiated IAA-pyrimidine mixtures were identified as reduced pyrimidines and photoadducts of pyrimidine and IAA. No dimers or photohydrates were formed. The products formed are consistent with the above electron transfer mechanism and differ from photoproducts formed by direct u.v. irradiation of pyrimidine solutions in the absence of sensitizers.

(1) T. R. Hopkins and R. Lumry, to be published.

LARGE MOLECULAR WEIGHT GLYCOGEN, STRUCTURE AND METABOLISM

R. Geddes
University of Auckland

Liver glycogen, when isolated by any of the modern, cold-water extraction methods, is very polydisperse material. A comparison of the sedimentation coefficient distributions of cold-water extracted material with that extracted by other methods (e.g. alkali, methyl sulphoxide) indicates the extent of degradation caused by these methods. The molecular weight spectrum of cold-water extracted glycogen varies from ca. 10^5 to ca. 10^9. Both the effect of β-amylase upon the molecular weight distribution of such polydisperse glycogen and measurement of the buoyant densities of various sub-fractions indicate that there is no structural difference between low and high molecular weight glycogen.

When radioactive glucose is introduced into the blood-stream of an animal, subsequent incorporation into glycogen may be measured. The glycogen may be fractionated by differential centrifugation or by zonal centrifugation in a sucrose gradient. The results indicate that in the normal animal there is some preferential synthesis of low molecular weight material but degradation of glycogen is effectively uniform.

BIOSYNTHESIS OF A GLYCOLIPID BY A MEMBRANE FRACTION FROM *S. PNEUMONIAE* TYPE 3 STRAIN A66R1-6.

Evelyn E. B. Smith and G. T. Mills
University of Auckland

A polyisoprenol phosphate is known to be a glycosyl carrier in the biosynthesis of *Salmonella* O-Antigen polysaccharides, the murein of some gram positive organism and the mannan of *M. lysodeikticus.* It is likely that a similar lipid may be involved in the biosynthesis of pneumococcal capsular polysaccharides which also have a regular repeating sequence of sugars.

The membrane fraction from the pneumococcal strain under study has previously been known to synthesise capsular polysaccharide from the substrates UDP glucose and UDP glucuronic acid, but at a rate slower than the wild type 3 organism.

In the present work, the membrane fraction enzyme digests which utilise ^{14}C UDP glucose alone which were fractionated on a charcoal-celite column in aqueous ethanol, and some 40% of the ^{14}C was eluted in 30% ethanol. Chromatography of this material on DEAE cellulose with ammonium acetate in 99% methanol and subsequently on Sephadex LH20 in methanol showed the labelled material to be a single component, and the elution position on the latter column suggested a molecular weight of about 1000.

Acid hydrolysis showed glucose to be the sole sugar component; P was present in a P:glucose ratio of 2:1. Controlled hydrolysis data would indicate that the glucose is linked to the lipid through a pyrophosphate group on position 1.

The nature of the lipid is still under investigation and will be discussed.

MOLECULAR SIZE AND POLYDISPERSITY OF TYPE 3 PNEUMOCOCCAL CAPSULAR POLYSACCHARIDES

E. E. B. Smith, R. Geddes and G. T. Mills
University of Auckland

Techniques which yield very pure pneumococcal capsular polysaccharides with high specific antibody binding capacity were used. The viscosity of type 3 pneumococcal capsular polysaccharides was greatly decreased by exposure of the polysaccharide to ultrasonic irradiation, along with some increase in antibody binding power. Gel chromatography of the original polysaccharide and its ultrasonicated product did not show any appreciable difference.

However, analysis of these materials in the ultracentrifuge by the approach-to-equilibrium method of Archibald as modified by Trautmann have indicated that

(1) the ultrasonicated material has undergone appreciable molecular size degradation.

(2) the original polysaccharide was of relatively discrete molecular size

and (3) the ultrasonicated product is polydisperse.

The reasons for the failure of gel chromatography to distinguish between the two materials and also the apparent rise in antibody binding power will be discussed.

A RATE-DETERMINING CONFORMATION CHANGE IN THE CATALYTIC STEPS OF FICIN- AND PAPAIN-CATALYSED HYDROLYSES

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University College, London

The ficin and papain-catalysed hydrolyses of esters are generally considered to proceed by a three step mechanism involving a thioacyl intermediate, E-S-$\overset{\overset{O}{\|}}{C}$-R ($EP^2$ below).

$$E + S \overset{K_S}{\rightleftharpoons} ES \xrightarrow{k_2} \underset{+P_1}{EP_2} \xrightarrow{k_3} E + P_2$$

Steady state kinetic studies ([substrate]>>[enzyme]) led to the conclusion that this mechanism applied for the hydrolyses of α-N-benzyloxycarbonyl-L-lysine (Z-lysine) esters with the k_3 step being rate-determining.

We used stopped-flow techniques to study the papain- and ficin-catalysed hydrolyses of Z-lysine *p*-nitrophenyl ester under non-steady state conditions and our results are not consistent with the above mechanism. With [enzyme]>>[substrate] we observed a first-order release of *p*-nitrophenol with a rate constant equal to k_3 whereas the mechanism given predicts that the rate constant would be related to k_2, and therefore much faster. Formation of Z-lysine occurs simultaneously with *p*-nitrophenol release at equal concentrations of enzyme and substrate instead of more rapidly. Furthermore, hydroxylamine, which should catalyse the k_3 step, has no effect on the rate of reaction.

We suggest that the reaction mechanism involves at least two additional steps, a rate-determining conformation change in the thioacyl enzyme followed by release of *p*-nitrophenol.

PROPERTIES OF *PENICILLIUM* GLUCOSE-6-PHOSPHATE DEHYDROGENASE

M. G. Shepherd and Anne A. Mason
University of Otago

Secondary plots of the initial velocity data for *P. duponti* glucose-6-phosphate dehydrogenase gave kM values of 4.25×10^{-5} and 1.6×10^{-4} for $NAPD^+$ and glucose-6-phosphate respectively. The inhibition by NADPH was competitive for both substrates with a k_I of 2.2×10^{-5} for $NADP^+$ and 3.0×10^{-5} for glucose-6-phosphate. This pattern of inhibition is not consistent with the sequential ordered mechanism observed for most dehydrogenases. An alternative mechanism will be proposed. Thermal denaturation studies show that glucose-6-phosphate dehydrogenase from the thermophile *P. duponti* is more heat stable than the glucose-6-phosphate dehydrogenase from the mesophile *P. notatum*. The enzyme from both sources is protected from heat inactivation by glucose-6-phosphate.

ANALYTICAL SECTION

ATOMIC FLUORESCENCE AND ATOMIC ABSORPTION WITH A CARBON FILAMENT

J. Aggett
University of Auckland

A number of graphite furnaces and similar devices have been investigated as atomisers for atomic absorption and atomic fluorescence spectroscopy. Among these is the carbon filament developed by T. S. West. The characteristics of this type of atomiser will be discussed, and its capabilities reported with particular reference to the atomic fluorescence of a) gold, and b) organic extracts of a number of elements.

STOPPED-FLOW GAS CHROMATOGRAPHY

Peter C. Rankin
Soil Bureau, DSIR, Lower Hutt

A versatile stopped-flow (interrupted elution) gas chromatographic system connected to an infrared spectrophotometer and mass spectrometer has been developed. It can be easily adapted to existing chromatographs without changing their original analytical function. The system provides good resolution gas phase spectra of each resolved component from a single glc injection using normal instrumental scanning times. Trapping efficiencies are $< 90\%$ on narrow or broad glc peaks by a procedure that avoids aerosol formation. Peak broadening normally observed under interrupted conditions has been minimised, and even allows routine spectroscopic analysis of partially resolved glc peaks.

IDENTIFICATION OF MONOGLYCERIDES BY MASS SPECTROMETRY

C. B. Johnson
Applied Biochemistry Division, DSIR

Differences in the mass spectra of 1- and 2-monoglycerides or their diacetates are not sufficient to provide a basis for the analysis of these compounds. However, mass spectra of the trimethylsilyl ether derivatives of 1- and 2-monoglycerides that contain saturated fatty acids, but not unsaturated fatty acids, are sufficiently different to provide a method of analysis of these compounds. The spectra of isopropylidene and benzylidene derivatives (intermediates in the preparations of the monoglycerides) may be used for distinguishing saturated and unsaturated monoglycerides. Cis and trans isomers of 1:2- and 1:3-benzylidene derivatives of monoglycerides have been separated by thin-layer chromatography.

SCHIFF BASES AS SOLVENT EXTRACTION REAGENTS

J. Aggett and R. A. Richardson
University of Auckland

Schiff bases, such as bis(acetylacetone)-ethylenediimine, bis(salicylaldehyde)-ethylenediimine and related compounds, possess two dissociable protons and are believed to function as doubly-charged anionic ligands in their complex formation reactions. Provided the solvent extraction process is not complicated by the presence of inorganic anions which normally have low complexing ability, these ligands should be rather selective reagents for cations of even charge. The solvent extraction behaviour of a number of these compounds will be reported and their possible use in analytical procedures discussed.

DETERMINATION OF ISONIAZID IN BIOLOGICAL MATERIALS

M. Lever
Greenlane Hospital, Auckland

Isoniazid (isonicotinic acid hydrazide) antagonises the action of pyridoxal phosphate and the nicotinamide coenzymes. It is widely used as a drug in the treatment of tuberculosis. Along with other aromatic acid hydrazides, it has been found to condense with β-diketones in aqueous solution; the products form yellow anions in the presence of strong bases. This reaction can be used for the rapid determination of isoniazid in biological material. A calorimetric procedure can determine less than 1 microgram in 1 ml serum; and a fluorometric procedure as little as 0.005 micrograms in 0.5 ml serum. The potential of this reaction for determining other biologically important materials will be discussed.

THE DETERMINATION OF TETRACYCLINE ANTIBIOTICS IN BIOLOGICAL MATERIAL

D. M. Wilson and M.Lever
Greenlane Hospital, Auckland

The toxicity of tetracycline antibiotics makes it desirable to monitor their concentration in body fluids. The most sensitive methods of determination are based on the fluorescence of metal chelates of the tetracycline ring system. Some recently introduced tetracyclines are therapeutically effective at about the lower limits of detection by existing procedures. One favoured method involves the formation of a highly fluorescent chelate of calcium with barbitone and tetracycline, and the extraction of this into an organic solvent. The original method has been adapted into a simple procedure with an increase in sensitivity. A new method has been developed in which the tetracycline is condensed with hydrazine to give an extractable derivative; this is intensely fluorescent in the presence of magnesium ions in basic solution. An exceptionally sensitive procedure has been developed on this principle. The relative merits of currently available methods for the analysis of tetracyclines in serum and other biological materials will be discussed.

INTERFERING FACTORS IN THE FLUOROMETRIC ASSAY FOR SERUM CORTICOSTEROIDS

M. Lever and D. M. A. Johnson
Greenlane Hospital, Auckland

Physiologically active steroids can be converted to fluorescent derivatives by reagents with high concentrations of sulphuric acid. This is the principle of the most generally used methods for determining serum corticosteroids as a measure of adrenal function. There are other fluorogens in serum that interfere with the assay. Serum lipids, especially cholesterol and phospholipids, account for a large part of these non-corticosteroid fluorogens. The non-corticosteroid fluorogens interact as expected for a very heterogenous mixture, but they interact only weakly with the cortisol derivative. Consequently the contribution of the non-corticosteroid fluorogens can be greatly reduced by reading the fluourescence a two pairs of excitation and emission wavelengths, one at the maximum for corticosteroid fluorescence, and a second where corticosteroid fluorescence is low but non-corticosteroid fluorescence is the same. Corticosteroid concentration can be calculated from the difference, and by this method close correlation with a competitive protein-binding method can be obtained.

CHEMICAL TECHNOLOGY SECTION

SUPERPHOSPHATE FROM CHRISTMAS ISLAND PHOSPHATES

M. S. White
N.Z. Fertlizer Manufacturer's Research Association

The precipitation of complex iron and aluminium phosphates and the failure of monocalcium phosphate monohydrate to crystallise cause difficulty in the manufacture of superphosphate from Christmas Island "A" phosphate rock (apatite) which contains ~ 5% R_2O_3 (R = Fe, Al). Calcination of Christmas "A" phosphate can make sufficient of the iron and aluminium insoluble to overcome these manufacturing problems. X-ray diffraction analysis and solubility measurements on Christmas "A" phosphate calcinated at 100° intervals from 200°C to 1300°C showed optimum deactivation of iron and aluminium at 1100°C.

Calcination of a mixture of Christmas Island "A", "B" and "C" phosphate ores, containing up to 18% R_2O_3 and as little as 13.6% P, with $CaCO_3$ at 1100°C results in a mixture of calcium phosphates containing 4.6% active R_2O_3 and provides a treatment for full utilisation of these ores. From this material superphosphate can be made that is slightly superior to that from uncalcinated Christmas "A". Calcination with calcium carbonate converts the minerals crandallite and millisite to calcium phosphate and corundum. Iron in these minerals and in geothite is converted to hematite. The addition of calcium carbonate to mixtures of "A", "B" and "C" ores containing more than 13% R_2O_3 is necessary to prevent the formation of soluble aluminium phosphate.

LEAD STABILISED PVC PIPES AND THEIR EFFECT ON POTABLE WATER

A. C. Kennett
Chemistry Division, DSIR

There is increasing use of rigid PVC pipes in potable water reticulation. Uncompounded PVC polymer is non-toxic, but lead compounds incorporated in the mixture to stabilise the polymer are toxic and may be leached out of the walls of the pipe by aggressive and potable waters.

The present methods of test for "Effect on Water" e.g. as given in NZS 1920 is based on BS 3505 "Specification for Unplasticised PVC Pipe for Cold Water Services". A simpler alternative test is suggested.

The effect of varying the lead content of the pipe and the carbon dioxide content of the water in contact with the pipe is discussed with particular reference to the requirements of the World Health Organisation for acceptable potable water.

The distribution of the lead salts in the walls of the pipes and the penetration of the water into the surface which is able to extract them from the pipe according to their solubility is used to assess the maximum possible lead concentration in distilled water contained in a PVC pipe of known composition.

Long term storage of water in PVC reticulations (such as may occur in large buildings after long periods of inactivity during construction and in the earlier days of occupation) and the effect on the water is reported.

The possibility of using non-toxic stabilisers in place of the more customary lead stabilisers is discussed briefly.

ON-LINE ACTIVATION ANALYSIS

C. R. Boswell
Massey University of Manawatu

On-line analysis of industrial processes provides an invaluable means of production control. Often, however, the technique has proved difficult to apply because of the physical condition of the sample or because of inhomogeneities in the material being examined. Activation analysis provides a means of overcoming these problems, due to the penetrating nature of both the neutrons producing the radioactive species and the gamma radiation emitted as the species decay.

As the process stream passes a source of neutrons, the material becomes radioactive and, after a suitable delay, the activity is measured using suitable radiation monitors. Because of the range of the radiation, it is possible to effectively examine large volumes for analysis, thereby reducing the problems associated with sample inhomogeneity. In addition, there is rarely any need for sample preparation because the processes involved are nuclear ones and generally do not depend on the chemical or physical condition of the material being examined.

The theory and general principles of on-line activation analysis will be discussed, and applications of the technique will be reviewed.

MOISTURE UPTAKE IN MILK POWDERS

R. J. Hubbard

N.Z. Co-op. Dairy Co., Hamilton

The aim of this investigation was to study moisture uptake in milk powders. As a starting point, moisture adsorption isotherms for the various powders were drawn up. It was found from these that all powders had the common characteristics of showing a rapid increase in hygroscopicity above 65-70% R.H. at 30°C. Further experiments were carried out to characterise the effect of time, temperature and relative humidity on the initial rate of moisture uptake. It was found that the principal driving force affecting the rate of moisture uptake was the vapour pressure difference between the surface of the milk powder particles and the surrounding air. A study of spray-drier characterisations and vapour pressure data for wholemilk powder allowed the computation of the surface vapour pressure on wholemilk powder particles. It was found that there was a large difference in surface vapour pressure between fresh and old powder. The vapour pressure difference between the surface of old and fresh powders and air at 65-70% R.H. at 30° was calculated. This can be said to represent a critical vapour pressure difference for moisture uptake. These critical vapour pressure differences were then converted to critical relative-humidities over the range of temperatures experienced under factory conditions.

ADSORPTION OF CASEINS TO PAPER COATING CLAYS

O. E. Mills and L. K. Creamer

New Zealand Dairy Research Institute

The smooth glossy appearance of some high quality paper is produced by applying a thin film of a casein and clay mixture, followed by calendering or polishing the surface flat. The bond between the casein adhesive and the clay particles has been investigated in the hope that data obtained will lead to the improvement of paper coating formulations.

Mixtures of casein and halloysite clay up to a ratio of 0.1 g/g were agitated continuously for 20 h at 20°C over a range of pH. Total protein analyses of the supernatants after centrifuging showed that casein binding is pH dependent (with greatest adsorption at low pH) and concentration dependent with an increase in concentration being followed by an increase in adsorption. Polyacrylamide disc gel electrophoresis of the supernatants showed that the order of attraction of the major casein components to the clay surface was γ-casein > β-casein > κ-casein. Except for κ-casein this series followed the order of increasing net negative charge. Because these proteins differed in their states of aggregation, chemical composition and conformation, the rule of decreasing attraction with increasing net negative charge needed further confirmation. Two acylated derivatives of β-casein were prepared, producing two proteins substantially the same as β-casein but differing in net charge and charge distribution. The above rule appeared to be followed. The adsorption of whole casein by halloysite and kaolinite in the presence of urea and 2-mercatoethanol (to minimise aggregation of the proteins) was studied to determine the effect of the clay in the adsorption.

Although it is still not clear how the caseins are bonded to the clays, the nature of the bond is discussed in the light of the results obtained so far.

USE OF DIFFERENTIAL SCANNING CALORIMETRY IN TECHNOLOGY OF MILKFAT

R. M. Dolby

New Zealand Dairy Research Institute

Methods of characterising milkfats have usually been limited to determination of fatty acids—crudely by iodine value or Reichert value or in more detail by GLC. Measurement of physical properties of the triglyceride mixture has usually been confined to softening point determination.

Estimation of solid fat index at several temperatures by dilatometry or NMR can give much fuller information on the properties of the fat.

Differential scanning calorimetry (DSC) is eevn more versatile as it gives detailed cooling and melting curves over a wide temperature range. It can be used not only for anhydrous fats but for emulsions such as creams or butter to show influence of previous thermal history on fat crystallization with the fat in globules as well as in bulk.

Use of DSC to study products of commercial fat fractionation has shown that the "liquid fraction' 'usually contains no triglycerides melting over 25°C. The "solid fraction" contains an increased proportion of these triglycerides contaminated with a considerable quantity of liquid fraction. Refractionation of the solid fraction can yield a product of narrow melting range (40-50° C).

Refractionation of the liquid fraction is more difficult owing to the large proportion of milkfat melting in the range 15-25°C.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30th APRIL, 1971

1970 $	*EXPENDITURE*	$	$
	Administration Expenses:		
1361	Printing, Stationery, Postages, Tolls, etc.	1197.65	
577	Travelling Expenses	749.98	
675	Salary, Registrar	700.00	
380	Branch Expense Allowances	360.00	
320	Honoraria (*Less* Proportion charged to Journal)	345.00	
105	Audit Fees	120.00	
50	Donation—S.A.N.Z.	50.00	
—	Manpower Survey Cost	50.00	
23	Depreciation	20.00	
20	Royal Society of New Zealand—Membership Fee	20.00	
(3511)			3612.63
3159	Cost of Journal	3851.95	
-2015	*Less* Revenue from Advertising	2464.20	
(1144)			1387.75
25	Prize—Conference Student	—	
—	Publicity Brochure	220.30	
—	"Careers in Chemistry" Publication	538.00	
402	"List of Members" Publication	—	
-68	Sundry Publications	26.14	
(359)			784.44
2142	Excess of Income over Expenditure for Year		1122.61
$7156			$6907.43

1970 $	*INCOME*	$	$
6884	Subscriptions—Annual		6624.75
	Interest Received		
92	Bank of New Zealand	106.37	
180	Local Body Stock	176.31	
(272)			282.68
$7156			$6,907.43

OVERSEAS VISITORS TRAVELLING FUND

$		$
33	Balance 30/4/70	84.57
195	Travelling Expenses Paid during Year	843.06
$228		$927.63

$			$
	Grant—Department of Education	50.00	
	D.S.I.R.	29.40	
—			79.40
143	Conference Profits		563.48
—	Donation		10.00
85	Balance 30/4/71		274.75
$228			$927.63

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

BALANCE SHEET AS AT 30th APRIL, 1971

1970 $		$	$
	CURRENT LIABILITIES		
105	Sundry Creditors	204.25	
228	Subscriptions received in Advance	367.00	
400	Royal Institute of Chemistry funds funds held in advance	400.00	
(733)	*Total Current Liabilities*		971.25
	SPECIAL FUNDS		
140	Education Fund (School Bulletins)	140.00	
85	*Less* Overseas Visitors Travelling Fund	274.75	
(55)			134.75 Dr.
	TRUST FUND		
2585	Balance 30/4/70	2587.58	
3	*Plus* Interest credited	2.61	
(2588)			2590.19
	ACCUMULATED FUNDS		
	Balance 30/4/70	6117.13	
	Excess of Income over Expenditure for Year	1122.61	
6117			7239.74
$9493			$10,666.43

1970 $			$	$
	CURRENT ASSETS			
49	Petty Cash Funds		4.62	
4714	Bank of New Zealand		2916.60	
874	Subscriptions in Arrears ...	679.00		
	Less Provision for Overdue Subscriptions ...	—		
-100			679.00	
76	Sundry Debtors		226.68	
163	Publication on Hand		125.34	
40	Advance—Conference		40.00	
(5816)	*Total Current Assets*			3992.24
	TRUST FUND INVESTMENTS AT COST			
88	Post Office Savings Banks		90.19	
1000	Hutt County Council, Redemption Loan		1000.00	
1500	Lyttelton Harbour Board Loan ...		1500.00	
(2588)				2590.19
	GENERAL FUND INVESTMENT			
1000	North Canterbury Hospital Board Stock		1000.00	
—	Bank of New Zealand Term Deposit		3000.00	
(1000)				4000.00
	FIXED ASSETS AT COST			
	Office Equipment	317.80		
	Less Depreciation	235.80		
87			82.00	
	Addressograph Plates ...	62.35		
	Less Depreciation	60.35		
2			2.00	
(89)	*Total Fixed Assets*			84.00
$9493				$10,666.43

AUDITOR'S REPORT

We have audited the books of the New Zealand Institute of Chemistry (Inc.) for the year ended 30th April, 1971, and have received all the information and explanations we have required. In our opinion, according to the best of our information and the explanations given to us as shown by the books of account, the Balance Sheet, Income and Expenditure Account, and Trust Fund Account are properly drawn up so as to give a true and fair view of the state of the Institute's affairs as at 30th April, 1971.

SHANAHAN & WINDER,
(Signed) M. P. Winder, Auditor.

Chartered Accountants.

BRANCH NOTES

AUCKLAND

Honour for Mr Brooker

Mr S. G. Brooker, Chief Chemist at Abels Ltd., was elected President of the N.Z. Institute of Food Science and Technology at the annual Food Technology Conference held at Massey University in May. Mr Brooker was a founder-member of the Auckland Branch of the Institute of Food Science and Technology. In recognition of his services a prize of $25 to be known as the Brooker Prize will be presented each year to the most distinguished student in Food Technology at Massey University. Mr Brooker is a Past-President of the N.Z. Institute of Chemistry.

N.Z. Breweries Ltd.

Mr J. R. Beck has been appointed General Manager of N.Z. Breweries Ltd. He was formerly Production Manager and Assistant Technical Manager, and has been closely associated with the development of the continuous brewing process, now widely used in the brewing industry.

Visitors

Dr R. D. Gillard, Reader in Chemistry at the University of Kent, visited Auckland in June and addressed the Auckland Branch on 'Origins of Asymmetry.' He gave several seminars at the university on research in inorganic chemistry and its application to biological processes.

Professor F. L. Warren, of the University of Cape Town, gave a lecture on 'The Sulphur Alkaloids, Cassipourine and Genardine: Structures and Partial Synthesis' at the university in June. Professor Warren is spending a year as Senior Research Fellow at Ruakura Agricultural Research Centre, Hamilton.

Personal

Miss Margaret Bridson, a graduate of the University of Auckland, has gained her Ph.D. in inorganic chemistry at the University of Newcastle.

Mr R. W. Olliff has returned from England where he spent 9 months study leave working on quantum chemistry with Professor C. A. Coulson at Oxford University..

Dr Joyce M. Waters and Professor T. N. M. Waters are in Oxford on study leave, investigating the structures of enzymes and other biologically active molecules, by X-ray crystallographic techniques.

Mr R. J. Sims has been appointed Chemist on the staff of the Chemical Inspector, Department of Health.

MANAWATU

N.Z. Dairy Research Institute

Dr W. A. McGillivray, Director of the Institute and currently President of the N.Z.I.C. was recently honoured by election to Fellowship of the Royal Society of New Zealand. In early September, Dr McGillivray will be travelling to Seoul, Korea, as a guest speaker at the 25th Anniversary of the Korean Chemical Society. He will then go on to Dublin, Eire, to attend the International Dairy Federation meetings, and subsequently visit a number of other centres of dairy interest in Europe.

Mr K. R. Marshall will be travelling to the First International Symposium on Advances in Microbial Engineering to be held at Marienbad, Czechoslovakia, in early September. He will then attend two further conferences on microbial engineering and visit a number of European and North American commercial firms and research institutes with interests in whey processing

Massey University

Dr J. C. Hawke leaves in September to spend a year in the Department of Biology at the University of York (U.K.). He will work on the problem of chloroplast development in association with Dr R. Leech.

Dr J. S. Ayers took up a lectureship in the Department of Chemistry and Biochemistry in June. Dr Ayers is a graduate of Canterbury University and has returned to New Zealand after spending almost three years as a postdoctoral fellow in the United States. He spent part of his time there working on problems in wood chemistry.

Professor H .A. Scheraga, from Cornell University was the main speaker at a one-day Symposium on Protein chemistry held in the Department of Chemistry and Biochemistry on June 4th. Professor Scheraga gave an outstanding lecture on theory and practice in the investigation of polytextile conformations. Other lecturers in the Symposium were: Dr E. N. Baker (Dept. of Chemistry and Biochemistry, Massey University) who spoke on Crystal Structure of Insulin; Dr W. B. Watkins (National Womens Hospital, Auckland), who discussed "Some Aspects of the Structure of Neurophysins"; and Dr T. Hopkins (Dept. of Biochemistry, Otago University). Whose subject was "Urea Denaturation of Chymotrypsin Derivatives". The Symposium concluded with a discussion led by Professor Scheraga on the use of computer techniques in determining protein conformations. Dr Sylvia Rumball of the Dept. of Chemistry and Biochemistry, has just completed a year of research with Professor Scheraga at Cornell.

Mr H. A. L. Morris has resigned his position from the Department of Food Technology to take a position with the United Nations Industrial Development Organisation. His first post will be in the Argentine.

Mr Malcolm Reeves (brother of Dr R. Reeves, Dept. of Chemistry and Biochemistry) has joined the staff of the Food Technology Department from the Sydney Branch of Mauri Brothers and Thompson.

Mr Gordon Robertson has also joined the Department of Food Technology. Previously he worked at Unilever, Hastings.

Mr Robin Fenwick has resigned his position in the Department of Food Technology to take the position of Technical Director (Processing) in the Korean Dairy Beef Company. He will be supported by the Asia New Zealand Development Consultants which was set up as a result of a World Bank Study of the Korean Dairy Industry.

Applied Biochemistry, D.S.I.R.

Dr E. Wong will travel overseas for three months and will include the Mass Spectrometry Conference in Sydney in his itinerary. During this trip he will familiarise himself with recent developments in the techniques and instrumentation involved in flavour chemistry as well as the biochemistry of plant phenolics.

Dr R. Lewis has been appointed to the staff of the Applied Biochemistry Division, D.S.I.R., to study mucus lipids. He graduated from the University of California, San Diego and has previously worked in New Zealand (1968) as a Senior Research Fellow at the Food Chemistry Division of D.S.I.R. Since that time he has been working at the Division of Food Science. C.S.I.R.O., Sydney.

CANTERBURY

Dr. D. A. R. Happer is spending a year's sabbatical leave with Professor F. G. Bordwell at Northwestern University, Chicago.

Dr. H. J. K. Powell has returned from study leave with Professor G. H. Nancollas at University of Buffalo, New York.

Dr. D. A. House left in August to spend a year's study leave with Professor Flemming Woldbye, an authority in the field of optical rotatory dispersion spectra of inorganic complexes. He will be involved in a teaching programme for advanced classes in inorganic reaction mechanisms.

Professor L. F. Philips is visiting U.K. on an Erskine Fellowship to attend the 2nd International Symposium on Gas Kinetics at Swansea and the Molecular Energy Transfer Conference at Cambridge. He will visit laboratories in U.S.A. on his way back.

Dr. R. C. Claridge is visiting South Africa and Israel on an Erskine Fellowship and will be returning via laboratories in Europe and U.S.A.

Dr. J. E. Fergusson is visiting the United States as an invited lecturer at the Gordon Inorganic Conference, New Hampton, New Hampshire.

Professor C. A. Winkler, Visiting Erskine Fellow, has returned to McGill University, Canada.

Professor G. Wilse Robinson, a low temperature spectroscopist from Californian Institute of Technology, will spend three months in the Chemistry Dept., University of Canterbury, as a visiting Erskine Fellow, with Professor L. F. Phillips.

Dr. C. G. Freeman presented a paper at the recent ANZAAS Congress in Brisbane.

Dr. P. J. McElroy has returned from Canada to take up a position as Lecturer in the Dept. of Chemical Engineering, University of Canterbury.

Mr. G. Mooyman has transferred from Wellington to Christchurch.

Recent visitors to the chemistry department have been Professor A. R. Katritsky, University of East Anglia; Professor Larry Strong, Earlham College, U.S.A.; Professor G. Pimental, University of California, Berkeley; Mr. D. St. Slack, Monash University; and Dr. A. Gillard, University of Canterbury at Kent.

OTAGO

Chemistry Department, O.U.

Several members of the Chemistry Department have been appointed to new posts as a result of administrative changes within the University. Professor H. N. Parton, Mellor Professor of Chemistry and Pro-Vice-Chancellor, has accepted the position of Acting Vice-Chancellor in anticipation of Vice-Chancellor R. M. Williams move to Wellington to the post of Director-General of Education.

Professor R. E. Corbett has been appointed Chairman of the Chemistry Department as from 1st July for a period of five years. Professor M. H. Pankhurst has been appointed Pro-Vice-Chancellor designate.

Dr. R. Smith has returned to a lectureship in organic chemistry after two and a half years in North America. Dr. Smith worked on natural product synthesis for eighteen months at Dartmouth College, Hanover, N.H., with Professor T. Spencer, and then spent a year with E. Wenkert at Indiana University, Bloomington, Indiana, where he studied organic reaction mechanisms.

Dr. B. M. Peake has accepted a lectureship in physical chemistry. Dr. Peake recently completed a Ph.D., degree on E.S.R. and N.M.R. spectra of free radicals under Dr. R. F. C. Claridge of the University of Canterbury. He takes up his position in February 1972. Meanwhile he will spend about six months working with Dr. F. Gerson at the Physikalisch Chemisches Institute der Universitat Basel, Switzerland.

Pharmacy News

The appointment of Dr. H. A. Taylor as Associate Professor of Pharmacy was reported last month. Dr. Taylor has now been appointed Foundation Professor and Chairman of the Department of Pharmacy. He was formerly head of the Pharmacy School of the Central Institute of Technology, and has previously taught in English schools of pharmacy.

Professor F. N. Fastier, who has been until now Acting Administrative Head of the Department of Pharmacy, as well as Professor in the Department of Pharmacology, will continue as Chairman of the Department of Pharmacology.

Mr. W. Thomas has returned from Burma after several months with the World Health Organisation. He was working on the indigenous production of sterile solutions.

Industry

Mr. J. D. Salinger has resigned from his position as chemist in charge of New Product Developments of Cadbury Fry Hudson Ltd., to become Chief Chemist at the Merck, Sharpe and Dohme Laboratories in Auckland. Mr. Salinger was a member of the Otago Branch Committee.

Visitors

Dr. R. D. Gillard, Reader in Chemistry at the University of Kent, visited Dunedin on 22-24 June. He gave two lectures in the Chemistry Department on his current research activities, namely "Reaction of Coordinated Ligands" and "Biological Effects of Platinum Metal Complexes."

N.Z.I.C. President Dr. W. A. McGillivray addressed the Otago Branch at the 22nd June meeting. Dr. McGillivray discussed recent work at the Dairy Research Institute on new processes for the dairy industry. The timing of his talk was especially appropriate—June 22 was the eve of the E.E.C. announcements on N.Z. dairy produce.

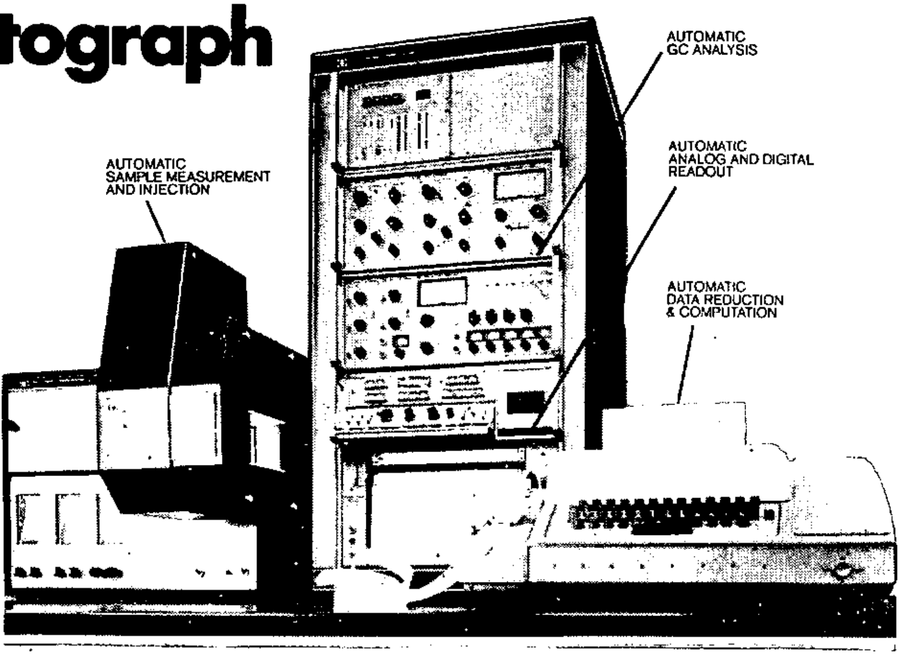
Another visitor to Dunedin was Dr. Joyce Fildes, who is microanalyst with the Department of Medical Chemistry, Australian National University, Canberra. Dr. Fildes' visits on 24-25 June and again on 3rd July gave many members an opportunity to discuss analytical problems. The main purpose of her visit was related to Zonta International, the women's service organisation.

Textile Chemistry

Dr. P. Barber has joined the School of Home Science, Otago University, as a lecturer in Textile Chemistry. Dr. Barber completed his Ph.D. in chemistry at the University of Manchester, and has since worked at I.C.I. Fibres, Pontypool, U.K., and more recently at the nylon plant of Dupont of Canada, at Kingston, Ontario.

Overseas

Dr. R. M. Carr, who left last November for a year in the United Kingdom has now completed his work at the Rothamsted Experimental Station and will spend the next six months in the Geology Department of the University of Manchester.



METRIC CHANGEOVER BOOKLET

A key document for New Zealand's changeover to the metric system has been published by the Standards Association of New Zealand. This is the New Zealand Standard for *The International System (SI) Units and their application*. It has been approved by the Metric Advisory Board as a means of promoting the correct use of SI units throughout New Zealand.

The standard provides a summary of the SI units and gives the rules as to how derived units of SI may be formed. It also includes reference to other units which, though not SI, have been recognised for use in association with SI units.

The document will answer the need for a guide to the correct use of the metric units now being introduced progressively in New Zealand.

Copies of NZS 6501P *The International System (SI) Units and their application* may be obtained at $1.25 ($1.45 by post) from the Sales Section, Standards Association of New Zealand, 6th Floor, New Zealand Display Centre Building, Sturdee Street, Wellington 1 (Private Bag, Wellington).

NOTICE

Annual General Meeting

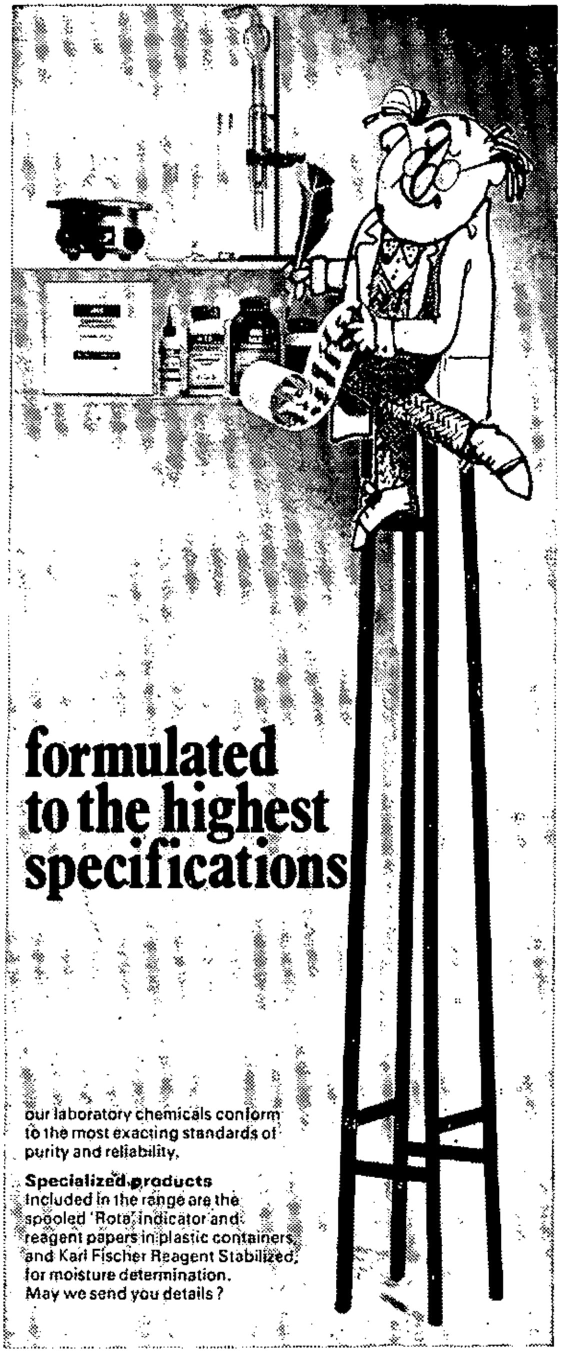
of

N.Z. Institute of Chemistry

Tuesday, August 24, 1971

at the

University of Waikato



Government of Hong Kong

There is a vacancy for a Chemist (Drugs and Food) in the Medical and Health Department, Hong Kong. Male or female candidates considered (female candidates must be unmarried). Age limit about 40 years. Appointment on agreement for three years in the first instance.

Selected candidates would be in charge of the examination and analysis of foods and drugs at Government Chemical Laboratory. Training and supervision of staff. Giving evidence in Court and advising Government and commercial interests on matters, e.g., legislation, relating to food chemistry and technology.

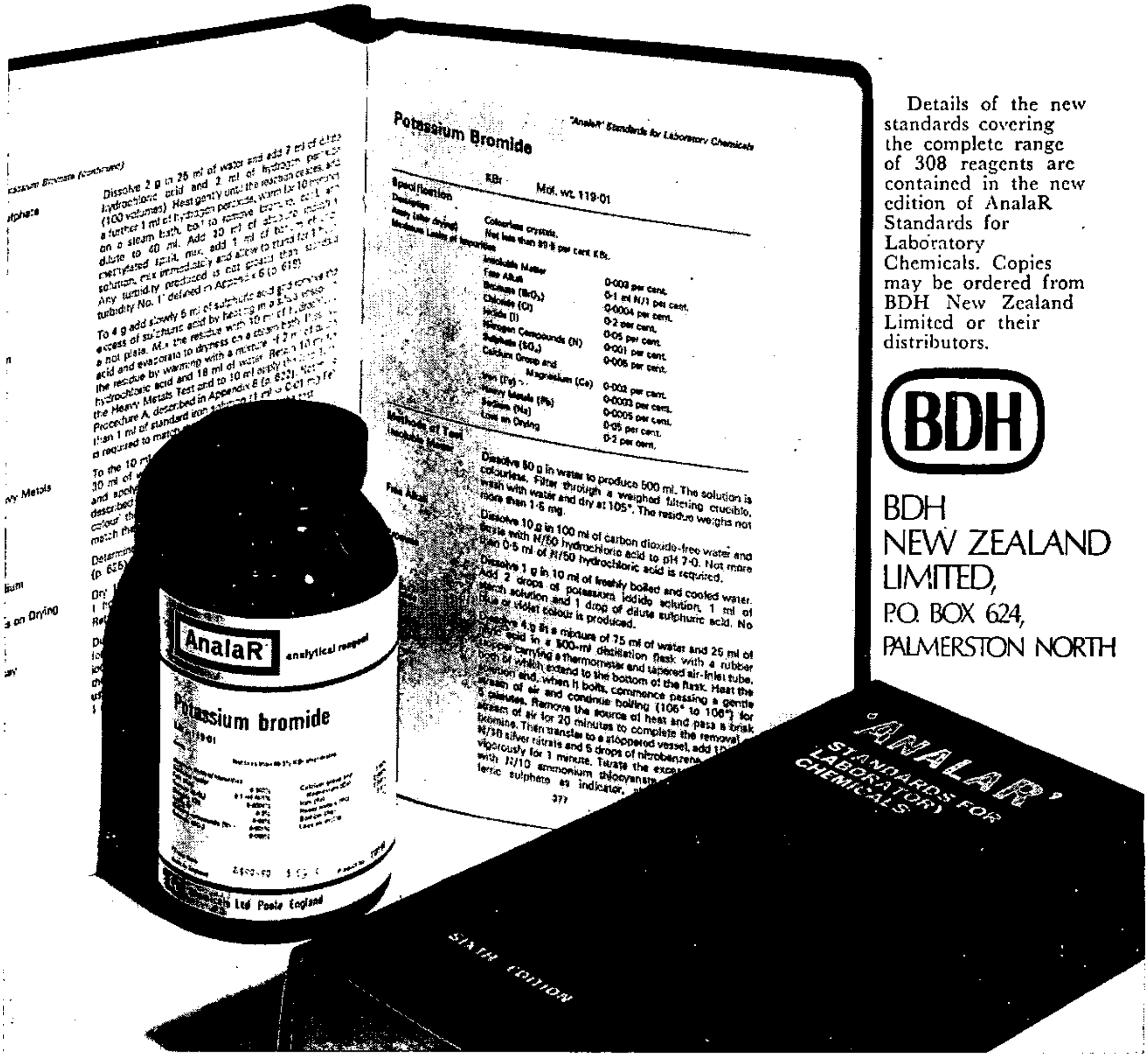
Qualifications required:

- (a) 1st or 2nd Class Honours degree in Chemistry from a British University or equivalent; OR
- (b) Associate Member of the Royal Institute of Chemistry;
- (c) preferably F.R.I.C. (Branch E) or M. Chem. A and some years experience in the general analysis of foods and drugs.

Salary scale by automatic annual increments equal to about $NZ4,020 to $NZ9,100 for men and $NZ3,480 to $NZ9,100 for women. Gratuity 17 per cent also payable on satisfactory completion of agreement. One increment granted for every completed year of post-qualification experience.

Free passages, education allowances, low income tax, subsidized accommodation, generous leave.

Further information obtainable from the Dominion Liaison Officer, Government House, Wellington.



Potassium Bromide
AnalaR analytical reagent
Potassium bromide
'ANALAR' STANDARDS FOR LABORATORY CHEMICALS
SIXTH EDITION

staff appointments

Shell offers employment to men and women with degrees in Chemistry, Civil or Mechanical Engineering, Agricultural Science, Commerce and Mathematics. There are also a few opportunities for graduates in other subjects, e.g. Economics, Law or Arts.

The Shell Group of companies which operates in more than 100 countries is engaged in New Zealand and throughout the world in the oil and chemical industries. The rapid development in both these industries requires highly competent and imaginative staff.

Positions available Most graduates will initially be employed in Wellington. Each man is appointed to a position best suited to his qualifications, talents and interests and he will follow a planned programme to enable him to make best use of his knowledge and ability. Employment with Shell is accepted as qualifying for corporate membership of professional Institutions or Societies.

Chemists will begin in the Central Laboratory in Wellington on product development and testing, technical service, and the supervision of quality control; they may also be employed in chemicals marketing.

Engineers are responsible for the design, development, construction and maintenance of oil storage facilities, processing plants, buildings, pipelines and road tankers.

Agricultural Science graduates are appointed to the Shell Agricultural trade organisation, which is responsible for the development and marketing of chemicals for farming.

Commerce graduates are employed primarily in Finance, where the responsibilities include quarterly accounts, treasury, taxation, credit, investment, audit, payroll, costing, budgets and management accounting. Shell operates an IBM 360/30 computer which provides opportunities for graduates with the necessary aptitude for systems analysis, programming, operations research, etc. Graduates are also employed in Marketing and Distribution.

Advancement As well as specialising initially in work for which he is qualified the graduate will be trained to take a comprehensive view of Shell activities to prepare him for more responsible work.

Shell Oil New Zealand Limited is staffed by New Zealanders, of whom the most able may be eligible for promotion to senior positions overseas. With individual recognition, supervision and guidance, each graduate is encouraged to progress towards the most senior position he is capable of filling. His own efforts towards self development may be aided in several ways, including overseas training for the most promising men. Promotion is on merit and from within the Company.

Salaries Recognition of graduate qualifications is given in commencing salaries. It is Shell's policy to offer salaries and conditions of employment (including retirement benefits) at least comparable to those offered by other large firms.

Vacation employment A few vacation jobs are also available in Wellington each summer for students in their second to last year of a degree course in Engineering, Commerce or Chemistry. Preference will be given to those seriously interested in the eventual prospect of a Shell career.

Applications may be made at any time during the year but a decision will not normally be made before October or November.

Enquiries More detailed information is available in the booklet 'A Guide to Graduate Employment with Shell Oil New Zealand Limited'. Copies of this booklet are available from the University or Shell Oil New Zealand Limited. Interviews can be arranged to suit any students who may be interested. Enquiries may be addressed to:
The Personnel Manager, Shell Oil New Zealand Limited, Shell House, The Terrace, PO Box 2091, Wellington. Telephone: 45-060 or Shell House, Albert Street, PO Box 1084, Auckland. Telephone: 78-880 or St Elmo Courts, Hereford Street, PO Box 2095, Christchurch. Telephone: 62-939.