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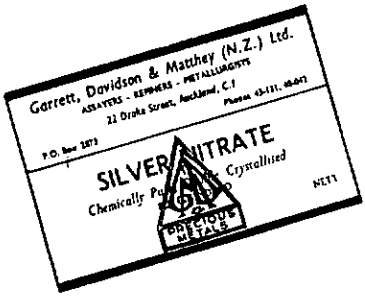

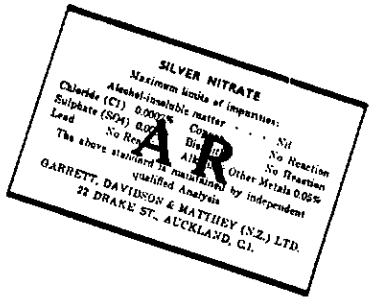

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CONTENTS

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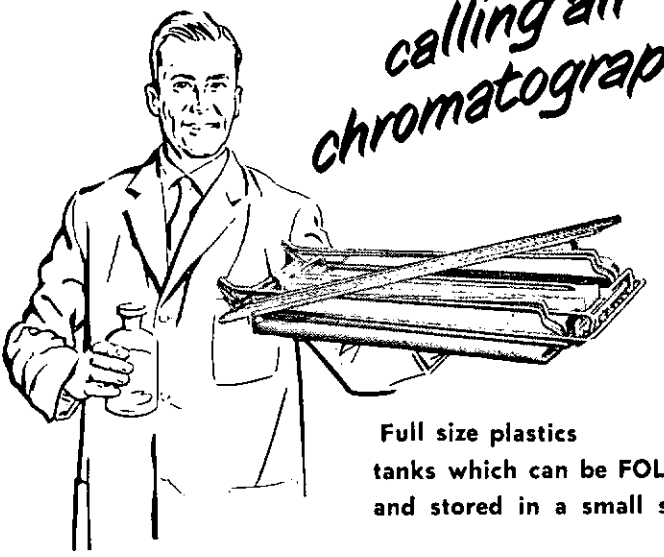

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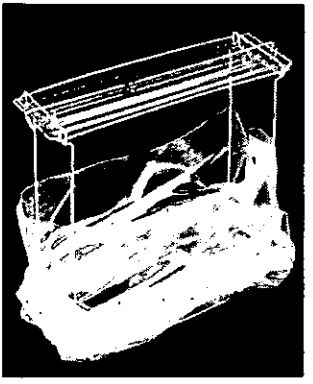

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1. Savvin, S. B., *Talanta*, 1961, 8, 673-85
2. Nemodruk, A. A. and Kochetkova, N. E., *C.A.*, 1962, 57, 11855h
3. Luk'yanov, V. F., Savvin, S. B. and Nikol'skaya, I. V., *C.A.*, 1961, 55, 8174e
4. Goryushina, V. G. and Romanova, E. V., *C.A.*, 1961, 55, 10210g

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STYRENE OXIDE

A very reactive and versatile intermediate, readily forming polymers and copolymers. With Grignard reagent 1:2- or 2:2-diphenyl-ethanol is produced[1]. The coloured reaction products from styrene oxide and pyridine or quinoline derivatives provide a method of colorimetric assay for this class of compound[2].

1. Karasch, M. S. and Clapp, M., *J. Org. Chem.*, 1938, 3, 355
2. Roth, H. J. and Schrimpf, H. O., *Arch. Pharm.*, 1960, 293, 22-8

SILVER DIETHYL-DITHIOCARBAMATE

A reagent for arsenic

A sensitive colorimetric test for arsenic as arsine depends on the measurement of the red colour formed in a 0.5% solution of silver diethyl-dithiocarbamate in pyridine[1]; the solution is stable for many months. The method has been successfully employed for determining arsenic in technical iron, in germanium dioxide, and in petroleum stocks and catalysts. Parts per billion of As in naphthas may also be determined[2].

1. Vasak, V. and Sedivec, V., *Chem Listy* 1952, 46, 341-4
2. Powers, C. W., *et al.*, *Analyt Chem.*, 1959, 31, 1589-93

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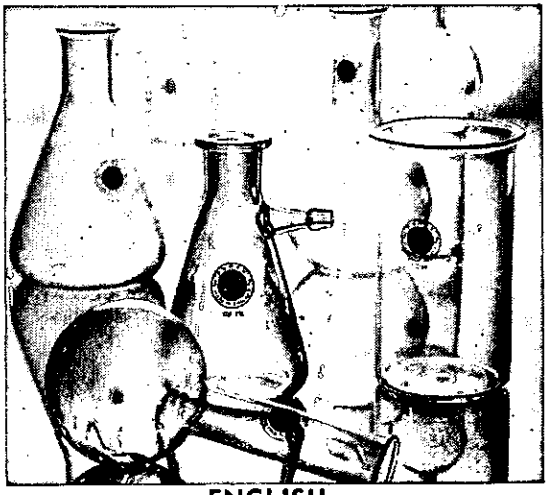

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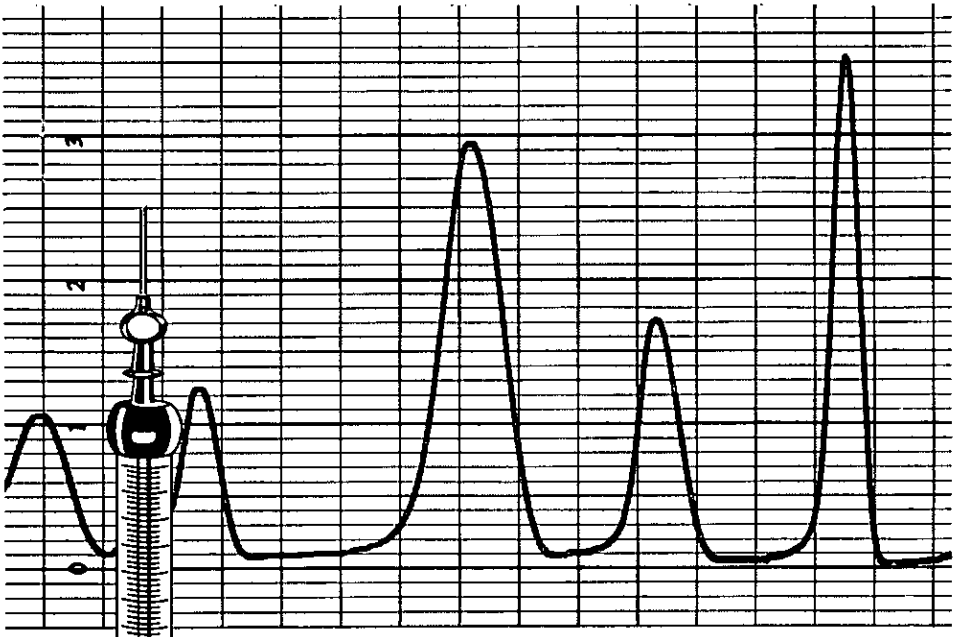

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JOURNAL OF THE NEW ZEALAND
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Vol. 28, No. 4 AUGUST, 1964

CONFERENCE PROGRAMME THOUGHTS

The last time the Institute Conference was held in Hamilton, in 1958, a contributed editorial point out that the meeting place, the Hamilton Girls' High School, was the site of the first Conference of this Institute (together with the New Zealand Section of the R.I.C.) twenty-three years earlier. Also it was stated that "the Waikato Branch differs from its five senior sibs in that it is not (yet) associated with a University".

This time the Conference will be held at the newly established University of Waikato, and, while the new University does not (yet) possess a science school, its first Vice-Chancellor, Dr D. R. Llewellyn, comes to his new post from the Chair of Chemistry at Auckland, is a Fellow of this Institute, and a former Conference Chairman. It is fitting that he should deliver the opening address for the 1964 Conference.

The Conference programme makes no departure from the general pattern established over the last few years. There are several invited addresses but most of the papers are those submitted by members and cover the usual diversity of subjects. There is no flavour peculiar to the Conference district and little that marks it as distinctively a conference of chemists working in New Zealand. This is not unexpected in view of the universal applicability of chemical principles and techniques.

The fact that Institute Conference programmes have settled into a fairly standard pattern is itself reason to consider whether some variation is desirable. It has been suggested that smaller conferences, not necessarily concurrent or at the same place, but organized around more definite symposia, would better meet the ever-increasing specialization in research. Such an idea, apart from increasing the cost and effort of organization, would destroy one of the main functions of our present conferences as a meeting where all types of chemists mingle. In chemistry as well as in biology there is often benefit in cross-fertilization. Furthermore the Conference is the one opportunity for discussion of Institute business, particularly the wider issues

which affect the whole profession. An alternative arrangement which should meet both requirements would be a conference with, say, two days in which specialists could meet in several different symposia, and two days devoted to interests (including getting to know one another) which are common to all chemists.

If the 1964 programme is compared with those of some years ago, the increase in contributions from university staff is apparent. Private industry has offered little as usual. Papers from Government laboratories also have a more basic approach than they had in our early conferences, reflecting the realization that the solution of specific problems in industry and agriculture requires examination of primary causes and processes.

This change in the origin and style of papers read at the Conference prompts some comment on the relationship between university chemistry departments and chemists in applied fields. In the earlier days of chemistry in New Zealand, men such as Black, Worley, Easterfield and Evans maintained a close interest in any attempts to apply the chemistry which they expounded to manufacturing or control, and some of them played a part in the formation of the D.S.I.R. and other organizations. Subsequently, with the growth of strong Government scientific units and the increasing burden of teaching, most of the university staff had little contact with applied chemistry. We well remember a professor who always referred to the Institute, not slightingly but in sheer misconception of its composition, as "the Industrial Chemists". In recent years, almost coincident with the increase in funds available for research in the universities, there have been signs that younger men are again finding interest, and scope for basic research, in subjects related to industrial and agricultural problems. Both academic and applied chemistry can profit thereby.

CONFERENCE 1964

GUEST LECTURER

Dr J. S. Shannon

The Guest Lecturer at the Conference is Dr J. S. Shannon, B.Sc., Ph.D., D.I.C., F.R.A.C.I., Leader of the Organic Chemistry Group of the Division of Coal Research, C.S.I.R.O., at North Ryde, Sydney.

Dr Shannon graduated with first-class Honours from the University of Adelaide (1949). Following 4 years' post-graduate study in the field of monocyclic terpenoid compounds, he joined a group at Imperial College, London, investigating homogeneous hydrogen-transfer reactions. Shortly after returning to Australia in 1955 he joined the Division of Coal Research, C.S.I.R.O., where, as Leader of the Organic Chemistry Group, his research work is, *inter alia*, concerned with the pyrolysis and photochemistry of aromatic compounds and catalytic-hydrogen exchange reactions. However, he is best known for his original contributions in the application of mass spectrometry to structural problems in organic chemistry. In this field his assistance has been widely sought, and he has undertaken collaborative investigations into structural problems of natural products with workers at universities and major research establishments throughout Australia, New Zealand and elsewhere.

VISITING SPEAKERS

In addition to the Guest Lecturer, two chemists visiting New Zealand will deliver addresses at the Conference.

PROFESSOR RICHARD M. NOYES, Chairman of the Chemistry Department, University of Oregon, is working at Victoria University of Wellington during the tenure of a Fulbright award. He will be in New Zealand from July until November, and will spend the remainder of his sabbatical year at the Max Planck Institute for Physical Chemistry at Göttingen.

Professor Noyes graduated from Harvard in 1939 and did his doctoral work at the California Institute of Technology. He remained there during the war as an instructor and was engaged on defence work. In 1946, he joined the staff of Columbia University, where he stayed until taking up his present Chair of Physical Chemistry at Oregon in 1958. He was a visiting Professor at Leeds University in 1955-56. He is a member of the Committee on Basic Research of the Office of Ordinance Research and of the Kinetics subcommittee of the National Research Council. He was the Chairman of the Division of Physical Chemistry of the A.C.S. in 1962.

Professor Noyes has published many papers, mainly on the kinetics of chemical reactions.

Professor and Mrs Noyes are both keen photographers and are active in a number of organizations in the U.S. concerned with the preservation of natural resources and the impacts of human development upon them.

Dr K. SUTHERLAND is visiting New Zealand for several weeks. He is Marketing Manager for Alginates (Austr.) Pty, Marrickville, N.S.W., a firm which has recently established a new industrial enterprise in the processing of Tasmanian seaweeds.

ABSTRACTS OF PAPERS

PHYSICAL METHODS OF IDENTIFYING AND ANALYSING PAINT FILMS

B. CLEVERLEY

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

Paint is an intimate mixture of polymers and pigments and it is difficult to analyse the components once the coating has dried and polymerized to a hard film. It is necessary, however, to analyse films when paints that have been supplied do not perform according to specification, when the effect of weathering or thermal degradation is being studied, and in forensic chemistry when paint chips or smears provide clues that could lead to the conviction of a criminal or the apprehension of a hit-and-run driver.

A number of different physical properties can be quickly determined on a small amount of sample, and one or two of these often provide all the information needed. X-ray diffraction, microscopy, emission spectroscopy, analysis of pyrolysis products, and infrared absorption spectrophotometry, are the physical methods most commonly employed. The infrared spectrum usually provides more information than any of the other measurements and is often sufficient on its own to identify the vehicle and the main organic and inorganic pigments. Methods have been developed to obtain infrared spectra of solid coating films that can be used quantitatively to differentiate between paints made up of similar components in different proportions. In this way it has been possible to identify similar paints made by different manufacturers and to identify cars involved in accidents.

SOLVENT EXTRACTION ENRICHMENT TECHNIQUES AND TRACE ELEMENT ANALYSIS

C. R. BOSWELL and R. R. BROOKS

Department of Chemistry and Biochemistry, Massey University of Manawatu, Palmerston North

Cyclic ketones and alcohols are able to participate in the formation of ion-association metal complexes more readily than the corresponding non-cyclic compounds because of reduced steric hindrance effects. Accordingly, the extraction coefficients of the chloro-complexes of Cu, Ag,

Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi into the three solvents cyclohexane, cyclohexanol, and cyclohexanone have been obtained. By varying the concentration of HCl in the aqueous phase, the variation of the extraction coefficients with acid strength has been studied.

From these data the optimum conditions for extraction have been chosen and, using these, solutions of rocks and other materials of geochemical interest have been examined.

Elements which are present in concentrations below spectrographic detection limits are thus enriched to the level of spectral sensitivity and their concentrations in the original material calculated.

OXIDATION KINETICS OF WOOL

I. K. WALKER

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

Problems in the ignition and combustion of porous solids present more difficulties than do corresponding problems with inflammable gases or liquids. One problem of this type that exists in New Zealand is the startling rapidity with which flame spreads in stores of baled wool, once fire has broken out. Although wool is generally regarded as the least inflammable of the textile fibres (excluding glass fibre), experience has shown that, once fire breaks out in a large store of baled wool, flames propagate throughout the building with amazing speed. This phenomenon is known to occur with wool that is not liable to spontaneous ignition at normal storage temperatures.

An investigation has been made of the oxidation kinetics of wool between 90°C and 150°C by calculating rates of generation of heat from the measured central temperature rises in spheres of wool held at constant ambient temperatures in atmospheres of air or oxygen. The reaction was found to have a conventional temperature coefficient over this temperature range. However, the variation of reaction rate with time cannot be explained by normal kinetic theory (in common with many other solid/gas interactions), nor has diffusion theory yet provided an explanation. Over extended periods of time the logarithm of oxidation rate shows a straight-line plot against the logarithm of time, indicating a power relationship. The same type of relationship has been found for the rate of adsorption of oxygen by coal at similar temperatures (Schmidt and

Elder *J.I.E.C.*, 1940, *32*: 249). The measured rates of oxidation show that at these elevated temperatures wool is not greatly different in its oxidation rate from other materials regarded as readily combustible in fires, and precautions should therefore be taken against spread of flame by thermal radiation in buildings containing baled wool. Water spray is the best method of achieving this.

In addition to this economic significance, the oxidation kinetics of wool offer an opportunity for experimental verification of the application to solids of Frank-Kamenetskii's theory of ignition (*Acta phys. chim. URSS*, 1939, *10*: 365). Previous attempts at experimental application to solids have been based on reactions of liquid fats and resins spread on porous solids, providing essentially homogeneous solution kinetics. Reaction orders higher than zero have therefore affected the reactant concentration in the liquid phase as time progressed, and the consequent spatial distribution of reaction rate. But the oxidation rate of wool depends only on temperature and time, and thus offers a means of testing the theory.

THE PROBLEM OF DETERMINING ISO-HUMULONES

H. O. ASKEW

N.Z. Breweries Ltd., Wellington

Humulones of hops as ordinarily understood consist of probably seven closely related substances which can isomerize apparently in more than one way. Moreover, further changes produce other substances which possess characteristic absorption in ultraviolet light similar to that of the *iso*-humulones. Attempts have been made to use buffer solutions under varying conditions to remove from solutions those compounds which are not not true *iso*-humulones. Absorption curves of the substances present in solution at the several extraction stages do not, however, show very great differences.

LYSYL- AND METHIONYL-sRNA SYNTHETASES FROM WHEAT GERM

ESAM MOUSTAFA

Plant Chemistry Division, D.S.I.R., Palmerston North

By using ammonium sulphate fractionation and calcium phosphate gel treatment lysyl- and methionyl-sRNA synthetases were purified from wheat germ about 600-fold and 160-fold, respectively. The two enzymes catalyse amino acid

dependent ATP-pyrophosphate exchange as well as the incorporation of ^{14}C amino acids into soluble RNA.

Some of the properties of the two enzymes will be reported.

HEMICELLULASES OF RUMEN MICRO-ORGANISMS

R. W. BAILEY
Plant Chemistry Division, D.S.I.R., Palmerston North
and
BLANCHE D. E. GAILLARD
Laboratory of Animal Physiology, Agricultural University, Wageningen, Holland

In addition to rumen bacteria, rumen oligotrich protozoa have now been shown to be rich sources of a water-soluble hemicellulase complex. The action of these enzymes has previously been investigated using arabinoxylans not necessarily from pasture plants. The hydrolysis, by both bacterial and protozoal hemicellulases, of the two main xylan and of the galactose-rich highly branched fractions of pasture plant hemicellulose has now been investigated. The various fractions are hydrolysed at different rates and uronic acid units appear to hinder attack on the pentose portions of the molecules. The hydrolysis rates of the three fractions by bacterial hemicellulase appear to depend on the diet of the animal from which the bacteria are obtained. Protozoal hemicellulase has been fractionated into separate arabinofuranosidase, xylanase and xylodextrinase. A glucanase associated with the protozoal enzymes hydrolyses a glucan contaminant of plant hemicellulose and also $\beta 1 \rightarrow 3 - \beta 1 \rightarrow 4$ linked glucan but not undegraded cellulose.

THE ACTION OF ORGANIC SOLVENTS ON LIPO-PROTEIN MEMBRANE SYSTEMS

M. G. RUMSBY
Department of Chemistry and Biochemistry, Massey University of Manawatu, Palmerston North

The myelin sheath of mammalian central and peripheral nerve has been shown to be derived directly from the cell membrane of the Schwann cell and thus the sheath represents a valuable source of lipo-protein membrane material on which the actions of solvents can be studied by physical and chemical techniques.

Using X-ray diffraction and electron microscopy, the actions of methanol, ethanol, chloroform and a 2:1 mixture of chloroform and methanol were studied on rat peripheral nerve myelin and it is clear that these solvents can be divided into two groups depending on their actions on the lipo-protein system.

Alcohol solvents appear to modify the myelin layering causing changes resembling those brought about by dehydration and freezing, while chloroform and solvent mixtures containing chloroform cause a rapid and total disorganization of the lipo-protein layering.

Thin layer chromatographic analyses of minute solvent extracts taken immediately after X-ray diffraction show that methanol, ethanol and 2:1 chloroform:methanol mixture had extracted substantial concentrations of different lipids from the lipo-protein but that chloroform alone had extracted only trace amounts of cholesterol and phosphatidyl ethanolamine while still retaining its disrupting action on the myelin sheath.

Further studies on the actions of different solvents suggest that the presence of a halogen atom in a solvent molecule is responsible for bringing about disorganization of the lipo-protein system.

Solvent extracts of three sub-cellular lipo-protein membrane fractions from bovine brain tissue were analysed for individual lipid content and results suggest that, in the membrane systems studied, a more labile lipid component, extractable with solvents like acetone, is present, while lipids which are more tightly bound to protein are extracted with solvents like chloroform:methanol mixtures.

FLAVONOID BIOSYNTHESIS IN CICER ARIETINUM

E. WONG
Plant Chemistry Division, D.S.I.R., Palmerston North

The flavonoid constituents of germinated garbanzo bean (*Cicer arietinum*) have been studied. The isoflavone, flavonol, dihydroflavonol, flavanone and chalcone, all having the 4'7-dihydroxy substitution pattern, have been identified as minor constituents. Biosynthetic studies have been carried out using ^{14}C labelled compounds and cell free extracts. The biogenetic interrelationships found for these compounds will be discussed.

MEASUREMENT OF THE CONDUCTANCE AND DIELECTRIC CONSTANT OF A LIQUID

W. S. METCALF

Chemistry Department, University of Canterbury, Christchurch

This paper will show how the apparent value of the conductance and dielectric constant of a liquid are affected by each other, and by the frequency used in the measurement.

HEATS OF MIXING OF CARBON TETRACHLORIDE + DIOXAN

I. R. McKINNON and A. G. WILLIAMSON

Chemistry Department, University of Otago, Dunedin

A number of systems have been investigated in which exothermic heats of mixing have been attributed to hydrogen bonding between the components of the mixture. In most cases the behaviour of such systems is interpreted in terms of an *ideal* mixture of three or more components —*i.e.*, the two compounds being mixed and one or more hydrogen bonded "complexes" formed between them. Generally no allowance has been made for contributions to the thermodynamic behaviour from non-specific interactions. The contribution of the non-specific interactions can be estimated from the thermodynamic behaviour of the corresponding system in which hydrogen bonding cannot occur. Thus for the systems $CHCl_3$ + acetone and $CHCl_3$ + dioxan the contribution of the non-specific interactions can be estimated from the heats of mixing of the systems CCl_4 + acetone and CCl_4 + dioxan. In investigating these contributions, we have measured the heats of mixing of CCl_4 + dioxan over the temperature range 25°C to 45°C and have found that the mixing is exothermic and that the heat of mixing decreases with increasing temperature. Such behaviour indicates a specific interaction between these two compounds presumably of the "charge-transfer" type. A brief survey of evidence for this type of interaction in other systems containing carbon tetrachloride is presented.

DIRECT POTENTIOMETRIC MEASUREMENT OF HYDROGEN ION CONCENTRATIONS

N. F. CURTIS and H. K. J. POWELL

Chemistry Department, Victoria University of Wellington

An attempt has been made to determine accurately the stability constants *Kc* for the reaction between some carbon substituted ethylenediamine ligands and H^+, Cu^{2+}, Ni^{2+}. In determining the equilibrium concentrations of components in such acid/base mixtures it is necessary to know the equilibrium hydrogen ion concentration. Potentiometric analysis of these solutions generally gives acidities in terms of hydrogen ion activities. This makes it necessary to use empirical activity coefficients to obtain the hydrogen ion concentration. In most cases, the coefficients used are those derived strictly for very dilute solutions of pure electrolytes. Their use in mixed electrolytes at higher ionic strength introduces unnecessary errors when it is possible to measure hydrogen ion concentrations directly.

In this work a glass electrode system has been rigorously calibrated to measure hydrogen ion concentrations rather than activities. Ethylenediamine/$HClO_4$ buffer in $NaClO_4$/$Ba(ClO_4)_2$ medium was used as a primary standard at 25°C. For this buffer, values of the concentration equilibrium constant *Kc*, have been previously determined at several ionic strengths by Pinsent and Everett. Their method involved no assumptions about the absolute value of any activity coefficients. Thus we could prepare buffer solutions of known hydrogen ion concentration.

The calibration of potential versus p[H] ($-\log_{10}[H^+]$) has been done at five ionic strengths (0.04–0.35 m/l) each in the p[H] range 4.00–10.50. A reproducibility of $\leqslant(\pm 0.003)$ p[H] units has been achieved. Within the concentration range used, the plot of potential versus p[H] is independent of the activity coefficients. Therefore the response of the glass electrode is proportional to the hydrogen ion concentration of the surrounding solution, and not to the hydrogen ion activity.

The subsequent results obtained for amine stability constants at different ionic strengths are considered reliable in view of the satisfactory extrapolation of log *Kc* values to zero ionic strength. This has given thermodynamic equilibrium constants consistent with the hypothetical standard state of infinite dilution. The satisfactory analysis of solutions containing several complex ions such as result from

the calorimetric determination of their heats of formation, requires very accurate concentration equilibrium constants. Those obtained in this work have given good results in calorimetric studies.

THE POLYMERIZATION OF METHANE BY ELECTRICAL DISCHARGES

C. B. JOHNSON
Fats Research Laboratory, D.S.I.R., Wellington
and
A. T. WILSON
Chemistry Department, Victoria University of Wellington

The production of high molecular weight polymers from mixtures of methane and water vapour in electrical discharges has been investigated. If this type of reaction is done in the presence of hydrogen sulphide and/or ammonia, sulphur and nitrogen can be incorporated into these polymers. The possible significance of these types of reactions in geochemistry and cosmochemistry will be discussed.

IDENTIFICATION BY MEANS OF PYROLYSIS AND GAS CHROMATOGRAPHY

D. F. NELSON
Chemistry Division, D.S.I.R., Auckland

Gas chromatography is now widely used for identification but its application is limited to substances which may be passed through the instrument as vapours. If solids or liquids of low vapour pressure are pyrolysed, the pyrolysis products may be suitable for study with a gas chromatograph. As individual compounds might be expected to give characteristic pyrolysis products, several groups of compounds have been examined to determine whether pyrolysis-gas chromatography would be useful and practicable for identification.

Although earlier workers first pyrolysed their samples and then injected part of the products into gas chromatographs, it is more convenient and usual to combine these two steps so that, immediately after pyrolysis, the products are swept on to the column. The equipment is designed with the pyrolysis chamber just before the column. The sample is inserted in the chamber on a platinum wire helix or on a platinum foil cup and the carrier gas is passed through the instrument. When the recorder is tracing a stable baseline, the sample is pyrolysed by passing an electric current through the platinum wire or foil.

It was found that various classes of plastics could be identified by this procedure, each sample giving its own characteristic set of peaks. Reproducibility of the pyrolysis chromatograms ("pyrograms") was satisfactory and adequate for identification purposes. When the temperature of pyrolysis was varied widely, differences were found among the minor peaks but moderate variations of pyrolysis temperature did not impair reproducibility. Observed chart tracings could be readily summarized by plotting the retention times of peaks on a logarithmic scale and arbitrarily classifying the peaks as large, medium or small.

The pyrolysis products of 27 substituted barbituric acids which may be used therapeutically have been studied. Free acids, their sodium salts and mixtures of free acid with anhydrous potassium carbonate were compared. As the pyrolyzates of each individual barbiturate produced a series of peaks which were reproducible in retention time and relative size, the method is suitable for identifying barbiturates.

As this identification based on pyrolysis and gas chromatography was empirical, the major pyrolysis products from a selected group of barbiturates were identified so that the validity of the technique might be evaluated. Nitriles were found to be important in both abundance and variety, the major product in each case being formed from the 5,5 substitutents and two of the ring carbons and one ring nitrogen.

THE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

A. D. CAMPBELL and A. R. KERR
Chemistry Department, University of Otago, Dunedin

The two most commonly used general methods for the determination of nitrogen in organic compounds are those of Kjeldahl and Dumas. Both have disadvantages. The Kjeldahl method, which involves estimation of ammonia formed on digestion of the sample in sulphuric acid, requires very careful temperature control during the digestion process to effect complete breakdown of most nitrogen heterocyclic systems. For research samples the method must be applied with caution because nitro and azo groups require reduction before proceeding with normal digestion methods.

The method of Dumas in which the sample nitrogen is converted to gaseous nitrogen is generally favoured

where the function of the nitrogen is unknown. However, it has been shown that certain types of compounds give low nitrogen values due, it is believed, to the formation of nitrogenous chars during the combustion. Normal combustion conditions (the sample is heated with copper oxide in an atmosphere of carbon dioxide) can hardly be described as favourable.

Various methods have been reported in which oxidizing agents other than copper oxide have been used. The authors wish to report and discuss the results obtained for a series of organic and organometallic compounds which have proved difficult to analyse by the normal methods. Results obtained on combustion of the sample in the presence of copper oxide, cobalt oxide and oxygen at various temperatures will be described. Results obtained using an automatic nitrogen analyser will also be compared with those obtained using conventional apparatus.

N.M.R. OF OCTAHEDRAL PARAMAGNETIC TRANSITION METAL-ION COMPLEXES

R. M. GOLDING

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

N.m.r. spectroscopy has mainly been used by chemists to determine organic molecular structures by proton magnetic resonance and the spectra are normally sharp, well-resolved, temperture-independent (ignoring the changes in the Boltzman distribution and exchange effects) lines. On the other hand n.m.r. spectra of paramagnetic complexes are usually broad and sometimes markedly temperature-dependent lines. A brief account of why the n.m.r. spectra of paramagnetic compounds are temperature-dependent will be given by outlining the results for octahedral complexes.

However, more emphasis will be placed on discussing the additional information that can be gained about the delocalization of the unpaired electrons over the entire molecule from the n.m.r. spectra of large paramagnetic molecules, with reference to ferric dithiocarbamate complexes. To explain these results, electron density distribution in aromatic rings, hyperconjugation and the inductive effect will be briefly mentioned. Finally, it will be outlined how n.m.r. experiments of paramagnetic complexes may supplement magnetic susceptibility and electron spin resonance measurements.

E.S.R. OF IRRADIATED INORGANIC SINGLE CRYSTALS

JANICE M. DE LISLE
Physics and Engineering Laboratory, D.S.I.R., Gracefield
and
R. M. GOLDING
Chemistry Division, D.S.I.R., Gracefield

The irradiation of inorganic solids provides a way of stabilizing, within the crystal matrix, a wide variety of chemical species whose properties have otherwise to be deduced indirectly. Electron spin resonance, e.s.r., spectra of the simple inorganic molecules CO_2^{2-}, NO_2, NO_2^{2-}, NO_3, NO_3^{2-}, PO_3^{2-}, SO_2^+, SO_2^-, SO_3^+ and SO_3^-, which have been produced by irradiation, have been studied. From the e.s.r. spectra, experimental g-values and hyperfine splitting constants are determined through the spin-Hamiltonian operator, $H = g\beta H.S. + A.S.I.$ The e.s.r. parameters are predicted for these molecules by using simple molecular orbital theory to determine the ground and excited state electronic configurations. Combining experimental and theoretical results enables the species to be identified. Such experiments strongly augmented by detailed theoretical calculations give us a powerful tool to test the validity of our molecular models first for simple molecules and later for the more complex molecules which occur in biological systems.

INVESTIGATIONS OF SOME TRANSITION METAL-ION COMPLEXES

G. R. BURNS, J. F. DUNCAN and K. F. MOK
Chemistry Department, Victoria University of Wellington

Complex inorganic compounds can be studied using a variety of physical techniques. A summary of the evidence produced and the conclusions drawn applying infra-red spectroscopy, n.m.r., magnetic susceptibility, and the Mössbauer effect to dithizone metal complexes and iron fatty acid complexes will be discussed.

1. 1,5-diphenylthiocarbazone (dithizone) forms complexes with a large number of metal ions. The chemistry and the structure of both the free organic ligand and of the complex compounds themselves have never been fully elucidated since Fischer's original work in 1933. The majority of the evidence obtained by us suggests that both in the solid and in solution dithizone forms strong hydrogen bonds probably both intermolecular and intra-

molecular. Both the Hg(II) and the Cu(II) metal complexes have been shown to have metal sulphur bonds and our work suggests that this also occurs with other metal ions.

2. Iron reacts with organic fatty acids to form polynuclear complexes which have anomalous magnetic moments at room temperature. Such magnetic moments can be explained by assuming iron-iron magnetic interactions and an investigation of the temperature dependence of the magnetic moments gives a measure of the extent of the interactions. A series of iron fatty acid complexes of the general formula $Fe_3R_6(OH)_2NO_3:xH_2O$, where R is the acetate, monochloroacetate, trichloroacetate and propionate radical, have been prepared. Formic acid forms the complex $Fe_3(HCOO)_8OH\ .2H_2O$. All these complexes have a magnetic moment of about 3.3 Bohr Magnetons at room temperature. The temperature dependence of the magnetic moment of the formate can be satisfactorily explained by a trinuclear model in which one iron site is slightly different from the other two in each molecule.

The recently discovered Mössbauer effect can also be used for studying polynuclear iron complexes. The Mössbauer spectrum of $Fe_3(CO)_{12}$ displays three peaks and is consistent with the linear model in which the central atom is octahedrally surrounded by bridging carbonyls. The iron fatty acid complexes are also being studied by this technique to supplement the information obtained from magnetic measurements.

MOSSBAUER EXPERIMENTS ON SINGLE CRYSTALS

J. F. DUNCAN
Chemistry Department, Victoria University of Wellington
and
R. M. GOLDING
Chemistry Division, D.S.I.R., Gracefield

Mössbauer spectroscopy studies the absorption of γ-rays (10-100 keV) between the ground and usually the first excited states of a particular nucleus. From a Mössbauer spectrum we are usually able to determine not only the energy difference between the ground and first excited states but also the magnitudes of magnetic and electric field interactions with the nucleus. The latter arise from the interaction between the intrinsic nuclear spin with the electrons in the molecule. However, in magnetically aligned

(*e.g.*, ferromagnetic) materials, the internal magnetic field predominantly determines the spectrum since the electric field gradient interaction is usually the smaller. But in diamagnetic and paramagnetic compounds the effective internal magnetic field is zero and the Mössbauer spectrum is dictated entirely by the electric field gradient at the nucleus. Consequently a typical Mössbauer spectrum of a powdered iron complex usually yields a couple of equally intense peaks. However, occasionally the peaks differ slightly in intensity and this has been attributed to a preferred orientation of the molecules in the powder such as may occur in a plate-like crystalline material.

In this study we are interested in examining the Mössbauer spectrum for a single crystal. For paramagnetic and diamagnetic single crystals of iron compounds the intensity ratio of the doublet becomes $3(1+\cos^2\theta):(5-3\cos^2\theta)$ where θ is the angle between the electric field gradient and the γ-ray axes. From these results we are now able to determine the direction of the electric field gradient in a single crystal and this will be illustrated for the Mössbauer spectra of single sodium nitroprusside crystals. Finally we shall consider the Mössbauer spectra when single crystals are placed in a laboratory magnetic field. Such experiments readily yield the relative signs and the magnitudes of the gyromagnetic ratios of the nucleus in the ground and the first excited states. These salient features of Mössbauer spectra of single crystals which we shall briefly outline illustrate the wealth of information that can be gained about electronic and nuclear interactions in molecules from this new field of spectroscopy.

FOETAL AND MATERNAL LIPIDS OF SHEEP

D. R. BODY and F. B. SHORLAND
Fats Research Division, D.S.I.R., Wellington

Investigations on the lipids of the Romney sheep have shown that, whereas the maternal tissues contain about 30% total lipids, consisting mainly of triglycerides, the foetal tissues have only 3% lipids, which consist largely of phospholipids.

Comparing the maternal and foetal triglycerides, it was found that, whereas the foetus contained a very simple fatty acid pattern comprising palmitic, stearic and oleic acids, the maternal tissues contained in addition traces of branched chain acids, together with the dienoic, trienoic and *trans* unsaturated acids. The fatty acids of the phospholipids, however, were not so distinctly different although

N.Z.I.C. CONFERENCE PROGRAMME
University of Waikato, Hillcrest, Hamilton
August 25–28, 1964

Tuesday Morning, August 25

9.00 a.m. onwards: Registration.
11.00 a.m. Opening of Conference.
11.30 a.m. Address by Dr D. R. Llewellyn.

Tuesday Afternoon

2.00 p.m. Presidential Address—Mr S. G. Brooker.
3.00 p.m. Afternoon tea.

Session A: **Pages 103–5**

3.30 p.m. Physical Methods of Identifying and Analysing Paint Films (B. Cleverley).
4.00 p.m. Solvent Extraction Enrichment Techniques and Trace Element Analysis (C. R. Boswell and R. R. Brooks).
4.30 p.m. Oxidation Kinetics of Wool (I. K. Walker).
5.00 p.m. The Problem of Determining Iso-humulones (H. O. Askew).

Session B: Biological Chemistry **Pages 105–7**

3.30 p.m. Lysyl- and Methionyl-sRNA Synthetases from Wheat Germ (E. Moustafa).
4.00 p.m. Hemicellulases of Rumen Micro-organisms (R. W. Bailey and Blanche D. E. Gaillard).
4.30 p.m. Action of Organic Solvents on Lipo-protein Membrane Systems (M. G. Rumsby).
5.00 p.m. Flavonoid Biosynthesis in *Cicer arietinum* (E. Wong).

Tuesday Evening

8.00 p.m. The Structure of Coal—Dr J. S. Shannon, Coal Research Divison, C.S.I.R.O., Sydney (*Guest Lecturer*).
At Ruakura Farmers' Hall.

Wednesday Morning, August 26

9.00 a.m. Oil Refining (G. Beavis).
10.00 a.m. Morning tea.

Session A: Physical Chemistry **Pages 108–9**

10.30 a.m. Measurement of the Conductance and Dielectric Constant of a Liquid (W. S. Metcalf).
11.00 a.m. Heats of Mixing of Carbon Tetrachloride + Dioxan (I. R. McKinnon and A. G. Williamson).
11.30 a.m. Direct Potentiometric Measurement of Hydrogen Ion Concentrations (N. F. Curtis and H. K. J. Powell).

Session B: Organic Chemistry **Pages 110–1**

10.30 a.m. The Polymerization of Methane by Electrical Discharges (C. B. Johnson and A. T. Wilson).
11.00 a.m. Identification by Means of Pyrolysis and Gas Chromatography (D. F. Nelson).
11.30 a.m. The Determination of Nitrogen in Organic Compounds (A. D. Campbell and A. R. Kerr).

Wednesday Afternoon

2.00 p.m. Recent Advances in Nucleic Acid Chemistry (G. B. Petersen).
3.00 p.m. Afternoon tea.

Session A: Electronic Structures of Some Inorganic Molecules

Pages 112–4

3.30 p.m. N.M.R. of Octahedral Paramagnetic Transition Metal-ion Complexes (R. M. Golding).
4.00 p.m. E.S.R. of Irradiated Inorganic Single Crystals (Janice M. de Lisle and R. M. Golding).
4.30 p.m. Investigation of Some Transition Metal-ion Complexes (G. R. Burns, J. F. Duncan and K. F. Mok).
5.00 p.m. Mossbauer Experiments on Single Crystals (J. F. Duncan and R. M. Golding).

Session B: Organic Chemistry

Pages 115–20

3.30 p.m. Foetal and Maternal Lipids of Sheep (D. R. Body and F. B. Shorland).
4.00 p.m. Lipids of Red Clover (*Trifolium pratense*) Leaves (R. O. Weenink).
4.30 p.m. The Origin of Methyl Ketones in Steam Distillates of Milk Fats (R. C. Lawrence, T. Gerson, J. C. Hawke, and F. B. Shorland).
5.00 p.m. Xanthones from *Gentiana bellidifolia* (K. R. Markham).

Wednesday Evening

6.30 p.m. Social Function ("Riverlea", Riverlea Rd., Hillcrest).

Thursday Morning, August 27

9.00 a.m. The Formation and Recombination of Radicals in Solution (Professor R. M. Noyes, University of Oregon).
10.00 a.m. Morning tea.

Session A: Surface Chemistry

Pages 121–2

10.30 a.m. Inorganic Surface Chemistry (A. T. Wilson).
11.00 a.m. The Surface Chemistry of Sulphate (P. C. Rankin and A. T. Wilson).
11.30 a.m. Anion Interactions with Carboxyl-bound Cations (D. J. Spedding and A. T. Wilson).

Session B: Organic Reactions

Pages 122–4

10.30 a.m. An Isotopic Study on the Hydrolysis of Organic Acids (Charmian O'Connor and D. R. Llewellyn).
11.00 a.m. Nitrating Species in Nitric Acid-Acetic Anhydride Mixtures (S. J. Dickson, A. Fischer, W. Yoong and J. Vaughan).
11.30 a.m. The Mills Nixon Effect (G. J. Welch and G. J. Wright).

Thursday Afternoon

2.00 p.m. The Chemistry of Marine Polysaccharides (K. Sutherland).
3.00 p.m. Afternoon tea.

Session A: Inorganic Chemistry

Pages 124–6

3.30 p.m. Synthesis and Orientation of Pyrophyllite (W. D. Means and J. Rogers).

4.00 p.m. Bismuth (III) Solution Chemistry (G. A. Wright).
(4.30 p.m. Electrodialysis with Ion-selective Membranes (A. M. Kennedy).
5.00 p.m. Kinetics of the Iodate-Iodide Reaction (A. F. M. Barton).

Session B: Organic Reactions **Pages 127–8**

3.30 p.m. Addition Reactions of Beta-Pinene Derivatives (M. P. Hartshorn and A. F. A. Wallis).
4.00 p.m. The Dehydrochlorination of DDT by Thiophenoxide Ion—Kinetics and Mechanism (B. D. England and D. J. McLennan).
4.30 p.m. Rearrangements in the Clemmensen Reduction (B. R. Davis and N. J. Cusack).
5.00 p.m. The Rearrangement of N,N'-Diphenyl-1,3-Propane Diamine (G. B. Russell).

Thursday Evening

8.00 p.m. N.Z.I.C. Annual General Meeting.

Friday Morning, August 28

9.00 a.m. Mass Spectrometry (Dr J. S. Shannon, Coal Research Division, C.S.I.R.O., Sydney). (*Guest Lecturer.*)
10.00 a.m. Morning tea.

Session A: Radiochemistry **Pges 129–30**

10.30 a.m. Stereochemical Effects in the Substitution Reactions of Tritium Recoils (A. L. Odell).
11.00 a.m. Tritium Labelling on Metal Catalysts (A. L. Odell and M. A. Long).
11.30 a.m. Phosphate Availability in Soils (Y. T. Shao and A. T. Wilson).

Session B: **Pages 130–1**

10.30 a.m. Toxic Hazards of Heated Cyanides (E. F. Hubbard).
11.00 a.m. Toxicity of Sporidesmin (D. E. Wright and I. T. Forrester).
11.30 a.m. Recent Development in Ultracentrifuge Techniques (J. W. Lyttleton).
12.00 a.m. Formal closing of Conference.

Friday Afternoon

Arrangements have been made for members remaining in Hamilton to visit the laboratories of the Artificial Breeding Centre (N.Z. Dairy Production and Marketing Board) at Newstead. Informal visits to the laboratories of the Ruakura Agricultural Research Centre will also be arranged.

ANNUAL GENERAL MEETING

The Annual General Meeting of the New Zealand Institute of Chemistry (Inc.) will be held at the University of Waikato, Hamilton, on Thursday, August 27, 1964, at 8.00 p.m.

AGENDA

(1) Apologies, welcome, etc.
(2) Confirmation of Minutes of the Annual General Meeting held at Massey University of Manawatu on Thursday, August 22, 1963.
(3) Institute Prizes for 1964.
(4) Officers for the coming year.
(5) Annual Report for the year ending July 31, 1964.
(6) Balance Sheet for the year ending April 30, 1964.
(7) New Rules.
(8) General.

W. E. HARVEY, *General Secretary*

the maternal lipids were richest in di- and polyunsaturated acids and in branched chain acids. These results show that the foetal fatty acids are not derived entirely from those of the mother.

The phospholipid fractions of the maternal and foetal lipids were similar and consisted of (by weight): phosphatidyl choline, 50%; phosphatidyl ethanolamine, 25%; sphingomyelin, 10%; phosphatidyl serine, 7%; phosphatidyl inositol, 3%; unidentified, 5%.

LIPIDS OF RED CLOVER (TRIFOLIUM PRATENSE) LEAVES

R. O. WEENINK
Fats Research Division, D.S.I.R., Wellington

The acetone-soluble fraction of red-clover leaves consists mainly of the mono- and digalactosyl diglycerides, with smaller amounts of hydrocarbons and other unsaponifiable constituents. Triglycerides occur in trace amounts only.

The acetone-insoluble fraction was fractionated on diethylaminoethyl cellulose and silicic acid columns to yield a wax fraction, digalactosyl diglycerides, phosphatidyl glycerol and unknown phospholipids. An uncharacterized fatty acid was shown to be preferentially attached to phosphatidyl glycerol.

THE ORIGIN OF METHYL KETONES IN STEAM DISTILLATES OF MILK FATS

R. C. LAWRENCE
Dairy Research Institute, Palmerston North
T. GERSON and F. B. SHORLAND
Fats Research Division, D.S.I.R., Wellington
and
J. C. HAWKE
Department of Chemistry and Biochemistry, Massey University of Manawatu, Palmerston North

Methyl ketones with odd numbers of carbon atoms from C_3 to C_{15} were found in steam distillates of milk fat. Exhaustive steam distillation of milk fat showed that the precursors of the methyl ketones were present in relatively small amounts.

The use of radioactive milk fat from a lactating cow which had been injected intravenously with (carboxy-^{14}C) acetate allowed a direct comparison to be made between the labelling patterns of the fatty acids and the correspond-

ing methyl ketones from the same milk source. The advantage of such a comparison was that two points on the biosynthetic pathway of milk fat (β-keto acid and the corresponding fatty acid) could be examined at the same time. The distribution of specific activities of fatty acids and methyl ketones from the radioactive milk fat was consistent with the origin of the fatty acids from at least two sources, which may and probably do intermingle to a substantial degree; namely, fatty acids transferred to the mammary gland from blood lipids (predominantly C_{12} to C_{18} acids) and the C_4 to C_{16} acids synthesized from acetate and D-β-hydroxybutyrate in the mammary tissue.

Acetone formed appreciable proportions of the total methyl ketones obtained from milk fat. Its low radioactivity in this investigation can be explained by assuming that most of the acetone precursor, presumably aceto-acetate, is derived from a non-isotopic source.

XANTHONES FROM GENTIANA BELLIDIFOLIA

K. R. MARKHAM
Chemistry Division, D.S.I.R., Gracefield

Ethanol extraction of the root material from the North Island Gentian *Gentiana bellidifolia* yields a mixture of pigments which are shown to be xanthones. I-R, U-V and n.m.r. spectral evidence will be presented together with chemical evidence to prove the structures of three of these pigments as 1,8-dihydroxy 3,5-dimethoxy xanthone (methyl bellidifolium), 1,5,8-trihydroxy 3-methoxy xanthone (bellidifolium) and 1,3,5,8-tetrahydroxy xanthone (desmethyl bellidifolium). The structures of two of these have been confirmed by a ten-step synthesis from resorcinol.

The structures of additional, minor pigments from this same plant will also be discussed. One of these is corymbiferin, previously isolated from G. corymbifera (Ross, D. J., 1950: *N.Z.J. Sci. Tech., 32* (3): 39).

INORGANIC SURFACE CHEMISTRY

A. T. WILSON
Chemistry Department, Victoria University of Wellington

Much of soil chemistry, biological chemistry and the chemistry of heterogeneous catalysis depends on the chemistry of materials adsorbed on to surfaces. Data will be presented to show that this chemistry can be quite different from conventional "three-dimensional" chemistry.

Despite its importance, inorganic surface chemistry is a little-studied branch of inorganic chemistry, mostly because of the experimental problems involved. At V.U.W. we have developed techniques which have enabled us to study this field. These techniques and the chemistry of phosphate on surfaces found in soil will be discussed, with particular reference to the problems of "fixation" and "availability" of soil phosphate.

THE SURFACE CHEMISTRY OF SULPHATE

P. C. RANKIN and A. T. WILSON

Chemistry Department, Victoria University of Wellington

A new technique has been developed for the study of adsorption of anions on to clay mineral surfaces. This paper is concerned with the adsorption of ^{35}S-sulphate on to the cation exchange surface of mica. The cleavage surface of mica is a common type occurring in clay minerals in the soil — *e.g.*, halloysite, kaolinite, montmorillinite. Extensive studies of mica have led to the elucidation of its surface structure. The study of the sulphate/mica system was facilitated by the fact that commercial end-window geiger counters have mica windows, enabling measurements of ^{35}S-sulphate adsorption.

Solutions of a known cation were prepared and the mica windows soaked in them. The majority of experiments were performed with adsorbed aluminium ions. Runs were also conducted with sodium-mica, hydrogen-mica, ammonium-mica, iron-mica and copper-mica. ^{35}S-sulphate was adsorbed on to these cation-mica surfaces and the rate of the desorption of the ^{35}S-sulphate, into a solution of known pH, followed with the geiger counter, a count rate meter and a strip chart recorder.

Resolution of the desorption curves gave the following results. ^{35}S-sulphate was retained by a mica surface having adsorbed divalent or trivalent cations. When monovalent ions were adsorbed, no sulphate was retained. The data from the chart recorder plot were transferred to semi-logarithmic paper. This curve was resolved into a series of straight lines. Each straight line corresponds to a different rate of desorption of ^{35}S-sulphate. These were characterized by their half-lives. Experiments showed that the half-lives were independent of pH, indicating that surface complexes were formed between sulphate ions and the cation-mica surface. The desorption reaction of these complexes was first order as shown by the logarithmic

desorption curve of each of the species. Resolution indicated five different surface complexes for the sulphate aluminium-mica system while iron-mica and copper-mica formed four each. Experiments were conducted with aluminium-mica in an effort to determine some of the chemistry of the sulphate-aluminium-mica surface complexes.

The advantage of this technique is that it allows the surface phenomena to be studied without the presence of the confusing and little-understood clay mineral edge effects. The data from this technique should, then, be of interest to soil chemists in studying the adsorption of sulphate on to a known clay mineral surface.

ANION INTERACTIONS WITH CARBOXYL-BOUND CATIONS

D. J. SPEDDING
Soils Department, Massey University of Manawatu, Palmerston North
and
A. T. WILSON
Chemistry Department, Victoria University of Wellington

Large molecules with carboxyl groups amongst their functional groups occur widely in nature and binding of metal ions by these carboxyl groups is known. However, little attention has been paid to the possibility of the interaction of anions with these carboxyl-bound cations. This paper will describe some investigations into anion-cation interactions on the surface of a carboxylic cation-exchange resin.

The following anions have been found to be removed from solution by a carboxylic resin saturated with certain cations: phosphate, molybdate, iodide, iodate, and chloride. Of the cations on the resin, ferric iron and aluminium play an important part in retaining the anions.

The implications, in soil science and biology, of these results will be discussed.

AN ISOTOPIC STUDY ON THE HYDROLYSIS OF ORGANIC ACIDS

CHARMIAN O'CONNOR and D. R. LLEWELLYN
Chemistry Department, University of Auckland

The exchange of the oxygen atoms of acetic acid, trimethylacetic acid, trifluoroacetic acid, trichloroacetic acid, aminoacetic acid and oxalic has been studied in solvent

water, using ^{18}O as tracer, over the hydrogen ion concentration range $4M > [H^+] > 10^{-11}M$ and between the temperatures 0 and 123°C. It was thought that these hydrolyses should involve similar mechanisms to esterification and ester hydrolysis.

The paths by which the oxygen atoms of a carboxylic acid or its ion may exchange with water are:

(1) Water attack on the protonated acid.

(2) Water attack on the acid or the chemically equivalent path—water attack on the protonated carboxylate ion.

(3) Hydroxyl ion attack on the acid or the chemically equivalent path—water attack on the carboxylate ion.

(4) Hydroxyl ion attack on the carboxylate ion.

We cannot distinguish between the alternatives in (2) and (3). The observed rates have been interpreted in terms of these four paths. Rate constants have been evaluated, together with corresponding activation energies, frequency factors, and entropies of activation.

With trifluoroacetic acid and trichloroacetic acid, in acid solution paths (1) and (2) make approximately equal contribution to exchange, whereas in alkaline solution path (4) is the only contributor.

The other acids studied exchange by paths (1) and (3), with perhaps small contributions from path (2).

NITRATING SPECIES IN NITRIC ACID-ACETIC ANHYDRIDE MIXTURES

S. J. DICKSON, A. FISCHER, W. YOONG and J. VAUGHAN
Chemistry Department, University of Canterbury, Christchurch

Reaction of *o*-xylene with nitric acid in acetic anhydride yields 3,4-dimethylphenyl acetate and lesser amounts of the expected 3- and 4-nitro-*o*-xylenes. Kinetics studies have shown that both the acetoxy and nitro compounds arise by reaction of the *o*-xylene with a protonated acetyl nitrate, itself formed from reaction of nitric acid with acetic anhydride. Although other alkyl-substituted benzenes give acetoxy as well as nitro derivatives on reaction with nitric acid in acetic anhydride, no acetoxy products are obtained from reaction of anisole or diphenylamine. From the kinetics of nitration of anisole and diphenylamine it is concluded that isomeric protonated acetyl nitrates are responsible for nitration of these compounds.

THE MILLS NIXON EFFECT

G. J. WELCH and G. J. WRIGHT
Chemistry Department, University of Canterbury, Christchurch

The effect of the fused saturated ring systems on the aromatic nucleus in the two compounds indan and tetralin has received little systematic study, although a number of papers, both experimental and theoretical, have been published. Two effects might be expected—differences between the two compounds in the favoured position of substitution on attack by electrophilic reagents, and some degree of bond fixation in the aromatic nucleus of the compounds arising from strain set up by the fused rings. The second possibility has been highlighted at the expense of the first since Mills and Nixon postulated (1930) the existence of fixed double bonds in indan and tetralin, and presented experimental evidence to support this view. All subsequent investigation has been concerned with this problem, which still remains in doubt.

This paper presents the results of a systematic investigation of the behaviour of these compounds towards electrophilic attack. Significant difference is found in the preferred position of substitution between indan on the one hand and tetralin and *o*-xylene on the other. An explanation for the results, and those of Mills and Nixon, is offered.

SYNTHESIS AND ORIENTATION OF PYROPHYLLITE

W. D. MEANS
Geology Department, University of Otago, Dunedin
and
J. ROGERS
N.Z. Geological Survey, D.S.I.R., Chemistry Department, University of Otago, Dunedin

A distinguishing feature of slates is almost perfect parallel orientation of minute platy grains of mica and other phyllosilicates. The familiar splitting property called slaty cleavage arises from this grain orientation pattern, or fabric. It is generally recognized that the mica in slates grows during metamorphism and that its orientation results from anisotropic stress conditions or consequent flow in rock bodies, but there is no general agreement on the geometric relation between slaty cleavage and directions of stress or flow. Experiments with model materials have shown that random platy particles can be made parallel by deformation of the enclosing plastic matrix.

This paper describes exploratory experiments in which the phylosilicate, pyrophyllite, $Al_2Si_4O_{10}(OH)_2$ was synthesized hydrothermally in material subject to anisotropic

stress. Under certain conditions of deformation and stress, oriented grain patterns, or fabrics, of pyrophyllite were obtained broadly similar to those of mica in slates.

BISMUTH (III) SOLUTION CHEMISTRY

G. A. WRIGHT

Chemistry Department, University of Auckland

Research work over the last 10 years, mainly by Swedish chemists, has shown that bismuth (III) in aqueous solution exists as the simple trivalent ion when the acid concentration is greater than 0.6 molar. At lower acid concentrations, hydrolysed and polymerized forms predominate. It was also established that complexes form with chloride, bromide and iodide ions, the maximum co-ordination number being six. With this knowledge it is now possible to carry out physico-chemical experiments with a view to understanding the behaviour of bismuth (III) in quantitative terms.

The bismuth amalgam electrode gave reproducible potentials in an oxygen-free system. It has been used to determine the standard electrode potential of Bi/Bi^{3+} as 0.292 volt in perchloric acid solutions. From this measurement the free energy of hydration of the gaseous bismuth ion is calculated to be -1166 kcal/mole. The hydrated ion is about 100 kcal less stable than would be predicted from a simple model which accounts quite well for the hydration energies of all the other aqueous cations. This deviation may be connected with the outer pair of *S* electrons on the bismuth ion.

Potentiometric titrations with the amalgam electrode were used to determine the stability constants of bismuth complexes with thiourea and an aromatic phosphine as ligands. *Hexa* co-ordination occurs and there is a marked increase of stability as the donor atoms become larger; thus sulphur and phosphorus bind much more strongly than oxygen or nitrogen. This is the reverse of the order expected on simple electrostatic grounds. It is also observed that the formation curve is steep — *i.e.*, complexes intermediate between the *mono* and *hexa* complexes are relatively unstable and have only a short range of existence.

The electrode potential indicates that bismuth ions should be readily reduced and it is of interest to consider the reduction mechanism. Flow tube experiments have shown that reduction by chromous ions is fast in the presence of ligands which complex with bismuth; when these ligands are absent there is an appreciable fall in the rate. Reduction of trivalent bismuth and its complexes at

the dropping mercury electrode results in a single polarographic wave in all cases and there is no evidence for an intermediate oxidation state.

ELECTRODIALYSIS WITH ION-SELECTIVE MEMBRANES

A. M. KENNEDY

Chemistry Department, University of Otago, Dunedin

With the advent of ion-selective membranes, electrodialysis is becoming an important industrial operation for processes involving the separation of electrolytes from solutions. This paper will discuss some of the properties of ion-exchange membranes, especially in relation to applications that are of possible commercial significance to New Zealand. These include the recovery of alkali metals from geothermal water, the concentration of sea-water as a first step in salt production, and the recovery of pulping chemicals from spent neutral sulphite liquor.

KINETICS OF THE IODATE-IODIDE REACTION

A. F. M. BARTON

Chemistry Department, University of Auckland

The kinetics of the halate-halide reactions have proved very complex, and progress in systematizing the observed rate laws has been slow. Kinetic studies of the well-known reaction between iodate and iodide had been made in the past by several techniques, but the more sensitive method of iodine determination by amperometry has now been used in order to obtain information over a greater range of reactant concentrations.

The initial, zero order rate of reaction was measured by the volume of sodium thiosulphate, added to the reaction mixture from a micrometer syringe, which was required to maintain the concentration of iodine at approximately 10^{-6} molar. The iodine concentration was obtained from the current (1 to 2 microamp) flowing between two platinum electrodes in the reaction vessel and measured as a potential difference by a recording potentiometer. Concentration ranges used were: iodate, 3×10^{-5} to 7×10^{-3} molar; iodide, 8×10^{-5} to 1×10^{-2} molar; pH 2 to 6 in perchloric acid, and in acetate and chloroacetate buffer solutions. The ionic strength was maintained at 1.00 with sodium perchlorate.

For acetate and chloroacetate a non-linear dependence of rate on buffer concentration was found, and this could be fitted by the expression

$$\text{Rate} = kB/(1+k'B)$$

where B = buffer concentration, for a constant concentration of all other reactants.

In perchloric acid, and in the buffered solutions at zero buffer concentration (obtained by extrapolation using a computer-calculated least squares method) the rate could be expressed

$$\text{Rate} = k_1[H^+]^2[I^-]^2[IO_3^-]^1 + k_2[H^+]^4[I^-]^3[IO_3^-]^2$$

The existence of the first term agreed with the results of earlier investigations, but the second term has not been reported previously.

ADDITION REACTIONS OF BETA-PINENE DERIVATIVES

M. P. HARTSHORN and A. F. A. WALLIS
Chemistry Department, University of Canterbury, Christchurch

Addition of hydrogen bromide to *cis*- and *trans*-pinocarveol proceeded with rearrangement to give 6-endo-bromocamphor and 6-endo-bromoisofenchone respectively. Reaction of pinocarvone with hydrogen bromide or bromine, however, gave pinane derivatives only.

THE DEHYDROCHLORINATION OF DDT BY THIOPHENOXIDE ION—KINETICS AND MECHANISM

B. D. ENGLAND and D. J. McLENNAN
Chemistry Department, Victoria University of Wellington

The correlation between the basicity of a reagent and its nucleophilicity as measured by the rate of nucleophilic substitution at a saturated carbon atom is generally poor. For example, mercaptide ions such as thiophenoxide are normally among the strongest nucleophiles despite their comparatively weak basicity. In elimination reactions, where the nucleophile attacks hydrogen, a better correlation would be expected but is not observed in the dehydrochlorination of *t*-butyl chloride by thiophenoxide. We have studied the corresponding reaction with DDT which, because of its resistance to substitution reactions, is a very convenient substrate.

In this elimination reaction, thiophenoxide is found to be 1,000 times less reactive than methoxide in solvent methanol, and this parallel between basicity and reactivity of the proton-abstracting reagent, together with the modified second-order kinetics observed for the DDT-thio-

phenoxide reaction, suggests a rare elimination mechanism involving reversible carbanion formation (the ElcB mechanism). But hydrogen isotope-exchange experiments rule out this mechanism, and the kinetics, which are, at first sight, incompatible with the more usual concerted process (E2), have been reconsidered and successfully reconciled with the latter.

Modern theories on E2 transition states and nucleophilicity can explain why thiophenoxide is comparatively un-reactive in the DDT reaction and why there is no correlation between basicity and reactivity in other cases. Bronsted and Hammett treatments provide an insight into the nature of the transition state for DDT dehydrochlorination and it is found that this transition state differs from the others in which thiophenoxide is a more reactive eliminating agent.

Detoxication of DDT and other chlorinated hydrocarbons by biological systems involves dehydrochlorination by mercaptide ions, and the present work affords a mechanistic interpretation of this process.

REARRANGEMENTS IN THE CLEMMENSEN REDUCTION

B. R. DAVIS and N. J. CUSACK
Chemistry Department, University of Auckland

The Clemmensen reduction—conversion of a ketone to a hydrocarbon with amalgamated zinc and concentrated hydrochloric acid—is shown to proceed anomalously when applied to 1,3-diketones. The known rearrangement of dimedone to a cyclopentanone derivative is shown to be a general reaction for acyclic 1,3-diketones, and some details of a proposed mechanism have been substantiated by synthesis of particular diketones and their possible rearrangement products.

Preliminary results suggest that the reduction of cyclic $\alpha\beta$ unsaturated ketones and 1,4-diketones also proceeds with rearrangement.

THE REARRANGEMENT OF N,N'-DIPHENYL-1,3-PROPANE DIAMINE

G. B. RUSSELL
Plant Chemistry Division, D.S.I.R., Palmerston North

When N,N'-diphenyl-1,3-propane diamine is heated under vacuum to 230°-250°C with 0.1 molar amounts of hydrobromic acid, decomposition occurs to give aniline, 1,2,3,4-

tetrahydroquinoline and julolidine, as volatile products. Using various substituted anilines, a variety of symmetrical diaryl-diamines were prepared and decomposed to give the appropriate anilines, tetrahydroquinolines (a mixture of 5- and 7- substituted isomers with the *meta*-substituted diaryl-diamines) and julolidines (in the cases where there were no *ortho* substituents). In each case the relative ease of decomposition was noted and a full product analysis made. These observations gave an insight into the effect of the substituent on the decomposition and allowed a mechanism for the cyclization step to be formulated.

The evidence favouring the proposed mechanism will be presented and some comments, on the interesting formation of julolidine, will be made.

STEREOCHEMICAL EFFECTS IN THE SUBSTITUTION REACTIONS OF TRITIUM RECOILS

A. L. ODELL
Chemistry Department, University of Auckland

Tritons produced in the $He^3(n,p)T$ reaction recoil with an energy of 0.2 meV. Such "hot" atoms react with hydrocarbons by substitution to form labelled hydrocarbons or by H abstraction to form H-T. The substitution reaction is not subject to the same stereochemical laws as thermally activated substitution reactions. In the expression Rate $= pZe^{-E'/RT}$, the exponential term approaches unity for "hot" atom reactions while p becomes a "hot" atom steric factor since the system does not react by the lowest "saddle" route. Evidence from product yields, effects of inert moderators and scavengers suggest that controlling effects in the course of a "hot" atom reaction is the angle of attack on the substrate molecule, "end on" collisions producing abstraction, while "side on" collisions produce substitution. Primary hydrogen atoms in hydrocarbon molecules show higher substitution/abstraction ratios than do secondary or tertiary hydrogen atoms. Early explanations for this effect were in terms of bond energy differences.

Experiments on recoil labelling of *iso* butane will be described which show that the controlling effect is stereochemical.

TRITIUM LABELLING ON METAL CATALYSTS

A. L. ODELL and M. A. LONG
Chemistry Department, University of Auckland

The exchange between tracer amounts of tritium gas and organic compounds with the aid of metal catalysts has been studied as a method of producing high specific

activity material. Cyclohexene, benzene, toluene and acetone have been labelled with a minimum of 95% purity. Further preliminary studies indicate that the method may be extended to the labelling of materials in carbon tetrachloride solution.

PHOSPHATE AVAILABILITY IN SOILS

Y. T. SHAO and A. T. WILSON
Chemistry Department, Victoria University of Wellington

The technique is an extension of "simultaneous isotope exchange kinetics" to a liquid/solid system. ^{32}P is used to follow the kinetics of phosphate exchange between the phosphate on the soil and the phosphate in the soil solution. The activity of the solution as a function of time can be expressed as the sum of a number of logarithmic terms each representing a different type of soil phosphate. Such concepts as "phosphate availability" and "phosphate fixation" are expressed in ordinary physical chemical terms. This technique gives a measure of the phosphate status of the soil from the point of view of the plant root, that is, absolute phosphate concentration of soil solution and the rate at which this phosphate will be replenished if removed by the plant root.

TOXIC HAZARDS OF HEATED CYANIDES

E. F. HUBBARD
Laboratory, Railway Workshops, Lower Hutt

When iron or steel is heated in the presence of certain cyanides, combination of iron with carbon and nitrogen will occur. This renders it capable of being hardened by quenching from a suitable temperature, in water or oil.

The cyanides commonly employed for this purpose are sodium cyanide, potassium cyanide, potassium ferrocyanide, either alone or as mixtures, or sometimes mixed with another salt such as sodium carbonate.

These cyanides may undergo transformations due to heat, or a reaction with metals and salts, or a reaction with moisture, all of which give rise to the emission of toxic vapours such as cyanogen, hydrocyanic acid, and the fume of vaporized potassium cyanide.

The nature of these products and the conditions under which they may occur will be described. Some experiments which have enabled the concentration of toxic fumes produced by cyanides to be determined under factory operating conditions will be reported.

The toxicity of these substances will be discussed, and some account of methods of first aid will be given.

TOXICITY OF SPORIDESMIN

D. E. WRIGHT
Ruakura Agricultural Research Centre, Hamilton
and
I. T. FORRESTER
Lincoln College, University of Canterbury, Christchurch

Sporidesmin, a sulphur-containing metabolite from *Pithomyces chartarum*, when dosed to animals causes pathological changes identical with those associated with facial eczema.

Experiments using guinea-pigs have shown that the toxin markedly influences the respiration of liver homogenates and mitochondria. These results together with analyses for nucleotides in livers will be discussed.

RECENT DEVELOPMENT IN ULTRACENTRIFUGE TECHNIQUES

J. W. LYTTLETON
Plant Chemistry Division, D.S.I.R., Palmerston North

The most common applications of the ultracentrifuge are:

(a) To examine a solution of large molecules to determine the relative concentration of molecules which sediment at different rates.
(b) To determine the molecular weights of large molecules.

The modern centrifuge, with schlieren, ultraviolet absorption and Rayleigh interference optics, has made possible many ways of obtaining this information. Some of the more generally useful of these will be described.

COURSE ON ENZYMOLOGY
Victoria University of Wellington

The Department of Chemistry, with assistance from the University's Department of Adult Education, will hold this course in its rooms in the Easterfield Building of the University between October 12 and 23, 1964.

The course is designed for graduates in Chemistry or Biochemistry and will deal with some current procedures in enzymology. The first week is primarily a lecture course (2 to 3 lectures daily) but some elementary laboratory work with enzymes will be provided for those who have had no previous formal course in biochemistry.

The second week will be primarily a practical course and will be arranged after discussions to suit needs of individual students so far as the facilities permit. Some indication of these requirements should be given on registration.

The following subjects will be considered: Separation techniques, Physical characterization, Structure determination, Particulate systems and Electron microscopy, Clinical applications.

Inquiries concerning the course should be addressed to the Director of Adult Education, Victoria University of Wellington, Box 2945, Wellington. A brochure will be available.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

BALANCE SHEET AS AT APRIL 30, 1964

1963 £		£ s. d.	£ s. d.
	Current Liabilities:		
90	Sundry Creditors	152 5 0	
15	Provision for Taxation	15 18 1	
77	Subscriptions Received in Advance	30 14 0	
—	Royal Institute of Chemistry: Funds held in Trust	200 0 0	
(182)			398 17 1
	Special Funds:		
28	Compounded Subscriptions	22 10 9	
75	Education Fund	75 0 0	
144	Overseas Visitors' Travelling Fund	4 4 9	
(247)			101 15 6
	Trust Fund:		
1326	As per statement attached		1286 16 11
	Accumulated Funds:		
	Balance as at 30/4/63	669 13 8	
	Add: Transfer from Trust Fund	44 0 0	
	Excess of Income over Expenditure for year	308 9 3	
670			1022 2 11
£2425			£2809 12 5

1963 £		£ s. d.	£ s. d.
	Current Assets:		
18	Petty Cash Funds	9 9 11	
443	Bank of New Zealand	813 19 2	
498	National Savings Account	515 2 5	
	Subscriptions in Arrears £152 14 0		
	Less: Provision for overdue Subscriptions 50 0 0		
56		102 14 0	
—	Local Members' *Journal* Subscriptions in Arrears	12 0 0	
20	Advance, Conference	20 0 0	
2	Monographs on Hand	0 10 0	
(1037)			1473 15 6
	Trust Fund Investments at Cost:		
283	Post Office Savings Bank	36 16 11	
500	Hutt County Council Debentures	500 0 0	
500	Lyttelton Harbour Board Stock	750 0 0	
44	Cash in General Account	—	
(1327)			1286 16 11
	Fixed Assets, at Cost:		
	Office Equipment £99 19 0		
	Less Depreciation 51 19 0		
60		48 0 0	
	Addressograph Plates £31 3 6		
	Less Depreciation 30 3 6		
1		1 0 0	
(61)			49 0 0
£2425			£2809 12 5

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED APRIL 30,1964

1963	EXPENDITURE	£ s. d.	£ s. d.
£			
	Administration Expenses:		
200	Salary, Registrar	220 0 0	
163	Travelling Expenses	206 4 1	
339	Printing, Stationery, Postages and Tolls	173 17 7	
150	Branch Expense Allowances	125 0 0	
50	Honorarium to Secretary	60 0 0	
21	Audit Fee	21 0 0	
20	General Expenses	18 8 3	
14	Depreciation	12 0 0	
(957)			836 9 11
308	Cost of *Journal*	313 16 2	
35	Honorarium to Editor	45 0 0	
(343)			358 16 2
27	*Chemistry in Action* — Net Cost		32 0 9
25	Chemistry Essay Prize		25 0 0
	Examination Expenses	16 13 9	
	Less Examinees' Fees Received	3 0 0	
8			13 13 9
15	Provision for Taxation		15 18 1
9	Excess of Income over Expenditure		308 9 3
£1384			£1590 7 11

1963	INCOME	£ s. d.	£ s. d.
£			
1350	Subscriptions — Annual	1483 19 7	
5	Proportion Compounded Subscriptions	5 1 7	
(1355)			1489 1 2
	Interest Received:		
6	Bank of New Zealand	8 9 10	
—	Local Body Stock	48 13 11	
18	National Savings Account	17 8 0	
(24)			74 11 9
5	Commission on *Journal* Subscriptions		6 10 0
—	Surplus on Distribution of "Education in Chemistry"		20 5 0
£1384			£1590 7 11

TRUST FUND ACCOUNT

1963		£ s. d.	1963		£ s. d.
£			£		
—	Transfer to Accumulated Funds (Debenture Interest received in year ended 30/4/63)	44 0 0	1275	Balance, 30/4/63	1326 15 0
1327	Balance, 30/4/64	1286 16 11	52	*Interest*: Post Office Savings Bank	4 1 11
£1327		£1330 16 11	£1327		£1330 16 11

OVERSEAS VISITORS' TRAVELLING FUND

1963		£ s. d.	1963		£ s. d.
£			£		
47	Travelling Expenses paid during year	278 0 0	106	Balance, 30/4/63	144 6 8
144	Balance, 30/4/64	4 4 9	75	Conference Surplus Credited to Fund	87 16 10
			10	Donations Received	50 1 3
£191		£282 4 9	£191		£282 4 9

AUDITOR'S REPORT

I have audited the books of the New Zealand Institute of Chemistry (Inc.) for the year ended April 30, 1964, and have received all the information and explanations I have required. In my opinion, according to the best of my information and the explanations given to me and 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 April 30, 1964.

J. W. SHANAHAN, A.P.A.N.Z.,
Auditor.

Christchurch:
June 19, 1964.

BRANCH NEWS AND NOTES

AUCKLAND

It was recently reported that the output of clay being processed by Clay Enterprises Ltd. is being increased to 20,000 tons per annum to provide for the needs of paper, cosmetic, paint and pottery manufacture. The clay will be obtained from a high-grade deposit of millions of tons discovered some time ago at Matauri Bay near Kaeo.

The subject "Phosphatic Fertilizers" was reviewed by Mr P. J. Gallaher in the Chairman's address to the branch in June.

At an international conference on water pollution, to be held in Tokyo during August, Mr R. Hicks is to lead the formal discussion on a paper on nitrogen removal from sewage and night-soil in stabilization ponds.

Dr H. C. Holland is chairman of the eleventh New Zealand Science Congress to be held in Auckland from February 11 to 17, 1965. The convener of the chemistry section is Mr G. R. White and enquiries about the programme for this section should be addressed to Dr F. J. B. Aggett, Chemistry Department, University of Auckland, Box 2175, Auckland, C.1.

MANAWATU

The Branch congratulates Dr R. M. Dolby on his appointment as Chief Chemist of the Dairy Research Institute.

Dr G. Petersen has returned to the Plant Chemistry Division, D.S.I.R., after three years overseas.

Tenders have been called for the construction of the new Dairy Research Institute Building, of an area of 26,600 sq. ft. It comprises an engineering wing on one side, a two-storey chemistry and bacteriology wing on the other side, and a linking two-storey section housing administration, library and cafeteria. It will be located opposite the present experimental factory, close to the Plant Physiology Division, D.S.I.R.

WELLINGTON

The Senior Lectureship in Spectroscopy at Victoria University has been filled by the appointment of Dr E. P. A. Sullivan, at present Lecturer in Chemistry at Sydney University. He had previously held lectureships at the University of Malaya and at Newcastle University College, University of Sydney.

The July meeting of the Wellington Branch took the form of a conversazione held by the Chemistry Department of Victoria University. After sherry and dinner, members of the branch met with staff and research students to discuss current research in the department and to see at first hand any practical aspects of their work.

Professor J. F. Duncan, of the Victoria University Chemistry Department, will be attending the Gordon Research Conference on Inorganic Chemistry, to be held at New Hampton, New Hampshire, U.S.A., from August 10 to 14, 1964.

The 1964 Mellor Lecture was delivered by Dr P. K. Foster, Director of the N.Z. Pottery and Ceramics Research Association. The title of his lecture was "Ceramic Research in New Zealand".

Dr T. P. Cotter, at present with the Chemistry Department, University of Canterbury, gave three lectures at Victoria University in June. These were entitled "Nuclear Rocket Propulsion Research", "Los Alamos — A Different American Laboratory and Community" and

"Thermionic Conversion of Nuclear Energy to Electricity". Dr Cotter, who holds a Fulbright award, is on leave from the Los Alamos Laboratories in New Mexico, U.S.A.

CANTERBURY

Two special meetings of the branch have been held recently. At the first of these, on June 29, Dr T. P. Cotter of the Los Alamos Scientific Laboratory gave an address entitled "Los Alamos — A different American laboratory and community". At the second special meeting on July 6 the President, Mr S. G. Brooker, gave an address entitled "Margarine". Earlier in the day many branch members attended a buffet luncheon to mark the Presidential visit.

OTAGO

The President of the Institute, Mr S. G. Brooker, spoke to the Otago Branch on Tuesday, July 7, and showed a film on the manufacture of margarine. Mr Brooker was entertained prior to the lecture at an informal dinner held at the University Union.

Following the successful series of lectures to school pupils last year, the Branch has again organized a series of three lectures for senior school pupils. The first of these "The water in our bodies", was given by Professor J. Robinson of the Physiology Department on June 5 and was attended by nearly 200 school pupils.

The July 24 Institute meeting will be held in Invercargill where Dr T. Hagyard will give an address on "Chemical Industry".

We wish to congratulate Dr P. K. Grant on the award of a Nuffield Fellowship for a year's study at Cambridge.

INSTITUTE BUSINESS

Items from the Minutes of the May, 1964, Meeting of Council

WELCOME, CONGRATULATIONS, ETC.

The President welcomed Dr Richards to the Council and referred to the fact that Mr G. A. Lawrence had been honoured in the New Year Honours list, and that Professor Siemon and Messrs K. E. Seal and A. W. Mackney had been appointed to the National Research Advisory Council.

CONFERENCE 1963

The final report of the 1963 Conference Committee was received. It was noted that Professor Alexander's fare had not been debited to the Conference account. If this is done, the Conference was run at a small profit.

Resolved: That the Conference Committee be thanked for their work and congratulated on their organization of the Conference and that the Conference profit be paid in to the Overseas fund.

CONFERENCE 1964

Mr Clare reported on the progress of arrangements for the Conference in Hamilton. It is proposed that members will be housed in hotels, private hotels and motels. *Resolved*: That all members of the Conference Committee with the exception of the

Secretary must pay the Conference Fee and that all members of the Committee are eligible to claim expenses.

AFFILIATION WITH THE ROYAL SOCIETY OF NEW ZEALAND

After delegates had outlined the views of branches, it was *Resolved*: That the Institute apply to the Royal Society of New Zealand to be accepted as an affiliated body subject to the condition that the Institute is under no direct financial obligation to the Society, and that the Society accepts the expenditure by the Institute on the *Journal* and on supporting visits from overseas scientists as satisfying the Society's Rules on the expenditure of the funds of affiliated bodies.

R.S.N.Z. SECTIONAL COMMITTEE ON CHEMISTRY

Resolved: That the Institute nominate Professor J. F. Duncan and Dr A. T. Johns for appointment to the R.S.N.Z. Sectional Committee on Chemistry.

Resolved: That the Institute inform the R.S.N.Z. that if the Institute is accepted as a member body of the Royal Society, the Council of the N.Z.I.C. would like to discuss with the Royal Society the future of the Sectional Committee on Chemistry.

NATIONAL COMMITTEE ON CHEMISTRY

In a letter, the President of the R.S.N.Z. considered that the suggestion that the President of the National Committee should be the President of the N.Z.I.C. was not a good one as continuity in office was desirable. *Resolved*: That the N.Z.I.C. recommends to the Royal Society that the National Committee on Chemistry should consist of the Sectional Committee together with the President and the First Vice-President of the N.Z.I.C.

ASSOCIATESHIP BY EXAMINATION

After a full discussion of the proposals under consideration it was *Resolved*: That the foreign language requirement for the Associateship examinations be deleted.

Resolved: That the syllabus for the Associateship examinations be defined as the Stage III (or equivalent) syllabus at a New Zealand University and that the Institute approach the universities to ascertain if they would be prepared to examine candidates on behalf of the Institute and provide assistance if required with syllabuses, texts, etc. (*Note*: It is assumed that the candidate would pay all fees, etc.)

It was agreed that it should be suggested to the Examination Committee that they consider the possibility of a candidate submitting a dissertation and having an oral examination in lieu of the special paper.

It was further agreed to invite the Chairman and Secretary of the Examination Committee to attend the next Council meeting.

CROSS-CREDITS, NATIONAL CERTIFICATE TO L.A.C.

On the recommendation of the Examinations Committee, it was *Resolved*: That the following cross-credits from the National Certificate in Science to the L.A.C. be approved.

Chemistry II as equivalent to Theoretical Chemistry.
Physics II as equivalent to Elementary Physics.
Mathematics I as equivalent to Elementary Calculations.

VICE-PRESIDENTS

Resolved: That the Rules of the Institute be amended to provide for two Vice-Presidents.

Resolved: That the two Vice-Presidents be designated First Vice-President and Second Vice-President.

Resolved: That the General Secretary be instructed to draft the necessary changes in the Rules for approval at the next meeting of Council and that the General Secretary be instructed to call for nominations for the office of Second Vice-President.

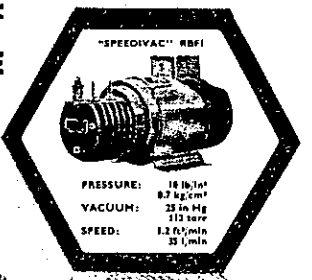
JOURNAL

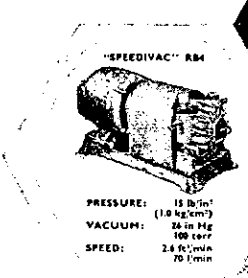
Resolved: That 1,000 copies of the article "Safety in the Laboratory" by A. H. Horn be reprinted.

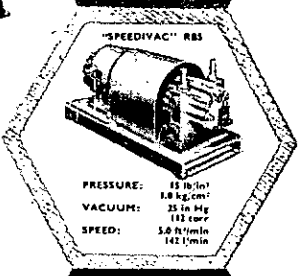
The Editor reported that Miss J. M. Mattingley had agreed to take the position of Editor in the near future.

W. E. HARVEY
General Secretary

A PERFECT COMBINATION OF VACUUM & PRESSURE







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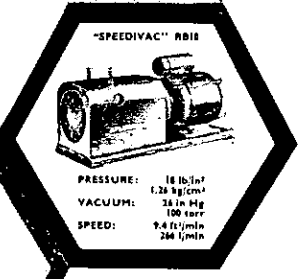

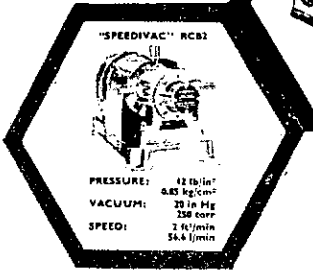

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a Sarong takes shape in Manchester

Sunrise in Java: on a river bank a group of chattering girls are drying cotton cloth, freshly printed in the brilliant colours favoured for sarongs. As the sun travels west, bringing a new day, printers and dyers of textiles in countless countries go to work: the bazaar craftsmen of Bombay, Bokhara and Cairo, the men who mind the intricate machinery of textile factories in Pekin, Vienna and Lyons. And in an ICI laboratory in Manchester, England, the day begins for the group of scientists who have provided the colour for sarongs and French couture fabrics alike—the inventors of 'Procion' dyestuffs.

Brilliant yet fast, economical and easy to use, the 'Procion' dyes were the first in the world to combine chemically with the fibres of cotton and linen. In the eight years since they were invented, technical service specialists from ICI have travelled millions of miles to explain their use and to give technical demonstrations lasting anything from three hours to three months. In more than 50 countries they have established the 'Procion' dyes as leaders in their field. With the 'Procinyl' fibre-reactive dyes for nylon and 'Procilan' for wool they represent yet another triumph for ICI research and a landmark in the history of colour chemistry.

The influence of I.C.I. research and production is felt today in every corner of the globe

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