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CONTENTS

page

Conference Guest Speakers:

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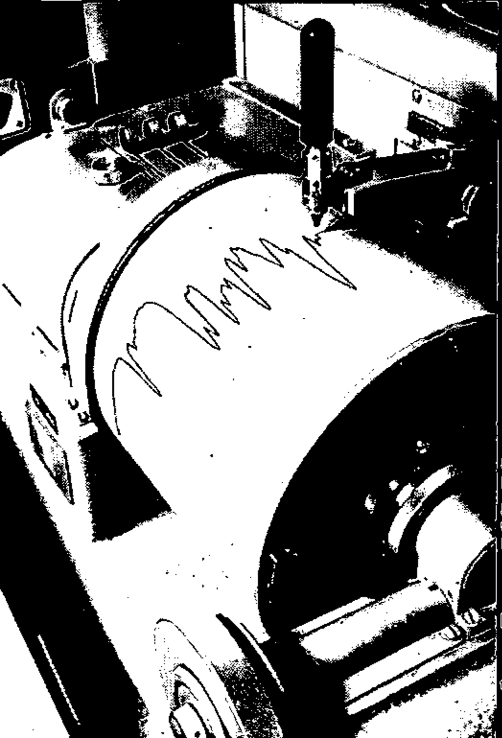

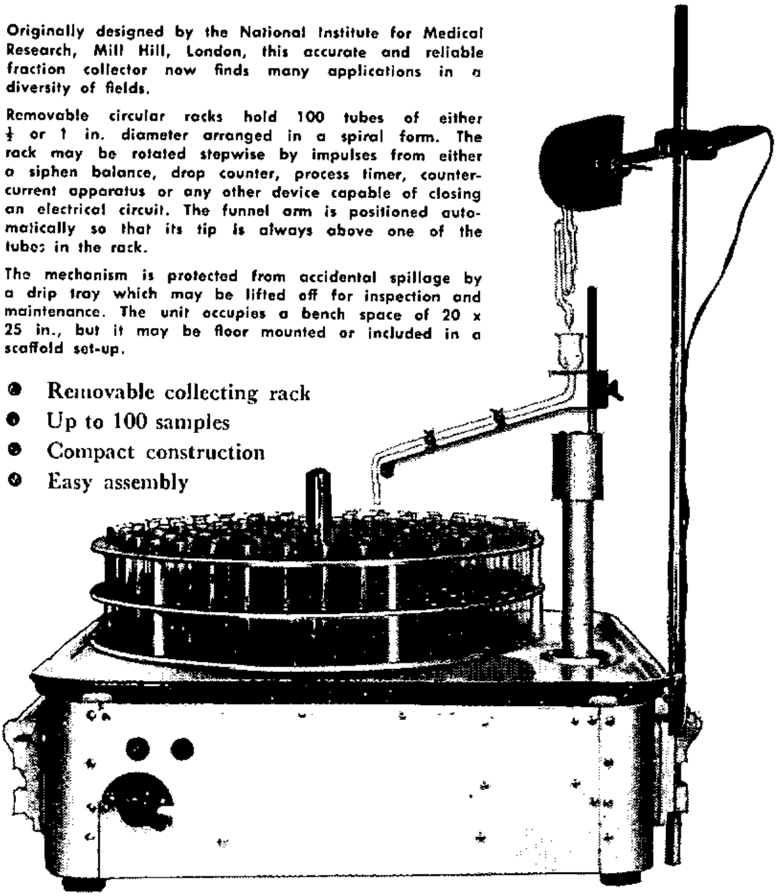

JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

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CONFERENCE 1965

A century ago William Skey left Dunedin to found a laboratory in Wellington which is now the Chemistry Division of D.S.I.R. Thirty years ago the first combined R.I.C.-N.Z.I.C. Conference was held in Hamilton. Since 1935 membership of the Institute has risen from just over 100, to 400 in 1951 and now to about 800. These are historical milestones. The Otago Branch of the New Zealand Institute of Chemistry looks forward to welcoming members again to Dunedin to celebrate their passing.

The current rapid growth of the Institute reflects increased numbers of chemists graduating from the universities. Visitors will notice the expansion of the facilities in the University of Otago's chemistry department since the 1959 Dunedin Conference. The most recent addition of approximately 4000 square feet is about to be occupied in an interim science building near the Home Science School. A new university union, a new library, and new halls of residence are other changes which visitors will appreciate.

The Minister of Science has accepted the invitation of the organising committee to open the Conference and to review the place of chemistry in research in New Zealand with particular reference to industrial development in the light of the report of the National Research Advisory Council and its working committees. Mr. Talboy's address will be the first of several occasions when members attending this meeting will hear about the part chemistry is playing, and will play, in our country's changing economy. The present and the future will be the concern of guest lecturers, Mr. Ivan Newham and Dr. J. S. Watt, as well as our president, Professor S. R. Siemon.

These addresses are the background for forty-two papers chosen from the fifty offered in response to the Conference Committee's request for papers and suggestions for symposia. The Committee's task therefore has been one of selection and arrangement. We thank all contributors of papers.

J. ROGERS,
Chairman, Conference Committee.

I. E. NEWNHAM,
M.B.E., M.Sc., F.R.A.C.I., M.A.I.M.M.

I. E. Newnham graduated M.Sc. from Melbourne University in 1940 and continued his post-graduate studies under Dr. J. S. Anderson until defence requirements resulted in his transfer to the Department of Aircraft Production in 1941. After collaborating with C.S.I.R. on the production of aircraft engine bearings, he joined the staff of P. J. Taylor (N'cle) Pty. Ltd. in 1944 and participated in the establishment of new processes for producing automotive bearings in Australia.

In 1947 he joined the CSIR Division of Industrial Chemistry where he studied the heavy mineral beach sands of Australia's eastern coastline. His major interest was the chemistry of titanium, zirconium and hafnium and in 1956-57 he worked in the National Distillers Corporation Research Laboratories at Cincinnatti, Ohio, on the development of a new process for separating zirconium and hafnium.

In 1961 he was appointed Chief of the CSIRO Division of Mineral Chemistry and he has spent the past four years fostering closer collaboration between the mineral industry, CSIRO and the Universities of Australia.

J. S. WATT

J. S. Watt was born in West Australia in 1908, and educated at Auckland Grammar School and Auckland University College. He was awarded a Rhodes Scholarship in 1931 and completed his doctorate (D.Phil.) in chemistry at University College, Oxford, in 1933. He joined I.C.I. in U.K. and subsequently transferred to I.C.I.A.N.Z. in Australia. After holding various technical and administrative positions in this company in Australia and New Zealand, he returned permanently to New Zealand in 1953 and subsequently joined Fletcher Holdings Limited. For ten years he was Managing Director of The Fletcher Industries Limited and at present is Chairman of Directors of this company. Other directorships: Pacific Steel, G.K.N. (N.Z.), Lusteroid, Nairn-Williamson (N.Z.). A past member of the Council of Scientific and Industrial Research, the Atomic Energy Committee and the Dairy Research Institute.

N.Z.I.C. CONFERENCE PROGRAMME

University of Otago, Dunedin

August 17-20, 1965

TUESDAY EVENING, AUGUST 17

7.00 p.m. Registration in Union.

8.00 p.m. Conference Opening.
His Worship the Mayor.
Vice-Chancellor of University of Otago.
The Minister of Science, Mr. Talboys.

WEDNESDAY MORNING, AUGUST 18

9.00 a.m. Guest Lecture—"Mineral Chemistry: Lost Art or Neglected Science?", Mr. I. E. Newnham, M.B.E., Mineral Chemistry Division, C.S.I.R.O., Melbourne.

10.00-10.30 a.m. Morning Tea.

Session A: Solid State Chemistry

10.30 a.m. Topotactic Reactions of Nickel Oxides (A. G. Freeman).

11.00 a.m. Kinetics of Formation of Spinels (J. F. Duncan and D. Stewart).

11.30 a.m. Growth of Mullite from Kaolin Minerals (K. MacKenzie, J. F. Duncan and P. K. Foster).

12 m.d. On the Analysis of Cristobalite (P. K. Foster and I. R. Hughes).

Session B: Organic Chemistry

10.30 a.m Triterpenes from Sticta Billardiarii (R E. Corbett and H. Young).

11.00 a.m. Nuclear Magnetic Resonance Studies of Some Aromatic Nitroso Compounds (A. Fischer).

11.30 a.m. The Westphalen Rearrangement (A. Fischer, M. P. Hartshorn, D. N. Kirk and S. W. Yoong).

12 m.d. Some Reactions of Epoxides of 12-Methylene-steroids (J. M. Coxon, M. P. Hartshorn and D. N. Kirk).

WEDNESDAY AFTERNOON, AUGUST 18

2.00 p.m. Easterfield Award Address.

3.00 p.m.-3.30 p.m. Afternoon Tea.

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

WEDNESDAY EVENING, AUGUST 18

Free (Geochemistry Group Meeting), (Branch Editors' Meeting).

THURSDAY MORNING, AUGUST 19

9.00 a.m. "Chemistry in Industry", Dr. J. S. Watt, Fletcher Industries.
10.00 a.m.-10.30 a.m. Morning Tea.

Session A: Physical Chemistry

10.30 a.m. Specific Interactions in Hydrofluorocarbons (I. D. Watson and A. G. Williamson).
11.00 a.m. Effect of Pressure on Very Fast Reactions (D. W. Howarth and W. S. Metcalf).
11.30 a.m. The Catalytic Properties of Palladium-Noble Metal Alloy Systems (A. Metcalfe).
12 m.d. Oxygen Exchange in Concentrated Mineral Acids between Acetic Acid and Water (Charmian J. O'Connor).

Session B: Organic and Biochemistry

10.30 a.m. Crystal and Molecular Structures of Strained Molecules (P. P. Williams).
11.00 a.m. Selenium and the Biosynthesis of Ubiquinone (K. R. Millar).
11.30 a.m. Lipid Biosynthesis in Higher Plants (J. C. Hawke).
12 m.d. Researches on Branched Chain Fatty Acids (F. B. Shorland and R. P. Hansen).

THURSDAY AFTERNOON, AUGUST 19

2.00 p.m. Presidential Address, Professor S. R. Siemon: "Looking Ahead".
3.00-3.30 p.m. Afternoon Tea.

Session A: Physical and Theoretical Chemistry

3.30 p.m. A Normal Co-ordinate Analysis of Thiocarbazide (G. R. Burns and J. F. Duncan).
4.00 p.m. Relationship between the Quadrupole Splitting and the Magnetic Susceptibility of Iron Complexes (R. M. Golding and J. F. Duncan).
4.30 p.m. Mössbauer Studies of Single Crystals (H. J. Whitefield, J. F. Duncan and R. M. Golding).
4.00 p.m. Spin Polarisation and Hyperconjugation in Organic Fragments (J. P. M. Bailey and R. M. Golding).

Session B: Organic and Biochemistry

3.30 p.m. The Action of Ammonia on Carbohydrates and Related Compounds (M. R. Grimmett and E. L. Richards).
4.00 p.m. Dehydration Studies on Nerve Myelin (M. G. Rumsby).
4.30 p.m. The Structure of the Cell Walls of some Thermophilic Bacilli (A. J. Wicken and I. T. Forrester).
5.00 p.m. Insect Detoxication Enzymes Utilizing Glutathione (F. J. Darby).

THURSDAY EVENING, AUGUST 19

6.30 p.m. Conference Dinner.

FRIDAY MORNING, AUGUST 20

9.00 a.m. "Isotopic Geochemistry and Biogeochemistry in New Zealand", Mr. T. A. Rafter.
10.00-10.30 a.m. Morning Tea.

Session A: Geochemistry

10.30 a.m. Chemical Equilibria in Natural Hydrothermal Systems (A. J. Ellis).
11.00 a.m. Regional Geochemistry of Thermal Waters in New Zealand (W. A. J. Mahon).
11.30 a.m. Studies of the Composition of Gases Associated with Steam from Drillholes at Wairakei, New Zealand (R. B. Glover).
12 m.d. Chemistry in the Antarctic (A. T. Wilson).

Session B: Inorganic and Structural Chemistry

10.30 a.m. Copper Ion Catalysis of the Racemisation of the Tris-Oxolato Chromium-III Anion (J. Kernohan, A. L. Odell and R. W. Olliff).
11.00 a.m. Nickel-anion Interactions in some Nickel Tetramine Salts (N. F. Curtis).
11.30 a.m. Structure and Bonding in Trinuclear Rhenium (III) Halides (J. E. Fergusson and B. R. Penfold).
12 m.d. A Compound Containing both 5 and 6 Co-ordinate Tin (IV) (F. W. B. Einstein and B. R. Penfold).

FRIDAY AFTERNOON, AUGUST 20

Session A: Geochemistry

2.00 p.m. Chemical and Analytical Applications of Discontinuous Countercurrent Solvent Extraction (C. R. Boswell and R. R. Brooks).
2.30 p.m. The Biogeochemistry of Trace Element Uptake by Marine Organisms (R. R. Brooks and M. G. Rumsby).
3.00 p.m.-3.30 p.m. Afternoon Tea.
3.30 p.m. Solubility of Orpiment in Sulfide Solutions to 200°C and 1500 bars (B. G. Weissberg).
4.00 p.m. Composition of Gases and Liquids within Inclusions of Minerals in some Ingeous and Metamorphic Rocks (R. L. Goguel).
4.30 p.m. Preparation of Molecular Sieves (R. M. Carr, G. A. Lawrence and G. L. Lyon).

Session B: Physical and Applied Chemistry

2.00 p.m. Bismuth Electrode Reactions (Helen G. Anderson, L. G. M. Gordon and G. A. Wright).
2.30 p.m. Photometric Observations on Reactions in Hydrogen Flames (M. J. McEwan and L. F. Phillips).
3.00 p.m.-3.30 p.m. Afternoon Tea.
3.30 p.m. Pulping Studies on Silver Beechwood (D. J. Brasch and P. I. Duncan).
4.00 p.m. Rot-proofing of Cellulose Materials (I. R. C. McDonald)
4.30 p.m. Lubricating Greases (A. A. Turner).

ABSTRACTS OF PAPERS

CONFERENCE, 1965

TOPOTACTIC REACTIONS OF NICKEL OXIDES

A. G. FREEMAN
Chemistry Department, Victoria University of Wellington

When water is added to α-$NaNiO_2$ crystals the Na ions are leached from the structure and replaced by protons. The ultimate products are γ-NiOOH, NiO, and $Ni(OH)_2$ but several intermediate steps have been recognised in the process. It is thought that γ-NiOOH is formed via an intermediate phase which is analogous to the so-called hydrate of van Bemmelen; this has the formula $4Fe_2O_3$. 1.4 Na_2O. 4-$6H_2O$. This intermediate phase has been partially characterised. Later, some γ-NiOOH is reduced, via $4Ni(OH)_2$ NiOOH, and $Ni_3O_2(OH)_4$, to $Ni(OH)_2$ and NiO. The reduction process is thought to occur by loss of oxygen from the structure and this implies that the reaction takes place at or near the surface of the crystal.

The final products of the reaction, and the intermediate phases, are all well oriented with respect to the original crystal of the γ-$NaNiO_2$ and the reaction may be explained in terms of an inhomogeneous topotactic mechanism.

KINETICS OF FORMATION OF SPINELS

J. F. DUNCAN and D. STEWART
Chemistry Department, Victoria University of Wellington

Some aspects of the formation of zinc ferrite in the solid state from zinc oxide and ferric oxide have been studied in detail. The techniques which have been used are as follows:

(a) study of the kinetics by X-ray methods;
(b) study of the structure of the spinel by infra-red spectroscopy;
(c) comparison of the iron environments by Mössbauer spectroscopy;
(d) investigation of the role of oxygen and the nature of the diffusing species in the reaction.

GROWTH OF MULLITE FROM KAOLIN MINERALS

K. MACKENZIE and J. F. DUNCAN
Chemistry Department, Victoria University of Wellington
P. K. FOSTER
N.Z. Pottery and Ceramics Research Association

The object of this research is to propose and test a model for the high temperature transformation of kaolinite minerals to mullite and cristobalite. The reaction sequence can be represented by the following equations:

$$\underset{\text{(kaolinite)}}{\mathrm{Al_2O_3.2SiO_2.2H_2O}} \xrightarrow[\text{—650°C}]{\text{550°C}} \underset{\text{(metakaolinite)}}{\mathrm{Al_2O_3.2SiO_2}} + \mathrm{2H_2O}$$

$$\underset{\text{(metakaolinite)}}{\mathrm{2(Al_2O_3.2SiO_2)}} \xrightarrow{\text{980°C}} \underset{\text{(Al-Si spinel)}}{\mathrm{Si_3Al_4O_{12}}} + \mathrm{SiO_2}$$

$$\underset{\text{(Al-Si spinel)}}{\mathrm{3(Si_3Al_4O_{12})}} \xrightarrow{\sim 1100\text{°C}} \underset{\text{(mullite)}}{\mathrm{2(Al_2O_3.2SiO_2)}} + \underset{\text{(cristobalite)}}{\mathrm{5SiO_2}}$$

An infrared method is being used in a detailed study of the transformation of metakaolin to spinel, and spinel to mullite. A quantitative internal standard analysis method has been developed. Frequency shifts of Al-O absorption bands during the reaction are also being studied. The IR bands in the mullite spectrum have tentatively been assigned, and a theoretical treatment of the spectrum has been made on the basis of the known structure of the mullite molecule.

A conductance apparatus for temperatures up to 1200°C has been designed for use in conjunction with an existing vacuum system, with a view to obtaining more information on spinel formation mechanism.

Radiometric measurements of diffusion constants of various ions through the kaolinite-mullite lattice should provide information on the role played by the exchangeable cations in the reaction sequence.

X-ray kinetic studies on mullite growth from kaolinite, halloysite and copper halloysite suggest that the mechanism of formation is the same for all three materials. The kinetics can be explained by rapid exponential nucleation of mullite from spinel followed by rapid crystal growth of a phase-boundary controlled type. Rate constants have been determined for the reaction, and the enthalpies of activation (87-96 K.cal mole^{-1}), free energies of activation, (108-130 K.cal mole^{-1}) and entropies of activation (-15.3— -28.8 cal.deg.$^{-1}$mole^{-1}) which are independent of the starting materials, are of the order of diffusive process energies.

ON THE ANALYSIS OF CRISTOBALITE

P. K. FOSTER and I. R. HUGHES

New Zealand Pottery and Ceramics Research Association

The decomposition of kaolin clay minerals to form mullite and silica is one of the most important of the high temperature solid state reactions which occur in the manufacture of ceramics. If the reaction is to be controlled, an understanding of the mechanism is essential. In pursuing this end solid state kinetics have been used as described elsewhere in this symposium. However, the kinetics of formation of mullite only can be used at this stage; studies of the rate of formation of silica which could yield valuable indications of the mechanism must be ignored until a valid quantitative analytical method is available for cristobalite, the crystalline form of silica which the reaction produces. In addition, cristobalite undergoes a structural inversion at 150-250°C and an associated change in specific volume. This has important technological implications which merit study. Quantitative analysis is a prerequisite for such work. The little that is known of the crystalline structure of cristobalite will be reviewed insofar as this limits the application of standard X-ray powder diffraction procedures for quantitative analysis, and attempts to relate X-ray diffraction intensities to the amount and type of crystalline silica present will be described.

Work to date indicates that the complete structural determination of silica is required for full understanding of the problems of quantitative analysis and of specific volume changes at inversion.

TRITERPENES FROM *STICTA BILLARDIARII*

R. E. CORBETT and H. YOUNG

Chemistry Department, University of Otago

Two new triterpenoids have been isolated from the lichen *S. billardiarii.* Infrared, ultraviolet, n.m.r. and mass spectral evidence, together with chemical evidence will be presented to prove that these compounds have the structures 7β-acetoxy-22-hydroxyhopane, and 15α-2-dihydroxyhopane. The structures of four rearrangement products of 7β-hydroxyhopane will also be discussed.

NUCLEAR MAGNETIC RESONANCE STUDIES OF SOME AROMATIC NITROSO COMPOUNDS

A. FISCHER
Chemistry Department, University of Canterbury
R. M. GOLDING and W. C. TENNANT
Chemistry Division, D.S.I.R., Gracefield

4-nitrosophenols in solution are tautomeric though much evidence suggests that the equilibria are generally heavily one-sided and sometimes solvent dependent.

In this paper we show from proton magnetic resonance studies that 2,6-dimethyl-4-nitrosophenol and 4-nitroso-l-naphthol exist in the quinone monoxide forms in dilute dimethylsulphoxide solutions, whereas 4-nitrosophenol exists in the phenolic form. However, in dilute chloroform solution 4-nitrosophenol also exists in the quinonoid form. The pmr spectra were found to be temperature independent so that significant amounts of the alternative tautomers are probably essentially absent.

THE WESTPHALEN REARRANGEMENT

A. FISCHER, M. P. HARTSHORN, D. N. KIRK
and S. W. YOONG
Chemistry Department, University of Canterbury

Reaction of the steroid alcohol $3\beta,6\beta$-diacetoxycholestan-5α-ol (I) with perchloric or other strong acids in acetic anhydride results in acetylation of the hydroxyl group and the formation of the triacetate $3\beta,5\alpha,6\beta$-triacetoxycholestane. Other 6β-substituted cholestan-5α-ols are also acetylated in this way. However, when reacted with sulphuric acid in acetic anhydride, (I) and the related 6β-chloro, 6β-fluoro and 6β-methoxy alcohols give a rearranged product in which the C-10 methyl group has migrated to C-5, as well as other products, all of which can arise via the formation of a C-5 carbonium ion intermediate. The details of the mechanism of the sulphuric acid-catalysed reaction have been elucidated by kinetic studies.

SOME REACTIONS OF EPOXIDES OF 12-METHYLENE-STEROIDS

J. M. COXON, M. P. HARTSHORN and D. N. KIRK
Chemistry Department, University of Canterbury

The preparation and stereochemistry of the epoxides of 12-methylenetigogenin will be discussed in relation to the limited data available in the literature.[1] The rearrangement of each epoxide using boron trifluoride or perchloric acid as a catalyst will be described.

REFERENCE

(1) P. Bladon and W. McMeekin, *J. Chem. Soc.*, 1960, 2191.

SPECIFIC INTERACTIONS IN HYDROFLUOROCARBONS

I. D. WATSON and A. G. WILLIAMSON
Chemistry Department, University of Otago

Recent investigations by Konecny and Deal of the solubility of 1-hydroperfluoroheptane indicate that while it is similar in behaviour to perfluoroheptane in aliphatic and aromatic hydrocarbons, it has enhanced solubility in polar or oxygenated hydrocarbons such as nitrobenzene and acetone. N.M.R. measurements on mixtures of acetone and 1-hydrofluoroheptane show the existence of a medium strength hydrogen bond, and it is thought that this is the cause of the solubility increase.

This paper discusses the solubility of 1-hydroperfluoroheptane and perfluoroheptane in dioxan and cyclohexane, and re-examines the results of Konecny and Deal. Our analysis of these combined data suggests, in contrast to Konecny and Deal, that there is also an enhancement of solubility of 1-hydroperfluoroheptane in aromatic hydrocarbons. Evidence for a specific interaction which might cause this is found in N.M.R. measurements of 1-hydroperfluoroheptane, and also chloroform in benzene.

EFFECT OF PRESSURE ON VERY FAST REACTIONS

D. W. HOWARTH and W. S. METCALF
Chemistry Department, University of Canterbury

The technique used to mount windows which will withstand a pressure of up to 20,000 atmospheres enables measurements of the intensity of fluorescence of solutions of 2:10 diphenyl anthracene in toluene or in methylcyclohexane to be made over a range of high pressures. If oxygen or carbon tetrachloride is also present in the solution, the fluorescence is reduced by an amount that depends on the pressure and concentration of these quenching substances.

The theory of the quenching of fluorescence allows a prediction of the effect of pressure. The experiments to be described are a test of this theory. The theory survives.

THE CATALYTIC PROPERTIES OF PALLADIUM-NOBLE METAL ALLOY SYSTEMS

A. METCALFE
Chemistry Department, University of Canterbury

Kinetic parameters for the para-ortho hydrogen conversion reaction on catalysts of the palladium-silver alloy system have been determined. These are compared with results found for the analagous palladium-gold system.

Both sets of data are interpreted in terms of a model for the rate determining step of the reaction, which involves the promotion of electrons from sub-fermi levels up to the fermi-surface of the electronic conduction band of a catalyst.

OXYGEN EXCHANGE IN CONCENTRATED MINERAL ACIDS BETWEEN ACETIC ACID AND WATER

CHARMIAN J. O'CONNOR
Chemistry Department, University of Auckland

The observed rate of exchange of the oxygen atoms between acetic acid (labelled with ^{18}O) and water is found to increase in hydrochloric acid up to 35% acid (w : w), but to reach a maximum in sulphuric acid and perchloric acid at 55% H_2SO_4 and 57% $HClO_4$ respectively. Experiments in the presence of phosphoric acid indicate that the rate depends solely on the water activity and is independent of the acidity function of the medium. When the observed rates are corrected for the water activities of the solvents they all increase steadily but more rapidly than those calculated for first order dependence on hydrogen ion concentration. At any one value of hydrogen ion concentration, the rates decrease in the order

$$R_{H_2SO_4} > R_{HCl} > R_{HClO_4}$$

A mechanism can be postulated to account for these results.

CRYSTAL AND MOLECULAR STRUCTURES OF STRAINED MOLECULES

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

The crystal structure of a bromine derivative of an isofenchone obtained unexpectedly from a rearrangement reaction has been determined for the purpose of determining the stereochemistry. The crystal and molecular structure of this molecule will be discussed in relation to other terpene type molecules involving five and four membered rings, and the strain in such molecules will be examined in detail. Although apparently highly strained, it will be shown how the strain is distributed throughout such molecules so that no one point is particularly reactive.

SELENIUM AND THE BIOSYNTHESIS OF UBIQUINONE

K. R. MILLAR
Department of Agriculture, Wallaceville

Ubiquinone, or coenzyme Q as it is sometimes called, is 2,3 dimethoxy-5-methyl-1:4-benzoquinone, substituted at the 6 position with an isoprene side chain.

Ubiquinone occupies a key position in the electron transport chain. Other roles, including its participation in oxidative phosphorylation and in cholesterol biosynthesis, have been proposed.

Selenium and vitamin E have been shown to affect the tissue levels of ubiquinone and ubichromenol (a cyclic isomer of ubiquinone) in the rat. Vitamin E deficiency leads to a decrease in concentration of these two compounds.

The way selenium acts in animal nutrition is still unknown. The effect of selenium and selenium-containing amino-acids on the enzyme systems which are concerned with the biosynthesis of ubiquinone and cholesterol from known precursors is being studied.

Results obtained will be given and an outline of experimental work proposed will be discussed.

LIPID BIOSYNTHESIS IN HIGHER PLANTS

J. C. HAWKE
Department of Chemistry and Biochemistry,
*Massey University of Manawatu, Palmerston North**

The characteristics of the lipid synthesizing activity of barley seedling tissue, which appears to be representative of the Graminae family, have been examined. A novel feature of these synthesizing systems is their ability to synthesize appreciable amounts of saturated fatty acids with 20 or more carbon atoms when acetate-1-^{14}C is used as substrate. Most of these fatty acids are incorporated into neutral lipids, and a few into polar lipids. Degradation of the labelled fatty acids shows that synthesis of the long chain fatty acids occurs by chain elongation of palmitate by a *de novo* pathway, viz:

$$16{:}0 \xrightarrow{C_2} 18{:}0 \xrightarrow{C_2} 20{:}0 \xrightarrow{C_2} 22{:}0 \xrightarrow{C_2} 24{:}0 \xrightarrow{C_2} 26{:}0$$

Fatty acids and OH-acid substrates of intermediate chain length were utilized for the synthesis of fatty acids up to and including C_{18} compounds. The biosynthesis of oleate from these substrates and the characteristics of cell-free systems will be discussed.

---

* This work was carried out at the Department of Biochemistry and Biophysics, University of California, Davis, and will be reported elsewhere in full, in co-authorship with Dr. P. K. Stumpf.

RESEARCHES ON BRANCHED CHAIN FATTY ACIDS

F. B. SHORLAND and R. P. HANSEN
Fats Research Division, Wellington

Branched-chain fatty acids which earlier had been thought to occur only in wool grease, the preen glands of ducks and geese, certain bacteria and the oils of the dolphin, were found by workers in the Fats Research Division to be present in ruminant fats and tall oil. In ruminants these acids consist mainly of odd and even-numbered *iso* acids ranging from C_{13} to C_{18} and odd-numbered *anteiso* acids from C_{13} to C_{17}. The origin of these *iso* and *anteiso* acids has been shown by overseas investigators to be in the micro-organisms of the rumen. As judged by experiments with the C_{15} and C_{17} *anteiso* members of the series, these acids when fed to anmials are deposited in the fatty depots and stored, and even after they have been withdrawn from the diet they remain in the body for some time. In 1951 this laboratory discovered a C_{20} multibranched fatty acid in butterfat. It was not conclusively identified until 10 years later when Swedish, followed by Dutch workers, independently employed mass spectrometry to establish its chemical constitution as 3,7,11,15-tetramethylhexadecanoic acid (phytanic acid). Subsequently the Fats Research Division has isolated and identified it from ox fat and sheep fat. It has also been found in varying proportions in ox plasma. The chemical structure of this acid is similar to that of phytol, from which it may originate. Particular interest in this acid has been aroused through Klenk and Kahlke and co-workers in Germany finding it in large amounts in the tissues, blood and urine of humans afflicted with the rare familial disease named Refsum's syndrome *(Heredopathia atactia polyneuritiformis)*. Investigations in the Fats Research Division on tissues kindly made available by Dr. W. S. Alexander, Pathologist, Lower Hutt, have confirmed these findings. It thus appears that the presence of substantial amounts of phytanic acid in the human body is diagnostic of the disease. Rat-feeding experiments carried out collaboratively between the Medical Research Unit of the Wellington Hospital and this laboratory have now shown that this acid is rapidly metabolised, and is stored only when fed in excessive amounts. The branched-chain fatty acids found in ruminants have not been observed to impart any detrimental effect except when fed in amounts vastly in excess of those present in normal diets.

A NORMAL CO-ORDINATE ANALYSIS OF THIOCARBAZIDE

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The infra-red spectra of thiocarbazide and thiocarbazide-d_6 have been obtained in the range between 4000 and 300 cm^{-1}.

A normal co-ordinate analysis of the in-plane molecular vibrations of thiocarbazide has been carried out using a Urey-Bradley force field. This has clarified the nature of the normal vibrations.

The development of an Algol programme to solve the secular equation and refine the force constants will also be discussed.

RELATIONSHIP BETWEEN THE QUADRUPOLE SPLITTING AND THE MAGNETIC SUSCEPTIBILITY OF IRON COMPLEXES

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and J. F. DUNCAN
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Recently we have predicted the quadrupole splitting for all iron compounds and calculated the magnetic susceptibility of Fe^{2+} and Fe^{3+} complexes, when the iron atom is in a crystal field of octahedral symmetry and tetragonal symmetry. The results have enabled us to relate the electric field gradient at the iron nucleus and the magnetic moment of high spin ferrous and low spin ferric compounds. This work has produced some very interesting results about the structure of iron complexes.

MOSSBAUER STUDIES OF SINGLE CRYSTALS

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To support our theoretical work in interpreting e.s.r., n.m.r., Mössbauer spectra and magnetic susceptibility measurements, we have investigated single crystals of $FeSO_4 7H_2O$, $K_3Fe(CN)_6$ and $K_3Fe(CN)_5NO2H_2O$. The results show that information can be obtained about the symmetry of the molecule and the direction of low symmetry distortion in the crystal lattice.

SPIN POLARISATION AND HYPERCONJUGATION IN ORGANIC FRAGMENTS

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In this paper we shall discuss the molecular orbital treatment of calculating spin-polarisation and hyperconjugation in molecules. We have determined a general expression for spin-polarisation along any organic fragment. The theory will be supported by experimental results from e.s.r. and n.m.r.

THE ACTION OF AMMONIA ON CARBOHYDRATES AND RELATED COMPOUNDS

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Carbohydrates undergo degradation in ammoniacal solution in a similar fashion to that in solutions of alkalies. Under ammoniacal conditions however, any α-dicarbonyl products condense with ammonia to form imidazoles. From a study of the structures of these imidazoles it is possible to deduce some of the products of alkaline degradation of carbohydrates. Attention has been focussed on α-dicarbonyl compounds which are suspected to be formed in alkaline solutions of reducing sugars. α-Hydroxycarbonyl compounds have also been found to produce imidazoles under ammoniacal conditions, suggesting that oxidation to the corresponding dicarbonyl compound is occurring. The isolation of high yields of 4(or 5)-methyl- and 2,4(or 2,5)-dimethylimidazole from a pyruvaldehyde-ammonia mixture indicates that mechanisms of imidazole formation are deficient if they do not allow for fission of the bond linking the carbonyl functions of pyruvaldehyde. A tentative reaction scheme is advanced to account for the breakdown of a hexose in ammoniacal solution.

DEHYDRATION STUDIES ON NERVE MYELIN

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It has been shown that changes in the periodicity of myelin layering occur in nerve segments during preparation of the tissue for electron microscopy. These changes are thought to be due to partial removal of water from the system by fixatives and can be followed by X-ray diffraction techniques.

Changes in structure within the myelin sheath of fresh nerve can also be brought about by allowing nerve tissue to dehydrate in air. Such modifications are considered to result from the removal of water from the lipo-protein system. X-ray diffraction studies suggest that these are far more complex modifications than those occuring during fixation for microscopy.

Results suggest that the original single-phase lipo-protein system present in fresh nerve myelin is extensively modified. Two separate phases become apparent after dehydration. One phase is thought to be derived from a contracted form of the original layering. The other phase arises from lipid components which are considered to have separated from the original lipo-protein on the loss of water.

This work indicates the importance of water in the normal membrane and suggests that the myelin lipo-protein system consists of a complex lipid-protein unit and a more labile lipid component. A study of the composition of the labile lipid should increase our knowledge of the structure of the myelin sheath and of the constituents of the cell membrane.

THE STRUCTURE OF THE CELL WALLS OF SOME THERMOPHILIC BACILLI

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Quantitative chemical analyses of isolated and purified cell walls from two species of facultative thermophilic bacilli, grown at 37° and 55°, have been carried out to determine the possible effects of growth temperature on wall composition. The major macromolecular constituents of these walls appear to be mucopeptide and unusual teichoic acids. Investigations of the structure of the latter, involving chemical and enzymatic degradations, will be described.

INSECT DETOXICATION ENZYMES UTILIZING GLUTATHIONE

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Glutathione is used in the enzymic formation of mercapturic acids. This is a common mechanism of detoxication of chlorinated hydrocarbons such as 3,4-dichloronitrobenzene. The initial step gives rise to a glutathione conjugate. It seems that there are three distinct enzymes involved, an aryl transferase, an alkyl transferase, and one which catalyzes conjugation with epoxides only (such as 2,3-epoxypropyl phenyl ether). We are particularly concerned with the glutathione-S-aryl transferase, for which a convenient assay has been developed using 2,4-dinitrochlorobenzene.

Comparisons have been made of the properties of the enzyme found in several different species in an endeavour to relate the detoxication activity of the grass-grub to that of other more studied species such as the housefly and rat liver. Activation energies, pH v. activity curves, behaviour on Sephadex and DEAE-cellulose columns and Michaelis constants are similar in all of them. For example, the activation energy of the grass-grub and housefly enzymes is 13.5 K cal/mole of substrate, while for grass-grub, housefly and sheep-liver the enzyme is always eluted at the same point as haemoglobin—120 ml. after loading on to a 120 × 1.5 cm.^{2} column of Sephadex G-100.

CHEMICAL EQUILIBRIA IN NATURAL HYDROTHERMAL SYSTEMS

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Natural hydrothermal solutions vary widely in their solute concentration and composition. A widely held theory is that the unusual element make-up of hot spring waters is derived from "magmatic" fluids rising from crystallising rock melt beneath the thermal areas. Recent laboratory experiments on rock/water interaction at temperatures of 150-600°C and pressures of up to 2000 atmospheres have given further information on the extraction and equilibrium processes that must occur in natural hot water systems. It appears that a "magmatic" fluid is not unique in composition, and that the compositions of many thermal waters could be explained simply by reference to the underground rock compositions and the temperature and pressure at which equilibrium with solution occurs.

The concentrations of most of the individual elements in thermal waters depend on one or more of several factors—element availability in the local rock, solubility of a secondary mineral, cation interchange, oxygen partial pressure, and interaction between solutes, including complexing and ionic strength effects. A comparison will be made between the concentrations of various elements found in natural hot solutions and those expected from known mineralogical and chemical equilibria at the temperatures.

The chemical processes which occur in volcanic hot spring systems are similar in many ways to those which occur during the formation of some types of metal sulphide ore bodies. As heavy metal sulphides are insoluble even in high temperature water, the mechanism of their transport in solution is of considerable interest. The likely composition of ore-bearing solutions is being outlined by high-temperature solution equilibrium studies, evidence from natural hydrothermal systems, and the compositions of fluid inclusions from crystals in mineralized zones. Examples are given of present day hydrothermal areas which show the trends in water composition which enable natural hot solutions to hold increasing equilibrium amounts of heavy metals in solution.

REGIONAL GEOCHEMISTRY OF THERMAL WATERS IN NEW ZEALAND

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Hot springs occur in both the North and South Islands of New Zealand. The temperature of the water discharged from the springs varies from a few degrees above ambient up to the boiling point for local atmospheric pressure. Most of the high temperature water (80-100°C) is discharged from springs within the North Island Volcanic Zone, where deep drillholes have revealed water temperatures of between 200 and 300°C at depths of 1000 to 4000 feet. Lower temperature springs (20-80°C) are found in the South Island, mainly along the Alpine Fault, and at many different localities in the northern half of the North Island.

There are four geological environments in New Zealand where thermal waters occur; (1) areas of active volcanism, e.g., White Island; (2) areas of recent volcanism, e.g., Taupo Volcanic Zone; (3) areas of old volcanism, e.g., Ngawha; (4) non-volcanic areas. Within the different geological areas some classification of the waters may be made by means of their chemical composition, although there are no distinct chemical boundaries between compositions in the various areas.

The compositions of natural hot waters are controlled by a number of factors, the most important of which are; the presence or absence of "magmatic" fluids, local geology (including rock type and chemical composition), water temperature, availability and composition of surface water, pH of the waters, rock permeability (determining rate of water turnover) and the extent to which the rocks have been hydrothermally altered.

In active volcanic areas the hot waters are mainly surface waters which have been heated by low-pressure, high-temperature magmatic steam. Water compositions are controlled by the composition of the steam and leaching of surface rocks. In recent volcanic areas there are a number of characteristic water types which are identified by their chemical composition, e.g., neutral chloride, acid-sulphate-chloride, and acid sulphate waters. The chemical similarity between some of these waters over large areas is demonstrated by the constancy in ratios of certain molecular and atomic constituents, e.g., Cl/B and Na/Li.

The composition of waters in areas of old volcanism and sedimentary rocks varies considerably. For example, at Morere the waters originate from Tertiary marine sediments and the mineral content of the waters is high. The Tarawera spring located close to the margin of rhyolitic rocks of the Taupo Volcanic Zone is associated with greywacke. Compared with Morere its mineral content is low. A similar comparison can be made between the chemical compositions of the Ngawha springs in North Auckland where the waters are heated by old basalt flows, and the Te Aroha springs which occur in andesites of Tertiary and Pleistocene age.

STUDIES OF THE COMPOSITION OF GASES ASSOCIATED WITH STEAM FROM DRILLHOLES AT WAIRAKEI, NEW ZEALAND

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Previous work indicates that the Wairakei hydrothermal system is fed at depths of more than 3000 feet by water at a temperature of 250-260°C. Carbon dioxide and hydrogen sulphide show differing solubility behaviour. This is used to investigate the steam separation processes. The pressures at Wairakei are such that the inflowing hot water at depth often loses a few percent of steam into the country before being discharged at the drillholes. The gas concentrations in the steam separating from and maintaining equilibrium with the water on release of pressure have been calculated and results indicate that the first few percent of steam are very rich in carbon dioxide and hydrogen sulphide, the water being quickly depleted of these gases. At all temperatures hydrogen sulphide is more soluble in the water phase than carbon dioxide. The steam therefore has a higher CO_2/H_2S ratio than in the original liquid. Correspondingly the CO_2/H_2S ratio in the residual water is lower than that in the original liquid. The ratio decreases with increasing steam separation.

When aquifer pressures are reduced, as for example when water levels fall, steam separation from water of a given temperature can occur at lower levels. Increased steam separation can occur and the enthalpy, gas content, and CO_2/H_2S ratio of the residual liquid will decrease. Changes of this nature which could be related to a single one stage separation mechanism were noted in some discharges between 1959 and 1961. Since then decreases have become more general. The low CO_2/H_2S ratios for the enthalpy now occurring in the discharges of many drillholes cannot be explained by a distinct one stage loss of steam. The values of CO_2/H_2S ratios for "multi-stage" steam separations have been calculated. In these the early flashed steam escapes from the water phase and the final gas-in-steam/gas-in-water equilibrium is governed by secondary flashed steam and not by the total steam flashed. This results in a much lower CO_2/H_2S ratio in the residual water. E.g., for an original CO_2/H_2S ratio of 30 in the hot water, one 4% steam separation reduces the ratio to 15.5; sixteen 0.25% separation steps reduce the CO_2/H_2S ratio to 6.4. It is suggested that in many cases "multi-stage" separations whereby the water gradually loses steam to its surroundings agree better with predictions from solubility data than a single one stage separation.

CHEMISTRY IN THE ANTARCTIC

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The use of chemical ideas and chemical methods to solve some of the scientific problems in Antarctica will be discussed. These include the use of chemical diffusion and accumulation of salts as a method of dating, the use of chemical techniques for working out ice budgets of glaciers, and for measuring ablation rates. The use of these techniques lead the author to the conclusion that the Ross Dependency region of the Antarctic was not extensively glaciated during the last ice age. This in turn leads to a new theory for the origin of Ice Ages.

COPPER ION CATALYSIS OF THE RACEMISATION OF THE TRIS-OXALATO CHROMIUM-III ANION

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The racemisation of the tris-oxalato chromium-III anion is catalysed efficiently by divalent transition metal ions, the effect increasing through the series Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, and falling again to Zn^{2+}. This order is to be expected from the Irving-Williams series and suggests the formation of a "metallated" complex as a reaction intermediate. The expected first order dependence on copper ion concentration is seen at lower copper ion concentrations but at higher concentrations the apparent order in copper decreases quite sharply although it is still greater than zero.

This kinetic pattern may be understood in terms of the rapid formation of mono-copperated and di-copperated species, the former of which racemises rapidly while the racemisation path through the latter is less efficient.

The reaction is also acid catalysed and there appears to be competition rather than addition between the Cu^{2+} and H^+ when both are present in appreciable concentrations.

NICKEL-ANION INTERACTIONS IN SOME NICKEL TETRAMINE SALTS

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Compounds of type NiN_4X_2 (where N_4 represents four monodentate amines, e.g. ammonia, or two bidentate amines, e.g. ethylenediamine or one tetradentate amine, e.g. triethylenetetramine) usually have structures in which the single charge anions, X^-, occupy two of the octahedral co-ordination sites about the nickel (II) ion. The **trans** configuration with minimum electrostatic repulsion between the anions would be expected. It has been observed for most such compounds for which X-ray crystallographic data is available. However, $Ni(en)_2Cl_2$ has been found to have a second type of structure, cis with chloro bridging, $[(en)_2NiCl_2Ni(en)_2]Cl_2$. Compounds with anions which can act as chelate co-ordinating agents sometimes adopt a third type of structure $[NiN_4X]X$ with one chelated and one "ionic" anion. For the last two types the non-co-ordinated anion can frequently be replaced by some other anion, giving compounds of the type $[N_4NiX_2NiN_4]Y_2$ and $[NiN'_4X]Y$ respectively. Compounds of the second type are formed with thiocyanate as well as halide ions, and compounds of the third type with anions such as nitrate, acetate and borohydride.

Methods of distinguishing the three types of structures, based on the infrared spectra of the anion and the visible spectra of the nickel (II) ion will be discussed.

STRUCTURE AND BONDING IN TRINUCLEAR RHENIUM (III) HALIDES

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It was discovered three years ago that the anion of composition $ReCl_4$ is trinuclear with a triangle of tightly bonded Re atoms. Since then work at the University of Canterbury, by F. A. Cotton's group at M.I.T. and by Colton and Martin at the University of Melbourne has made it possible to place chemical, structural and bonding aspects of these Re(III) compounds on a firmer basis.

At M.I.T. X-ray structural studies have been completed on $ReCl_3$ itself and on salts containing $Re_3X_9L_3$ (where L is a neutral ligand) and Re_3Br_9 as discrete groups. At Canterbury X-ray structure analyses of salts of $Re_3Cl_{11}^{2-}$ and $Re_3Br_{11}^{2-}$ have revealed some significant variations in the detailed configurations of the anions (in particular the non-equality of Re-Re lengths within the triangle). U.V.-visible spectral studies and radio-chlorine exchange studies have been made in attempt to establish the basic entity in solution. Colton and Martin have made detailed magnetic studies and have deduced that Re(IV) chloride should also possess a trinuclear structure.

We propose a bonding scheme in which a σ-bond framework is combined with π molecular orbitals encompassing the Re_3 triangle which can explain the outstanding structural features.

A COMPOUND CONTAINING BOTH 5 AND 6 CO-ORDINATE TIN (IV)

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Two unusual discrete ions $[SnMe_2Cl_3]^-$ and $[SnMe_2Cl\ \text{terpyridyl}]^+$ make up the compound $Sn_2Me_4Cl_4$ terpyridyl, which crystallizes in the spacegroup $\overline{P1}$.

The anion is a near perfect trigonal bipyramid with two methyl groups and a chlorine atom in the equatorial plane. Bonds to the two apical chlorine atoms are 0.20 Å longer than the bond to the equatorial chlorine atom.

The cation is a distorted octahedron with the chlorine atom trans to the middle pyridine ring. This chlorine atom is linked to the tin by an unusually long bond (2.64 Å).

This structure and terpyridyl geometry will be discussed.

CHEMICAL AND ANALYTICAL APPLICATIONS OF DISCONTINUOUS COUNTERCURRENT SOLVENT EXTRACTION

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Although discontinuous countercurrent liquid solvent extraction has been used extensively in the past for the separation and purification of organic and biological compounds its applications in inorganic chemistry have been relatively few.

When using a Craig-type countercurrent extraction apparatus it is possible to obtain an expression relating the number of the tube containing the maximum concentration of a solute and its distribution coefficient in that solvent system. From this it is possible to obtain an expression relating the number of the tube containing the maximum concentration of a solute and its percent extraction. The combination of a Craig-type countercurrent extraction apparatus with an emission spectrograph gives a very rapid method for determining the extraction characteristics of a large number of inorganic ions simultaneously. By this means the extraction of the elements Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Sb, In, La, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, and Bi from HCl into methyl isobutyl ketone has been studied as a function of acid concentration.

From the results obtained it is possible to separate Fe from the majority of the elements present in a cyclohexanone extract of a rock solution by partition on a Craig countercurrent extraction apparatus.

Discontinuous countercurrent extraction has also been used to enrich trace elements in sea water up to spectrographic detection limits for their quantitative determination.

THE BIOGEOCHEMISTRY OF TRACE ELEMENT UPTAKE BY MARINE ORGANISMS

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Spectrographic determination of Ag, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, V and Zn were carried out on three species of New Zealand bivalves: *Ostrea sinuata, Pecten novaezelandiae* and *Mytilus edulis.* Analyses were performed on the sediment, on the whole animals and on the individual dissected organs. All the elements concerned showed some degree of enrichment in the shellfish compared with the marine environment. The results are discussed in the light of modern chemical theory and conclusions have been made concerning the geochemical and biochemical processes involved in trace element uptake by the biosphere.

SOLUBILITY OF ORPIMENT IN SULFIDE SOLUTIONS TO 200°C AND 1500 BARS

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Orpiment (crystalline As_2S_3) is an unusual mineral of restricted distribution which occurs in a few hot springs and in some shallow seated hydrothermal ore deposits closely associated with realgar, stibnite, cinnabar, gold, and the gangue minerals quartz and calcite. A field and petrographic investigation of several deposits containing orpiment and realgar in the western United States was done to ascertain from the field relations, mineral associations and the sequences of deposition of orpiment and associated minerals, the probable limits of the physico-chemical conditions involved in the deposition of orpiment. Conclusions are: (1) orpiment is commonly part of the main sequence of epithermal ore deposition and is not always formed by supergene alteration of pre-existing minerals; (2) the temperatures of deposition were probably above 100°C and certainly below 300°C; (3) the pressures at the time of deposition were probably in the lower half of the range 1 to 100 bars; (4) the solutions from which orpiment was deposited were probably dilute aqueous sulfide solutions.

A laboratory investigation was carried out to ascertain which processes lead to the deposition of orpiment, by determining the solubility of orpiment in aqueous solutions containing from 0.55

to 3.43 weight percent of sodium sulfide, at temperatures ranging from 25° to 200°C, and at pressures ranging from 100 to 1500 bars. Conclusions are: (1) change in pressure is unimportant; (2) dilution and evaporation are unimportant; (3) decreasing temperature is the major physical control. The experiments indicate that reactions reducing sulfide ion concentration of the transporting solutions, such as acidification, oxidation, or reaction with wall rocks, are also probably involved.

COMPOSITION OF GASES AND LIQUIDS WITHIN INCLUSIONS OF MINERALS IN SOME IGNEOUS AND METAMORPHIC ROCKS

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The investigation of fluid inclusions is the only direct way to obtain information about gases and liquids present during the formation of a rock. Gases and liquids are trapped as bubbles of mainly microscopic and submicroscopic size during the crystallisation of the rocks (primary inclusions), and at any subsequent time by the healing of cracks in the rock (secondary inclusions). The analysis of the contents of such inclusions can be done by two methods.

1. Microscopical studies including the measurement of optical data of the inclusion contents, and the observation of their phase transformations with heating and cooling.
2. Extraction of the gas and liquid phases from the minerals for chemical analysis.

The first method requires inclusions of relatively large dimensions. These are extremely rare in most minerals.

The second method, offering broader application, will be discussed in a way that shows the possible contaminations in the different extraction processes. Results obtained by extraction in a vacuum ball mill will be compared with those obtained by another common method—the degassing of the mineral crystals at high temperatures in vacuo.

Vacuum ball milling is considered by the author to be the more appropriate method, and was used with a great number of minerals separated from granitic, pegmatitic, and metamorphic rocks. The geochemical significance of the results will be discussed.

PREPARATION OF MOLECULAR SIEVES

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Aluminium silicates have a variety of structures, e.g. discrete ions, chains, rings, bands, sheets and three-dimensional frameworks. Many species have been synthesised under hydrothermal conditions at high temperatures and pressures. Of all aluminium silicates only the species known as molecular sieves have been prepared from aqueous solution at atmospheric pressure and temperatures as low as 100°C. Molecular sieves are hydrated framework aluminium silicates and usually belong to the class of minerals known as zeolites. A few are felspathoid minerals.

Little attention has been given to the low-temperature synthesis of zeolites and felspathoids with the exception of those species which are commercially produced. All of the available results indicate that zeolites and related substances can be prepared from aqueous solutions containing excess alkali at 100°C. The starting composition often bears little relationship to the composition of the products. In some cases the reported syntheses are not entirely reproducible.

Studies of the kinetics of formation of basic sodalite (a synthetic felspathoid) and K-G (a synthetic chabazite) from aqueous gels have been attempted. The formation of sodalite is complex. Linde Sieve A first appears and decomposes to form either a phillipsite phase or basic sodalite. K-G forms relatively rapidly after an initial induction period. The growth of crystalline phases was followed by measuring the intensities of X-ray reflections. The effect of variables such as composition (water, alkali, $Al_2O_3 : SiO_2$ ratio) and temperature have been investigated in an attempt to find reproducible synthesis conditions for pure samples of each phase.

BISMUTH ELECTRODE REACTIONS

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The electrode formed by bismuth metal in contact with various aqueous solutions has been studied by two experimental methods. The aim was to learn the molecular mechanism of the process taking place and the nature of the oxides or other phases which appear at the interface.

In the *galvanostatic* method a constant current was passed through the electrode and the steady state potential was observed with respect to a reference electrode. In aerated solutions oxygen will oxidise the metal surface and this can be opposed by a constant cathodic current in the range 0 to 100 microamp./cm^2 so that a steady state is achieved after a few hours. Thus in chloride solutions a layer of BiOCl of average thickness less than 300 Å is formed. Its presence can be deduced from the dependence of the electrode potential on pH and chloride concentration according to the equation $BiOCl + 2H^+ + 3e^- = Bi + H_2O + Cl^-$.

In the *potentiostatic* method a constant potential was applied to the electrode and the current as the dependent variable, observed. The anodic polarisation curves of bismuth have been determined by measuring the current as a function of increasing positive potential. Regions of active bismuth dissolution followed by passivation were observed and gave a sharp peak in the polarisation curve. The effect of pH and ligands has been studied and a simple mechanism involving protection of the surface by an oxide layer explains the results reasonably well.

PHOTOMETRIC OBSERVATIONS ON REACTIONS IN HYDROGEN FLAMES

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Many high-temperature processes and equilibria can be studied by using the hot, burnt gases of an $H_2/N_2/O_2$ flame as a reaction vessel. In the present work equilibria involving the formation of metal halides and hydroxides, and chemiluminescent processes involving IO, BrO, CuH and metal atoms, have been studied at temperatures between 1400° and 2600°K by measuring the intensity of light emission from a series of flames into which traces of various additives had been introduced.

PULPING STUDIES ON SILVER BEECHWOOD

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Recent work by the New Zealand Forest Service has shown that there are considerable supplies of accessible and marketable beech woods in the Nelson area, and it has been suggested that it might be possible to use these beeches to supplement *Pinus radiata* as a raw material for the manufacture of rayon grade dissolving pulp by the prehydrolysis-sulphate process. Pilot-plant pulping studies at the Chemistry Division, D.S.I.R., show that good quality rayon pulp can be readily prepared from silver beechwood *(Nothofagus menziesii)* in yield and quality comparable to *Pinus radiata* rayon pulps. Silver beech has some technical advantages over *Pinus radiata*. For example, the sulphate digestion time required to produce pulps with the same permanganate number and pentosan content is of the order of 30% less for silver beech than for the pine, and the quantity of active alkali required is about 50% lower. Further, because of the milder sulphate pulping conditions it is possible to prepare unbleached pulps from silver beech which have a much higher intrinsic viscosity than those from *Pinus radiata,* although the actual viscosity level desired can be readily achieved by modifications to the prehydrolysis stage. The specific effect of the first stage of a prehydrolysis-sulphate digestion on the hemicellulose fraction of wood means that the high pentosan content of silver beech is in no way detrimental to the preparation of high alphacellulose pulps, and the pentosan content of the pulps can be readily reduced to a very low level. Preliminary experiments on red beech wood *(Nothofagus fusca)* indicate that this wood will have similar pulping characteristics to silver beech in the prehydrolysis kraft process.

It is thus technically feasible to use the native beeches from the Nelson Conservancy as an additional or alternative source of raw materials for the preparation of rayon grade dissolving pulp.

ROT-PROOFING OF CELLULOSE MATERIALS

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Methods will be described that enable cellulose materials to be successfully preserved with conventional aqueous copper-chrome-arsenate timber treating solutions. The effectiveness of treatments will be compared with conventional rot-proofing chemicals under soil burial and accelerated weathering conditions. The method of fixation of the insoluble chemicals and the form of the chemicals in the treated material will be discussed. Some practical experiments conducted with the treated materials will be considered and the application of this knowledge to the wider field of timber preservation will be described.

LUBRICATING GREASES

A. A. TURNER
Shell Oil New Zealand Limited, Christchurch

A lubricating grease has been described as a combination of petroleum products and soaps suitable for lubrication. A review of the lubricating grease field is given which indicates that any suitable definition of these products must include reference to the fact that liquids other than petroleum oils, in particular synthetics, can be used and that thickeners can include such diverse materials as silica gel, metal glycerides and organic dyes.

Greases are basically three-component systems. The subject will be treated under the following headings:

(a) Thickener. (b) Vehicle or lubricating medium.
(c) Additives.

Reference will be made to the conventional greases which are composed of mineral oil and soap. It will be shown that the desired properties can be obtained by judicious choice of components such as fatty material and alkali, and how the manufacturing process used influences the final product. The use of synthetics compared with conventional ingredients will be discussed and an indication given of their future possibilities.

THE UNIVERSITY OF MELBOURNE

POST-DOCTORAL RESEARCH FELLOWSHIP IN INORGANIC CHEMISTRY

Applications are invited for appointment to a Post-doctoral Research Fellowship in the Department of Inorganic Chemistry. The position has the status of a University Lecturer and is renewable annually with a maximum tenure of three years. The salary range is £1,850-£2,600 per annum and commencing salary will be fixed according to qualifications and experience. Reasonable travel and removal expenses will also be provided.

The research activities of the Department are currently focussed on the chemistry of transition metal compounds. A wide range of modern instruments is available including several high resolution infra-red spectrophotometers (4000-200 cm^{-1}); visible and ultra-violet-recording spectrophotometers; magnetic susceptibility balance and cryostat (77-400°K); Varian HR-60 NMR spectrometer, double focus high resolution MS-9 mass spectrometer; recording optical rotary dispersion spectrophotometer (including circular dichroism); Philips 1010 X-ray generator, diffractometer and associated spectrographic equipment.

Specific inquiries should be made with Professor R. L. Martin, Department of Inorganic Chemistry. Applications in duplicate and giving full details of qualifications and experience should be sent to the Registrar, University of Melbourne, Parkville, N.2., Victoria, Australia, by 31st August, 1965.

F. H. JOHNSTON, Registrar.

Reprinted by courtesy of R.A.C.I., from the Proceedings of the Royal Australian Chemical Institute, September, 1964.

A NEW ION CHARGE SYMBOLISM IN MASS SPECTROMETRY

J. S. SHANNON

Division of Coal Research, C.S.I.R.O., New South Wales, Australia

The recent flow of papers into the chemical press dealing with the application of mass spectrometry has revealed an urgent need for the general adoption of appropriate symbolisms in the formulation of ion structures and electron shifts. This paper briefly reviews the current situation and proposes a new ion charge symbolism.

Structure elucidation of chemical compounds by mass spectrometry requires the rationalization of their mass spectra in terms of ion structures and ion reactions. When a compound is first admitted into the mass spectrometer, molecular ions are formed due to the emission of single electrons from the molecules of the compound.

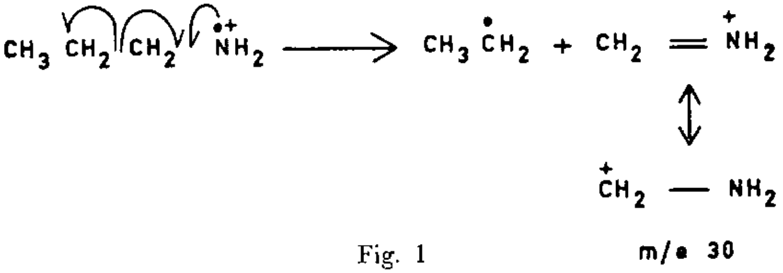


Fig. 1

These odd-electron molecular ions may then dissociate in one of two ways; first, by the elimination of a free radical (cf. Fig. 1) to produce an even-electron ion (carbonium, oxonium, nitronium, etc.); or secondly, by the elimination of a neutral molecule (Fig. 2) to produce an odd-electron ion (radical ion). Thus peaks in a mass spectrum may be due to either or both of two different types of ions.[5]

In order to predict and illustrate the corresponding ion structurs and reactions correctly, it is necessary to differentiate both between one- and two-electron shifts and also between odd- and even-electron ions. Recently, the frequent failure to draw the

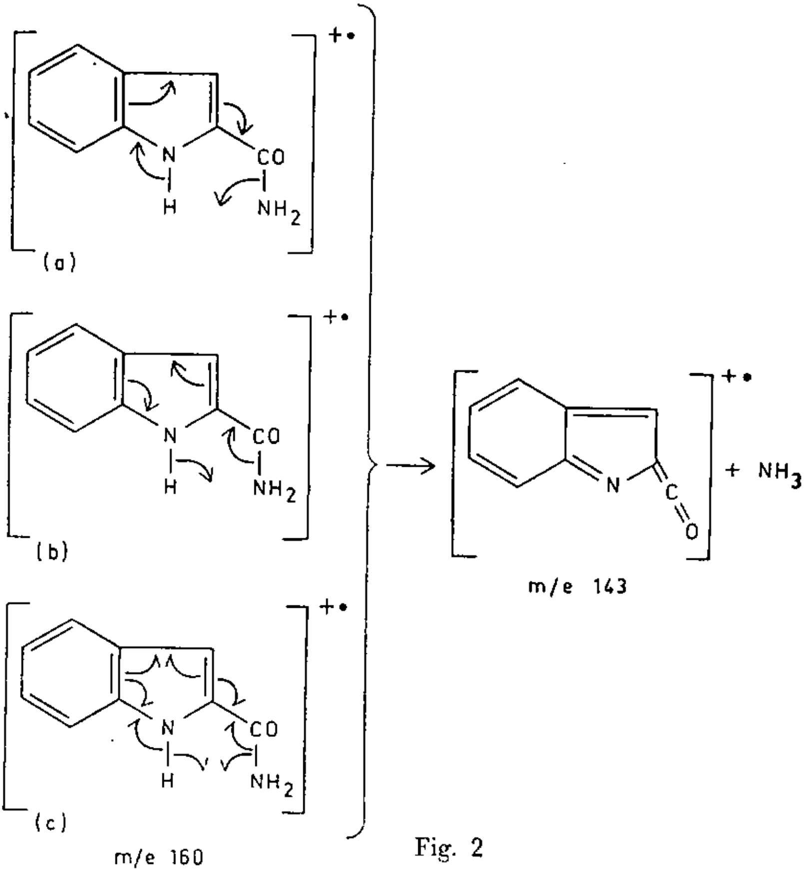


Fig. 2

first of these distinctions has been discussed and a suitable remedy proposed.[1] For example, one- and two-electron shifts may be symbolized by the arrows shown in Fig. 3.*

ONE-ELECTRON SHIFT TWO-ELECTRON SHIFT

Fig. 3

For drawing the second necessary distinction, namely that between odd-electron and even-electron ions, a symbolism which has been used by the present author[3] and independently by Silverstein and Bassler[4], is now proposed for general adoption.†

In most current and recent publications a + sign has been used in the formulation of both odd- and even-electron ions. For example,

(a) (b)

Fig. 4

the benzene (molecular) ion (a) and the tropylium (carbonium) ion (b) are commonly depicted as in Fig. 4 despite their fundamental difference. The proposed new symbolism retains the + sign for even-electron ions but introduces a $\underset{\cdot}{+}$ sign for odd-electron ions (see, for example, Tables 1 and 2).‡

With the new symbolism it is possible to differentiate between odd- and even-electron ions when the common abbreviation, M, is used. Thus M^{+} has been used for the molecular ion, and $(M\text{-}28)^{+}$ or $(M\text{-}CO)^{+}$ for the ion due to the elimination of a molecule of carbon monoxide from a molecular ion. These symbols now become $M^{+\cdot}$, and $(M\text{-}28)^{+\cdot}$, and $(M\text{-}CO)^{+\cdot}$ respectively. With even-electron ions the + sign is retained, e.g. $(M\text{-}CH_3)^{+}$ or $(M\text{-}15)^{+}$. The symbolism may be used to distinguish also the two types of doubly charged ions—first, for example, the type formed by the loss of one electron from an odd-electron ion:

$$M^{+\cdot} \rightarrow M^{\pm +} + e$$

and secondly, the odd-electron type formed by the loss of an electron from an even-electron ion. For example:

$$(M\text{-}15)^{+} \rightarrow (M\text{-}15)^{++\cdot} + e$$

Further, the symbolism may be used when illustrating ion transitions, e.g., those involved in the dissociation of the phenol molecular ion. Hitherto these have been written:

$$94^{+} \rightarrow 66^{+} + 28$$
$$66^{+} \rightarrow 65^{+} + 1$$

It is now proposed that they be written:

$$94^{+\cdot} \rightarrow 66^{+\cdot} + 28$$
$$66^{+\cdot} \rightarrow 65^{+} + 1.$$

The corresponding ion reactions are as shown in Fig. 5.

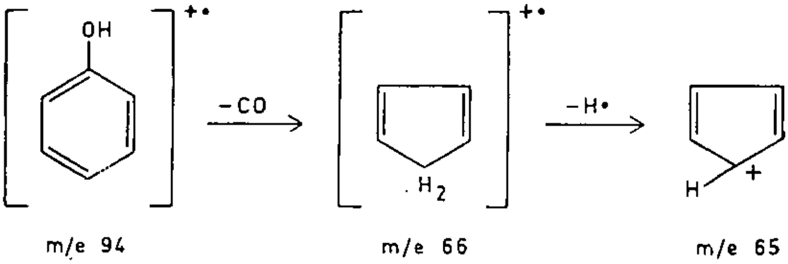


Fig. 5

With the advent of high-resolution mass spectrometry there will no longer be any doubt as to the molecular formulae of ions formed even in the most complex reactions, or whether the ions are of the odd- or even-electron type. Consequently there will be no difficulty in general usage of the $\underset{\cdot}{+}$ symbolism.

Examples are now given of its application for illustrating some ion reactions.

First, we have the reaction of molecular ions in which the location of the charge is uncertain, as, for example, in Fig. 2.§

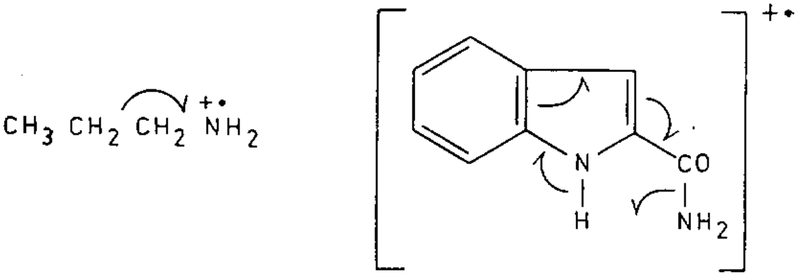
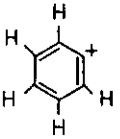


Fig. 6

Since this reaction and other similar hydrogen-transfer reactions proceed via cyclic transition states in which there may be some electron delocalization, it is uncertain which of the processes (a), (b), and (c), depicting the transfer of a proton, hydride

Table 1.—Even-electron Ions

Ions from aliphatic compounds	$CH_3CH_2CH_2\overset{+}{C}H_2$ $CH_3CH_2\overset{+}{C}H\ CH_3$
Allylic ions	$CH_3CH{=}CH{-}\overset{+}{C}H_2$
Aromatic ions	Tropylium ion (see (b) in Fig. 2)
Phenyl ions	

ion, and hydrogen atom respectively, best approximates to the true reaction. In practice, other things being equal, it is sufficient to show only one of these possible processes.

Secondly the $\underset{\bullet}{+}$ symbolism may be used with molecular ions containing hetero- or metal-atoms, where the charge may be presumed to be localized (see, for instance, Fig. 1 and examples quoted in Reference 1).

---

* These are recommended as more suitable for printing than the arrows originally used by the present author[2, 3].

† Prof. C. Djerassi and the Stanford group have indicated (private communication) their complete concurrence with, and are in fact already following, this proposed convention.

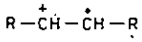
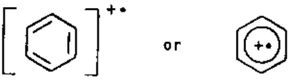
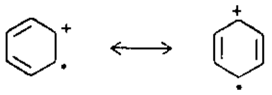
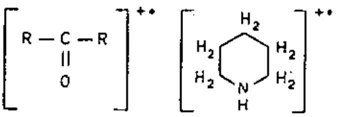
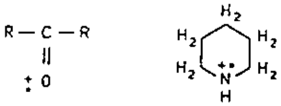
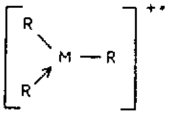
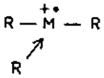
‡ The symbol $+\cdot$ and the symbol $\underset{\bullet}{+}$ are considered to be identical and are therefore used indiscriminately.

§ For the sake of simplicity in formulations including single electron shifts Budzikiewicz, Djerassi, and Williams[1, 2] delete one of the paired one-electron arrows ("fish hooks"). Applying this practice to the formulae in Figs. 1 and 2 (c), they would appear as in Fig. 6.

ACKNOWLEDGMENTS

The author is grateful to his colleagues for valuable discussions and to Mr. W. T. Cooper for help in the preparation of the manuscript.

Table 2.—Odd-electron Ions

Aliphatic radical ions		$(CH_3CH_2CH_2CH_3)^{+\cdot}$
Olefinic radical ions		$(R-CH=CH-R)^{+\cdot}$ or  $R-\overset{+}{C}H-\overset{\bullet}{C}H-R$
Aromatic radical ions		 These formulae are equivalent to 
Radical ions containing hetero-atoms	Charge delocalized	
	Charge localized	
Radical ions of organo-metallic or co-ordination compounds	Charge delocalized	
	Charge localized	

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(2) Budzikiewicz, H., Djerassi, C., and Williams, D. H. (1964). "Structure Elucidation of Natural Products by Mass Spectrometry". Vol. I. "Alkaloids", p.2. (Holden-Day: San Francisco.)

(3) Inter al., Hodges, R., White, E. P., and Shannon, J. S., (1964). Tetrahedron Letters No. 7, 371.

(4) Silverstein, R. M., and Bassler, G. C. (1963). "Spectrometric Identification of Organic Compounds", Chapter 2. (John Wiley: New York.)

(5) McLafferty, F. W., in "Mass Spectrometry of Organic Ions" (1963). F. W. McLafferty (ed.). (Academic Press: New York.)

Notice of Meeting

The

Annual General Meeting

of the

New Zealand Institute of Chemistry

will be held at the

University of Otago, Dunedin

on

Wednesday, 18th August, 1965

at 3.30 p.m.

W. E. Harvey,
General Secretary.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30th APRIL, 1965

1964 £	EXPENDITURE	£	s.	d.	£	s.	d.
	Administration Expenses:						
206	Travelling Expenses ..	378	13	5			
174	Print., Stationery, Postages & Tolls	326	3	10			
220	Salary, Registrar	240	0	0			
125	Branch Expense Allowances	210	0	0			
60	Honorarium to Sec. ..	60	0	0			
21	Audit Fee	25	0	0			
18	General Expenses	16	17	7			
12	Depreciation	10	0	0			
(836)					1,266	14	10
314	Cost of Journal ..	216	15	7			
45	Honorarium to Editor ..	45	0	0			
(359)					261	15	7
32	Chemistry in Action—Net Cost				—	—	—
25	Chemistry Essay Prize				—	—	—
	Examination Expenses .	8	8	0			
	Less: Examinees' Fees Received	1	7	6			
14					7	0	6
16	Provision for Taxation .				20	4	4
308	Excess Income over Expenditure				189	4	2
£1,590					£1,744	19	5

1964 £	INCOME	£	s.	d.	£	s.	d.
1,484	Subs.—Annual	1,604	2	4			
5	Proportion Compounded Subscriptions	5	1	7			
(1,489)					1,609	3	11
	Interest Received:						
8	Bank of N.Z.	20	5	11			
49	Local Body Stock ..	69	13	9			
17	National Savings Ac. ..	8	1	11			
(74)					98	1	7
7	Commission on Journal Subscriptions				9	9	6
20	Surplus on Distribution of Publications				28	4	5
£1,590					£1,744	19	5

TRUST FUND ACCOUNT

1964 £		£	s.	d.	1964 £		£	s.	d.
44	Transfer to Accumulated Funds	–	–	–	1,327	Balance, 30/4/64	1,286	16	11
1,287	Balance, 30/4/65	1,287	18	6		Interest:			
					4	Post Office Savings Bank	1	1	7
£1,331		£1,287	18	6	£1,331		£1,287	18	6

OVERSEAS VISITORS' TRAVELLING FUND

1964 £		£	s.	d.	£ 1964		£	s.	d.
278	Travelling Expenses Paid during year	143	13	0	144	Balance, 30/4/64	4	4	9
4	Balance, 30/4/65	116	1	2	88	Conference Surplus Credited to Fund	83	11	2
					50	Donations Received	171	18	3
£282		£259	14	2	£282		£259	14	2

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

BALANCE SHEET AS AT 30th APRIL, 1965

1964		£	s.	d.	£	s.	d.
£	**Current Liabilities:**						
152	Sundry Creditors	25	10	0			
16	Provision for Tax ..	20	4	5			
31	Subscriptions Received in Advance	113	18	0			
	Royal Inst. of Chem.:						
200	Funds held in Trust	200	0	0			
(399)					359	12	5
	Special Funds:						
23	Compounded Subs. ..	17	9	2			
75	Education Fund	75	0	0			
4	Overseas Visitors' Travelling Fund	116	1	2			
(102)					208	10	4
	Trust Fund:						
1,287	As per statement attached				1,287	18	6
	Accumulated Funds:						
	Balance as at 30/4/64	1,022	2	11			
	Add: Excess of Income over Expenditure for year	189	4	2			
1,022					1,211	7	1

1964		£	s.	d.	£	s.	d.
£	**Current Assets:**						
	Petty Cash Funds ..	9	18	8			
814	Bank of N.Z. . .	1,082	9	8			
515	National Savings Ac. ..	—	—	—			
	Subs. in Arr. 124 15 0						
	Less: Prov. Overdue Subs. .. 50 0 0						
103		74	15	0			
—	Sundry Debtors	53	6	6			
12	Local Members' Journal Subs. in Arrears ..	—	—	—			
20	Advance, Conference ..	20	0	0			
1	Monographs on Hand ..	—	—	—			
(1,474)					1,240	9	10
	Trust Fund Investments, At Cost:						
37	P.O.S.B.	37	18	6			
500	Hutt County Council Redemption Loan .	500	0	0			
750	Lyttelton Harbour Bd. Stock	750	0	0			
(1,287)					1,287	18	6

			General Fund Invest.:			
		—	North Canterbury Hospital Board Stock ..			500 0 0
			Fixed Assets, At Cost:			
			Office Equip.	99 19 0		
			Less: Depc. ..	61 19 0		
		48			38 0 0	
			Addressograph Plates ..	31 3 6		
			Less: Depc. ..	30 3 6		
		1			1 0 0	
		(49)				39 0 0
£2,810	£3,067 8 4	£2,810				£3,067 8 4

AUDITOR'S REPORT

I have audited the books of the New Zealand Institute of Chemistry (Inc.) for the year ended 30th April 1965 and have received all the information and explanations I have required. In my opinion, according to the best of my information and the explanations given to me and as shown by the books of account, the Balance Sheet, Income and Expenditure Account, and Trust Fund Account are properly drawn up so as to give a true and fair view of the state of the Institute's affairs as at 30th April 1965.

Christchurch,
7th July, 1965.

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

THE UNIVERSITY OF MELBOURNE

Applications are invited for the following position:

LECTURESHIP OR SENIOR LECTURESHIP IN INORGANIC CHEMISTRY

The research activities of the Department are at present focussed broadly on the chemistry of transition metals. Specific topics include elucidation of the mechanisms of inorganic reactions, physiocochemical studies of volatile inorganic compounds (especially metal fluorides), spectroscopic and magnetic studies of co-ordination compounds, solvent extraction and new analytical techniques, X-ray structural studies.

A wide range of modern instruments is available including several high resolution infra-red spectrophotometers (4000-200 cm^{-1}); visible and ultra-violet-recording spectrophotometers; magnetic susceptibility balance and cryostat (77-400°K); Varian HR-60 NMR spectrometer, double focus high resolution MS-9 mass spectrometer; recording optical rotary dispersion spectrophotometer (including circular dichroism); Philips 1010 X-ray generator, diffractometer and associated spectrographic equipment.

SALARY: £2,400 x £105—£3,150 (Lectureship).
£3,250 x £110—£3,800 (Senior Lectureship).

Initial salary will be determined according to qualifications and experience.

Further information, including details of F.S.S.U. type superannuation, travel and removal expenses, housing assistance and conditions of appointment, is available from the Registrar, University of Melbourne, Parkville, N.2. Victoria, Australia, and applications should reach him by 31st August 1965.

F. H. JOHNSTON, Registrar.

Minutes of a meeting of the Council of the New Zealand Institute of Chemistry (Inc.) held at Victoria University, Wellington, on Wednesday, 2nd June, 1965, at 10 a.m.

PRESENT: Dr. A. T. Johns (1st Vice-President, in the Chair), M. S. Carrie (2nd Vice-President), Dr. G. A. Nicholls (Auckland), Dr. E. B. Davies (Waikato), D. W. King (Manawatu), Dr. P. P. Williams (Wellington), T. A. Mitchell (Canterbury), C. W. Thomson (Otago proxy), D. J. Hogan (Registrar), Miss J. M. Mattingley (Editor) and Dr. W. E. Harvey (General Secretary).

ASSOCIATESHIP BY EXAMINATION: Regulation 1 covering the above, drawn up by the Examinations Committee was approved.

SALARY SURVEY: The Secretary outlined discussions he had had with Dr. R. B. Miller about the form of the questionnaire and the timing of the survey. It was agreed that Dr. Miller be authorised to proceed with the salary survey and the reply paid envelopes be supplied.

JOURNAL: The Editor outlined difficulties that had arisen over the publication of the Journal, with particular reference to the repeated late appearance of the Journal and certain technical production difficulties. After long and full discussion it was **resolved** (2nd Vice-President/Canterbury) **that** Council reaffirms its view that the Editor alone should be responsible for the content of the Journal. It was further **resolved** (2nd Vice-President/Canterbury) **that** the arrangement under which Editorial Services Ltd. prints and publishes the Journal be terminated forthwith.

RESOLVED (Auckland/Canterbury): THAT a sub-committee consisting of the Editor, the Wellington Delegate and the General Secretary be empowered to arrange for the printing and publishing of the Journal and related matters.

INSTITUTE PRIZES: The Secretary detailed the entries for the Institute Prizes. Assessors were appointed, where appropriate.

NATIONAL COMMITTEE FOR CHEMISTRY: Miss Mattingley reported that the Royal Society had resolved to establish a National Committee for Chemistry which would inter alia take over the duties and responsibilities of the Sectional Committee.

CHEMISTRY IN ACTION: **Resolved** (Canterbury/Waikato) **that** 2,500 copies of "Chemistry in Action" be printed and that no charge be made for this publication this year.

JOURNAL MATERIAL: **Resolved** (Chair/Wellington) **that** Council reaffirms its view that the text of lectures delivered before Branches should be offered to the Editor of the Journal before being submitted for publication elsewhere.

WELLINGTON HOSPITAL BOARD

DEPARTMENT OF BIOCHEMISTRY

WELLINGTON HOSPITAL

Applications are invited from graduates in Science, preferably with Chemistry or Biochemistry to a higher level for the following two positions.

(a) Hospital Scientific Officer in charge of Auto-analysis. This officer will be in charge of the analysis of blood constituents using an auto-analyser and will assist in the expansion of this service.

(b) Hospital Scientific Officer to carry out analysis in the metabolic investigation of patients. This officer will have considerable scope for expanding analytical methods connected with the above investigations and will work in close association with the Physician in Charge of the Endocrinological Unit.

The successful applicants will be graded in the Hospital Scientific Officer Scale of £940 to £1,280 or £1,330 to £1,480 according to experience and qualifications.

Further information may be obtained from the Director of Pathology, Wellington Hospital with whom applications close at 9 a.m. on Friday, 3rd September, 1965.

BOOK REVIEW

Introduction to Chemical Pharmacology, by R. B. Barlow.
Published by Methuen & Co., London, 1964. 452 pages.
Price £4/4/- in U.K.

Although pharmacology owes much to chemists, their contribution to it has been largely indirect. Many chemists employed in the drug industry have been merely providers of compounds for pharmacological testing. An empirical approach to drug testing is still frequently employed by pharmacologists because they believe that their chemist colleagues are unlikely to make useful deductions from the structure-activity relationships noted in the course of a research. This belief may well be justified so long as the chemists concerned fail to take account of the many factors which can modify pharmacological activity.

Having himself experienced the difficulty of coming to pharmacology from chemistry without previous training in the biological field, Barlow is an experienced guide for others in a similar situation. It is a tribute to his skill that his book now appears in a second edition (which is a great improvement on the first). Probably much of the demand for it has come from pharmacologists who are particularly concerned with the interpretation of structure-activity relationships and realize their need for expert chemical guidance. My major criticism is that this book would give an extremely restricted view of pharmacology to any chemist who depended on it solely. Thus one might infer from Barlow's choice of material that pharmacologists were concerned almost exclusively with drug effects on nerve and muscle; there is not even the barest reference to such types of drug as antibiotics and other chemotherapeutic agents, hormones and their synthetic analogues, haematinics, diuretics, antacids, anti-inflammatory agents. Moreover, too much emphasis has been given to factors which influence the capacity of a drug to interact with receptors at the expense of factors which influence the capacity of a drug to reach these receptors and to remain in contact with them. When a better balance is achieved, this will be a very good book indeed.

F.N.F.


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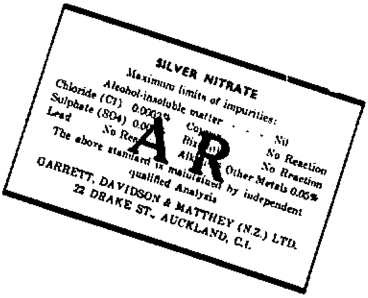
SILVER NITRATE
Maximum limits of impurities:
Alcohol-insoluble matter
Chloride (Cl) 0.0002%
Sulphate (SO4) 0.00
Lead
No Rea
Nil
No Reaction
No Reaction
Other Metals 0.05%
The above standard is maintained by independent qualified Analysis
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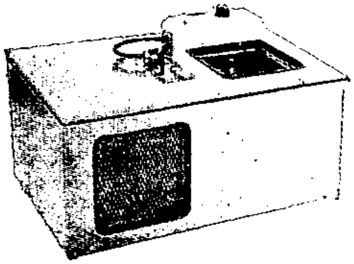

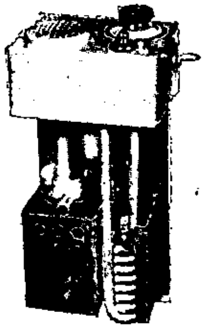

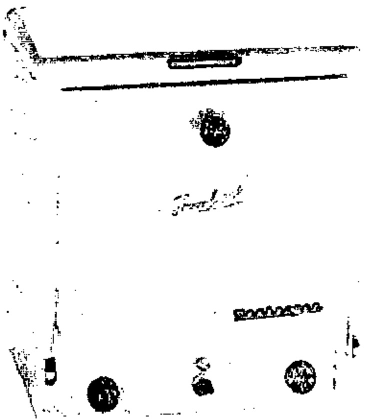

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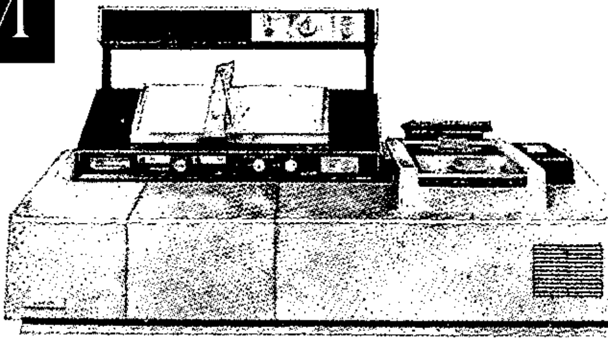


for routine U.V. analysis and Complete Automation

Spectrophotometer

For faster and even more efficient operation Unicam offer a set of automation accessories.

SP.820 Constant Wavelength Scanner
SP.825 Programme Controller
SP.830 Automatic Cell Changer
SP.850 Scale Expansion Accessory

Facilities are provided for the automatic interchange of up to 4 sample and 4 reference cells, automatic re-cycling over any preselected wavelength range and automatic recording at predetermined time intervals.

Many time consuming operations become simple with Unicam automation, particularly

ENZYME REACTION RATES
MONITORING LIQUID COLUMNS
ALL ROUTINE SPECTROSCOPY

Specification

SP.800A—Double beam recording ultraviolet and visible spectrophotometer with linear wavelength scale 190-700 mμ. Complete with tungsten and deuterium lamps, automatic lamp interchange, fused silica prism in thermostatted monochromator, automatic slit programme, attenuator combs giving linear absorbance scale 0-2A, photomultiplier detector and automatic gain control, integral flat bed recorder, holders for standard cells in both normal and second sample position with two 10 mm. stoppered silica cells with case, instruction manual, 300 sheets chart paper, ring binder for completed spectra, test filters for wavelength and stray light, two absorbance scale attenuators, set of fuses and one spare pen.

SP800B—As SP.800A but with linear wavelength scale 190-850 mμ and special red sensitive photomultiplier.

SP800C—As SP.800A but with linear wavelength scale 52,500 cm^{-1} to 14,000 cm^{-1}.

SP.800D—As SP.800A but with linear wavenumber scale 52,500 cm^{-1} to 11.500 cm^{-1} and special red sensitive photomultiplier.

This elegantly styled instrument automatically records absorbance against wavelength or wave number throughout the ultraviolet and visible region of the spectrum. One of four different models may be selected to suit the applications in hand.

Performance

Wavelength (SP.800A, SP.800B)

Accuracy ± 0.4 mμ at 200 and 250 mμ, ± 2 mμ at 500 mμ.

Reproducibility ± 0.1 mμ at 200 and 250 mμ, ± 1 mμ at 500 mμ.

Wavenumber (SP.800C, SP.800D)

Accuracy ± 40 cm^{-1} at 50,000 cm^{-1}, ± 80 cm^{-1} at 20,000 cm^{-1}.

Reproducibility ± 15 cm^{-1} throughout range.

Photometric

Accuracy ± 0.02A
Reproducibility ± 0.005A

Absorbance Zero Flatness

± 0.01A (adjustable)

Resolution

190-370 mμ, 0.1-0.4 mμ; 370-700 mμ, 0.4-2.0 mμ.

Stray Light Less than 1 % at 200 mμ.

Sample Compartment

$9.4 \times 4.9 \times 4.8$ inches high.
$24.0 \times 11.0 \times 12.5$ cm high.

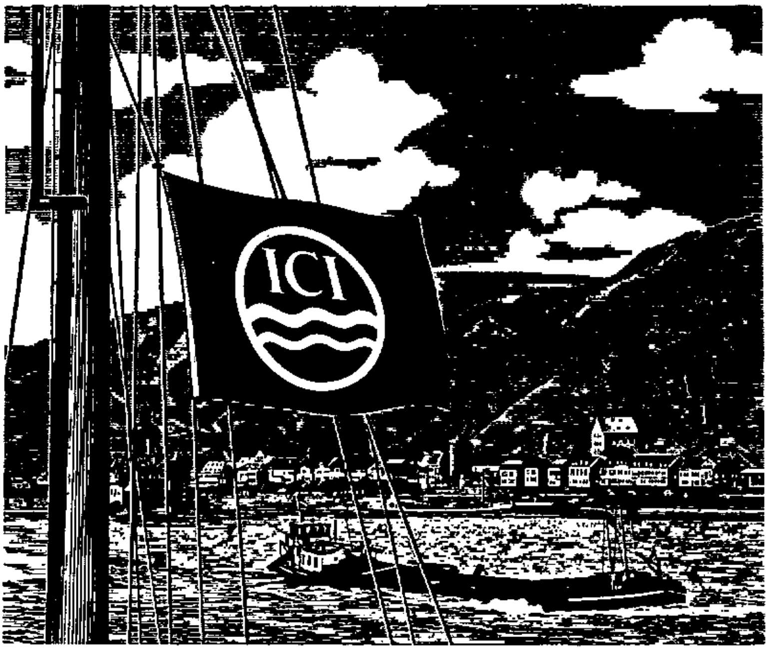
Overall Instrument Dimensions

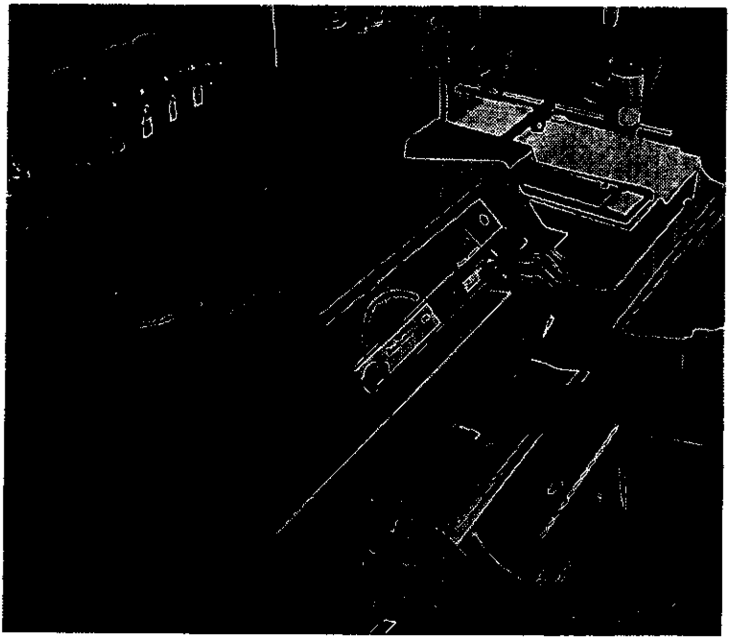
$37 \times 23 \times 15\frac{1}{2}$ inches, 211 lb weight.
$94 \times 59 \times 40$ cm, 96 kg weight.

REPRESENTED EXCLUSIVELY IN NEW ZEALAND BY

GEO. W. WILTON & CO. LTD.

Box 367, WELLINGTON **Box 1980, AUCKLAND**





The BECKMAN DB SPECTROPHOTOMETER

is a compact, direct-reading, easy-to-operate *double-beam* instrument for making transmittance and absorbance measurements in the 205 to 770 mμ wavelength range. It is a low-cost instrument that can be installed in your laboratory for less than £1,150. The DB provides both the accuracy and the versatility usually found only in much higher priced spectrophotometers. Over five years user experience in New Zealand has proved the reliability of this instrument. The DB may be used as a direct reading instrument, or it may be made a double-beam ratio-recording spectrophotometer by connecting it to a recorder such as the Beckman Potentiometric Recorder or the Beckman Linear and Log Recorder, Combined with a Beckman Linear and Log Recorder and a Beckman Scale Expansion Accessory, the DB offers the versatility of double-beam ratio-recording spectrophotometers costing twice as much. The wide range of accessories available to increase the versatility of this instrument includes Sequential Sampler, Flow and Micro Cells, Programmed Scanning, Atomic Absorption, and Reflectance Attachment.

Full servicing and maintenance available from . . .

WATSON VICTOR LTD

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Also at Auckland, Christchurch, Dunedin.

"Serving Science and Medicine since 1888"

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