CHEMISTRY IN NEW ZEALAND

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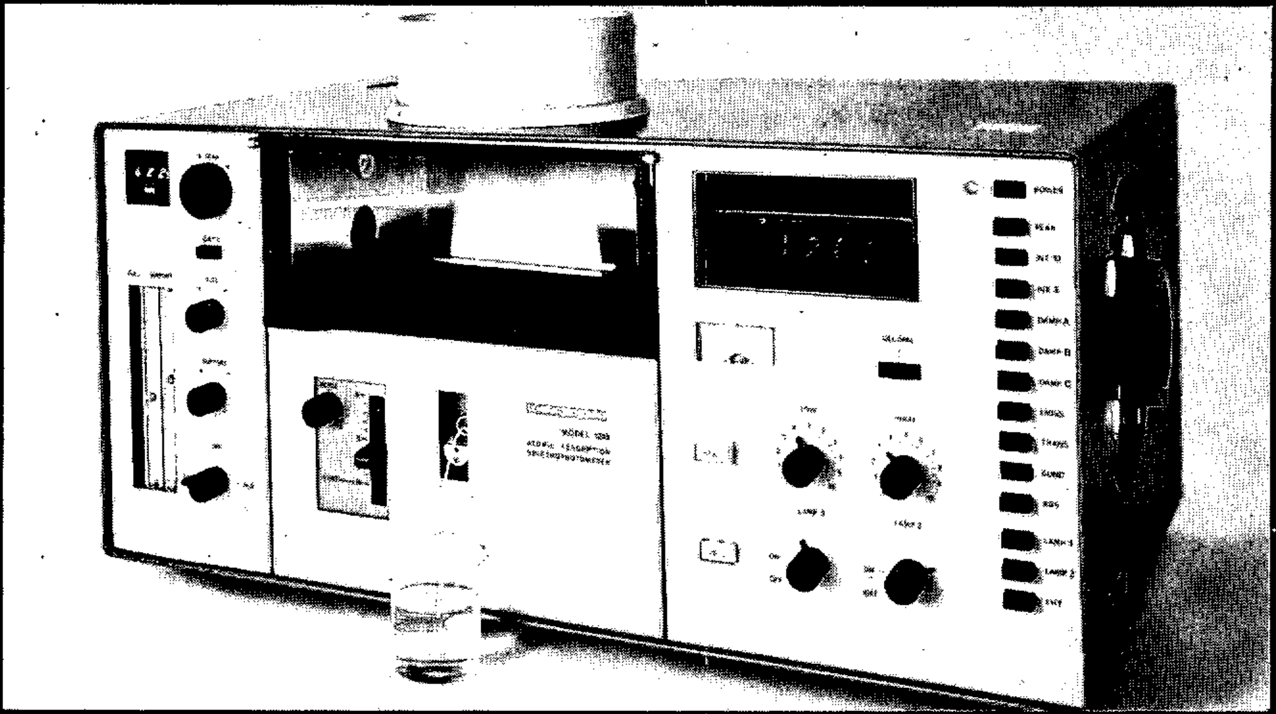

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CHEMISTRY IN NEW ZEALAND

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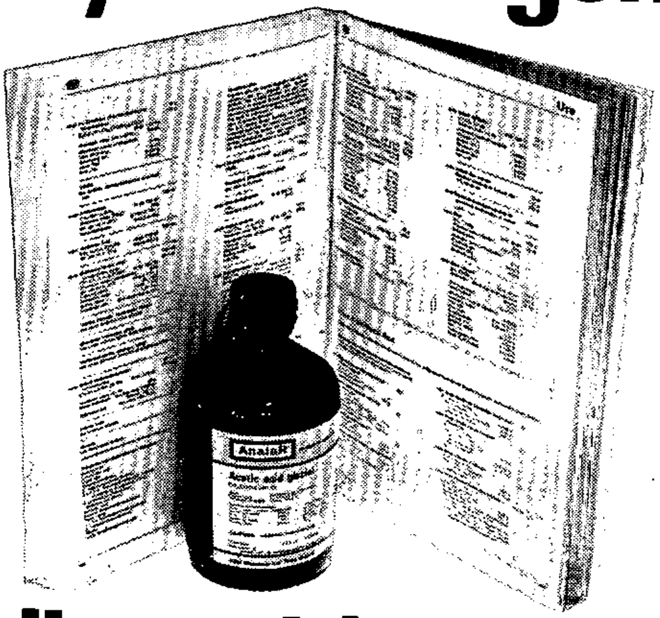

CONFERENCE 1972

Welcome to Wellington

Wellington. To residents outside the capital city what does this name bring to mind? Perhaps thoughts of hurried travel; of Head Offices and central committee meetings; of lobbying for money or equipment; of politics, papers and people. Travel to Wellington is often more in the class of a necessity than a pleasure. However, the Wellington Committee has endeavoured to arrange a programme which will make your attendance at the 1972 Conference both a necessity *and* a pleasure.

The Wellington-Lower Hutt area contains a particularly high population of chemists, and about one quarter of the approximately one thousand total NZIC members work here. The Wellington Conference therefore gives an unusually good opportunity for meeting with fellow chemists at Sessions and later in their laboratories. The Conference this year has a compact programme contained within three days. Within this time there is a programme of strong review papers in several areas of chemistry, together with papers selected from the best of New Zealand research in particular fields. The opening speaker will be the Minister of Science, the Hon. L. W. Gandar, and there will be several distinguished overseas visitors at the Conference, including our special guest lecturer Professor J. O'M. Bockris, a world figure in electrochemistry.

The general plan in the Conference is to give N.Z.I.C. members the opportunity of getting up-to-date with modern developments in various chemical disciplines. It is a Conference planned for chemists rather than for public relations. A good variety of research papers have been offered and will be presented within a series of concurrent Sessions on the Wednesday. There are several social functions to keep the atmosphere relaxed.

Several of the Specialist Groups of the Institute have arranged special symposia. These include Chemical Thermodynamics, Organic Chemistry, Geochemistry, and Biochemistry. Visits to laboratories on the Friday are proving popular with those who have registered already. You will be able to see new techniques and equipment in the Government and University laboratories, and to inspect industrial processes.

The Annual Conference is the feature of the N.Z.I.C. year. We hope that you find it stimulating and entertaining.

A. J. Ellis,
Conference Chairman.

CONFERENCE PROGRAMME

Circumstances have forced a number of changes to the outline of the Conference Programme as given in the second conference circular.

Professor E. N. Lightfoot was originally to deliver the guest lecture on Tuesday, but as he now has to return at an earlier date to the U.S., Professor Bockris has been asked to deliver the guest lecture, and Professor L. G. Hepler of the University of Lethbridge, Alberta, has been invited to deliver a review lecture on Electrolyte Chemistry.

Mr. J. E. Allan is unable to head the section "Inorganic Analysis Today", due to illness, and Dr. H. Keyser (V.U.W.) has agreed to deliver the review lecture.

SYMPOSIA

The conference will be preceded on Monday, 21st August, by two symposia:

(1) *ORGANIC CHEMISTRY SYMPOSIUM*

Those interested in the above symposium should contact Dr. J. T. Craig, Department of Chemistry, Victoria University of Wellington.

(2) *CHEMICAL THERMODYNAMICS SYMPOSIUM*

The following tentative programme has been arranged:

DR. A. G. WILLIAMSON (Chairman), Dept. of Chemical Engineering, Canterbury University: "Experimental Measurement of Second Virial Coefficients of Pure Condensable Vapours". DR. D. V. FENBY (Secretary), Department of Chemistry, Otago University: "Aromatic Fluorocarbon Mixtures". DR. D. E. JONES, Department of Chemistry, Otago University: "Light Scattering in Liquid Systems". DR. P. J. McELROY, Department of Chemical Engineering, Canterbury University: "The Supercooling of Water". DR. H. K. J. POWELL, Department of Chemistry, Canterbury University: "Protonation Reactions of some Polydentate Basic Ligands". DR. I. D. WATSON, Department of Chemistry, Biochemistry and Biophysics, Massey University: "Prediction of Excess Properties of Mixtures using a Hard Sphere Model".

BIOCHEMICAL SYMPOSIUM

This will be held on Friday 25th, and will combine members of the Biochemical Institute and those members of our Institute having biochemical interests.

GEOCHEMISTRY

This group will meet on Wednesday 23rd. Interested members will be given more information on registration.

ROYAL SOCIETY

The Royal Society of N.Z., under the auspices of the National Committee for Chemistry, intends to convene a meeting during the conference. This meeting is to discuss:

(a) The objects and present achievements of I.U.P.A.C. in relation to N.Z.

(b) The possibility of chemical companies becoming company associates of I.U.P.A.C.

(c) New Zealand national representatives on I.U.P.A.C. commissions.

(d) Chemistry teaching in schools.

As it is unlikely that the N.Z.I.C. President, Mr. K. E. Seal, will be able to attend the conference, the above meeting may be held instead of the Presidential Address. A reception will follow. All delegates are strongly urged to attend this meeting and the earlier trades display activities.

CONFERENCE SESSIONS

Guest Lecturer: J. O'M. BOCKRIS (Flinders University, South Australia)

ABSTRACTS: SECTION A: SPECIAL SESSIONS — INVITED SPEAKERS

NOTE: Asterisk indicates the speaker for multi-authored papers.

ELECTROCHEMISTRY

Review Lecture:

L. G. Hepler (University of Lethbridge, Alberta).

Research Papers:

G. A. Wright (University of Auckland).

S. I. Smedley (Victoria University).

ELECTRODE PROCESSES ON METALS

G. A. Wright

Chemistry Department, University of Auckland

Electrochemical process industries in New Zealand include the manufacture of chlorine, hydrogen, aluminium and cuprous oxide; electroplating of Cu, Zn, brass, Ni, Cr, Cd and Ag; anodising of aluminium; and electrolytic sewage treatment. Electrochemical reactions are also involved in the corrosion of metals; and many ships, pipelines and other vulnerable structures are cathodically protected. Much New Zealand research on electrode reactions has been concerned with trouble-shooting or improvement of existing processes.

More fundamental work has been concerned with the behaviour of freshly-cut surfaces on reactive metals (University of Canterbury), diffusion and detection of intermediates at rotating electrodes (Victoria University), and the kinetics of dissolution and passivation of metals (University of Auckland). The last mentioned studies have involved potentiostatic polarisation, cyclic voltatmmetry and film growth experiments on Tl, Ni, Co, Cu and Bi electrodes.

On actively dissolving metal surfaces, adsorbed intermediates of low valence play a key role (NiOH on Ni, Cu^+ on Cu, BiOH on Bi). The addition of adsorbable species generally has a marked effect on the reaction rate, particularly if there is a strong tendency to co-ordinate with the dissolving metal atom. Thiourea adsorbs strongly on bismuth and changes the mechanism, while chloride, bromide and iodide catalyse the anodic dissolution of nickel.

On a passive metal surface a film of oxide (Cu_2O on Cu) or similar compound (BiOCl on Bi) acts as a protective coating for the surface. Film growth and dissolution are controlled by the point defects present in the film, usually cation vacancies, electrons, or electron holes. The motion of these defects requires a high electric field, but the incorporation of impurity ions can increase the conductance.

RECENT DEVELOPMENTS IN EQUILIBRIUM AND NON-EQUILIBRIUM THEORIES OF IONIC LIQUIDS

S. I. Smedley

Victoria University

For the purpose of this discussion an "Ionic Liquid" will be defined as a liquid composed purely of ions.

During the past 12 years there has been an intense world-wide research effort into the properties of ionic liquids. Thus we now have quite a detailed knowledge of the effects of temperature, pressure and composition on the transport properties of glass-forming and non glass-forming ionic melts. Among the thermodynamic properties that have been studied are heat capacities, compressibilities, phase equilibriae and excess functions of mixing. However, despite this wealth of information, theoretical attempts to account for the observed properties of ionic liquids are still very naive, as is the case for all types of liquids. In view of the many theories that have been applied to ionic liquids, the discussion will briefly outline some of the more successful attempts. These include the conformal solution theory, the significant structures theory for both equilibrium and non-equilibrium properties, and the kinetic theory of transport in liquids.

FOOD CHEMISTRY

Review Lecture:

E. L. Richards (Massey University).

Research Papers:

C. L. Davey (M.I.R.I.N.Z.).

D. A. Heatherbell and J. R. Surawski (Plant Diseases Division, D.S.I.R.).

E. Wong and C. B. Johnson

THE BIOCHEMISTRY OF THE COLD SHORTENING OF MEAT

C. L. Davey

Meat Industry Research Institute, Hamilton

Muscle, unlike other animal tissue, lives on for a period after death and can be stimulated to contract until the state of rigor mortis is achieved some 18-24 hours post mortem. Muscle is toughened by being shortened and depending upon the degree of contraction can be so tough as to be virtually inedible.

Pre-rigor chilling is one quite unexpected way of stimulating a muscle to contract. This cold shortening phenomenon is therefore of considerable economic importance since chilling and freezing of pre-rigor carcasses are essential aspects of efficient meat processing in New Zealand. As a first step in finding means for overcoming cold shortening, background biochemical information on the phenomenon has been obtained.

The biochemical changes of cold shortening are the same as those in normal physiological contraction. Adenosine triphosphate is split to supply the energy for the shortening and as expected the splitting rate increases with the muscle doing work against an external load. Adenosine triphosphate breakdown is initiated by calcium ions. In relaxed muscle these are stored in the sacs of the sarcoplasmic reticulum surrounding each fibril.

An active calcium pump ensures the storage of all calcium ions within the sacs and therefore maintains the relaxed state of muscle. On activation of a muscle the pump fails to prevent the discharge of calcium ions from the sacs to the muscle fibrils which therefore contract. The temperature coefficient of pumping activity is large meaning that pumping is greatly reduced at low temperatures. Under these circumstances pumping is presumed to be so weak that leakage of calcium ions to the fibrils cannot be prevented. The fibrils therefore cold shorten.

GLC DETERMINATION OF SUGARS AND NON-VOLATILE ORGANIC ACIDS IN NEW ZEALAND GROWN SUB-TROPICAL FRUITS

D. A. Heatherbell* and J. R. Surawski
Plant Diseases Division, D.S.I.R., Auckland

It is useful to have rapid and convenient methods for separating, identifying and quantifying acids and sugars, and for determining their distribution characteristics in fruit and fruit products. This information can aid adulteration investigations, the nutritionist, the processor and the taxonomist. A rapid method for extraction and determination of non-volatile organic acids and sugars by gas liquid chromatography (GLC) of their trimethyl silyl (TMS) derivatives was developed. From ethanolic fruit extracts, acids were precipitated as their lead salts and the sugars in the remaining supernatant partitioned into aqueous methanol. These preparations, with suitable internal standards, were dried and converted to their TMS derivatives for GLC. Sugars and acids identified and quantified include (figures in parenthesis represent percentage on a fresh weight basis):

Chinese gooseberry: Glucose (3.8), fructose (2.4), sucrose (1.3), citric (1.1), quinic (0.9), malic (0.5), ascorbic (0.07), glucuronic (0.08), and traces of sorbitol, oxalic, succinic, fumaric and shikimic acids.

Tamarillo: Glucose (1.0), fructose (0.8), sucrose (2.7), citric (2.1), malic (0.1), quinic (0.01), and traces of ascorbic, aspartic, cinnamic and p-coumic acids.

Feijoa: Glucose (1.2), fructose (0.7), sucrose (4.5), inositol (0.05), citric (0.8), malic (0.2), quinic (0.01), glucuronic (0.02), and traces of ascorbic, oxalic, fumaric, and p-coumaric. In some instances identification was confirmed by thin layer chromatography or mass spectrometry.

Application of the method to maturity studies on these fruits and to processed products is discussed.

MUTTON FLAVOUR

E. Wong* and C. B. Johnson
Applied Biochemistry Division, D.S.I.R., Palmerston North

Although lamb and mutton are highly acceptable in countries such as Britain and New Zealand, they are not favoured in most other countries. Their low popularity has been attributed to the characteristic odour produced on cooking. At Applied Biochemistry Division, research is underway to characterise the undesirable odours of cooked sheep meats.

Starting with the assumption that fats play an important role in producing the distinctive flavour of sheep meats, we have succeeded in isolating samples of volatile materials possessing the characteristic odours by distillation of sheep fats. The samples have been further fractionated and at least two fractions have been found to have distinctive smells that could contribute to the "sheep" odour.

Gas chromatography of the "sheep smelling" fractions has separated these into many components and the undesirable odours can be detected by nose in the course of analysis. Further resolution of the complex mixture awaits application of more sophisticated high-resolution gas chromatographic techniques and attempts have to be made to establish the significance of individual peaks to the total off-flavour profile. Study of the chemical nature of these odour components, at the level of complexity and sensitivity involved, requires the technique of combined gas chromatography-mass spectrometry.

STRUCTURAL DETERMINATIONS IN CHEMISTRY

Review Lecture:

E. Sinn (Victoria University).

Research Papers:

W. T. Robinson (University of Canterbury).

W. C. Tennant (Chemistry Division, D.S.I.R.).

G. A. Bowmaker and R. Whiting (University of Auckland).

THE USE AND USEFULNESS OF SINGLE CRYSTAL X-RAY STRUCTURE ANALYSIS

Ward T. Robinson

University of Canterbury

The 1960's saw increasing applications of this technique to structural problems in many areas of research chemistry. Combination of automatic diffractometers with large fast computers, and suitably trained personnel, will ultimately result in service laboratories for recording and analysing X-ray reflection intensities. Presently commercial service is not viable because real costs are far beyond most research budgets for "outside work". However, honest costing of man hours and instrumentation would show many classical and spectroscopic structure investigations even more expensive, and certainly less definitive, than modern X-ray analysis.

Presently excellent facilities for this work exist in local university and Government laboratories and expanding research collaborations span many areas of contemporary academic interest. These will be illustrated by reference to some exciting investigations currently under way in New Zealand.

SOME STRUCTURAL APPLICATIONS OF ELECTRON SPIN RESONANCE

W. C. Tennant

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

The ESR experiment is briefly described with particular reference to the spectra obtainable from transition ions in crystalline environments. The relations between the ESR parameters and crystallography are briefly considered and the use of the paramagnetic ion as a sensitive probe to investigate site symmetry, site occupancy and site distortion discussed. The sort of information obtainable from observation of "fine" structure and nuclear and ligand hyperfine structure is also briefly covered.

The principles discussed are illustrated by results from recent studies involving Mn^{2+} ions in a natural single crystal of the mineral tremolite and also from a series of Mn(III) dithiocarbamates. Finally, in more detail an ESR spectrum from an "unknown" paramagnetic species in a tetraethylthiouram crystal is analysed to illustrate how one identifies the species and locates it in the crystal.

For paper by G. A. Bowmaker and R. Whiting please see page 105.

THEORETICAL CHEMISTRY

Review Lecture:

L. F. Phillips (University of Canterbury).

Research Papers:

R. G. A. R. Maclagan (University of Canterbury).

B. M. Peake (University of Otago).

R. W. Olliff (University of Auckland).

VALENCE-BOND STUDIES OF AH_2 MOLECULES

R. G. A. R. Maclagan

University of Canterbury

A computational procedure for performing valence-bond calculations using the Prosser-Hagstrom biorthogonalisation technique will be outlined. A comparison will be made with the molecular-orbital SCF method. The results of minimal Slater basis set calculations on BeH_2, H_2O and CH_2 will be discussed. The results of "full" valence-bond calculations, molecular orbital calculations, valence-bond calculations neglecting ionic structures and calculations using the perfect-pairing and resonance approximations will be compared. The behaviour of hybrid orbitals as a function of bond-angle will be discussed. They are found to continue to point in approximately their equilibrium directions and not to closely follow the hydrogen nuclei as the bond angle is varied.

MO CALCULATIONS OF SPIN DENSITIES FOR SOME ORGANIC RADICAL IONS

B. M. Peake

University of Otago

The ESR spectra of some peri-alkyl substituted naphthalene radical ions have been successfully analysed in terms of certain hyperfine coupling constants. Theoretical calculations of spin densities in thes species have been made using simple Huckel and SCF MO theory, and these will be discussed in terms of the observed coupling constants.

CORRELATON ENERGY AND TERM SEPARATIONS OF 3d^n ATOMS AND IONS

R. W. Olliff

University of Auckland

Spectroscopic term separations of 3d^n atoms and ions are always calculated, even at the Hartree-Fock limit, to be somewhat greater than the observed separations, the discrepancy being attributed to correlation effects in the 3d^n electron configuration. A technique for calculating this effect will be outlined.

The results show that the correlated Slater-Condon Parameters (F^k) which determine the term separation are related to the Hartree-Fock calculated values (F^k_∞) by the relations

$$F^k_\infty = \text{const. } \alpha$$

$$F^k = F^k_\infty + A + \frac{B}{\alpha}$$

where α is the effective nuclear charge seen by the d-electrons, and A and B are constants. Semi-empirical evaluation of A and B allows us to correct the calculated F^k_∞ for the effects of electron correlation.

INORGANIC ANALYSIS TODAY

Review Lecture:

H. Keyser (Victoria University).

Research Papers:

J. Aggett (University of Auckland).
J. Rogers (N.Z.F.M.R.A. (Inc.)).
N. E. Whitehead (I.N.S., D.S.I.R.).

ANALYTICAL APPLICATIONS OF SCHIFF BASES

J. Aggett

University of Auckland

The combination of solvent extraction procedures with analytical techniques such as spectrophotometry frequently enhances both the selectivity and sensitivity of the basic procedure. In this respect studies on the solvent extraction of inorganic cations by quadridentate Schiff Bases have revealed a number of systems of analytical interest. The results of investigations on these will be discussed to illustrate the use of solvent extraction in combination with spectrophotometry, atomic absorption spectroscopy, and spectrofluorimetry.

SOME APPLICATIONS OF THE FLUORIDE ELECTRODE IN FERTILISER RESEARCH

J. Rogers

N.Z. Fertiliser Manufacturer's Research Association

The classical method of Willard and Winter (1933) for the determination of fluorine in phosphate rocks and fertilisers, which involves first separation by distillation followed by analysis, requires considerable experimental skill and time even when recent colorimetric techniques are used, such as the lanthanum alizarin fluorine blue procedure. Solution in dilute acid followed by analysis with the fluoride electrode provides an accurate and rapid alternative to this traditional method. (Evans, Hoyle and Macaskill, New Zealand Journal of Science 143, 1970; 851, 1971).

The pF ion activity-concentration relationship of the fluoride electrode will be compared and contrasted with the glass electrode measurement of pH. Since 1968 the fluoride electrode has been used at The New Zealand Fertiliser Manufacturers' Research Association as follows:

1. To determine fluorine in phosphate rocks and phosphate fertilisers, fluorine in gaseous and liquid effluents from superphosphate manufacture and fluorine in herbage.
2. In a study of the vapour pressure of solutions of HF and H_2SiF_6.
3. To study ways of increasing the recovery of fluorine during superphosphate manufacture.

Results will be summarised and some problems encountered discussed.

THE USE OF PROTON INELASTIC SCATTERING AS AN ANALYTICAL METHOD

N. E. Whitehead

I.N.S., D.S.I.R.

Proton inelastic scattering, a new method of non-destructive instrumental analysis, relying on excitation of nuclear energy levels, was used for chemical analysis of a number of samples and surfaces. Volcanic ashes gave analysis figures in the range 3-4% Na, 9-16% Al_2O_3, and 300-900 ppm F. Corresponding means for a rather heterogeneous flint were 630 ppm, 0.23%, and 210 ppm. Silica proved difficult to determine due to a non-linear calibration curve. Qualitative examination of a "space ball" showed the presence of titanium, vanadium and aluminium. Using the technique, leaching was demonstrated in the surface layers of some human fossil remains from Australia, indicating which sections were unlikely to give reliable C-14 dates.

MODERN ORGANIC ANALYTICAL METHODS

Review Lecture:

I. R. C. McDonald (Chemistry Division, D.S.I.R.).

Research Papers:

M. Lever (Green Lane Hospital).
J. W. Blunt and M. H. G. Munro (University of Canterbury).
A. W. Missen and H. M. Stone (Chemistry Division, D.S.I.R.).

ANALYSIS OF SOME DRUGS BY FORMATION OF FLUORESCENT CHELATES WITH CATIONS IN NON-AQUEOUS SOLUTION

M. Lever
Pathology Department, Green Lane Hospital

Analytical techniques used in clinical laboratories must be suitable for batch processing of samples and must be able to give rapid and reliable results in the hands of unsupervised technical staff. For analysis of low levels of drugs in body fluids the following fluorometric technique is convenient. The drug itself or a fluorescent derivative is extracted and the derivative extracted into a suitable fluorescene reagent in a stoppered tube that also serves as a fluorometer microcuvette. Many drugs or drug derivatives form fluorescent chelates with non-transition metal cations, and these chelates are exceptions to the generalisation that maximum fluorescence is obtained in solvents that do not favour hydrogen bonding. Fluorescence responses are high in ethanediol, a solvent available free of fluorescent impurities. Ethanediol is immiscible with amylacetate which is a suitable extraction solvent.

Analytical procedures for tetracycline and rifomycin antibiotics, and for isoniazid, will be described. The drug (or the hydrazone with pentan 2,4 dione of isoniazid) is extracted into amyl acetate and back-extracted into an ethanediol solution containing magnesium ion (tetracyclines and rifomycins) or zinc ion (isoniazid). Using 0.1 to 0.5 ml serum, levels less than 10% of the minimum effective level can be determined in serum.

RADIOCHROMATOGRAM SCANNING

J. W. Blunt* and M. H. G. Munro
University of Canterbury

The technique of radioscanning of thin-layer and paper chromatograms will be described. The use of this technique in such diverse applications as reaction mechanism studies, quantitative analysis and the study of biosynthetic pathways will be discussed.

ALCOHOL ANALYSIS BY THE HEADSPACE METHOD

A. W. Missen and H. M. Stone*
Chemistry Division, D.S.I.R.

A brief account will be given of the development of glc headspace analysis, and its application to an automated determination of alcohol in blood. The optimisation of glc conditions, and the relative merits of using internal or external standards will be discussed.

BIOCHEMISTRY

Review Lecture:

R. D. Batt (Massey University).

Research Papers:

A. M. Robertson (University of Auckland).
G. G. Midwinter (Massey University).
P. A. Sullivan (University of Otago).

ENERGY METABOLISM IN BACTERIA

A. M. Roberton
University of Auckland

Studying the mechanism and efficiency of bacterial energy conservation is more difficult than studying analogous systems in animals. Whilst animal mitochondria can be isolated in an intact form, bacterial cell-free material carrying out oxidative phosphorylation is always partly degraded.

In aerobic bacteria, ATP formed by oxidative phosphorylation has recently been measured in intact cells. $\frac{P}{O}$ ratios (moles ATP per atom oxygen) were comparable to those of animal mitochondria, and higher than in bacterial cell-free systems. Nevertheless, it is likely that many bacteria do have low $\frac{P}{O}$ ratios in vivo due to their possessing fewer coupling sites, loose coupling, branched electron-transfer chains, etc.

Anaerobic bacteria usually obtained their energy by fermentation (though anaerobic oxidative phosphorylation is used by a few bacteria). Studies on ATP production most frequently involve measurements of growth yields Y (gm. dry wt. of bacteria divided by moles of substrate degraded). Y is related to the ATP formed by a factor Y_{ATP} (gm. dry wt. per mole ATP). The conditions under which Y should be measured, and the corrections necessary will be discussed. It is of interest that some exceptions have been discovered which do not conform to the empirical finding that Y_{ATP} is reasonably constant for all different types of bacteria. The reason is not understood.

THE USE OF MASS SPECTROMETRY IN THE DETERMINATION OF THE PRIMARY STRUCTURE OF PROTEINS

G. Midwinter
Massey University

Recent studies have extended the usefulness of low resolution mass spectrometry as an aid in the determination of the primary structure of proteins. In an investigation of the sequence of the microbial enzyme ribitol dehydrogenase: MWt 35,000, 51% of the total structure was obtained by mass spectrometry. Peptides suitable for mass spectrometry were obtained by limited proteolysis of the carboxymethylated enzyme followed by gel filtration and ion-exchange chromatography.

Volatile derivatives of the peptide mixtures were made by N-acetylation and permethylation and the sequence of the peptides was determined on an AEI MS902 using the direct insertion probe.

Modification of the permethylation procedure permitted the sequencing of peptides containing the previously difficult amino acids histidine and methionine.

The procedures used and the results obtained to date will be described.

THE REACTION MECHANISM OF L-LACTATE OXIDASE

P. A. Sullivan
University of Otago

The flavoenzyme L-lactate oxidase catalyzes the following reaction:

$$\text{L-lactate} + O_2 \longrightarrow \text{acetate} + CO_2 + H_2O$$

The object of this investigation was to describe the catalytic mechanism of this enzyme and to compare the general properties with other flavoenzymes.

1. Anaerobic experiments using the stopped-flow system have shown that lactate oxidase reacts rapidly with substrates such as L-lactate, β phenyl-L-lactate, L-α-hydroxy-β-methylvalerate and L-α-hydroxyisovalerate to form an intermediate which decays slowly to form the fully reduced flavoenzyme.

2. The rate of formation of this intermediate and the rate of the reaction of the intermediate with molecular oxygen are fast enough to be involved in the catalytic cycle.

3. The intermediate detected by stopped flow studies can also be produced by mixing anaerobic solutions of reduced enzyme with the corresponding keto-acid.

4. Free peroxide is not formed in appreciable quantities during catalysis.

5. Recent progress in the general understanding of flavoenzyme catalysis suggests that the primary steps proceed via an ionic mechanism [1,2]. This could involve the formation of a flavin-substrate adduct followed by the abstraction of αH of the substrate as a proton.

---

[1] L. E. Brown and G. A. Hamilton, J. Am. Chem. Soc., (1970) 92, 7225.

[2] C. T. Walsh, A. Schonbrunn and R. H. Abeles, J. biol. Chem. (1971) 246, 6855.

ABSTRACTS: SECTION B: GENERAL SESSIONS (CONTRIBUTED)

INORGANIC CHEMISTRY

INFRA-RED STUDIES OF OXYGEN ADSORBED ON EVAPORATED GERMANIUM FILMS

A. Metcalfe

University of Canterbury

An experimental method has been developed for the observation of molecules adsorbed on germanium surfaces. The interaction of oxygen with evaporated Ge films has been investigated, and the observed spectra interpreted in terms of the preliminary formation of O_2^- over bare surfaces with subsequent formation of Ge-O-Ge, and the identification of interstitial oxygen during growth of thick oxide layers following the formation of Ge-O^- in the surface.

ADSORPTION OF SO_2 FROM THE ATMOSPHERE ON TO IRON

J. R. Duncan

University of Auckland

It has been suggested that sulphate nests are formed in corrosion of iron in atmospheres containing SO_2 by the diffusion of adsorbed SO_2, or sulphate from SO_2(ads), through the electrolyte layer on the surface to anodic areas. Adsorption of $^{35}SO_2$ from a controlled atmosphere on to high-purity, rust-free iron, followed by autoradiography illustrates that there is adsorption at particular points on the iron surface even under conditions when the solution layer on the surface might be expected to be too thin to support the proposed diffusion process.

Similar experiments using potentials of +1, zero (earth) and —1 Volts on samples of iron exposed to an atmosphere containing sulphur dioxide showed no difference in adsorption between the three samples, and the adsorption at isolated sites noted previously still occurred. These were interpreted as meaning that the low potentials applied here, which will be comparable to those generated in the corrosion cell, were not sufficient to affect adsorption from the atmosphere.

It is known that many types of oxides and hydroxides are present on a still-shiny iron surface. It is suggested that a possible explanation for the observed effect is preferential adsorption of SO_2 onto one particular type of oxide.

INVESTIGATIONS OF STRUCTURE AND BONDING IN HALOCUPRATE(I) COMPOUNDS BY N.Q.R. SPECTROSCOPY

G. A. Bowmaker* and R. Whiting

University of Auckland

The naturally occurring isotopes of copper, ^{63}Cu and ^{65}Cu, both have nuclear spin $I = 3/2$, and are therefore capable of giving rise to nuclear quadrupole resonance in the presence of an electric field gradient. The symmetry of the metal site in copper complexes is very often low enough to allow the appearance of a non-vanishing field gradient, but in spite of this, very little work appears to have been done on copper n.q.r. to date. Cu(I) complexes are particularly interesting for an n.q.r. study, since the different bonding theories which have been proposed for d^{10} complexes in the past predict quite different values for the field gradient at the copper nucleus.

We have studied the halogen and copper n.q.r. of compounds containing the discrete halocuprate(I) ions $CuCl_2^-$, $CuBr_2^-$, and $Cu_4I_6^{2-}$. The information concerning structure and bonding in these ions which can be obtained from the n.q.r. spectra will be discussed. A tetrahedral structure for the previously unreported $Cu_4I_6^{2-}$ ion is proposed, and an analysis of the results for the linear $CuCl_2^-$ and $CuBr_2^-$ ions suggests that the field gradient at the copper nucleus is due to a partial d orbital vacancy.

DETERMINATION OF WEAR METALS IN ENGINE OILS BY ATOMIC ABSORPTION WITH A GRAPHITE ROD ATOMIZER

R. D. Reeves

Massey University

The analysis of used engine oils for traces of metal particles in 0.1-50μg cm^{-3} concentrations has been used for some years as a means of identifying normal and abnormal engine wear. Atomic absorption has been extensively used for this purpose, although there is inconvenience and loss of sensitivity, because of the need to dilute the oils with an organic solvent before they can be aspirated into a conventional burner.

This paper discusses the use of direct atomization of microlitre samples of oils from a cavity in a graphite rod. The concentrations of Ag, Cr, Cu, Fe, Ni, Pb, and Sn have been determined in more than twenty jet-engine and reciprocating-engine oils taken from the U.S. Air Force Spectrochemical Oil Analysis Program (S.O.A.P.) during the period May 1969-December 1971. This enabled a comparison to be made with results obtained for flame atomic absorption in the laboratories participating in S.O.A.P. The results for Ag, Cu, Fe, Ni and Pb were almost all within one standard deviation of the flame atomic absorption mean values. The graphite rod atomizer gave values for Cr that were 60-70% higher than those found with an air-acetylene flame. Most of the Sn concentrations were near, or below, the levels detectable with flame atomization.

The graphite rod atomizer provides a useful alternative to flame atomization for this type of sample, offering better sensitivity with a smaller sample, combined with greater speed and ease of handling.

PHYSICAL CHEMISTRY

THE STABILITIES OF CARBONIUM IONS

I. J. Miller
Chemistry Division, D.S.I.R.

An empirical bond energy scheme for carbonium ions is derived which gives good agreement with experimental values for some primary, secondary and tertiary ions. If the chemical bonds are considered as polarizable, the bond energy scheme, and some reactions of carbonium ions, can be rationalised solely from the application of classical electrodynamics. As examples it is deduced that dienylic ions are less stable than the cyclopentenylic ions and cyclohexentenylic ions. It is also shown that the activation energies for the cyclization of dienylic ions is largely composed of electrostatic repulsion between the equally charged ends. While the results are mainly applicable for the gas phase an approximate discussion of solvation energies shows that, while all C-C bonds stabilise a carbonium ion centre to a greater extent in the gas phase, a methyl will stabilise positive charge to a greater extent than, say, on ethyl in aqueous solution if the positive charge is less than 0.6e. That is, the Baker-Nathan order is predicted in solution if the charge is delocalised. It is concluded that the concept of hyperconjugation is unnecessary for a description of carbonium ions.

INTRACELLULAR pH

Sharon F. Hannan
University of Auckland (Student paper)

For some years there has been a controversy over the interpretation of measurements of intracellular pH, in that the value 7.0 calculated from the distribution of a weak acid is one whole pH unit higher than that derived by inserting a pH sensitive microelectrode into the cell.

Various explanations have been proposed to account for this discrepancy:

(a) Heterogeneity of the cells;
(b) A large difference in liquid junction potentials;
(c) Errors in measuring extracellular volume; and
(d) Binding of the acid by cell proteins.

None of these in itself could account for such a large difference. In order to estimate the magnitude of the first I am developing a weak base to be distributed across the membrane, thus giving an independent estimate of the heterogeneity.

It has recently been suggested that the water inside cells is surface-oriented rather than bulk phase. Thus, the intrinsic structuring of the water is enhanced, the energy of water-structure-making ions is increased, and that of water-structure-breaking ions is decreased.

If the H^+ ion is considered a water-structure-maker, as much evidence suggests, then the apparent discrepancy between the two pH measurements can be resolved.

THE ELECTROCHEMICAL BEHAVIOUR OF TRANSITION METAL IONS IN AN ALUMINOSLICATE GLASS

I. W. M. Brown
Victoria University (Student paper)

Aluminosilicate glasses, formed by quenching the clay mineral kaolinite ($Al_2O_3.2SiO_2.2H_2O$) from high temperatures, can be devitrified by reheating to 950°C. Transition metal ions may be placed in well defined sites in the glass by fusion of the appropriate metal oxide in the melt, resulting in some unusual oxidation states and magnetic phenomena.

A study of the behaviour of these glasses in a d.c. electric field has shown (a) the dopant ions migrate to the cathode, enhancing the recrystallization of mullite and cristobalite in that region; different products are formed at the anode and cathode faces.

(b) At temperatures up to the recrystallization temperature the major conduction process is electronic while at higher temperatures ionic conduction becomes much more significant.

These experimetns suggest that solid state electrolysis techniques might be useful for controlling ion migration and phase separation in diffusion-doped semiconductors and synthetic gemstones, and for separation and analysis of metal ions in solids.

A KINETIC APPLICATION OF ION-EXCHANGE SEPARATIONS

Claire Couldwell
University of Canterbury (Student paper)

As part of a programme to investigate the mode of acid hydrolysis of some analogous cobalt(III) and chromium(III) complexes the rate of halide release from some tetraamines has been studied in acid solution. One technique that has been used in the course of this work is that of ion-exchange chromatography. Some of the fundamental properties of ion-exchange resins and the mechanisms of ion-exchange separations will be discussed. The experimental conditions chosen in this research will be described along with the reasons for using the particular type of column, the cation-exchange resin, and the column length. The general technique of ion-exchange chromatography will then be applied to a kinetic problem. An experiment will be described in which a primary hydrolysis study of a chromium(III) tetraamine in acid solution has been made using a modification o fthis method. The reasons for tackling the problem in this way will be discussed as will the significance of the results.

THE PROPERTIES OF COLLOIDAL PARTICLES FROM STUDIES OF LOW AREA SYSTEMS

A. G. Langdon

University of Waikato

The study of colloidal systems is often made tedious and uncertain by the procedures necessary to separate the colloidal phase from the suspending media. Thus techniques were developed to render the properties of individual particles accessible to direct investigation. This has been achieved by adsorbing a monolayer (or less) of the particles at an inert interface.

The system used for these studies was the mica-hydrous iron (III) oxide system. Working with such systems it is essential that adequate precautions be taken to avoid contamination. Electron microscopy showed that treatment of a clean mica surface with a hydrous iron (III) oxide suspension resulted in the adsorption of a monolayer of spherical particles 5-10 nm in diameter. Isotope dilution studies were used to construct sorption isotherms for sorption from P-32 labelled phosphate solutions. At the highest phosphate concentrations employed, Fe:P ratios approaching unity indicated the formation of an iron (III) phosphate phase. The kinetics of P-32 labelled phosphate sorption and desorption were followed by a continuous monitoring method. Although these are demonstrably complex processes, some progress has been made in the interpretation of the results in terms of a diffusion model.

MOLECULAR ORBITAL CALCULATIONS ON BONDING OF MOLECULAR OXYGEN TO HAEMOGLOBIN

Margaret P. Halton

Victoria University

Cyt. P-450, haemoglobin, and aqueous haemoglobin all have different reactions of the iron II to molecular oxygen. Theoretical models have been developed to examine the nature of the iron-O_2 bonding in haemoglobin, and the models tested by comparison with Mössbauer data. Formation of a stable monomeric oxygen adduct can be understood in terms of a two electron donation to the iron, to compensate for the iron-oxygen electron transfer and prevent simple oxidation from occurring. Different geometries of the bound iron-O_2 system can account for the observed differences in reaction of Cyt. P-450 and haemoglobin.

EXCESS FREE ENERGIES OF MIXING FOR AQUEOUS TWO-SALT SOLUTIONS OF SODIUM AND POTASSIUM CHLORIDES AND DIHYDROGEN ORTHOPHOSPHATES: A TEST OF THE CROSS SQUARE RULE

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The cross-square rule of T. F. Young and his co-workers concerns the mixing at constant total ionic strength of equal amounts of two aqueous single salt solutions. It has been applied to volumes and enthalpies of mixing and, more recently, to the excess free energies of mixing G^E. The rule states that if the four salts formed from two cations and two anions are mixed in pairs, then the sum of the excess free energies of mixing of the four common ion mixings will equal the sum for the two mixings in which there is no common ion.

The rule has been shown to hold for a number of systems including Na, K, Cl, Br and Na, K, Cl, SO_4 and Na, Mg, Cl, SO_4 but departures from the rule have been observed in the systems Na, K, Cl, NO_3 and Mg, Ca, Cl, NO_3. These departures have been ascribed to ion-pairing.

Excess free energies have now been determined from isopiestic measurements for the system Na, K, Cl, H_2PO_4. All of the Cl-H_2PO_4 mixings show large positive excess free energies of mixing. Common ion mixings involving the same pair of unlike ions have similar excess free energies of mixing. The cross square rule is obeyed within the experimental uncertainties of the measurements.

PROTON MAGNETIC RELAXATION IN LANTHANIDE COMPLEXES

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Proton spin-lattice relaxation times (symbol T_1) are sensitive to the presence of paramagnetic ions. The relatively small effect of certain lanthanide ions has been attributed to the short electronic relaxation times characteristic of those ions. One interesting implication of this theory is that the small residual influence should be independent of molecular motion, while remaining proportion to the inverse sixth power of the lanthanide-proton distance.

It is proposed that this dependence of T_1 could be a useful supplement to the established, but somewhat ambiguous, technique of using lanthanide-induced n.m.r. shifts to deduce molecular geometries. To test this proposal, T_1 measurements have been made for individual resonances in the n.m.r. spectrum of the adduct formed by addition $Pr(dpm)_3$ to camphor.

DIRECT SYNTHESIS OF POLYTHIO CARBOHYDRATE DERIVATIVES

G. S. Bethell* and R. J. Ferrier
Victoria University

Acid catalysed thiolyses of some esterified aldose derivatives have revealed that thioacetals are produced as expected, but also that thio-groups are introduced at other positions and that polythio products are formed. A study of some specific cases has revealed the nature of the reactions involved.

From 3,5,6-tri-O-benzoyl-1,2-O-isopropylidene-D-glucofuranose crystalline 4,5,6-tri-O-benzoyl-2,-3-di-S-ethyl-2,3-dithio-D-allose diethyl dithioacetal is obtainable directly in 65% yield. It will be shown that the reaction involves attack of ethanethiol at C-1 and ester-assisted migration of ethylthio groups from this position to C-2 and thence to C-3.

With the possibility opened that polythioaldose derivates could be prepared by successively "feeding" thiol groups into C-1 and that these could "chase" a suitable migratory leaving group from the reducing end of the molecule, various aldose derivatives have been thiolysed. Findings will be presented.

ORGANOMETALLIC-COORDINATION CHEMISTRY

REACTION STUDIES OF GROUP IV-TRANSITION METAL COMPOUNDS

B. W. L. Graham
University of Waikato (Student paper)

Organometallic compounds containing metal-metal bonds show a wide variety of chemical reactions. There are at least four different positions for attack by any reagent—at either metal atom or at the ligands on either metal atom—and this study attempts to determine some of the factors influencing the reactivity and choice of reaction site in a few of these compounds.

Much of the work was done on compounds of the general form $R_3GeM(CO)_x$ (especially $M = Mn, Co$; $R_3 = H_3$, or H_2Me). Initially a number of simple reagents were used, including hydrogen halides and pseudohalides, olefins, and Lewis bases, with a variety of reaction conditions. Exchange reactions between related systems have also been studied.

The results from these reactions will be used to make an initial interpretation of the chemical nature of this class of compounds.

THE ELECTRONIC NATURE OF THE TRICOBALTCARBON CLUSTER

A. Cartner
University of Otago (Student paper)

Methinyltricobalt enneacarbonyls, of which the Co_3C cluster is the structural core, are potential carbonylation catalysts. It has been shown that the reactivity of these clusters is determined by the coordination environment of the cobalt atoms and the apical substituent Y. This paper describes some kinetic and infrared studies undertaken with a view to elucidating the peculiar electronic structures of these molecules.

Rate constants for the first-order reactions

$$YCCo_3(CO)_9 + L \rightleftharpoons YCCo_3(CO)_8L + CO$$
$$L = R_3P \text{ etc.}$$

have been evaluated utilising changes in the carbonyl stretching frequencies. It will be shown that trends in ΔH^* and ΔS^* follow the inductive capacity of Y. A model, based on the concept of a delocalised Co_3C cluster, which can explain the experimental observations will be discussed.

COMPLEX FORMATION BY OXIMES, AMINES AND KETONES

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University of Canterbury

Oxime reagents have widespread use in Analytical chemistry but there is little quantitative data on the stabilities of their metal complexes. This paper will discuss the stabilities of the copper(II) complexes formed with structurally related oxime, amine and ketone ligands; comparison of these ligands will be based on potentiometric (log K) and calorimetric (ΔH) data.

THE COORDINATION OF THIO LIGANDS BY MERCURY

P. C. McMorran and C. J. Wilkins*
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In common with other heavy metals mercury shows a marked preference for bonding highly polarisable ligands. With trimethylarsine oxide and trimethylarsine sulphide several series of mercury compounds can be obtained for direct comparison with cadmium and zinc derivatives. Where isomorphous mercury and cadmium compounds exist, e.g. $ML_4(ClO_4)_2$ with L = Me_3AsO and Me_3AsS, the ratios of the infrared frequencies ν(M-S)/ν (M-O) are considerably higher for mercury than for cadmium. The small separation of the 5d and 6s mercury levels seems adequate as a basis for explaining the greater strength of the Hg-S bond, but there is undoubtedly also some specific factor weakening the Hg-O bond, ass hown by other infrared evidence and by long Hg-O bond distances.

As examples of the systematic interpretation of infrared spectra it will be shown that the series $HgX_2.R_3AsS$ gives ν(Hg-X) bands from both terminal and bridging halogens. For $HgX_2.R_3AsO$, on the other hand, there are no bridging halogen frequencies, but features characteristic of *oxygen* bridging. Mercury differs from cadmium in not producing coordination numbers higher than four with these ligands.

AN ESR STUDY OF SOME SUBSTITUTED PYRIDINE N-OXIDE COPPER(II) COMPLEXES

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The ESR (methanol solution, frozen solution, powder, and single crystal) spectra of $[CuL_4](ClO_4)_2$ where L = pyridine N-oxide, α-picoline N-oxide, β-picoline N-oxide, γ-picoline N-oxide, and 2,6-lutidine N-oxide and of $[CuL_6](ClO_4)_2$ where L = pyridine N-oxide and γ-picoline N-oxide have been obtained. The preparation of hexa(γ-picoline N-oxide) copper(II) perchlorate is reported for the first time.

The solution and frozen solution spectra indicate very similar bonding in all the complexes, with the metal-oxygen bond being moderately ionic. The powder spectra reveal all the tetrakis complexes to be axially symmetric; though tetra(γ-picoline N-oxide) copper(II) perchlorate shows a reversal of the usual order of the g-values. This is explained in terms of the packing interactions within the crystal structure, rather than metal-ligand interaction. The single crystal spectra are all characteristic of axially symmetric complexes. Hexa(pyridine N-oxide) copper(II) perchlorate gives an isotropic ESR spectrum, but this is not believed to be due to exchange interaction. Hexa(γ-picoline N-oxide) copper(II) perchlorate gives an axial ESR spectrum with considerable tetragonal misalignment.

THE SYNTHESIS AND REACTIVITY OF SOME CHALCOGENIDE OLEFIN COMPLEXES OF RHODIUM (I) AND IRIDIUM (I)

E. W. Ainscough, A. M. Brodie* and E. Mentzer
Massey University

Complexes in which an olefin and a phosphorus donor ligand are simultaneously co-ordinated to a transition metal atom are well known. However, similar sulphur or selenium complexes are rare. In the course of our studies of organometallic chalcogenide compounds we have isolated the new square planar complexes (cod)MClL (cod = cyclo-octa-1, 5-diene; M = Rh, Ir; L = Me_3PS, Me_2PhPS, Me_2PhPSe, Me_3AsS).

Spectroscopic studies confirm the chalcogen atom is bonded to the metal. It is of interest that the iridium (I) complexes are readily obtained in refluxing benzene from an iridium (III) precursor, $[(cod)IrHCl_2]_2$, and the appropriate chalcogenide ligand, HCl being eliminated. In contrast phosphine and phosphite ligands react with $[(cod)IrHCl_2]_2$ giving iridium (III) hydride derivatives. The rhodium complexes are obtained from the reaction of $[(cod)RhCl]_2$ and the chalcogenide. Of the ligands investigated, Ph_3PS has the least ability to undergo the bridge splitting reactions indicating reduced donor properties. Furthermore, unlike phosphines and phosphites, none of the chalcogenides will displace the coordinated cyclo-octadiene.

The new complexes readily undergo oxidative addition reactions (e.g. with MCl, I_2) but in contrast to their phosphine analogues, reactions can be complicated by attack also occurring at the chalcogenide ligand. (e.g. with Cl_2).

METHYL MERCURY

M. Zobel

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Microbial action on mercury-bearing effluents in rivers and lakes produces methyl mercury. The uptake of this toxic compound into edible fish is the cause of much concern.

The analytical techniques used to quantify methyl mercury in biological specimens is discussed in the light of its ecological importance.

ORGANIC CHEMISTRY

TETRACYCLIC DITERPENOID BIOSYNTHESIS: AN ALTERNATIVE HYPOTHESIS

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For nearly two decades the accepted hypothesis† for tetracyclic diterpenoid biosynthesis has required cyclisation of the 13-vinyl group of the pimarene and isopimarene skeletons to an electrophilic centre at the angular 8-position. From a mechanistic viewpoint this is unrealistic and evidence will be briefly discussed in support of this claim.

An alternative hypothesis requires cyclisation of suitable derivatives of Δ^8-pimarene-15,16-diol and Δ^8-isopimarene-15,16-diol. Mechanistic and biosynthetic implications of this alternative hypothesis will be presented.

SYNTHESES IN THE FUMAGILLIN SERIES

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Fumagillin is a mould metabolite which exhiibts anti-tumour properties but which is too toxic for clinical use. Structurally fumagillin is a 1,2,3,4-tetrasubstituted cyclohexane, unusual not least in that it contains two epoxides. The structure and stereochemistry were established some years ago, and current synthetic studies have as their aim the development of methods which may prove useful for the elaboration of analagous compounds of known stereochemistry, which may be biologically active.

TRITIUM LABELLING OF HYDROCARBONS ON GAMMA-IRRADIATED SILICA GEL

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Gamma-irradiated silica gel (previously degassed at temperatures above 300°C for more than ten hours) functions as an effective reagent for the promotion of an exchange reaction between tritium gas and hydrocarbons. Good yields of labelled hydrocarbons can be obtained, particularly with branched-chain compounds, with up to 50% of the tritium being incorporated in reaction products, and 97-99% of the incorporated tritium in the parent hydrocarbon.

LEWIS ACID-CATALYSED ISOMERISATIONS OF NAPHTHALENE TETRACHLORIDES

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Solutions of naphthalene tetrachlorides (1,2,3,4-tetrachlorotetralins) in the presence of Lewis acid catalysts ($AlCl_3$, for example) have been found to undergo regiospecific epimerisations at the 1- and 4-positions. Specifically, when the heterogeneous catalyst system, $AlCl_3/CS_2$, is used, the three isomers with a trans-disposition of the chlorine atoms at the 2- and 3-positions each isomerise to give the same relative proportions of each other. Of the three isomers with a cis-disposition of the chlorine atoms at the 2- and 3-positions, one is readily available, the second is obtainable in very low yield only, and the third is unknown. Thus, whilst the readily available isomer is, in principle, capable of isomerising to the difficulty obtained isomer and the unknown isomer, the reaction does, in fact, proceed only slightly. Attempts to increase the magnitude of this small change, particularly with regard to the possibility of obtaining the unknown isomer, will be described.

Rates of isomerisation with regard to the various isomers, and variations in the nature of the catalyst, including the use of homogenous systems, also will be outlined.

Finally, an example of the use of this catalysis will be given, in which the tetrachloride obtained by the heterolytic addition of chlorine to 1,5-dichloronaphthalene is converted, almost completely, to the isomer, hitherto unknown, possessing the opposite configuration at the 4-position.

ACID-CATALYSED REARRANGEMENTS OF SOME C5-OXYGENATED STEROIDS

E. T. J. Bathurst, J. M. Coxon and M. P. Hartshorn*

University of Canterbury

On reaction with sulphuric acid-acetic anhydride-acetic acid $3\beta,6\beta$-substituted-cholestan-5α-ols un-

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† E. Wenkert, Chem. and Ind., *1955*, 282.

dergo the Westphalen rearrangement to give 5β-methyl-Δ^9-compounds. In contrast the 6α-acetoxy-compounds yield Δ^4-olefins in which no rearrangement has occurred.

In addition the C4-stereochemistry has an effect on the reactions of the 4-acetoxy-5α-hydroxycholestanes, the 4β-acetoxy compound undergoing rearrangement to give 5β-methyl compounds, while the 4α-epimer yields Δ^5-olefins and no rearrangement products.

This marked influence of the C4- and C6-sterochemistry on the fate of the intermediate C5-carbonium ion can be rationalised in terms of the preferred conformation of rings A and B for each of the 4-acetoxy- and 6-acetoxy- C5-carbonium ions.

The importance of conformational effects on the reactions of 5-hydroxysteroids is further exemplified by the absence of 5β-methyl compounds from among the products of the reaction of 4β-acetoxy-5β-hydroxycholestane, the C5-epimer of which gave exclusively 5β-methyl rearrangement products.

IN VIVO AND IN VITRO SYNTHESES OF THE TETRANORTRITERPENOID BITTER PRINCIPLES

R. J. Weston

Chemistry Division, D.S.I.R.

The tetranortriterpenoids are a class of bitter principles which occur in the three closely related plant families, Meliaceae, Rutaceae and Simaroubaceae. Componds from the first two families only will be discussed. These naturally occurring compounds have many structural features in common but differ in small yet significant details which arise from a divergence of the final stages of metabolism in the three families, e.g., the limonoids all have cleaved rings A and D, while the miliacids have an intact ring A and rings B, C and D may be cleaved. The postulated biosynthesis of these tetranortriterpenoids will be illustrated by arranging the naturally occurring products in order of increasing oxidation.

Some work will be described directed towards the synthesis of some of the more complex products using less complex natural products as starting material.

INTERMOLECULAR HYDROGEN BONDING IN BARBITURATES

P. P. Williams

Chemistry Division, D.S.I.R.

X-ray crystallographic studies of several polymorphs of Phenobarbitone and Nostal have been carried out with the aim of investigating the molecular interactions which can occur in the solid state. A variety of hydrogen bonding modes have been observed, and these will be described, as well as results obtained in other similar investigations. The conformational variations in phenobarbitone molecules, and the possible relevance of the hydrogen bonding modes to pharmacological activity will be discussed.

BIOCHEMISTRY

CORRELATION OF OLEORESIN MONOTERPENE COMPOSITION WITH GENETIC VARIABILITY AND DISEASE SUSCEPTIBILTY IN *PINUS RADIATA*

S. Chou, D. R. Smith and J. A. Zabkiewicz*

Forest Research Institute

There has been a long-standing interest in monoterpenes but they have been considered of little practical or metabolic significance. Recently, with the advent of gas chromatography ,there has been a revival of interest in this class of compound for chemotaxonomic purposes. Work done previously on *Pinus radiata* had been based on extracts from oleoresin samples taken from trees at breast height. Since it was considered desirable to "fingerprint" or typecast trees as early as was practicable—the present technique involves sàmpling from the current growth in the leader (top shoot). When this was done, quite a different monoterpene composition was obtained which instigated studies on (a) the monoterpene composition within individual trees, (b) comparisons of composition between trees, particularly of clonal stock.

Variation between clones led to speculation that disease susceptibility could be indicated by monoterpene composition—specifically in response to attack by the fungus *Diplodia pinea.* Some "naturally" resistant trees had been observed in the field: examination of their monoterpene composition showed that the "resistant" trees had a higher than normal Δ^3-carene content. Furthermore, there was an inhiibtion of *Diplodia* growth and spore germination by Δ^3-carene.

PROPERTIES OF PROTEASE FROM *ACTINIDIA CHINENSIS* (CHINESE GOOSBERRY)

J. M. Boland

Massey University (Student paper)

Actinidin, the anionic protease from *Actinidia chinensis* berries, has been purified to constant specific activity, and crystallised. Uultracentrifugation indicates that the protein has a M.W. of about 25000. Studies on a series of homologous NCBZ amino acid p-nitrophenol esters shows the enzyme to have a preference for lys >> try $\neq$ ala > tyr $\neq$ leu > gly; thus basic side chains are preferred.

Furthermore inhibitor studies using arginine derivatives showed a papain-like preference for an aromatic group in the penultimate site.

The enzyme activity has been shown to be dependent on a thiol group. The reaction mechanism is likely to involve a thioester intermediate, formed by nucleophilic attack of the thiol sulphur atom on the carboxyl carbon of the amino acid, with elimination of the alcoholic (phenolic) group.

Recent evidence suggests that the mechanism of ficin-catalysed hydrolysis of NαCBZ-lysine p-nitrophenol ester is more complex than the above, with a third intermediate in the reaction.

Evidence for this type of mechanism in actinidin will be presented.

PESTICIDES AND SERUM PROTEINS

D. G. Ferry

Toxicology Research Unit

Medical Research Council of New Zealand

The organochlorine insecticides have been detected in the fat and blood of people in many countries. Differences in the concentrations of insecticides occur in different groups of people for various reasons.

It has been observed that subjects on long-term anticonvulsant therapy have lower blood and fat levels than the general population. The mechanism of this reduction is believed to be by enzyme induction but it has been suggested that displacement of the pesticides from protein binding might be the explanation.

We have examined and confirmed the above observation, investigated the displacement hypothesis and determined the distribution of DDT, dieldrin and lindane in serum proteins of different animal species including man.

The results of these experiments indicate that although the displacement suggestion may alter the level of lindane and dieldrin it is unlikely to be significant in reducing DDT levels in humans.

THE BINDING OF THE DYE, METHYL ORANGE TO SERUM PROTEINS OF PATIENTS WITH RENAL FAILURE

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Department of Medicine, Auckland Hospital

Several workers have reported that patients with renal failure have a lower serum protein binding capacity for organic dyes than serum proteins from normal volunteers. This descrease could be due either to drug or metabolic product competition for the dye binding sites or to a change in the conformation of the protein molecules lending to a decrease in the total number of binding sites available for dye binding.

The serum protein binding capacities of patients with varying degrees of renal failure as well as those on the artificial kidney and transplantation programmes were determined in an attempt to elucidate the cause of this desorption.

Increased serum fatty acid levels seem to be largely responsible for this altered binding capacity in renal failure.

The results of this work as well as the significance of the desorption phenomenon to drug therapy will be discussed.

THE EFFECT OF LOW CONCENTRATIONS OF SULPHUR DIOXIDE ON THE METABOLISM OF BARLEY LEAVES

D. J. Spedding and (the late) W. J. Thomas

University of Auckland

Barley seedlings were exposed to $^{14}CO_2$ in pairs so that one seedling received no SO_2 and the other seedling received about 5ppm SO_2. After the $^{14}CO_2$ exposure the leaves were extracted with water and ethanol and the ^{14}C-labelled compounds were separated by paper chromatography. The striking difference in the ^{14}C-labelling pattern between the two seedlings was the appearance of up to 30% of the ^{14}C-label in glycolic acid in the SO_2-treated seedlings. ^{14}C-glycolic acid was undetectable in the extracts from seedlings exposed to $^{14}CO_2$ in the absence of SO_2. It is postulated that the S^{IV} species formed in cell solution by the dissolution of SO_2 themselves form aldehyde bisulphite compounds which are known competitive inhibitors of the enzyme glycolic oxidase. It has been postulated that glycolic oxidase is related to stomatal opening in plant leaves and it is known that SO_2 affects stomatal opening. There is a possibility that aldehyde-bisulphite compounds are the connecting link between SO_2 and its effect on stomatal opening.

ORGANIC (ANALYTICAL)

QUANTITATIVE ANALYSIS OF METHYL KETONES IN MILK FAT

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Dairy Research Institute, Palmerston North

A series of odd-numbered (C3-C15) aliphatic methyl ketones formed in milk fat during heating or storage may impart an unacceptable stale flavour to high-fat dairy products such as evaporated milk and whole-milk powder. The same compounds, however, are responsible for the characteristic flavour of mold-ripened cheeses and at lower levels may also contribute to the flavour of Cheddar cheese. Methyl ketones, together with saturated and unsaturated aldehydes are often isolated and identified from milk fat as their 2,4 dinitrophenylhydrazones. Since methods currently available for the separation of hydrazones into classes and individual compounds have some shortcomings, new techniques have been investigated to aid in the identification and quantitative analysis of methyl ketones.

Methyl ketones and aldehydes are quantitatively regenerated from their hydrazones by elution in pentane from a column of celite impregnated with sulphuric acid. Aldehydes may be selectively oxidised by elution from a column of celite impregnated with potassium permanganate. After concentration the complete series of methyl ketones are separated by gas-liquid chromatography on a 10 ft. x ⅛ in. column packed with 15% FFAP on Varaport 30, temperature programmed from 90° to 210°C. Detector response factors have been determined for individual ketones.

RAPID G.L.C. ANALYSIS OF LOW MOLECULAR WEIGHT FREE FATTY ACIDS

P. G. Robinson
Auckland University

The methods used for analysis of low molecular weight free fatty acids are briefly reviewed. The effect of column length and column packing particle diameter on retention time and resolution has been investigated and an optimum column length of 0.5 m found, the complete analysis of C_2 to C_5 acids taking only 8 minutes. The separation of the C_2 to C_8 N-acids in under 2 minutes is demonstrated.

Methods of extracting low m.w. free fatty acids from biological samples are reviewed and discussed.

QUANTITATIVE ANALYSIS OF FREE FATTY ACIDS IN DAIRY PRODUCTS

I. K. Gray* and N. J. Walker
Dairy Research Institute, Palmerston North

Free fatty acids make an important contribution to the flavour of dairy products. Depending upon the level present in a particular product the resulting flavour may be either desirable or undesirable. Since methods currently available for the quantitative estimation of these acids have several disadvantages, a simple technique has been developed for the isolation and accurate analysis of the complete series (C2-C18) of fatty acids.

Free fatty acids in milk fat derived from the product under investigation are converted to salts by titration with methanolic potassium hydroxide. The non-volatile salts are extracted from the fat and quantitatively reconverted to fatty acids on a gas-liquid chromatographic column by formic acid vapour in the carrier gas. The fatty acids are separated on the column packed with 7% diethyleneglycol succinate on Chromosorb W, temperature programmed from 95° to 210°C.

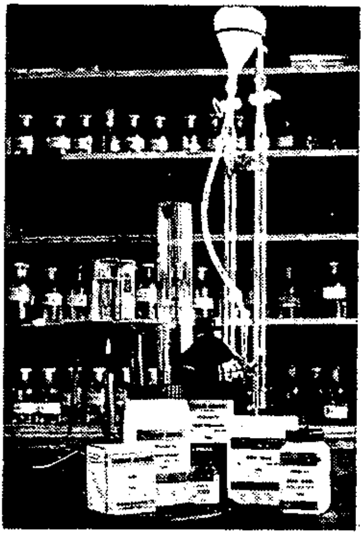
Studies with reference fatty acids have demonstrated 100% conversion from potassium salt to free acid using the above technique which eliminates possible loss of short chain acids prior to injection. In addition detector response factors have been established for individual fatty acids.

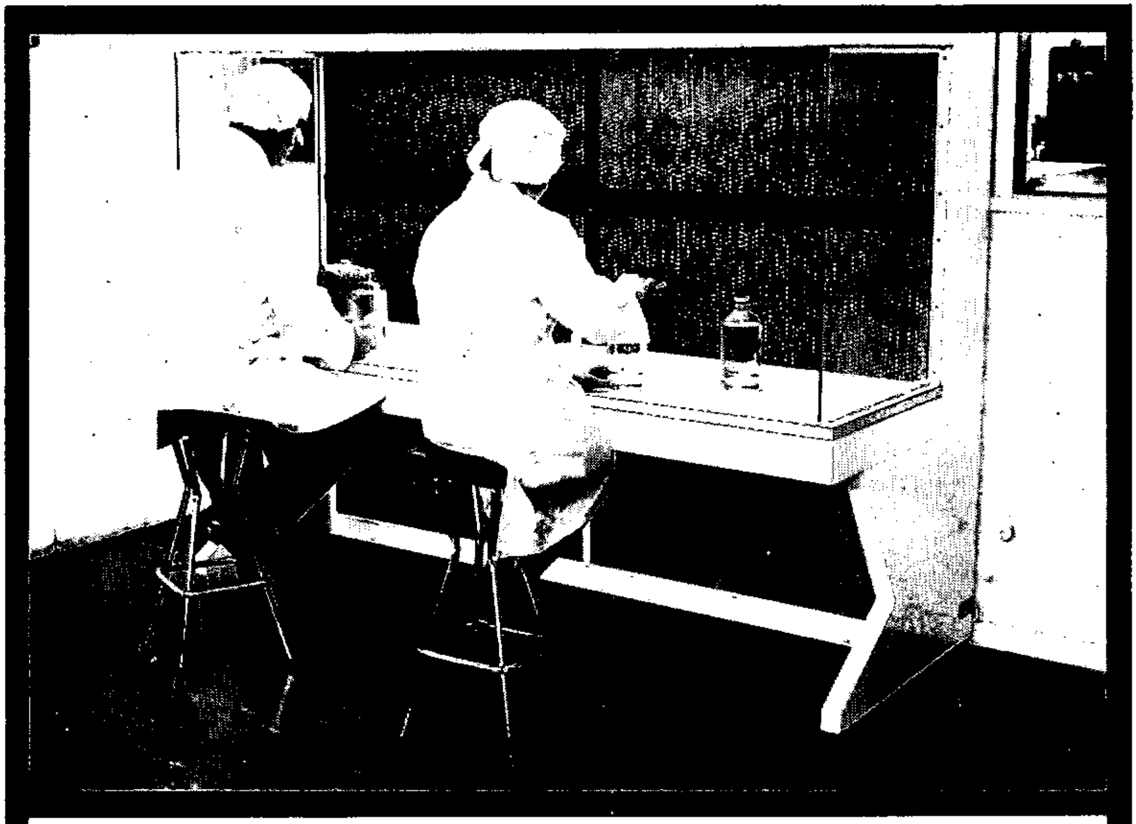
GLUCOSE AND CALCIUM DETERMINATIONS WITH 4-HYDROXYBENZOIC ACID HYDRAZIDE DERIVATIVES

M. Lever
Pathology Department
Green Lane Hospital, Auckland

Reducing sugars react with aromatic acid hydrazides in dilute aqueous alkali to give bis aroyl hydrazones of glyoxal and methyl glyoxal. These hydrazones form anions with intense absorbance in the near U.V. An exceptionally intense colour is given with 4-hydroxybenzoic acid hydrazide (PAHBAH), and the anion in this case forms a yellow chelate with calcium or cadmium ions (absorption max. about 415 nm). These reactions have been applied to carbohydrate analysis. To determine glucose in serum less than 10 microlitre sample is required when this is heated with a reagent containing PAHBAH, calcium citrate and sulphite in 0.3M NaOH. This procedure has been adapted for use with the Technicon "Autoanalyser". Less than microlitre/ml glucose can be determined colorimetrically with 0.5 ml sample. Using the lanthanum chelate of the derivative in diethanolamine solution, a sensitive fluorometric assay has been developed which can determine less than 50ng/ml glucose with 0.5 ml sample.

The bis-hydroxybenzoylhydrazones of α diketones are potential reagents for cations. The derivative of butan 2,3 dione has been prepared and gives a clearly visible yellow colour in the presence of 1 ppm calcium. The chelate is fluorescent, but a linear relationship between calcium concentration and fluorescence has not been obtained in the systems so far studied.





OFFICIAL NOTICE

An Annual General Meeting of the New Zealand Institute of Chemistry (Inc.) will be held in Room E006, Victoria University, Wellington, on Thursday, 24 August 1972, at 5.30 p.m.

AGENDA

1. Apologies.
2. Minutes of the Annual General Meeting held at the University of Waikato on 24 August 1971.
3. Presidential Remarks.
4. Annual Report for the year ended 31 July 1972.
5. Balance Sheet and Statement of Accounts for the year ended 30 April 1972.
6. Officers for 1973.
7. Institute Prizes.
8. General.

W. E. HARVEY,
General Secretary.

OBITUARY

N. J. R. Field, M.A., D.Phil. (Oxon)

Nigel Field died suddenly on the evening of Saturday, June 10, aged 29; he left a wife and two young children.

He was appointed to a visiting lectureship in the Chemistry Department at Victoria in February of 1969 where he taught physical chemistry at all levels. He quickly established a reputation as a commanding lecturer and, particularly, as a gifted personal teacher.

Dr. Field was an active research worker and had established a group in photochemistry, studying particularly fast photo-chemical reactions in solution with the aid of an electrochemical monitoring technique. A skilful, ingenious and patient experimenter he mastered the difficult techniques involved and successfully constructed a complex and novel apparatus with which his group had already studied a wide range of photochemical reactions. For his expert knowledge of this field and also for his willingness to collaborate with colleagues in other areas of research he will be greatly missed in the department.

A great lover of music and the arts, he enjoyed the concerts of the chamber music society, the symphony orchestra, plays at Downstage, and almost everything the University and the City had to offer. In leisure moments he enjoyed squash and cricket and being outdoors with his children.

He will be remembered with great affection and regard at Victoria, by his students and colleagues, and by his many friends.

J.W.T.

APOLOGY AND CORRECTION

Many readers noticed that the photograph which appearel on page 87 of the June issue was not of Mr. G. A. Lawrence, who appears below. It was, in fact, Mr. R. J. Laurenson, a well-known Wellington businessman. Our apologies go to the friends and relatives of Mr. G. A. Lawrence, and to Mr. R. L. Laurenson and our readers.

The late Mr. G. A. Lawrence

SALARIES FOR CHEMISTS

P. K. Foster, M.Sc., Ph.D., D.I.C.

N.Z. Pottery and Ceramics Research Association

Summary

1. The recent salary surveys carried out by the N.Z. Institute of Chemistry for its professional members confirm quantitatively that State and private sector remunerations for chemists are determined on quite different bases. Comparability of rates of remuneration is not possible for this special class of employee.

2. Recent (post 1969) salaries for chemists have risen at only half the rate in industry compared with that in Government. Rates of increase in Government salaries in this period are comparable with the average overall rate of increase in the private sector, and therefore salaries of chemists in industry have decreased relative to other rates in the private sector.

3. Under current stabilisation regulations and in the economic circumstances prevailing in much of New Zealand industry, it appears that the above situation with respect to salaries of chemists employed in industry is due to policies generally adopted by industry managements in the face of rapidly increasing costs.

Introduction

Consideration of chemists' remuneration is appropriate for several reasons:

(a) The employees' interest is obvious, particularly under conditions of rapid inflation.

(b) Employers are concerned to keep costs down to maintain profitability of their enterprise. In scientific organisations, or in scientific sections of other organisations, salaries are the largest single item of expenditure.

(c) Public concern with the adjustment of State salaries is highlighted by the Royal Commission currently sitting.

(d) The effects of the Stabilisation of Remuneration Regulations are of great importance.

(e) The 1969 and 1971 Salary Surveys conducted by the N.Z. Institute of Chemistry provide a factual base from which to discuss the above important issues.

Comparability of Chemists' Salaries in the Public and Private Sectors

In a brief discussion of the 1971 salary survey it was pointed out that the statistically significant factors of age and major function accounted for quite different proportions of the variance of salaries in the Government and Industry employment groups, and that Government salaries were more accurately described by the simple linear additive model adopted. The figures confirm quantitatively, for the first time to the writer's knowledge, the extent to which salaries in the wo sectors are determined on quite different bases:

(a) In industry, the job is rated, often by standard evaluation techniques, and compared with other non-technical functions. Generally, to receive promotion in addition to cost of living adjustments, you change your job. In a given job, the age of the incumbent is of minor importance.

(b) In Government, a personal merit system evaluates the employee rather than the job. To reecive promotion in addition to cost of living adjustments you have to become more valuable in the same job. To the extent that experience contributes to ability to tackle a greater range of problems more efficiently, the greater contribution of age as a statistical factor in Government employment is explained.

It is therefore meaningless to talk of comparability of remuneration between the two employment sectors.

It is further noted that it was not possible to establish a statistically significant difference between the two employment groups in either salary survey.

Recent Rates of Increase of Chemists' Salaries in the Public and Private Sectors

The salary surveys showed that while Government salaries increased by 35 percent, industry salaries increased by only 18 percent between 1969 and 1971. While no proof could be offered of the statistical significance of the difference, there is little doubt of its reality and accuracy. In both surveys, the samples analysed were approximately two-thirds of the Institute membership. In the worst possible case, therefore, half the returns analysed were from the same people. On the grounds that those who declined to submit returns in 1969 would tend to react in the same way in 1971, it is believed that much more than 50 percent of the samples analysed comprised the same people. It is pointed out that a significant difference in rates of increase between surveys does not conflict with the inability to establish a difference between the employment groups in either survey. The latter requires a distribution sufficiently narrow within each group in relation to the numbers in the samples and the difference between the means, for statistical significance to be established. The distributions were too broad to say other than that differences were due to chance variations.

The difference in rate of increase is open to alternative interpretations:

Either: Government chemists' salaries increased out of proportion to the total private sector;

Or: Industry chemists' salaries decreased relative to the rest of the private sector.

These can be examined by comparing Government salaries and the Labour Department's six-monthly surveys of the overall average weekly remuneration excluding overtime. The latter is compared with a Government scientists' scale position in Table I. Since the common factor of time ensures a correlation, the data are reduced to percentages over the April 1965 figure as a base for comparison of *rates* of increase with time. (Table II and Fig. 1). Because of the dis-

TABLE I

MOVEMENT IN AVERAGE PRIVATE SECTOR REMUNERATION AND A POSITION ON GOVERNMENT SCIENTISTS' SCALE

		Private Sector Av. Weekly $	*Govt. Salary Scale $*
April	1965	33.12	3040
October	1965	33.72	3140
April	1966	34.20	3140
October	1966	35.09	3280
April	1967	36.50	3350
October	1967	36.99	3380
April	1968	37.92	3440
October	1968	39.44	3600
April	1969	40.46	3600
October	1969	40.92	3830
April	1970	42.95	4150
October	1970	46.51	4510
April	1971	51.07	4950
October	1971	53.64	5180

TABLE II

PERCENTAGE INCREASES IN REMUNERATION OVER APRIL 1965 FIGURE

		Private Sector	*Government*
April	1965	0	0
October	1965	1.8	3.3
April	1966	3.3	3.3
October	1966	5.9	7.9
April	1967	10.2	10.2
October	1967	11.7	11.2
April	1968	14.5	13.1
October	1968	19.1	18.4
April	1969	22.2	18.4
October	1969	23.6	26.0
April	1970	29.7	36.5
October	1970	40.4	48.4
April	1971	54.2	62.8
October	1971	62.0	70.4

continuity in Table II and Fig. 1, the data from April 1970 was treated similarly (Table III).

TABLE III

Percentage increases in remuneration over April 1970 figures

		Private Sector	*Government*
April	1970	0	0
October	1970	8.2	8.7
April	1971	18.9	19.2
October	1971	24.9	24.8

It is important that the lines drawn in Fig. 1 were *not* drawn as the best lines through the data. They are the *theoretical* lines *for equal rates of increase* from the two bases taken. It is clear that Government chemists salaries have increased at a rate reasonably comparable with the private sector.

It can therefore be concluded that industry chemists' salaries have significantly decreased relative to the average of the total private sector, to the extent of at least 20 percent. This figure is a minimum estimate in that the difference between Government and indutsry has almost certainly widened since the survey taken in 1971.

The Impact of the Stabilisation of Remuneration Regulations 1972

These regulations provide that no salary increases, other than for promotion on the basis of substantially increased responsibilities or merit promotion on accepted scales, can be made without application to, and the consent of, the Remuneration Authority, and that generally consent may be given only to the minimum extent necessary to remove or relieve serious anomalies. Anomalies may not be claimed on the basis of comparison with State Services rate of remuneration, directly or indirectly. This would appear to constitute a serious hurdle to increases in industry chemists' salaries.

While the Regulations specifically exclude the use of the comparison made in the preceding section of this paper, it can be deduced that their effect is more apparent than real as far as industry chemists are concerned.

Because industry chemists are at least 20 percent worse off relative to the average of the private sector than they were in 1969, it is probable that anomalies within some firms do in fact exist to an extent sufficient to form the basis of applications to the Remuneration Authority, even under he more stringent guidelines of the 1972 Regulations.

It follows that the position with respect to industry chemists' salaries is a result of managements' decisions not to make such applications. It is also very probable that most other permanent salaried staff groups in industry are in the same position. This is borne out by similar observations by the N.Z. Institution of Engineers to those resulting from the N.Z. Institute of Chemistry salary surveys.

The industry chemists' arguments must be made with their managements, who have adopted their salary policies in order to maintain their entrprises' profitability and therefore their survival in the face of rapidly increasing costs in other directions.

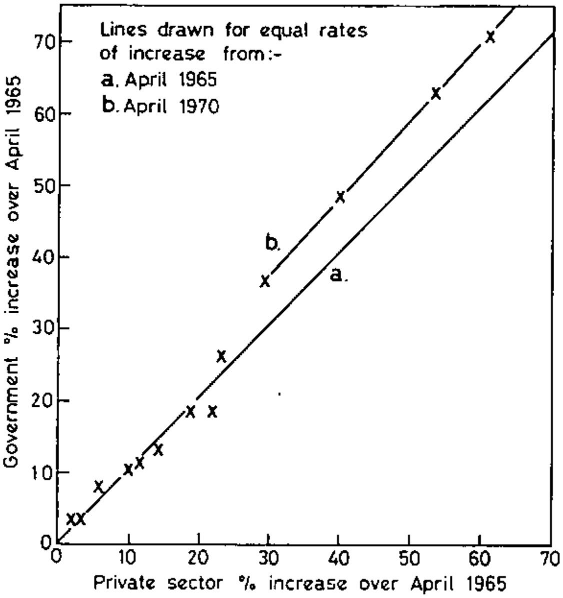


Fig. 1. Comparison of Data from Table 2.

OBITUARY

John Leighton Mandeno

Jock Mandeno, who died on 2nd May, 1972, after an unrelenting illness from which he seemed earlier to be making steady progress towards recovery, was a long-standing and well known member of the Institute. During the whole of his career, in which he moved from Government employment to industry, he always maintained a characteristic geniality, a friendliness of approach, and unfailing wisdom and good sound sense in all his actions. He was more than generous with his advice, his time and his services in so many spheres, and was the type of man people naturally turned to for help, knowing how readily and willingly he would respond.

Coming originally from a prominent family in the Auckland province, he attended Auckland Grammar School before coming to Wellington in 1929 to take up a cadetship in the then Dominion Labortory. Concurrent University studies at Victoria College gained him an M.Sc. degree in Chemistry in 1934.

As he possessed an early inclination towards the application of chemical knowledge to practical problems, it was a fortunate coincidence that about that time the Dominion Laboratory was entering upon a development stage, and expanding into applied research activities. He became one of a small team working on the gas storage of apples, and there will still be some of his contemporaries who remember the special gas chambers built in an adjoining garage.

His next activity in Dominion Laboratory was to head up a newly formed Paint Section, a step which was to set the seal upon his subsequent field of endeavour. Then in 1945 he was awarded an overseas study tour to further his knowledge not only of paint technology, but also of building materials, preparatory to setting up a relevant Section on his return with a view to expanding into building research. It was at this time that he developed the strong leaning towards the application of standard specifications which was to stand him in such good stead in his final occupation.

However, the call of industry eventually became attractive ,and in 1949 he began his industrial career, firstly as technical superintendent with Pinchin Johnson N.Z. Ltd., then for a period with Stipplecote Products Ltd., and lastly as Chief Chemist with Giant Paints Ltd.

On his retirement in 1970, he still felt much too active to be without a full-time occupation, and joined the Standards Association of N.Z. as a Technical Adviser with responsibility for paints, plastics, dairy products, explosives and glass. He was still in that position when overtaken by his untimely illness.

In Institute affairs, Jock played his part capably and conscientiously in the earlier days of the Wellington Branch by serving on the Committee, as Secretary, and eventually as Chairman. He was always a regular attender at Branch meetings, and formerly also at Conferences. In addition he was an active member of the Royal Society of New Zealand, and was a member of the steering committee which brought into being the N.Z. Section of the Oil and Colour Chemists Association, becoming the first Chairman in 1952.

The late Mr. J. L. Mandeno

It was characteristic of his inherent humanity, that, in addition to his professional activities and to his full and happy family life, he could still find the time and energy to devote himself wholeheartedly to the service of his Church. He was not only an elder of St. Ninian's in Karori, but engaged in many duties for the Wellington Presbytery, including being a Church Property Trustee for over ten years and Chairman of the Trust at the time of his death.

Of his many other interests, mention of only two will suffice to round out this appreciation of his many-sided personality—he was a member of the Karori Masonic Lodge and a regular player at the Karori Bowling Club. Of all too few of us can it be said, as it can of Jock Mandeno in full measure, that he was truly a chemist in the community.

E.S.B.

BOOK REVIEWS

Alicyclic Chemistry, by F. J. McQuillin. Cambridge University Press, 1972, 185pp., U.K. £4.20 (cloth), £1.80 (paper).

Authors of standard texts have in the past tended to gloss over the chemistry of alicyclic systems or have restricted their treatment to the simple five- and six-membered ring systems which, apart from their utility for introducing concepts of conformational analysis and stereochemistry have been regarded as close relatives of their acyclic analogues. Yet few areas have proved to be more fruitful for the development of principles of wide general significance, from the simple ideas of ring strain as enunciated by Baeyer to the far-reaching generalisations made possible by the Woodward Hoffmann approach to orbital symmetry. Dr. McQuillin states in the preface to this book that he has "attempted to illustrate these developments by means of simple examples" and this he has succeeded in doing in a concise and readable manner.

The first three chapters deal with the physical properties of alicyclic compounds with particular emphasis on spectroscopic properties, conformation, and the effect of ring size on reactivity. Cycloadditions and related reactions are dealt with in the next chapter, then follows a systematic treatment of rings of various sizes, bridged rings, and cage molecules, and finally fused ring systems (with the noteworthy omission of the steroid, diterpene, and triterpenoid systems). Throughout the text is concise and clear with well produced structural formulae illustrating reaction schemes, and references at the end of each chapter adequate to enable readers to find more detailed information. This is not a book for beginners in organic chemistry, but for students at the Stage III or Honours level it is a mine of information on modern approaches to the subject.

W.E.H.

Industrial Chemistry — Organic, by D. M. Samuel. Royal Institute of Chemistry Monograph for Teachers No. 11, Second Edition, 1972, 140pp., U.K. £1.50.

This edition bears only a formal resemblance to the first edition which appeared some six years ago. It is very much larger, includes new sections on basic raw materials and on high polymers and surface active agents, and gives more information on the end-use of the products described. Whether it is any more relevant to the New Zealand scene is debatable. The monograph deals only with the production of basic aliphatic and aromatic compounds: no mention is made of the manufacture of fine chemicals, pharmaceuticals, biochemical products, etc., so that none of the processes described, with the possible exception of the sulphonation of aromatic hydrocarbons, is operated in this country. Not surprisingly the author has concentrated on European, and in particular U.K. practice, with only brief mention of U.S. processes where they differ, and most of the statistical data on production, cost, etc., refer primarily to the U.K. Despite these shortcomings the book should be read by all teachers of organic chemistry even if only to remind them of the differences between laboratory and industrial methods, and to impress upon them the scale of operation which is essential for economy. How many chemists or teachers would estimate that the U.K. production of ethylene oxide, regarded here as almost a curiosity, is approximately 175,000 tons per annum?

Throughout the book pressures are expressed in pascals. This is perhaps laudable, but at least the values so obtained could have been rounded off to make them more realistic. Thus we see that butane can be isomerised with an aluminium chloride catalyst at a pressure of 1.013-3.343 MPa, i.e. 10-33 atmos. And if one wishes to embrace S.I. units so completely why quote production figures in lbs.?

W.E.H.

ERRATUM

The following introduction should have been used for Dr. Ferguson's article on page 77 of our June issue. The editor regrets any misunderstanding the omission of this introduction may have caused.

"This short article has been written by Dr. J. E. Ferguson as an outline of the work for which he was awarded the Institute's I.C.I. Prize for 1971. It is not intended as a formal paper on the subject".

BRANCH NEWS

Auckland

The Auckland University held a very successful Open Day on 10 June when the Chemistry Department really impressed those who saw through it. Mr. G. White arranged extensive demonstrations and films and is to be congratulated on his efforts.

Information on pollution of the Waitemata Harbour has been requested by the Branch from the Auckland City Council as a start in involving the Branch in affairs of public concern.

The Branch made a donation in May to send a party of eleven observers to the widely publicised Human Environment Conference recently held at Stockholm.

Dr. Devereaux, using details supplied by the University Registrar, is spear-heading a successful membership drive by contacting new graduates in chemistry from the Auckland University.

In his Presidential address to the Branch Mr. K. E. Seal developed the theme that the chemist could be an important member of the community if he and the Institute strove to establish themselves in the public eye. Respect for a chemist's talents has to be earned and it is about time chemists did something to influence both government and popular opinion on newsworthy matter, when he is qualified to sepak.

Personal

Congratulations to Professor D. Hall on being elected a Fellow of the Royal Society.

Mr. J. Hawthorne is now Chairman of the N.Z.I.C. Committee investigating Technician Training and Education. Submissions are welcome and can reach him through the Branch Secretary, P.O. Box 23-594, Papatoetoe.

Dr. I. Devereaux has completed one year as Chairman, Auckland Branch N.Z. Geological Society, recently addressing that Branch on "Stable Isotope Geochemistry".

Mr. J. R. Beck has been promoted to Head of Brewery Operations in N.Z. Breweries Ltd.

Mr. G. Maskill-Smith has joined the Building Research Association in Wellington as Head of Building Materials Research.

Heavy Metals in the Environment

It is proposed to hold a symposium at the Auckland Technical Institute on 18 October 1972 from 9 a.m. to 4.30 p.m. This would take the form of a group of invited speakers from Government, Industry and University followed by speakers contributing papers on analytical methods, pollution abatement, biological and health implications of the processing of heavy metals in the environment.

The meeting will conclude by the invited speakers forming a question and answer panel. The running of this symposium will depend upon the amount of support given by people offering papers.

Enquiries or offers of papers can be made to J. K. Johannesson, Auckland Technical Institute, P.O. Box 5044, Auckland 1.

Manawatu

Mr. K. Seal delivered a stimulating presidential address to the branch entitled "Chemists in the Community", in which he discussed the role of the Institute in N.Z. today.

New Zealand Dairy Research Institute

Dr. L. K. Creamer has been granted an Institute Fellowship to travel to Bradford, England, where he will carry out research into the clotting of milk by rennet. He will also attend the International Dairy Federation Symposium on casein micelle structure in the Netherlands.

Mrs. Patricia M. Boon, who recently graduated M.Sc. from Victoria University, has been appointed as a Research Officer to the milk powder section.

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

Dr. A. Cashmore has returned to work in this Division after overseas post-doctoral study at the M.R.C. unit in Cambridge in Britain and in the Molecular Biology Department at the University of California, Berkeley.

Massey University

Dr. W. S. Hancock, who completed his Ph.D. at Adelaide University Organic Chemistry Department, has arrived to take up a position as Lecturer in Chemistry. Dr. Hancock has had two years post-doctoral experience at the Department of Biochemistry at Washington University, St. Louis, on the chemical synthesis of proteins which involved the preparation of Acyl Carrier Protein.

Dr. G. G. Midwinter has recently returned from England where he spent a year at the M.R.C. laboratory of Molecular Biology, Cambridge, on the determination of the primary structure of proteins using low resolution mass spectrometry.

Dr. R. D. Reeves has recently returned from a year spent with Professor J. D. Winefordner at the University of Florida, Grainesville, where he worked on the development, behaviour and applications of a graphite-rod atomizer system for atomic absorption and atomic fluorescence. Dr. Reeves addressed a meeting of the branch with a talk entitled "Recent Developments in Analytical Atomic Spectroscopy."

Wellington

Chemistry Department, V.U.W.

Through Dr. Nigel Field's death the Department has suffered an enormous loss. An obituary notice appears on p. 117.

Drs. E. Sinn and B. Halton have now returned from their teaching visits to the Universities of Virginia and New South Wales, respectively.

Professor R. J. Ferrier is to give invited papers at the VIth International Symposium on Carbohydrate Chemistry in Madison, Wisconsin, and at the 164th National American Chemical Society Meeting in New York City in August.

The awards of the New Zealand Ramsay Memorial Fellowship and of a U.K. Commonwealth Scholarship to Mr. C. R. Clark are announced. Mr. Clark will be studying under Dr. R. W. Hay at the University of Stirling for the Ph.D. degree.

Chemistry Division

Mr. H. J. Todd of the Physical Chemistry Section left in May for a private visit to England. While there he will spend three weeks on behalf of Chemistry Division studying advances in spectrographic techniques and equipment.

Mr. G. G. Page of the Metallurgy Section left early in July for a private visit to England. While he is away he will spend three weeks visiting ferrous and non-ferrous metals, water, and building research establishments on behalf of Chemistry Division.

Dr. I. J. Miller will be in Australia for two weeks in July. He will spend a few days at the University of New England, Armidale, on behalf of Chemistry Division, investigating their ^{13}C N.M.R. facilities.

Mr. T. Marshall, who is Deputy Director at Chemistry Division, and in charge of the Chemical Engineering and Mineral Processing Sections, will leave New Zealand in August in order to study industrial and mineral developments in Western Australia, South Africa, United Kingdom, Scandinavia, Mexico, U.S.A., Canada and Japan.

Institute of Nuclear Sciences

Dr. W. H. Melhuish visited Gaithersburg in Maryland, U.S.A., in March, at the invitation of the National Bureau of Standards, and gave one of the principal lectures at their conference on Accuracy in Spectrophotometry and Luminescence Measurements.

Two visiting scientists have recently joined the Institute. They are Dr. M. Kusakabe of Tokyo Kyoiku University who will spend two years on isotope geochemistry studies, and

and Mr. C. Siri-Upathum from Thailand who arrived in April to take up a 9-month fellowship awarded by the International Atomic Energy Agency.

Mr. D. C. Lowe is spending 6 months as a visiting scientist at the Scripps Institution of Oceanography in U.S.A. in connection with his work on the analysis of atmospheric gases.

Mr. W. J. McCabe gave a lecture to the Physics Section of the Royal Society on the Institute's work on pollution studies.

Drs. C. J. Adams, G. L. Lyon and B. W. Robinson attended a 2-day Vulcanological Conference in Rotorua during May, and Dr. Robinson lectured on his studies of base metal deposits in relation to volcanic rocks.

Canterbury

Professor B. R. Penfold has been awarded an Erskine Fellowship by the University of Canterbury and will be the N.Z. delegate at the Ninth International Congress of Crystallography in Kyoto, Japan, from 26 August to 7 September 1972. He will then be making laboratory visits in U.S.A. and the United Kingdom.

Dr Ward T. Robinson will also attend the Congress prior to going to Stanford University, California, to spend a year working with Professor James P. Collman.

Dr. K. E. Richards leaves in August to spend 10 months at the University of Guelph, Ontario, Canada, working with Professor A. K. Colter in the general field of chemical behaviour of charge transfer complexes.

Dr. R. A. G. Maclagan, at present Visiting Lecturer in the Chemistry Department, has been appointed to a lectureship in the department.

Mrs. M. G. Metcalf of the Medical Unit, the Princess Margaret Hospital, has been awarded a Ph.D. degree by the University of Otago for studies on gas chromatographic assays for steroids in urine. This is the first doctorate awarded by the Otago Medical School for work done in another centre.

The Junior Chemical Society's second meeting for the year was addressed by Professor J. Vaughan and Dr. G. A. Rodley on "Colour".

Otago

President's Visit

The President, Mr. K. Seal, addressed a well attended meeting of the Branch last month. His lecture on "The Chemist in the Community" was mainly concerned with the public image of the Institute and the ways in which this image might be enhanced.

Chemistry Department, O.U.

Professor E. Lightfoot of the University of Wisconsin visited the Department in early July and lectured on "Applications of Transport Phenomena to the Description of Ultra Filtration". Professor Lightfoot is an Erskine Fellow of the University of Canterbury.

Professor A. D. Campbell has been appointed to the Fertilizer Processing Technical Committee of the New Zealand Fertilizer Manufacturer's Association.

Secondary Schools

The annual Branch lecture to Dunedin secondary school pupils was given this year by Dr. D. Fenby. His lecture, "Variations on a Laser Beam", was very successful and well attended.

NEW ZEALAND COMMITTEE FOR WATER POLLUTION RESEARCH

Professor R. L. Earle, head of the Biotechnology Department of Massey University, was elected Chairman of the New Zealand Committee for Water Pollution Research at its first annual meeting in Wellington. Also elected to the executive of the Committee were a vice-chairman, D. A. Ferrier, Chief Public Health Engineer, Ministry of Works, President, Water Supply and Disposal Association of New Zealand and a member of the Council of The New Zealand Institution of Engineers, a secretary/treasurer, K. R. Davis, Secretary, Water Supply and Disposal Associ- Chemist and Plant Superintendent of the ordinator, R. Hicks, until recently Chief ation of New Zealand, and a technical co- Auckland Regional Authority, and New Zealand member of the Governing Board of the International Association for Water Pollution Research.

Other directors are: Dr. V. M. Stout, Senior Lecturer in the Department of Zoology, University of Canterbury and President of the Limnological Society. Dr. M. E. U. Taylor, Chief Chemist, Auckland Regional Authority. Dr. R. H. Thornton, Director, Cawthron Institute, Nelson. Dr. G. R. Williams, Controller of Wild Life, Department of Internal Affairs. Vice-President, New Zealand Ecological Society.

The Committee will aim to promote seminars on water pollution research, review water pollution research in New Zealand and indicate areas requiring priority, and to encourage communication, co-operative effort and maximum exchange of information on water pollution research and water quality management between those bodies in New Zealand active in these fields. In these activities, it will work in conjunction with the Engineering and Scientific Committee on Water (E.S.C.O.W.) and with the Royal Society of New Zealand and its associated member bodies.

In the international sphere, the Committee's principal objective is to provide an independent organisation through which qualified New Zealand Societies, Institutes and reesearch organisations whose members are concerned with water pollution research, can be represented on the Governing Body of the International Association on Water Pollution Research. The general objectives of the International Association, which are shared by the Committee, are:

(a) To encourage international communication, cooperative effort and a maximum exchange of information on water pollution research and water quality management;

(b) To sponsor regular international meetings and conferences where reports on important reesearch in water pollution control are presented;

(c) To provide a scientific medium for publication of research reports and activities of the Association;

(d) To shorten the time lag between development of research findings and their application in engineering design.

Formation of the Committee has received wide support from research organisations in the universities, in industry and in government, and from engineering and scientific bodies and societies.

The Committee will welcome enquiries from interested groups who may not yet know of its activities. Enquiries should be addressed to The Secretary, New Zealand Committee for Water Pollution Research, P.O. Box 12241, Wellington.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

INCOME AND EXPENDITURE ACCOUNT FOR YEAR ENDED 30th APRIL, 1972

1971 $		$	$
	EXPENDITURE		
	Administration Expenses:		
1,198	Printing, Stationery, Postages, Tolls, etc.	1,218.30	
700	Salary, Registrar	950.00	
750	Travelling Expenses	665.46	
345	Honoraria (*Less* Proportion charged to Journal)	535.00	
360	Branch Expense Allowances	360.00	
120	Audit Fees	150.00	
50	Donation—S.A.N.Z.	50.00	
20	Royal Society of New Zealand—Membership Fee	20.00	
20	Depreciation	16.00	
50	Manpower Survey Cost	—	
(3,613)			3,964.76
	Publications:		
3,852	Cost of Journal	4,888.73	
- -	List of Members	1,140.48	
		6,029.21	
—2,464	*Less* Revenue from Advertising	3,622.98	
(1,388)			2,406.23
538	"Careers in Chemistry"		- -
221	Publicity Brochure		—
26	Sundry Publications		—
1,122	Excess of Income over Expenditure for Year		1,556.24
$6,908			$7,927.23

1971 $		$	$
	INCOME		
6,625	Subscriptions—Annual		7,367.29
	Interest Received:		
107	Bank of New Zealand	228.58	
176	Local Body Stock	191.88	
(283)			420.46
—	Donation		10.00
—	Examination Fees		120.00
—	Net Proceeds Sundry Publications		9.48
$6,908			$7,927.23

OVERSEAS VISITORS TRAVELLING FUND

$		$
84	Balance 30.4.71	274.75
843	Travelling Expenses Paid during year	454.00
$927		$728.75

$		$
79	Grants	—
564	Conference Profits	547.83
10	Donation	—
274	Balance 30.4.72	180.92
$927		$728.75

BALANCE SHEET AS AT 30th APRIL, 1972

1971 $		$	$
	CURRENT LIABILITIES		
204	Sundry Creditors	105.00	
367	Subscriptions received in advance	178.50	
400	Royal Institute of Chemistry funds held in advance	400.00	
(971)	*Total Current Liabilities*		683.50
	SPECIAL FUNDS		
140	Education Fund (School Bulletins)	140.00	
—275	*Less* Overseas Visitors Travelling Fund	180.92	
(135 Dr.)			Dr. 40.92
	TRUST FUND		
2,587	Balance 30.4.71	2,590.19	
3	*Plus* interest credited	2.70	
(2,590)			2,592.89
	ACCUMULATED FUNDS		
2,587	Balance 30.4.71	7,239.74	
	Excess of Income over Expenditure for Year	1,556.24	
7,240			8,795.98
$10,666			$12,031.45

1971 $			$	$
	CURRENT ASSETS			
5	Petty Cash Funds		34.75	
2,916	Bank of New Zealand		3,804.24	
679	Subscriptions in Arrears		930.00	
227	Sundry Debtors		274.00	
125	Publication on Hand		247.57	
40	Advance—Conference		80.00	
(3,992)	*Total Current Assets*			5,370.56
	TRUST FUND INVESTMENTS AT COST			
90	Post Office Savings Bank		92.89	
1,000	Hutt County Council, Redemption Loan		1,000.00	
1,500	Lyttelton Harbour Board Loan ...		1,500.00	
(2,590)				2,592.89
	GENERAL FUND INVESTMENT			
1,000	North Canterbury Hospital Board Stock		1,000.00	
3,000	Bank of New Zealand Term Deposit		3,000.00	
(4,000)				4,000.00
	FIXED ASSETS AT COST			
	Office Equipment	317.80		
	Less Depreciation	251.80		
82			66.00	
	Addressograph Plates ...	62.35		
	Less Depreciation	60.35		
2			2.00	
(84)	*Total Fixed Assets*			68.00
$10,666				$12,031.45

AUDITOR'S REPORT

We have audited the books of the New Zealand Institute of Chemistry (Inc.) for the year ended 30th April, 1972, 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, 1972.

SHANAHAN AND WINDER,
Chartered Accountants.

M. P. Winder,
Auditor.

DEFINITIONS, TERMINOLOGY, AND SYMBOLS IN COLLOID AND SURFACE CHEMISTRY—I

This Appendix to the **Manual of Symbols and Terminology for Physicochemical Quantities and Units** (Butterworths, 1970) has been prepared by the Commission on Colloid and Surface Chemistry of the Division of Physical Chemistry of IUPAC. It is the outcome of extensive discussions within the Commission, with other IUPAC Commissions, and with persons and organisations outside IUPAC, over the period 1961-1971. A tentative version of these proposals were issued by IUPAC as **Tentative Nomenclature Appendix** No. 3 (January 1970) to the **Information Bulletin:** the text has been revised in the light of the criticisms, comments, and suggestions which were received.

The Appendix consists of three Sections; the first concerned with definitions and terminology and with recommenadtions for appropriate symbols; the second is a list of recommended sysmbols; and the third an alphabetical index of terms defined, together with the corresponding symbols. The areas dealt with are: Adsorption and Spread Monolayers; Mechanical and Thermodynamic Properties of Surfaces and Interfaces; Definition and Classification of Colloids; Preparation and Processing of Colloidal Systems; Stability of Colloidal Systems, Aggregation, Coagulation, Flocculation; Surface Active Agents; Fluid Films; Colligative and Related Properties; Attraction and Repulsion; Sedimentation, Creaming, Centrifugation, and Diffusion; Electrochemical Terms in Colloid and Surface Chemistry; Electrokinetics.

Available as a reprint from: IUPAC Secretariat, Bank Court Chambers, 2-3 Pound Way, Cowley Centre, Oxford OX4 3YF, UK. (v + 56 pages) US $2.25 (£0.75) Cash with order, postage free.

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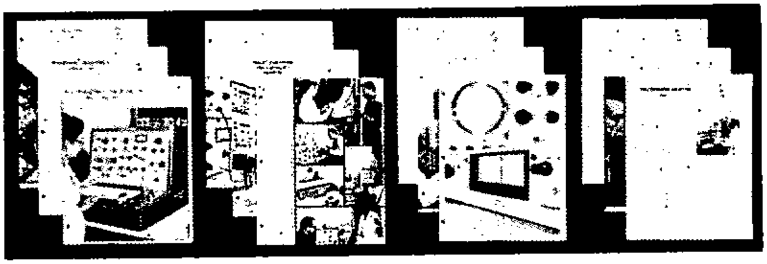

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STAFF APPOINTMENTS

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 chemicals 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.

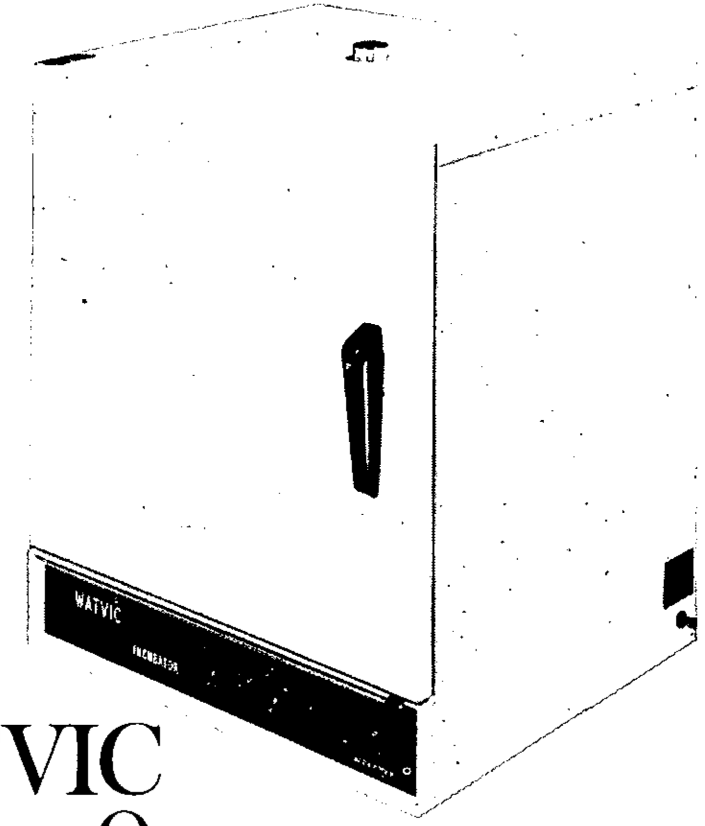
Application may be made at any time during the year, but a decision will not normally be made before October or November.

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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