JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

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Conference Programme

SHELL OIL NEW ZEALAND LIMITED

CHEMISTS

Shell has always been an employer of graduates. Of the salaried staff at present employed in the marketing company throughout New Zealand, 24% hold degrees or professional qualifications. In the top 30 positions the proportion is 70%. These percentages are likely to increase because the work to be done steadily becomes more difficult and intricate.

The Shell Group of Companies, although primarily U.K. owned, is international in character and in scope but Shell Oil New Zealand Limited is staffed by New Zealanders, of whom the most able may be eligible for promotion to senior positions overseas.

Young graduates have a special salary scale and 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.

Graduates in chemistry are employed in three principal departments of Shell Oil New Zealand Limited—in the laboratory, in the Technical Division and in the marketing of petrochemicals. Appropriate training is given within and outside the Company to enable graduates to keep themselves informed on the latest developments in the petroleum and chemical fields. They are encouraged to belong to, and participate in the activities of scientific bodies, and employment at the Central Laboratory is approved for Associate Membership of the N.Z. Institute of Chemistry.

Since the function of a Shell marketing company is to produce the income to pay for oil exploration, research and transport, and to earn dividends for Shell shareholders, considerations of productivity, costs and return on investment are always important. Therefore the graduate as well as specialising initially in work for which he is qualified, will be trained to take a comprehensive view of the oil industry, and of Shell activities generally.

In any responsible jobs in Shell, staff members must acquire breadth of knowledge and competence, and be willing and able to work with others, often under conditions of difficulty and pressure.

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, and these could include overseas training or appointments for the most promising men.

The trade of the Shell Group of Companies, in keeping with that of the oil industry generally, is now five times as large as in 1939, and since the war the demand for oil has been developing and expanding at such a rate that it virtually doubles every fifteen years, as well as becoming more and more complex. These trends show every indication of continuing.

More detailed information is available in the booklet "A guide to graduate employment with Shell Oil New Zealand Limited."
Enquiries may be addressed to:

The Staff Manager, Shell Oil New Zealand Limited,
Shell House, The Terrace, P.O. Box 2091, Wellington. Telephone 45-060
or Shell House Albert Street, P.O. Box 1084, Auckland. Telephone 32-240
or St. Elmo Courts, Hereford Street, P.O. Box 2095, Christchurch. Telephone 62-939.

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JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

Vol. 30, No. 4 AUGUST, 1966

EDITORIAL

CONFERENCE 1966

This year the Annual Conference is to be honoured by the presence of His Excellency, The Governor General Sir Bernard Fergusson, at the opening ceremony. His attendance is a tribute to the standing of the Institute in New Zealand.

The Annual Conference of the Institute offers an opportunity for chemists to meet their contemporaries in industry, university, or research institution; to present original research results; and to learn of the advances in all fields of the subject. However, the increasing complexity of modern chemistry and the necessary high degree of specialisation can lead to a situation in which a lecturer is understood only by a small group of his audience. This tendency is accentuated by the use of words and methods of expression that are often quite specific for the subject discussed. This observation is not original, and many previous Conference committees have recognised the problem and have arranged review lectures by established chemists and directors of research.

This year's committee decided that, without changing the proven research format of past conferences, the time was opportune to introduce to the programme subjects of possibly more general interest. Accordingly, our guest lecturer, Professor R. D. Brown, was invited to give his stimulating views on the education of chemists in Australia and a symposium on the subject "Chemical Education" has been arranged to follow this lecture. Educators at the Secondary and University level have agreed to participate and future employers of chemists have been asked to express their

views on the qualities they require and expect in graduates. I am sure the various points of view expressed will be both provocative and instructive. Two visiting educators, Professor L. A. Woodward from Oxford and Professor W. C. Edmister of Oklahoma, will be present at this symposium and their opinions should add to a valuable discussion.

It is anticipated that the provision of buildings, equipment, maintenance of equipment and safety in laboratories will be of general interest to many members. Accordingly, a session in which papers on these subjects will be presented has been arranged.

As chemists, many members play an important role in the secondary industries in New Zealand so Dr. W. B. Sutch has been invited to present his views on the Development of Secondary Industries in New Zealand. This lecture will be held on Wednesday evening and the public will be invited to attend.

The National Research Advisory Council must have an increasing influence upon the development of science in New Zealand and the views of the Chairman, Mr. J. T. Andrews, will be welcomed. Mr. Andrews has agreed to describe in broad detail the work of N.R.A.C.

In all other respects the conference will follow the well established pattern and some 45 papers have been accepted for presentation. The committe regrets that the contributions from members in industry do not allow more than one session for this work, and hopes that in future conferences the views of industrial chemists will be more loudly heard.

I. R. C. McDONALD,
CONFERENCE CHAIRMAN.

NOTICE OF MEETING

The Annual General Meeting of the New Zealand Institute of Chemistry will be held on Wednesday, August 17, 1966, at 4 p.m. in Room 006, Easterfield Building, Victoria University of Wellington.

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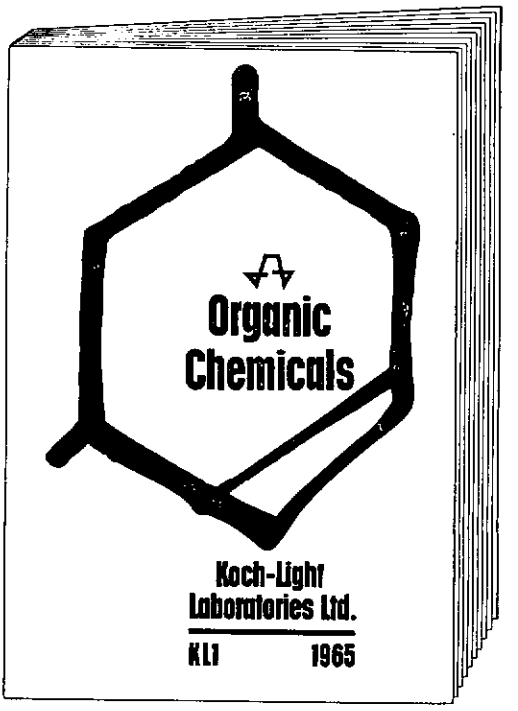

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N.Z.I.C. CONFERENCE PROGRAMME
VICTORIA UNIVERSITY OF WELLINGTON, WELLINGTON
AUGUST 16 to 19, 1966

●

TUESDAY MORNING, AUGUST 16

9.15 - 10.30 a.m. .. Registration in Easterfield Building.
11.00 - 12.00 a.m. .. Conference Opening—His Excellency the Governor General. Student Union Building.
12.00 - 2.00 p.m. .. Luncheon.

TUESDAY AFTERNOON, AUGUST 16

2.00 - 3.00 p.m. .. Guest Lecture—Prof. R. D. Brown.
3.00 - 3.30 p.m. .. Afternoon Tea.
3.30 - 5.30 p.m. .. Symposium: Chemistry and Education:
Mr. I. D. Dick,
Mr. Roy,
Dr. M. H. Panckhurst,
Mr. D. Watkins.

WEDNESDAY MORNING, AUGUST 17

9.15 - 10.15 a.m. .. Presidential Address: Dr. A. T. Johns.
10.15 - 10.45 a.m. .. Morning Tea.

Session A: Physical Chemistry (Dr. A. J. Ellis)

10.45 a.m. .. .. Study of the silica gel-water system using simultaneous isotope exchange kinetics (P. C. Rankin and A. T. Wilson).
11.15 a.m. .. .. The influence of magnetic and electrostatic fields upon equilibria in chemical systems (A. Metcalfe).
11.45 a.m. .. The interaction of Ni(II) and Zn(II) ions with cysteine methyl ester (L. J. Porter and R. Hay).
12.15 p.m. .. .. Electronic configurations in organic molecules (J. P. M. Bailey and R. M. Golding).

Session B: Biochemistry (Dr. W. A. McGillivray)

10.45 a.m. .. .. Isolation and properties of a chalcone-flavanone isomerase from soya beans (E. Moustafa and E. Wong).
11.15 a.m. .. .. Aurone biosynthesis (E. Wong).
11.45 a.m. .. .. Asparagine biosynthesis in plants (M. Lever and G. W. Butler).
12.15 p.m. .. .. An acetylesterase from orange skins (E. M. Sampey, E. C. Webb and B. Zerner).

Session C: Laboratory Design and Equipment (Dr. I. K. Walker)

10.45 a.m. .. .. Designing a chemical laboratory (R. F. Mulliner).
11.15 a.m. .. .. Guidance in the purchase of scientific equipment (K. W. Rhodes and I. E. Marklew).
11.45 a.m. .. .. The maintenance and servicing of chemistry's modern equipment (J. R. Vickerman).
12.15 p.m. .. .. Laboratory hazards (J. F. Burgess).

WEDNESDAY AFTERNOON, AUGUST 17

Session A: Physical Chemistry (Continued)

2.00 p.m. .. .. Models for ions in solution: transfer of ions between solvents (K. H. Khoo and M. H. Panckhurst).

2.30 p.m. .. .. The association of the ions Cu en_2^{2+} and $S_2O_3^{2-}$ in solution (R. A. Mathieson).

3.00 p.m. .. .. Pure nuclear quadrupole resonance spectroscopy (E. P. Sullivan).

Session B: Co-ordination Chemistry (Prof. A. L. Odell)

2.00 p.m. .. .. Homogenous activation of hydrogen by transition metal complexes (J. F. Young).

2.30 p.m. .. .. The transition metal ion catalysed hydrolysis of histidine methyl ester and the methyl ester of 2,3 diamino propionic acid (P. J. Morris and R. W. Hay).

3.00 p.m. .. .. Spectroscopic measurement of the degree of distortion from octahedral symmetry of inorganic complexes (R. M. Golding).

Session C: Pesticides (Mr. P. J. Clark)

2.00 p.m. .. .. Oxidation of methyl groups in some N-methyl carbamates (G. E. R. Hook and J. N. Smith) *and* Phosphate conjugation: a detoxication mechanism in insects (F. J. Darby, M. P. Heenan and J. N. Smith).

2.30 p.m. .. .. Techniques in pesticides residues analysis (H. V. Brewerton).

3.00 p.m. .. .. Quality control in the manufacture of herbicides (O. K. Sewell).

3.30 - 4.00 p.m. .. Afternoon Tea.

4.00 - 5.30 p.m. .. Annual General Meeting N.Z.I.C.

8.00 p.m. .. .. Public Guest Lecture: The development of secondary industries in New Zealand (Dr. W. B. Sutch).

THURSDAY MORNING, AUGUST 18

9.15 - 10.15 a.m. .. Guest Lecture: Mr. J. T. Andrews (Chairman, N.R.A.C.).

10.15 - 10.45 a.m. .. Morning Tea.

Session A: Biochemistry (Continued)

10.45 a.m. .. .. The use of polyvinylpyrrolidine (PVP) in the isolation of mitochondria and other enzymes from plant tissues (J. R. L. Walker).

11.15 a.m. .. .. Species differences in glutathione aryltransferase (A. G. Clark, F. J. Darby and J. N. Smith).

11.45 a.m. .. .. Studies of nucleotide sequences in deoxyribonucleic acid (G. B. Peterson and Janice M. Reeves).

Session B: Solid State Chemistry (Dr. P. K. Foster)

10.45 a.m. .. .. The kinetics and mechanism of the dehydroxylation of crocidolite (M. W. Clark and A. G. Freeman).

11.15 a.m. .. .. A new application of transition state theory to a solid state reaction (J. F. Duncan and K. J. D. McKenzie).

11.45 a.m. .. .. The use of the Mössbauer effect to study the reaction of ferric oxide and zinc oxide in the solid state (J. F. Duncan and D. J. Stewart).

THURSDAY AFTERNOON, AUGUST 18

1.45 - 4.30 p.m. .. Conference Tours.

7.30 p.m. .. .. Conference Dinner (Student Union Building).

FRIDAY MORNING, AUGUST 19

9.15 - 10.15 a.m. .. Guest Lecture: Raman Spectra (Dr. L. A. Woodward).

10.15 - 10.45 a.m. .. Morning Tea.

Session A: Inorganic Chemistry (Prof. C. J. Wilkins)

10.45 a.m. .. .. The chemistry of rhenium and technetium (J. E. Ferguson and Mrs. J. H. Hickford).

11.15 a.m. .. .. Mössbauer and NMR studies of iron phosphides (R. E. Bailey and J. F. Duncan).

11.45 a.m. .. .. Photochemistry of aqueous zinc oxide-lead oxide mixtures (W. C. Tennant).

12..15 p.m. .. .. Some aspects of the halide chemistry of transition metals (J. E. Fergusson).

Session B: Industrial Chemistry (Mr. E. S. Borthwick)

10.45 a.m. .. .. Planning industrial research and development work (A. F. Wilson).

11.15 a.m. .. .. Some diffusion phenomena of heavy vapours (E. F. Hubbard).

11.45 a.m. .. .. Internal stresses in ceramics (P. K. Foster and I. R. Hughes).

12.15 p.m. .. .. The production of a durable railway tarpaulin (I. R. C. McDonald and R. M. Sinclair).

FRIDAY AFTERNOON, AUGUST 19

Session A: Physical Organic Chemistry (Prof. J. Vaughan)

2.00 p.m. .. .. Kinetics and mechanism of the decarboxylation of some aromatic acids (K. R. Tate, M. J. Taylor and R. W. Hay).

2.30 p.m. .. .. The Clemmensen reduction of difunctional ketones (K. M. Baker, J. G. Buchanan, B. R. Davis and P. D. Woodgate).

3.00 p.m. .. .. The acid catalysed hydrolysis of tetramethylethylene oxide (C. D. Stevenson and M. D. Carr).

Session B: Co-ordination Chemistry (Continued)

2.00 p.m. .. .. Geometric isomerism in octahedral complexes of multidentate ligands (D. A. House).

2.30 p.m. .. .. Molybdenum (II) halides and their co-ordination behaviour (C. J. Wilkins).

3.00 p.m. .. .. The crystal and molecular structure of *cis* cyclotetramine tetraene Ni(II) perchlorate (M. F. Bailey, I. E. Maxwell and P. P. Williams).

Session C: Analytical and Industrial Chemistry (Prof. J. F. Duncan)

2.00 p.m. .. .. Biochemical prospecting for molybdenum in N.Z. (R. R. Brooks and G. L. Lyon).

2.30 p.m. .. .. Atomic absorption in a medical laboratory (J. Pybus).

3.00 p.m. .. .. Mössbauer spectroscopy as a tool in analytical chemistry (M. Avrahami and R. M. Golding).

3.30 p.m. .. .. Close of Conference.

Abstracts of Conference Papers

STUDY OF THE SILICA GEL-WATER SYSTEM USING SIMULTANEOUS ISOTOPIC EXCHANGE KINETICS

P. C. RANKIN and A. T. WILSON

Victoria University of Wellington

The technique of studying simultaneous exchange reactions has been developed at Victoria University to study surface phenomena; for example, the adsorption of water on clays, wool and textile fibres.

This paper is concerned with the study of the silica gel-water system. Approximately 4 mgms. of silica gel is placed in a specially modified gas geiger counter and equilibrated at a known relative humidity. High specific activity tritiated water vapour is then added to the system and the drop in activity, as the tritiated water vapour exchanges with the water adsorbed on the silica gel, is measured. Mathematical analysis shows that the activity as a function of time consists of a constant term plus a number of logarithmic terms. The number of logarithmic terms indicates the number of ways the water vapour interacts with the surface under study. Analysis of results also gives information about the amounts of each form of adsorbed water on the surface being studied.

Investigations on the specially prepared silica gel indicated the presence of one form of adsorbed water (i.e. one type of adsorption site). Results also show that at low relative humidities the number of adsorption sites increases with increasing relative humidity. Mechanisms for the adsorption of water on the silica gel and for the exchange of the hydrogen atom of the SiOH group with adsorped water vapour will be postulated.

THE INFLUENCE OF MAGNETIC AND ELECTROSTATIC FIELDS UPON EQUILIBRIA IN CHEMICAL SYSTEMS

A. METCALFE
Chemistry Department, University of Canterbury

Calculations have been made of the effects of such fields upon the values of the equilibrium constants for some typical systems. While these effects for the macroscopic fields of modest intensity available in the laboratory are of a very small order, those caused by local fields due to presence of polar and charged species within the system are of greater importance.

THE INTERACTION OF NICKEL(II) AND ZINC(II) IONS WITH CYSTEINE METHYL ESTER

L. J. PORTER and R. W. HAY
Victoria University of Wellington

The solution chemistry of the Ni(II) and Zn(II)-cysteine methyl ester system has been investigated potentiometrically and spectrophotometrically and a variety of solid complexes have been isolated. A variety of dimeric and trimeric species are formed along with mononuclear species.

The basic hydrolysis of the ester was followed using a pH-stat and activation parameters were determined. The catalytic effects of Zn(II) and Ni(II) were studied and the bis-complexes were found to hydrolyse by consecutive first-order kinetics. Rate constants were evaluated by computer calculations via the time-ratio method.

ELECTRONIC CONFIGURATIONS IN ORGANIC MOLECULES

J. P. M. BAILEY and R. M. GOLDING
Chemistry Division, Gracefield

Extended Huckel M.O. calculations of the electronic configurations of large organic molecules permit the hitherto inaccessible study of some of the physical properties (e.g. reactivity, structural predictions, conformational analysis, e.s.r., n.m.r. and U.V. spectra) of these molecules. We shall discuss some of the predicted properties of molecules such as alkyl naphthalene derivatives.

ISOLATION AND PROPERTIES OF A CHALCONE-FLAVANONE ISOMERASE FROM SOYA BEANS

E. MOUSTAFA and E. WONG
Plant Chemistry Division, Palmerston North

This paper reports the existence in soya bean seedlings of an enzyme which catalyses the conversion of 2,4,4'-trihydroxy-chalcone to (-)-4', 7-dihydroxyflavanone. A method for the purification of this enzyme will be given and some of its properties will be discussed.

AURONE BIOSYNTHESIS

E. WONG
Plant Chemistry Division, Palmerston North

Results from recent tracer studies have shown that a chalcone is the primary C_{15} intermediate in flavonoid biosynthesis. The biosynthetic pathways from chalcone to the various classes of flavonoid compounds remain to be elucidated. With the use of enzyme extracts of soybean seedlings, an intermediate in the biosynthesis of aurone from chalcone has been found. The structure, stereochemistry and probable mode of formation of this intermediate will be discussed.

ASPARAGINE BIOSYNTHESIS IN PLANTS

M. LEVER and G. W. BUTLER
Plant Chemistry Division, Palmerston North

Asparagine is an amino acid which occurs in plant proteins. In higher plants it appears to have an additional function, that of nitrogen storage. It accumulates under conditions of starvation when the plant is probably mobilising nitrogenous substances for energy. Under these conditions it can, in some species, account for over 10 per cent of the weight of the plant.

The biogenesis of asparagine is obscure in both plants and animals. Despite the efforts of a number of workers, no convincing evidence has been obtained for the biosynthesis of asparagine from aspartate by an asparagine synthetase analogous to glutamine synthetase. Some bacteria have an asparagine synthetase, the mechanism of which is quite different from that of glutamine synthetase. This enzyme has not been found to occur in higher organisms.

A possible biosynthetic route involving cyanide and β-cyano-alanine has recently been found to occur in all the plants that

have been studied. Its metabolic significance is uncertain as most plants are not known to synthesize cyanide. Some properties of the enzyme catalysing the synthesis of β-cyanoalanine from cyanide and cysteine will be described, and possible roles for this enzyme discussed.

AN ACETYLESTERASE FROM ORANGE SKINS

ELIZABETH M. SAMPEY, E. C. WEBB and B. ZERNER
Department of Biochemistry, University of Queensland

An acetylesterase has been purified from the acetone powder of orange skins and some of its properties have been studied. Electrophoresis on starch gel has shown that there is more than one esterase component present in the crude extract. Gel filtration on Sephadex G 100 has shown that some of these components have different molecular sizes.

The main component, which migrates to the cathode at pH 8.6 on starch gel, has been isolated and purified 800-fold. The K_m for the enzyme with phenyl acetate as substrate has been found to be 7.2×10^{-4}M at 38°C and pH 7.2, in the presence of 0.15M sodium chloride. Salt is necessary to maintain the activity of the enzyme in the assay mixture but the purified enzyme appears to be stable in 0.01M buffers at 4°C for over one week.

DESIGNING A CHEMICAL LABORATORY

R. F. MULLINER
Chemistry Division, Gracefield

It is no longer possible to push a laboratory into some unused corner of an existing building. Over the past 20 years laboratories have become major projects on which considerable sums of money have been and still are being spent.

Many directors of scientific establishments have found themselves in the position of having to brief an architect on exactly what they want in their new building. This has often taken considerable effort on the part of the director and his staff.

Designing a chemical laboratory is a complicated business and the internal furniture and fitments and services are considerably more complex than in an ordinary office building.

This paper describes the basic things which have to be taken into account when setting out to plan a chemical laboratory.

GUIDANCE ON THE PURCHASE OF SCIENTIFIC EQUIPMENT

K. W. RHODES and I. E. MARKLEW
Geo. W. Wilton & Co. Ltd.; Watson Victor Ltd.

The purchase and supply of scientific equipment in New Zealand involves negotiations which are often subject to misunderstandings and frustrations. Frequently these can be avoided.

Adequate instructions to the suppliers in connection with quotations requested and orders placed, together with an understanding of the factors affecting the importation of goods into New Zealand, can result in much better service being achieved.

THE MAINTENANCE AND SERVICING OF CHEMISTRY'S MODERN EQUIPMENT

J. R. VICKERMAN
Chemistry Division, Gracefield

Modern chemistry is requiring more and more items of complex electronic and optical equipment which are often treated as "black boxes" by the chemist. How does the chemist know whether odd results are the result of the "black box" or himself? This difficulty will be illustrated by considering problems which have occurred in recorders, pH meters, spectrophotometers and gas-chromatographs.

LABORATORY HAZARDS

J. F. BURGESS
Victoria University of Wellington

Laboratory staff need to be aware of the potential dangers in their work. It is necessary to make education in safety interesting and therefore effective. Common hazards, with preventive measures and established safe practices, will be discussed.

MODELS FOR IONS IN SOLUTION: TRANSFER OF IONS BETWEEN SOLVENTS

K. H. KHOO and M. H. PANCKHURST
Chemistry Department, University of Otago

Using the simple model for an ion in solution of a charged sphere in a continuous dielectric medium, the Born equation gives the electrostatic contribution to the free energy of hydration

of an ion. The failure of this equation to represent experimental data is well known and attempts have been made to modify the equation. Stokes[1] has recently shown that by using a calculated Van der Waals radius for the ion in the gas phase, the crystal radius in solution, and alowing for dielectric saturation, excellent agreement is obtained with experimental data.

The major term in the electrostatic free energy of hydration expression is the self energy of the gaseous ion so that comparison with experiment does not give a critical test of the model for ions in solution. Such a critical test can be carried out by investigating the free energy of transfer of ions between different solvents. This will be done in the present paper using precise ionic products for thallium I and chloride ions obtained from solubility measurements in water and water-methanol mixtures. It will be shown that Stokes's model for ions in solution gives poorer agreement with experiment than does the simple model, using reasonable assumptions for solvation of ions in water-methanol mixtures.

[1] Stokes, R. H., J. Amer. Chem. Soc., 1964, Vol. 86, p. 979.

THE ASSOCIATION OF THE IONS Cu en_2^{2+} and $S_2O_3^{2-}$ IN AQUEOUS SOLUTION

R. A. MATHESON

Victoria University of Wellington

Some years ago Yoneda made a spectrophotometric study of the association of the ions Cu en_2^{2+} and $S_2O_3^{2-}$. His value for the association constant was much greater than would be expected from simple electrostatic considerations. Because of this and because of inconsistencies in his data we made a fresh determination of this constant. We found no differences between values of the association constant calculated from experimental data obtained at different wavelengths, after taking care to avoid the formation of other absorbing ions. Our value for the association constant is much lower than Yoneda's. The significance of this result and the assumptions involved in calculating the association constant from spectrophotometric data will be discussed.

PURE NUCLEAR RESONANCE SPECTROSCOPY

E. P. SULLIVAN
Victoria University of Wellington

When an atomic nucleus in a molecule possesses a spin quantum number greater than one-half, the small energy differences found in the molecule may be described mainly by the interaction of the electric quadrupole moment of the nucleus and the electric field gradient at the nucleus due to the molecular electrons.

Such relatively "close" energy levels may be observed as fine structure in microwave transitions in some such molecules.

Pure nuclear quadrupole resonance spectroscopy is concerned with the direct observation of such transitions in solids. A brief historical and conceptual introduction to the subject will be given, followed by a description of the experimental procedure and some experimental parameters. An indication of the use of this branch of spectroscopy as an aid to solving structural problems will be given.

HOMOGENEOUS ACTIVATION OF HYDROGEN BY TRANSITION METAL COMPLEXES

J. F. YOUNG
Chemistry Division, D.S.I.R.

This is a brief account of work carried out at Imperial College with Professor G. Wilkinson. The homogeneous hydrogenation of olefins and acetylenes using soluble complexes of rhodium will be discussed. The kinetics of the reaction and the possible mechanism will be considered and evidence presented for the formation of rhodium hydrides and olefin complexes as reaction intermediates. The formation of transition metal hydrides by direct reaction with hydrogen is a more general phenomenon than has been formerly realised.

THE TRANSITION METAL ION CATALYSED HYDROLYSIS OF HISTIDINE METHYL ESTER AND THE METHYL ESTER OF 2,3-DIAMINOPROPIONIC ACID

P. J. MORRIS and R. W. HAY
Victoria University of Wellington

The basic hydrolysis of histidine methyl ester and the methyl ester of 2,3-diaminopropionic acid have been studied at 25°C and I = 0.1 M, using a pH-stat. Copper (II) and Nickel (II) ions in-

crease the rate of hydrolysis by a factor of about 200 times due to the formation of metal complexes. The catalytic activity is due to a combination of inductive, statistical and electrostatic effects.

SPECTROSCOPIC MEASUREMENTS OF THE DEGREE OF DISTORTION FROM OCTAHEDRAL SYMMETRY OF INORGANIC COMPLEXES

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

Many transition metal ions form octahedral complexes where the transition metal ion is assumed to be in a crystal field environment of octahedral symmetry. Deviations from this symmetry may arise. Certain physical measurements such as e.s.r., n.m.r., Mössbauer, U.V. and I.R. may lead to a measure of the degree of this distortion, some techniques being more sensitive than others. This will be illustrated theoretically and experimentally.

OXIDATION OF METHYL GROUPS IN SOME N-METHYLCARBAMATES

G. E. R. HOOK and J. N. SMITH
Victoria University of Wellington

The carbamate insecticides are notable for the degree of selectivity they exhibit between species. It is possible that this specificity is related to differences in ease of oxidation of either the *N*-CH_3 or the alkyl group in different species. We have therefore measured, in a preliminary survey, the rates of oxidation of methyl groups attached either to the aromatic ring or to the carbamate residue.

Oxidation rates of ring methyls are not affected by other ring substituents in any simple manner. They are about the same as oxidation rates of the *N*-methyl and much faster than the rate of ring hydroxylation. When methyl groups are present in both the ring and the carbamate group both are oxidised and the products are effective anticholine esterases.

The significance of oxidation in the detoxication and design of carbamate insecticides will be discussed.

PHOSPHATE CONJUGATION: A DETOXICATION MECHANISM IN INSECTS

F. J. DARBY, M. P. HEENAN, and J. N. SMITH
Victoria University of Wellington

Phenols are detoxified in insects by conversion to sulphate or β-glucosides (Smith 1964)[1] and these reactions have been confirmed in the grass grub and the flies *lucilia* and *musca*. Grass grubs however, form a third conjugate which is the major metabolite when 1-naphthol or a variety of other phenols are administered. A similar conjugate is present in blowflies and houseflies after administration of phenols.

These conjugates have been identified as the phosphate esters of the phenols by chromatographic, ionophoretic and isotope dilution techniques. Quantitative assays have been made of the amount of phosphate, sulphate and glucoside conjugates formed from labelled 1-naphthol.

The relevance of these observations to the study of carbamate insecticides will be discussed.

[1] Smith, J. N. (1964), J. N.Z. Inst. Chem. 28: 153.

TECHNIQUES IN PESTICIDE RESIDUES ANALYSIS

H. V. BREWERTON
Chemistry Division, D.S.I.R.

The contribution of analytical chemistry to the world-wide effort to limit pesticide residues in consumer products is outlined. The three main steps in pesticide trace analyses in biological matter, namely extraction, clean-up, and measurement, are discussed in relation to the two major groups of insecticides, the organo-chlorines and the organo-phosphates.

QUALITY CONTROL IN THE MANUFACTURE OF HERBICIDES

O. K. SEWELL
Ivon Watkins-Dow Ltd., New Plymouth

Quality control in herbicide manufacture starts with raw material testing, through in-process control to finished product analysis. This is quite an extensive programme with the main hormone-type weedkillers such as 2.4-D and 2,4,5-T. Some typical problems in herbicide quality control will be dealt with,

and examples will be given of analytical development work carried out on some of the main weedkillers. Applications of techniques such as U.V. and infrared spectrophotometry and G.L.C. will be given.

THE USE OF POLYVINYLPYRROLIDONE (P.V.P.) IN THE ISOLATION OF MITOCHONDRIA AND ENZYMES FROM PLANT TISSUES

J. R. L. WALKER
Cawthron Institute, Nelson

The preparation of enzymically active particles from plant tissues is often complicated by the presence of phenolic materials which during isolation procedure polymerise, bind on to the cell proteins and inactivate the enzymes. The use of several new polymeric compounds such as dextrans, nylon powder and P.V.P. have recently been investigated. This paper reviews their use during the isolation of mitochondria from apple peel, a tissue rich in phenolics. The protective role of P.V.P. is related to its reactions with mitochondrial phenolase. Recent work on this subject will be discussed.

SPECIES DIFFERENCES IN GLUTATHIONE ARYLTRANSFERASE

A. G. CLARK, F. J. DARBY, and J. N. SMITH
Victoria University of Wellington

Gammexane is metabolised in insects and vertebrates by conversion to an S-dichlorophenylglutathione (Clarke *et al.* 1966).[1] This appears to be the major product of detoxication in insects. Since glutathionases are likely to be involved in the process we have examined the effects of inhibitors on these enzymes in extracts of sheep liver and of grass grubs.

Sulphonphthaleins with pKa values more acid than 7 are effective inhibitors of insect enzyme but do not significantly inhibit the vertebrate enzyme. The related phthalein, Bromsulphalein, acts similarly and behaves as a competitive inhibitor to glutathione in the reaction using insect enzyme. With vertebrate enzyme it is a poor inhibitor and acts noncompetitively towards glutathione.

[1] Clark, A. G., Hitchcock, M., and Smith, J. N., 1966, **Nature, London**, 209: 103.

Studies of the kinetics of the enzymic reaction suggest that the active site may contain a histidine residue and two lysines, and allow a tentative specification for an irreversible inhibitor to be drawn.

STUDIES OF NUCLEOTIDE SEQUENCES IN DEOXYRIBONUCLEIC ACID

G. B. PETERSEN and JANICE M. REEVES
Plant Chemistry Division, Palmerston North

In the past year we have made considerable progress in our development of techniques for studying the distribution of nucleotide sequences in DNA.

Progress to date will be reported and the application of the methods to the study of the DNA of bacterial viruses will be outlined.

THE KINETICS AND MECHANISM OF THE DEHYDROXYLATION OF CROCIDOLITE

M. W. CLARK* and A. G. FREEMAN
Victoria University of Wellington

The dehydroxylation process of crocidolite, a fibrous amphibole, has been studied under vacuum conditions. The crocidolite anhydride has essentially the same structure as crocidolite, and for this reason a mechanism based largely on proton migration and cation counter-migration had previously been suggested. The present kinetic work shows that the process is diffusion controlled over most of the reaction range, and that the results best fit a model for radial diffusion out of a cylinder. The activation energy for the process suggests that the rate controlling step is the diffusion of OH^- or H_2O through the lattice of the crystal. In order to explain the structural and kinetic data it is suggested that the process takes place in two stages: proton delocalization (this implies the migration of a cation into each unit cell of crystal, or alternatively, the conversion of $Fe^{2+} \rightarrow Fe^{3+}$ per formula unit) then recombination of protons and oxide ions at, or near, the surface of the crystal to form water which then diffuses out of the crystal.

* Now at Department of Soil Science, Massey University.

A NEW APPLICATION OF TRANSITION STATE REACTION

J. F. DUNCAN and K. J. D. MACKENZIE
Victoria University of Wellington

The high temperature solid state reaction sequence kaolinite $\xrightarrow{650°C}$ metakaolinite $\xrightarrow{980°C}$ Al-Si spinel $\xrightarrow{1,100°C}$ mullite + cristobalite was followed by quantitative X-ray powder analysis and mullite growth curves were determined at temperatures in the range 1,100-1,220°C. These curves were mathematically analysed and rate constants for the reaction metakaolinite → spinel → mullite were obtained. From these, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$, the activation thermodynamic functions were calculated. Theoretical entropies due to disorder were calculated and compared with the activation entropy changes obtained from the kinetic data. It was concluded that the slow step is the transformation of metakaolinite into a number of intermediate phases, each becoming progressively more mullite-like, and differing from each other only in the degree of ordering of the octahedral aluminium ions. This conclusion was confirmed by (1) the observation of a frequency shift of an Al-O band in the IR spectrum, which is interpreted as a progressive exchange of octahedral aluminium for tetrahedral silicon, and (2) by studies in Mössbauer spectroscopy of clay minerals doped with ^{57}Co. Thus the mechanism of this reaction is such that there is no single transition state as is assumed in the normal usage of Absolute Rate Theory.

MOSSBAUER STUDIES OF THE SOLID STATE REACTION OF FERRIC OXIDE WITH ZINC OXIDE

J. F. DUNCAN and D. J. STEWART
Victoria University of Wellington

The Mössbauer effect has been used for quantitative analysis of the following solid state reaction:

$$Fe_2O_3 + ZnO \rightarrow ZnFe_2O_3$$

By comparing the kinetic curves obtained by this method with those obtained by an X-ray powder method, information about the diffusing species is obtained. It is found that the oxygen lattice of the product ferrite spinel is established first, and that the diffusion of the iron ions is a slower step.

MOSSBAUER AND N.M.R. STUDIES OF IRON PHOSPHIDES

R. E. BAILEY and J. F. DUNCAN
Victoria University of Wellington

The iron phosphides FeP, Fe_2P and Fe_3P have been prepared and their Mössbauer and ^{31}P N.M.R. spectra studied as a function of temperature. The quadrupole splitting and isomer shift of FeP decrease with increasing temperature over the temperature range studied. The ^{31}P Knight shift increases.

Only one of the iron sites of Fe_2P shows quadrupole splitting.

Ferromagnetic Fe_3P has a complex Mössbauer spectrum at low temperatures.

The correlation of Mössbauer spectra and crystal structure wil be discussed in detail.

PHOTOCHEMISTRY OF AQUEOUS ZINC OXIDE-LEAD CHLORIDE MIXTURES

W. C. TENNANT
Chemistry Division, Gracefield

Irradiation of aqueous ZnO-$PbCl_2$ mixtures by ultraviolet light (3660 A) results in the decomposition of the $PbCl_2$. The decomposition is shown to be a solid state reaction photosensitized by ZnO but is dependent in the first instance on the non-photochemical aqueous interaction of ZnO and $PbCl_2$. The extent of decomposition varies widely with different grades of ZnO and is directly related to the fluorescence type of the oxide. From a study of the influence of the properties of ZnO samples on $PbCl_2$ photolysis, a detailed mechanism of the reaction is proposed. The application of this mechanism to ZnO-photosensitized photolyses of other inorganic salts is also discussed.

THE CHEMISTRY OF RHENIUM AND TECHNETIUM

J. E. FERGUSSON and (Mrs.) J. H. HICKFORD
University of Canterbury

Recent work on the co-ordination chemistry of rhenium and technetium will be reviewed. The chemistry of these two provides a good example of similarities in the properties of the

second and third row transition metals as distinct from the first row. A survey of the known compounds for the two elements also makes it possible to illustrate the trends in the co-ordination behaviour of different oxidation states of transition metals. Technetium and rhenium which occupy a central position in the periodic classification of the transition metals provide a link between the elements to the left and the "platinum" metals on the right. The chemistry of the two elements wil be reviewed in order to demonstrate these inter-relations.

SOME ASPECTS OF THE HALIDE CHEMISTRY OF TRANSITION METALS

J. E. FERGUSSON
University of Canterbury

A survey will be made of the chemical properties of transition metal halides and their complexes where relevant. Our present state of knowledge on transition metal halides is considerable and it is therefore possible to survey trends in the type of halides that are known, from the point of view of their structures and reaction chemistry. The halogens differ in their co-ordination behaviour. The stability of the transition metal halides shows very marked trends as the halogen is changed and also as the metal is changed. These trends give information about the nature of the metal-ligand bond.

PLANNING INDUSTRIAL RESEARCH AND DEVELOPMENT WORK

A. F. WILSON
N.Z. Forest Products Ltd., Auckland

Recent overseas trends in the planning of industrial research and development are surveyed, with particular attention given to the folowing topics: Research work as a part of a company's total planning; evaluation of new projects; transferring research results to operations; co-ordination of research effort with the work of other departments in the company.

SOME DIFFUSION PHENOMENA OF HEAVY VAPOURS

EDMUND F. HUBBARD
N.Z. Railways, Lower Hutt

When certain inflammable liquids such as benzol, hexane and heptane are vapourised the vapours have a density several times greater than air. These heavy vapours behave sometimes as gases and sometimes as liquids. Some unusual diffusion phenomena which are produced have resulted in fires and explosions under conditions which were considered safe. Discussion of these phenomena will include some illustrative experiments.

INTERNAL STRESSES IN CERAMICS

P. K. FOSTER and I. H. HUGHES
P.A.C.R.A., Gracefield

The inversion temperature of cristobalite (SiO_2) varies according to whether or not it is restrained in a matrix. Substitution in the Clausius-Clapeyron equation of the difference in inversion temperature yields quantitative indications of high internal stresses in ceramics. Thermal expansion measurements indicate the stress distribution.

THE PRODUCTION OF A DURABLE RAILWAY TARPAULIN

I. R. C. McDONALD and R. M. SINCLAIR
Chemistry Division, Gracefield

Railway tarpaulins are essential for the protection of goods transported in open trucks. The tarpaulins in present use have a very limited life. Studies have been made in order to extend their life. The main problems encountered were how to rotproof the linen flax canvas and how to waterproof it with a plastic coating. Problems of tear strength in relation to accelerated weathering and of waterproofing the stitched seams will be discussed.

KINETICS AND MECHANISM OF THE DECARBOXYLATION OF SOME AROMATIC ACIDS

K. R. TATE, M. J. TAYLOR and R. W. HAY
Victoria University of Wellington

Carboxylic acids normally decompose by a unimolecular mechanism $RCOOH \rightarrow RH + CO_2$ and some decarboxylations of this type will be discussed. In 1948 Schenkel and Schenkel-Rudin suggested that certain organic acids are decarboxylated by a bimolecular electrophilic substitution mechanism:

$$H^+ + RCO_2H \rightarrow HR + CO_2 + H^+$$

Convincing experimental evidence for this mechanism has been lacking. Some carboxylic acids which decarboxylate by this mechanism have now been studied.

THE CLEMMENSEN REDUCTION OF DIFUNCTIONAL KETONES

K. M. BAKER, J. G. BUCHANAN, B. R. DAVIS and P. D. WOODGATE
University of Auckland

Clemmensen reduction of a variety of difunctional ketones has been shown to involve rearrangement, postulated as occurring through small ring intermediates. Cyclic and acyclic $\alpha\beta$-unsaturated ketones are reduced to a mixture of two saturated ketones, and the intermediacy of a cyclopropanol is rendered likely by the acid catalysed rearrangement of such compounds. Reduction of β-diketones leads to rearranged α-ketols and ketones. The rearrangement undergone by the likely cyclopropanediol intermediate will be discussed. The various pathways by which γ-diketones are reduced will be presented and likely pathways described.

THE ACID-CATALYSED HYDROLYSIS OF TETRAMETHYLETHYLENE OXIDE

C. D. STEVENSON and M. D. CARR
Victoria University of Wellington

Acid-catalysed hydrolyses of epoxides have been assigned both the A-1 and the A-2 mechanisms. There has been a good deal of controversy over the mechanism and many empirical criteria (Ho, entropy of activation, volume of activation, Burnett's ω func-

tion) have been used in an attempt to choose between the two mechanisms. In the case of tetramethylethylene oxide these criteria give conflicting answers. However, there is a more direct experimental approach which shows that the mechanism is clearly A-2.

GEOMETRIC ISOMERISM IN OCTAHEDRAL COMPLEXES OF MULTIDENTATE LIGANDS

D. A. HOUSE
University of Canterbury
CLIFFORD S. GARNER
University of California, Los Angeles, California, U.S.A.

The preparation and properties of optical and geometric isomers of $[M(trien)X_2]Y$ and $[M(tetren)X]Y_2$ (M = Co, Cr; trien = triethylenetetramine, tetren = tetraethylenepentamine) are described. One of the three possible $[Cr(trien)X_2]Y$ isomers, one of the four possible $[Cr(tetren)X]Y_2$ isomers and two $[Co(tetren)X]Y_2$ isomers have been isolated. Infrared spectra have been used to distinguish geometric isomerism, and of the two forms of $[Co(tetren)Cl]ZnCl_4$, one has been resolved. Structural assignments are made on the basis of infrared spectra, optical activity, ring strain and reaction rate measurements.

MOLYBDENUM(II) HALIDES AND THEIR CO-ORDINATION BEHAVIOUR

C. J. WILKINS
University of Canterbury

The molybdenum(II) halides and their derivatives contain Mo_6X_8 cages with halogens at cube corners and molybdenum atoms close to the centres of the cube faces. Within these cages there is direct bonding between metal atoms. In the halides themselves individual cages are linked through bridging halogens, but reaction with ligands destroys this interlinking. In the co-ordination complexes the Mo_6X_8 unit behaves as a pseudo atom with a marked preference for six co-ordination as in the compounds $H_2[(Mo_6Cl_8)Cl_6]8H_2O$, $[Mo_6Cl_8)Cl_4Py_2]Cl_2$, $[(Mo_6Cl_8)Cl_3(Ph_3P)_3]Cl$, and $[Mo_6Cl_8Cl_2Dipy_2]Cl_2$. The mode of attachment of bidentate ligands to the cage is unsolved, but possibilities will be discussed. In derivatives of the types $Mo_6Cl_8(SO_4)_2$ and $Mo_6Cl_8(C_2O_4)_2$ the sulphate and oxalate groups are covalently linked.

THE CRYSTAL AND MOLECULAR STRUCTURE OF *cis* TETRA-ENE Ni(II) PERCHLORATE

I. E. MAXWELL, M. F. BAILEY
Victoria University of Wellington
and
P. P. WILLIAMS
Chemistry Division, Gracefield

cis-$(C_{16}H_{28}N_4)Ni^{II}(ClO_4)_2$ forms deep red crystals which are orthorhombic, space group Pbcn. The unit cell dimensions are:
$a = 10.62 \pm 0.03$, $b = 11.18 \pm 0.03$, $c = 18.81 \pm 0.04$A.
The calculated density of 1.587 g/cc for 4 molecules per unit cell agrees well with the observed density, 1.59 g/cc. The initial problem to be solved by the x-ray structure was the molecular configuration, and since the approximately planar framework of the complex lies on a crystallographic 2-fold axis, the molecule is required to be in the *cis* configuration.

The ClO_4^- ions are sandwiched between parallel cyclic tetramine Ni(II) cations, but are neither directly above nor within bonding distance of the nickel ions. The structure and bonding of this square planar nickel complex will be discussed in detail.

BIOGEOCHEMICAL PROSPECTING FOR MOLYBDENUM IN NEW ZEALAND

R. R. BROOKS and G. L. LYON
Massey University of Manawatu

Biogeochemical prospecting for molybdenum has been carried out at Copperstain Creek, Takaka, Nelson Province. It was discovered that spectrographic analysis for molybdenum in the ash of *Oleana rani* (A. Cunn.) Druce, Compositae, gave an indication of anomalous areas similar to those obtained by analysis of the soil. Three other species which were analysed, though giving indications of molybdenum mineralization, did not show regular correlation with soil analyses. It was concluded that concentrations of molybdenum greater than 15 p.p.m. in the ash of *O. rani* are an indication of mineralization in the area. The available evidence points to this species having a partial exclusion mechanism at low molybdenum concentrations which breaks down with increasing amounts of the element in the soil. Although all species studied were

able to accumulate copper, no correlation with concentrations in the soil was observed. *O. rani* was found to concentrate zinc strongly. It was concluded that biochemical prospecting will be useful in the future for the development of the natural resources of New Zealand.

ATOMIC ABSORPTION IN A MEDICAL LABORATORY

J. PYBUS
Auckland Hospital

The Auckland Hospital has used an atomic absorption spectrophotometer for the past eighteen months for the routine estimation of calcium, magnesium, copper, lead and iron.

Both calcium and magnesium, in serum or urine, are measured on a single dilution containing added strontium and perchloric acid. Conservatively, thirty estimations are performed in an hour. This method has replaced the Clark and Collip method for calcium and the Titan yellow method for magnesium.

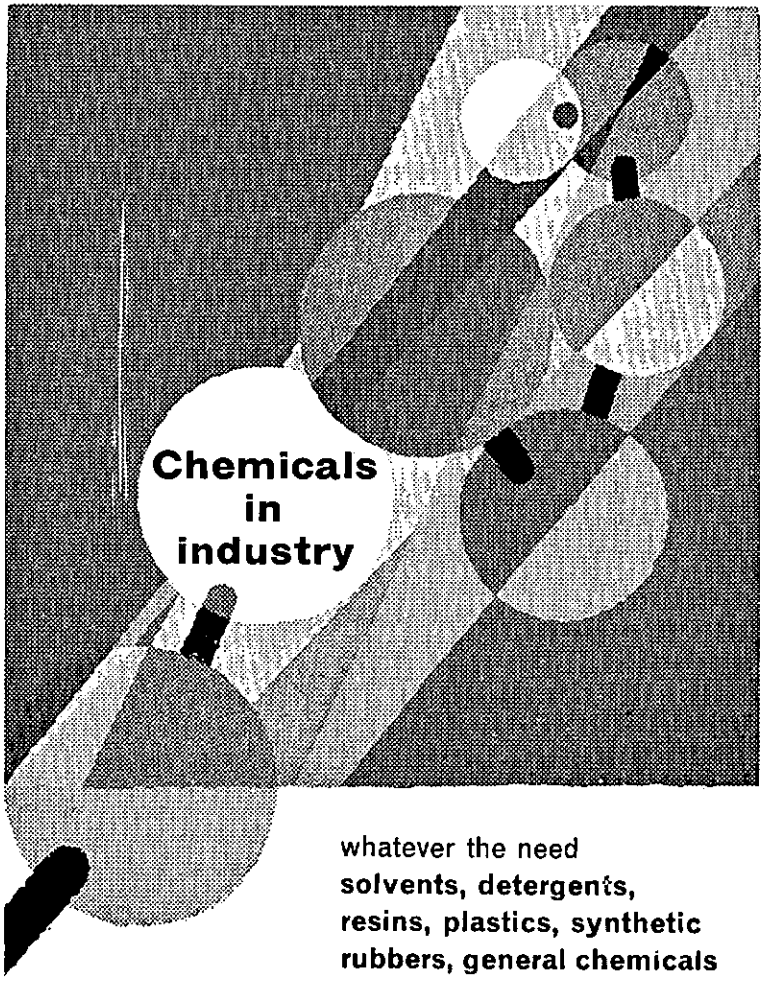
For the estimation of lead in blood, lead is extracted directly from haemolysed red cells with ammonium pyrrolidine dithiocarbamate into methyl isobutyl ketone. A similar procedure is used for serum copper, urinary copper and lead. The method for serum iron has a similar sensitivity to colorimetric methods, but is free from difficulties asociated with turbidity.

The advantages of atomic absorption techniques are simplicity, specificity, sensitivity and precision.

MOSSBAUER SPECTROSCOPY AS A TOOL IN ANALYTICAL CHEMISTRY

M. AVRAHAMI and R. M. GOLDING
Chemistry Division, Gracefield

Various ferrous and ferric ilmenites and ulvites in which the Fe : Ti ratio varied from 0.5 : 1 to 6 : 1 were prepared and their Mössbauer spectra determined. Once their quadrupole splitting $\triangle E_Q$ and isomeric shift δ have been established, unknowns (e.g. ores, preparations, etc.) could be identified qualitatively and, after standardization of the method, quantitatively. The Mössbauer spectra in some cases may yield additional information and a comparison with X-ray diffraction spectra will be discussed. The method can also be utilized effectively in following solid state reactions such as the formation of naturally occuring iron-titanium minerals.



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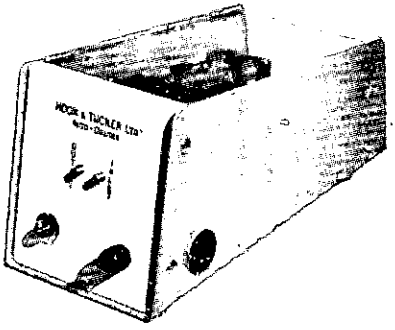

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THE NEW ZEALAND INSTIT

BALANCE SHEET A

1965 £		£ s. d.	£ s. d.
	Current Liabilities:		
26	Sundry Creditors	202 12 6	
20	Provision for Taxation ..	67 17 4	
114	Subscriptions Received in Advance	177 5 0	
200	Royal Institute of Chemistry: Funds held in Trust	200 0 0	
(360)			647 14 10
	Special Funds:		
17	Compounded Subs. ..	12 7 7	
75	Education Fund	75 0 0	
116	Overseas Visitors' Travelling Fund	148 4 10	
(208)			235 12 5
	Trust Fund:		
1,288	As per Statement attached		1,289 0 9
	Accumulated Funds:		
	Balance as at 30/4/65 ..	1,211 7 1	
	Less Excess of Expenditure over Income for Year	516 6 11	
1,211			695 0 2
£3,067			£2,867 8 2

AUDITOR'S

I have audited the books of the New Zealand Institute of have received all the information and explanations I have rec and the explanations given to me as shown by the books of acc and Trust Fund Account are properly drawn up so as to give as at April 30, 1966.

Christchurch, June 27, 1966.

TE OF CHEMISTRY (INC.)

AT APRIL 30, 1966

1965		£	s.	d.	£	s.	d.	£	s.	d.
	Current Assets:									
10	Petty Cash Funds ..				12	14	8			
1,082	Bank of N.Z.				809	1	11			
	Subs in Ar. ..	154	7	0						
75	Less Prov. for O'due Subs.	50	0	0						
					104	7	0			
53	Sundry Debtors				87	7	10			
20	Adv'ce. Con.				20	0	0			
—	Publications on Hand ..				13	16	0			
(1,240)								1,047	7	5
	Trust Fund Investments, at Cost:									
38	P.O.S.B. ..				39	0	9			
500	Hutt County Council Redemp. Loan				500	0	0			
750	Lyttelton Harbour Bd. Stock ..				750	0	0			
(1,288)								1,289	0	9
	General Fund Investment:									
500	North Cant. Hospital Bd. Stock ..							500	0	0
	Fixed Assets, at Cost:									
	Office Equip.	99	19	0						
	Less Deprec.	69	19	0						
38					30	0	0			
	Addr'ss'gr'ph Plates ..	31	3	6						
	Less Deprec.	30	3	6						
1					1	0	0			
(39)								31	0	0
£3,067								£2,867	8	2

REPORT

Chemistry (Inc.) for the year ended April 30, 1966, and
uired. In my opinion, according to the best of my information
ount, the Balance Sheet, Income and Expenditure Account,
a true and fair view of the state of the Institute's affairs

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

THE NEW ZEALAND INSTITUTE

INCOME AND EXPENDITURE ACCOUNT

EXPENDITURE

1965 £		£ s. d.	£ s. d.
	Administration Expenses:		
326	Printing, Stationery, Postages and Tolls	456 8 2	
379	Travelling Expenses	338 4 9	
240	Salary, Registrar	240 0 0	
210	Branch Expense Allowances	221 17 6	
25	Accountancy and Audit Fees	67 0 0	
60	Honorarium to Secretary	60 0 0	
17	General Expenses	10 19 11	
10	Depreciation	8 0 0	
(1,267)			1,402 10 4
	Cost of Journal (including proportion of Editor's Honorarium £45)	870 12 1	
262	Less Net Revenue from Advertising	213 0 8	
			657 11 5
	Chemistry in Action—		
—	Net Cost		159 11 5
—	Chemistry Essay Prize		25 0 0
	Examination Expenses	31 10 0	
7	Less Examinees' Fees Received	25 18 0	
			5 12 0
—	Instrument Survey		20 0 0
20	Provision for Taxation		67 17 4
189	Excess Income over Expenditure		— — —
£1,745			£2,338 2 6

OF CHEMISTRY (INC.)

FOR YEAR ENDED APRIL 30, 1966

INCOME

1965 £		£ s. d.	£ s. d.
1,604	Subscriptions—Annual ..	1,655 6 4	
5	Proportion Compounded Subscriptions	5 1 7	
(1,609)			1,660 7 11
	Interest Received:		
20	Bank of New Zealand ..	28 4 8	
70	Local Body Stock ..	76 1 6	
—	Taxation Prepaid ..	5 4	
8	National Savings Account	— — —	
(98)			104 11 6
—	Donation		5 0 0
28	Surplus on Distribution of Publications.. ..		51 16 2
10	Commissions on Journal Subscriptions		— — —
			1,821 15 7
—	Excess of Expenditure over Income for year		516 6 11
£1,745			£2,338 2 6

TRUST FUND

1965 £		£ s. d
1,288	Balance, 30/4/66	1,289 0 9
£1,288		£1,289 0 9

OVERSEAS VISITORS'

1965 £		£ s. d.
143	Travelling Expenses paid during year ..	– – –
116	Balance, 30/4/66	148 4 10
£259		£148 4 10

JOURNAL ADVERTISING

	£ s. d.	£ s. d.
Direct Expenses Attributable to Advertising:		
Commission to Printers on Advertising Obtained	18 0 0	
Postages and Stationery	12 1 2	
		30 1 2
General Journal Costs:		
Printing	989 15 8	
Honorarium to Editor .. .	45 0 0	
Postages and Stationery	35 3 0	
General Expenses	10 6	
	1,070 9 2	
Less Proportion not attributable to Advertising on basis of page utilisation (200/245)	873 16 10	
		196 12 4
		226 13 6
Net Advertising Income		213 0 8
		£449 14 2

OF CHEMISTRY (INC.)

ACCOUNT

1965 £		£ s. d.
1,287	Balance, 30/4/65	1,287 18 6
	Interest:	
1	Post Office Savings Bank	1 2 3
£1,288		£1,289 0 9

TRAVELLING FUND

1965 £		£ s. d.
4	Balance, 30/4/65	116 1 2
83	Conference Surplus Credited to Fund ..	32 3 8
172	Donations Received	– – –
£259		£148 4 10

REVENUE ACCOUNT

	£ s. d.
Gross Income from Advertising	439 14 2
	£449 14 2

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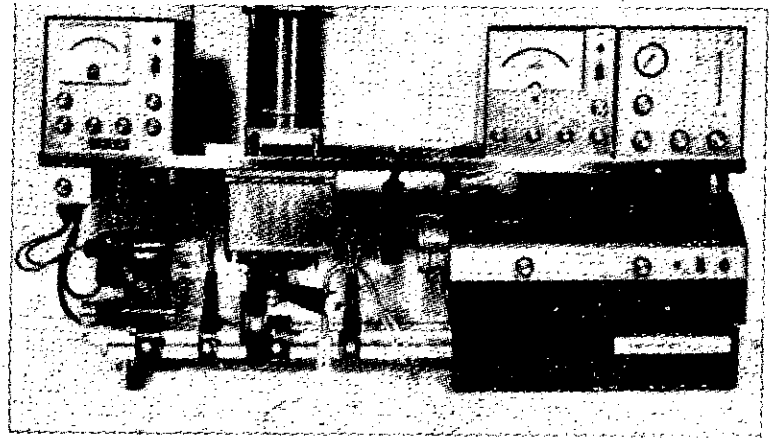

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CHANGING FASHIONS IN CHEMISTRY: ELECTROLYTE SOLUTIONS 1887-1966

by

M. H. PANCKHURST

Chemistry Department, University of Otago

(From the 1966 Chairman's address to the Otago Branch)

In this paper I intend to trace the development of ideas in one part of a branch of physical chemistry, electrolyte solutions, from 1887 to the present day. The part to be dealt with is that concerned with the problem of the extent of dissociation or ionization of electrolytes in aqueous solution.

Such a study as this, the development of ideas, has its own particular interest. Whether or not it is of any use, in the sense that it could show us pitfalls to avoid in future, is very debatable. It is doubtful whether in this sense the study is of much use, because science is very much a human activity and is subject to all the human weaknesses such as rigidity of thought, unwillingness to learn from the past and a tendency to follow fashions.

If I wanted a text it would come from E. A. Guggenheim. Writing in "Discussions of the Faraday Society" in 1957 Guggenheim said: "The long-standing question whether typical strong electrolytes are completely ionized in dilute aqueous solution has received answers depending partly on experiment, and partly on prejudice, fashion and especially on the interpretation of the words 'completely ionized'." For my purposes I consider this long-standing question to have arisen in 1887. This was the first year of publication of Ostwald's famous journal Zeitschrift fur physikalische Chemie. In the first volume there appeared two important papers: "The role of osmotic pressure in the analogy between solutions and gases", by J. H. van't Hoff, and "On the dissociation of substances in aqueous solution", by Svante Arrhenius. Both authors had first published their ideas some years earlier but their theories only became widely read and argued about after publication in this new journal.

In 1887 van't Hoff, a Dutchman, was 35 and Arrhenius, a Swede, was 28. Arrhenius's interest in dissociation arose from measurements he had carried out on the conducting power of electrolyte solutions. In 1883 he presented this work and his speculations on it, to the University of Upsala as a dissertation for the doctorate of the University, with the well known result—he was awarded a fourth class for his dissertation and a third

class for his defence of it. Brilliant new ideas have often not been recognised by lesser men and Arrhenius was not pleased. He sent copies of the work to Clausius, Lothar Meyer, Ostwald and van't Hoff. "These celebrated men", he says, "with whom the Upsala professors are not to be compared treated me as a colleague and not as a stupid schoolboy."

Van't Hoff, who obtained his doctorate from the University of Utrecht in 1874 at the age of 22, was a little more worldly wise. His dissertation title was "A contribution to our knowledge of cyanacetic acid and malonic acid", a title which has a curiously modern ring. Sir James Walker in his van't Hoff Memorial Lecture to the Chemical Society remarks that the work was of a routine character and not at all remarkable. This is rather surprising since van't Hoff had published his famous pamphlet on the stereochemistry of carbon compounds some months before. Walker goes on "It argues well for the sound common sense of the young van't Hoff that he presented a humdrum piece of practical work for his dissertation rather than the startling innovation contained in his pamphlet, for the latter might have had an even worse fate than the equally famous thesis of Arrhenius". Perhaps there is good advice here for Ph.D. candidates.

In his paper in the first volume of Zeitschrift fur physikalische Chemie van't Hoff showed both experimentally and theoretically, using kinetic arguments, that the laws describing the behaviour of ideal gases, summed up in $PV = RT$, also applied to dilute solutions, in which case P was the osmotic pressure. However, in both cases, there were exceptions to the general laws. Van't Hoff cites NH_4Cl which as a vapour has a higher vapour pressure than predicted because of dissociation into NH_3 and HCl. He suggests the same explanation for the exceptions in solution and formally takes account of this by writing $PV = i\,RT$, with i greater than or equal to one. In solution the exceptions included most salts, acids and bases. Van't Hoff and Arrhenius had corresponded before the publication of their papers and van't Hoff says "I should not have adopted this course (emphasising the exceptions) had not Arrhenius privately written to me the probability that salts and the like are decomposed into ions". The symbol i is thus to be interpreted in the context of the equilibrium $MX \rightleftarrows M + X$ where if α is the proportion of MX molecules dissociated, $i = 1 - \alpha + 2\alpha = 1 + \alpha$ (for a 1 : 1 dissociation) and i gives a direct measure of the degree of dissociation.

Arrhenius in his 1887 paper carried on where van't Hoff left off. He postulated that salts, bases and acids are, using modern terminology, partially dissociated into ions at moderate concentrations. Further, that as the dilution increases, at its limit these substances become completely dissociated into ions. Using his work on the conductivity of solutions Arrhenius asserted that the ratio $\frac{\lambda c}{\lambda \infty}$ equals the degree of dissociation α, where λ_c is the molecular conductivity at concentration c and λ^∞ is the limiting molecular conductivity. Using this assertion Arrhenius then showed that for some 80 compounds α calculated from conductivity measurements agreed very well with α calculated from osmotic pressure measurements. He further showed that his ideas could be used to give a satisfactory interpretation of measurements of heats of neutralization, densities, refractive indices and freezing point depression.

The idea that ions are present in solution was of course not new. The interpretation of electrolysis and conductivity experiments in particular depended on this idea. However, before Arrhenius the extent of ionization was considered to be very small and perhaps even to be produced by the application of the electric potential—a view which is still held by many candidates for the University Entrance examination. Arrhenius's contributions were to emphasize that dissociation was a normal state of affairs, that it became complete at extreme dilutions and that the extent of dissociation could be quantitatively estimated.

Arrhenius and van't Hoff continued to make notable contributions to solution theory for many years (van't Hoff was awarded the first Nobel prize in Chemistry in 1901; Arrhenius was awarded it in 1903). My purpose now is to show the way in which their ideas were taken up by others and changed into the forms which we have today. To avoid producing a catalogue of names I shall do this by reference partly to some individual contributions and partly to the Discussions of the Faraday Society. The Faraday Society is the premier British society for physical chemists and its discussions of topics of current interest in physical chemistry usually bring together the leading experts in a given field.

Arrhenius's ideas initially met with a great deal of opposition, partly because of the low temperature at which ionization was asserted to take place; the gas phase dissociation of molecules was familiar at high temperatures but not at low temperatures.

It must also be remembered that the electron was not yet discovered, that there was no model for the atom and that ions were rather mysterious. There was general reluctance to accept the concept of charged particles in solution. As an example of the type of opposition met I quote from Professor H. E. Armstrong. Armstrong was a forceful and influential British chemist, a member of the Council of the Chemical Society from 1873 to 1937, at various times Secretary, Vice-President and President of that body, and Professor at the Central Institution which became Imperial College in 1911. Writing in the correspondence columns of "Nature" in November 1896 Armstrong says:

> "All are agreed that Arrhenius and van't Hoff and their satellites have rendered inestimable service by their generalisations, and the consequent application they have made of them; certainly the world has shown its esteem of their work. Moreover, there can be no doubt, as I stated not long ago in my presidential address to the Chemical Society, that in so far as weak solutions are concerned a law has been discovered which is broadly true in mathematical form: yet I have no hesitation in asserting that the fundamental premises on which it is based are destitute of common sense in the opinion of those who look at these matters without leaving chemical experience out of account; and I venture to think that this is not only their position, but also that of many physicists.
>
> I shall continue to be, as I have been from the outset, a determined opponent of what, I think, may fairly be termed the nonsensical hypothesis of ionic dissociation, for there is no other appropriate term for a view which asserts that hydrogen chloride and a few other compounds are so loosely strung together that they fall to pieces when dissolved in water: out of sheer fright, it would seem, as no valid motive is suggested for such self-sacrifice; and no such charge of unprincipled levity of conduct is brought against the vast majority of compounds other than a few acids and akalies! I believe the view in question to be in entire opposition to the teachings of chemical experience; inapplicable to the explanation of the greater number of facts."

Opposition of this sort gradually died down but as the ionization hypothesis was made more quantitative other difficulties appeared. According to Ostwald's dilution law the dissociation constant,

$$K = \frac{\alpha^2 c}{1-\alpha} = \frac{\alpha^2}{(1-\alpha)v},$$

should be constant. K was shown to be constant for weak electrolytes such as acetic acid but was far from constant for strong electrolytes such as KCl. This became known as the anomaly or abnormality of strong electrolytes, for by the first decade of this century Arrhenius's postulate that ionization is complete at infinite dilution but not at higher concentrations had become accepted, so that thinking was in terms of this postulate. Many possible reasons for the anomaly were advanced. Some of these, suggested by Arrhenius himself in 1911, were:

1. change of ionic friction with dilution;
2. electric attraction of ions;
3. influence of foreign substances on the osmotic pressure;
4. hydration of ions.

These effects are now all recognised, if not completely understood, but they were not made quantitative until much later.

In 1909 Niels Bjerrum, Professor at the Royal Veterinary and Agricultural College at Copenhagen, taking a new direction, suggested that strong electrolytes are completely ionized at all concentrations. He based this suggestion on spectral measurements in the visible region of the molecular absorption of chromium salts, it being shown that this absorption was independent of concentration. This indicated either no dissociation or complete dissociation and since these salts are electrolytes the former alternative is ruled out. Accepting complete dissociation, Bjerrum then stated that the anomaly of strong electrolytes ". . . must be due to the action of the electric charges on each other."

The new concept of complete dissociation represented a considerable modification of the Arrhenius hypothesis, but during the next few years there were many advances which strengthened the case for the new concept. These advances included the formulation of the ideas of activity and activity coefficient [related to concentration by $a = cf$, the activity coefficient f thus being the factor by which the concentration c must be multiplied to give agreement between, for example, osmotic pressure measurements and pressures calculated by the van't Hoff equation]. Initially f was largely unexplained, but in 1913 Milner carried out the first numerical calculations of f, attributing all deviations from ideality to electrostatic interactions. Milner did not obtain an analytical formula for f (which no doubt delayed acceptance of his ideas) but Bjerrum and others made extensive use of Milner's tabulations

and arrived at what Bjerrum calls an interpolation formula for the activity coefficient,

$$-\log f = kc^{1/3},$$

k being a constant depending only on temperature and solvent.

Thus by 1919 the idea of the complete dissociation of strong electrolytes might be considered to have been reasonably well established. In that year the Faraday Society held a discussion on "The present position of the ionization theory" and a reading of these papers makes it quite clear that the idea of *incomplete* dissociation was still dominating the field—the prevailing fashion was hard to change.

The Ostwald dilution law had long been known to be inadequate for strong electrolytes; many of the papers at this Discussion described attempts to obtain empirical dilution laws to explain the experimental observations, one such being:

$$K = \frac{\alpha^2}{(1-\alpha)(v + \varepsilon\alpha)},$$

in which ε is another constant. Arrhenius himself contributed to the Discussion and concluded his comments by saying: "The idea of Bjerrum that the dissociation of KCl and other salts is complete seems not to agree very well with experience." One of the few voices raised in favour of complete dissociation was that of Milner. (Bjerrum was not present.)

The next Faraday Discussion on electrolyte solutions was held in 1927. This was preceded in 1923 by the classic papers of Debye and Huckle on the theoretical calculation of ionic activity coefficients based on the model of complete ionization to rigid charged spheres, charges z_+ and z_-, with a minimum internuclear separation a°. One of their formulae was

$$-\log f = \frac{Az_+ z_- I^{\frac{1}{2}}}{1 + Ca^\circ I^{\frac{1}{2}}} \qquad \ldots\ldots\ldots\ldots (1)$$

I being the ionic strength. Speaking of the 1927 Discussion at a later date R.P. Bell has said: "The classical paper of Debye and Huckel was only four years old. . . . Most of the discussion, therefore, centred round the theory of interionic attraction and its application to very dilute solutions, and the success of this essentially physical attack on the problem carried with it a tendency to discount any specific chemical explanations. . . . [A] good deal of time was spent in demolishing spurious degrees of dissociation arrived at by ignoring interionic forces."

In four years, the prevailing fashion had changed completely and dramatically, the emphasis being now almost entirely on complete ionization.

Over the next few years this remained so and, among other subjects, attention was turned to the problem of mixed electrolyte solutions. For such solutions it was shown, for mathematical and thermodynamic reasons, that the Debye-Huckel formula (1) was not applicable, but that it could be replaced by an extended formula,

$$-\log f = \frac{A z_+ z_- I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - BI = f(I) - BI \quad \ldots\ldots (2)$$

As the interpretation of ionic interactions was further refined the BI term in (2) was replaced by Guggenheim by a series of terms which were designed to account for specific interactions between oppositely charged ions. For example Guggenheim's equation for the activity coefficient of NaCl in a mixture with KBr solution can be written as

$$-\log f_{Na.Cl} = f(I) - \tfrac{1}{2}\left(\beta_{Na.Cl}(C_{Na} + C_{Cl}) + \beta_{Na.Br} C_{Br} + \beta_{K.Cl} C_{K}\right) \quad \ldots\ldots (3)$$

Each of the terms $\beta_{M.X}$, called interaction coefficients, can be determined from measurements on single electrolytes, and is specific to the particular pair of oppositely charged ions M and X. These interaction coefficients can be regarded as taking care of specific properties of the ions as contrasted with the non-specific coulomb interactions. Such specific properties may include polarization, dielectric saturation, size variations, solvation and so on. Formulae such as (3) can be said to sum up the physical explanation of the anomaly of strong electrolytes, as opposed to Arrhenius's essentially chemical explanation—incomplete dissociation.

There were no further Faraday Conferences on electrolyte solutions until 1957 and by this time the President, R. P. Bell, could say "Since 1927 the idea of incomplete dissociation has been gradually creeping back into the subject. . . ." Chemical interactions were once more fashionable.

One of the problems which has been exercising us at Otago is the determination of the stage at which the physical explanations break down and incomplete dissociation must be assumed.

For typical strong electrolytes such as NaCl interaction coefficients have values of about 0.1, and this figure has itself become fashionable as indicative of complete dissociation. However, some electrolytes such as thallium (I) chloride have interaction coefficients, when regarded as completely dissociated, which are much more negative than 0.1, the figure for thallium (I) and chloride ions being about —1.3. Such large negative values indicate very specific interactions. But are these interactions so specific that they indicate incomplete dissociation? The best modern measurements on solutions of thallium (I) chloride alone can be equally well represented by assuming *either* a large negative $\beta_{Tl,Cl}$ *or* some association to give a TlCl complex, the remaining free ions having a $\beta_{Tl,Cl}$ value of about 0.1. Using purely thermodynamic measurements the choice between these alternatives has been largely one of fashion. I say "has been" because I think, for thallium (I) chloride, we have decided between these alternatives.

It is not my purpose to go into technical details of our research work here but our work can be illustrated by the plots in Figure 1. This figure shows the results of the analysis of the solubilities of thallium (I) chloride in nine different series of electrolyte solutions. The line labelled NaCl is for the solubilities of thallium (I) chloride in a number of sodium chloride solutions of varying concentrations. These measurements in sodium chloride can be interpreted by assuming that the concentration of TlCl complex is zero (complete dissociation) or, equally well, by assuming values for C_{TlCl} up to about 0.001 moles litre $^{-1}$, as in the figure. Different values for C_{TlCl} correspond to different $\beta_{Tl,Cl}$ values for the free ions, as shown. $\beta_{Tl,Cl}$ is found using equations such as (3), all $\beta_{M,X}$ values except $\beta_{Tl,Cl}$ being known. The same holds for measurements in other electrolyte solutions so that the problem of whether or not there is association cannot be decided from measurements in any one electrolyte. But it is a condition for equilibrium in all these solutions that C_{TlCl} must be a constant, whatever its value. Therefore if thallium (I) chloride is completely dissociated, all lines in Figure 1 should intersect at $C_{TlCl} = 0$, within experimental uncertainty. This is not the case, but the value $C_{TlCl} = 7.6 \times 10^{-4}$ mole l^{-1} and the corresponding value $\beta_{Tl,Cl} = -0.02$ l. mole $^{-1}$ do describe all measurements within the experimental uncertainty. The detailed analysis of these uncertainties has been done elsewhere. In this particular case therefore we believe that both physical and chemical interactions are necessary to explain the properties of thallium (I) chloride solutions. We are investigating this and other systems using a

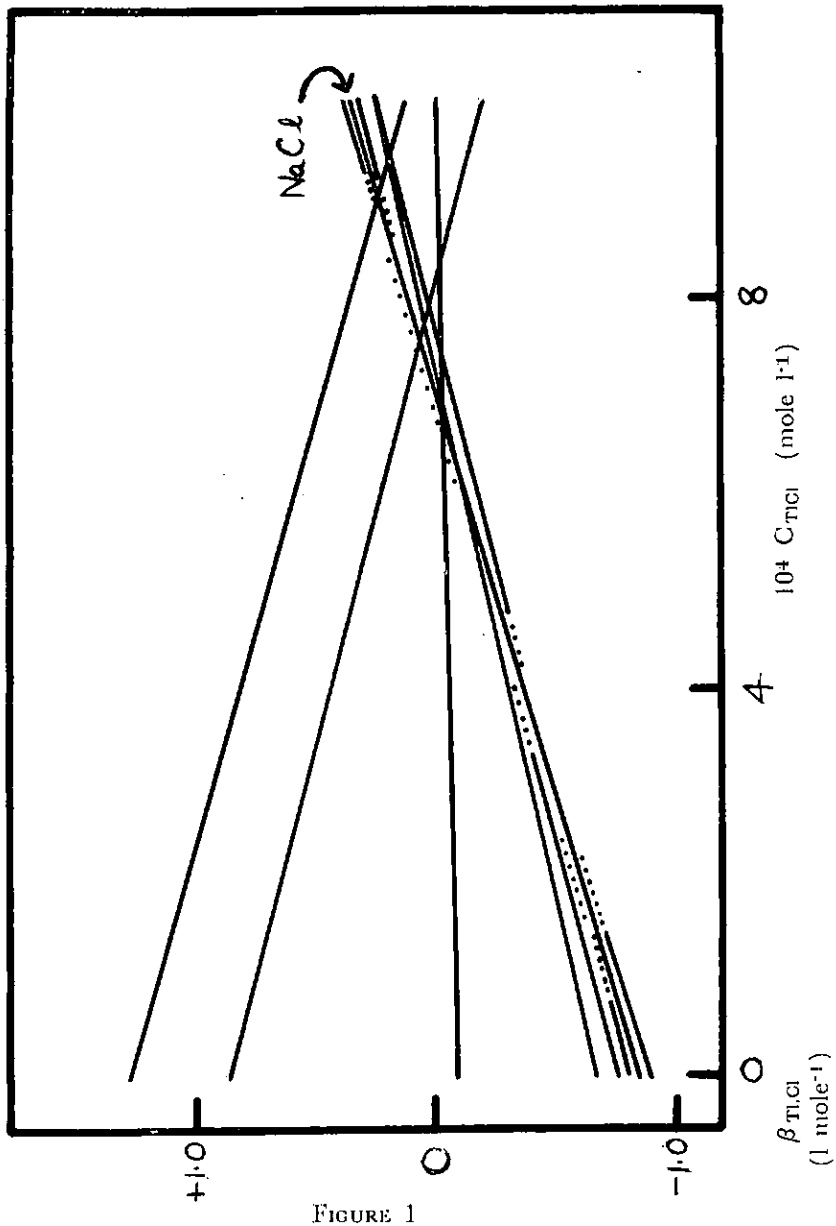

FIGURE 1

Plots of $\beta_{Tl,Cl}$ against C_{TlCl}, the concentration of TlCl complex. Each line is obtained from the analysis of the solubilities of TlCl in varying concentrations of a particular electrolyte solution. Each such set of measurements is equally well represented by any pair of values of $\beta_{Tl,Cl}$ and C_{TlCl} as in the plots, but *all* sets of measurements can only be represented by a limited range of values of these parameters.

variety of experimental techniques, including, to bring the story back to the beginning, osmotic pressure measurements.

This paper has been necessarily somewhat superficial, omitting many important features of modern electrolyte theory. But I think enough has been said to ask whether or not the title, "Changing Fashions in Chemistry", was an appropriate one. Perhaps "Changing Directions" would have been better? On the whole I think that "fashions" in the sense of prevailing customs is still an appropriate word. After all, the fact is, that from 1887 to 1923 this field of chemistry was dominated by the idea that the so-called strong electrolytes were never completely dissociated in solution, except at extreme dilutions. This was despite the very good evidence (as we see it now) to the contrary. The change in fashion was brought about very dramatically in 1923 by an important theoretical development —the Debye-Huckel theory. This sort of change is by no means rare in science, e.g. the current activity in inorganic chemistry brought about by important theoretical developments. For at least 20 years after 1923 complete dissociation was the prevailing fashion. We have now reached the stage where we are occupying a position between the two extremes, recognizing in particular cases the necessity for both physical and chemical interactions. This leaves us with the uncomfortable question: to what extent is our current work dictated by fashion or custom or prejudice, call it what you will?

BRANCH NOTES

Manawatu

A recent meeting of the branch was held in conjunction with the Manawatu Branch of the Royal Society. The speaker was Mr. R. B. Thompson, Superintendent of the Antarctic Division, D.S.I.R., Wellington, who gave an address, supplemented with a film and slides, entitled "The Work of the Antarctic Division, D.S.I.R."

Dr. J. Lyttelton, Plant Chemistry Division, D.S.I.R., has recently been elected a Fellow of the Royal Society.

Dr. M. G. Rumsby, Lecturer in Biochemistry at Massey University, has accepted a Research Fellowship to work with Professor R. J. Rossiter, at the University of Western Ontario, on phospholipid biosynthesis. He will take up his new position early in 1967.

Dr. E. L. Richards has rejoined the Department of Chemistry and Biochemistry after a year's leave at Purdue University.

Dr. R. R. Brooks, Senior Lecturer in Physical Chemistry at Massey University, will be leaving in August to spend a year in the Department of Geology, U.C.L.A.

Dr. E. Conn will be returning in July to his position at the University of Davis, California.

Mr. A. Cashmore has returned to Plant Chemistry Division from Auckland, where he has been working for his Ph.D.

Mr. J. G. Clarke, D.R.I., has recently visited a number of South East Asian countries where he has been assisting in the manufacture of recombined milk products.

Mr. A. K. R. McDowell is on a two-month visit to the United States.

Wellington

Lower Hutt members of the Wellington Branch showed their appreciation of having the venue for the April meeting on their own territory by providing Mr. T. Marshall with an interested audience for his talk on "Development of Smelting Processes of Titaniferous Ores". Much of the success of the evening can be attributed to Wiltons Ltd., and in particular to Mr. K. Rhodes, for the excellent facilities which they provided. Members are looking forward to the possibility of holding further meetings there.

Dr. R. A. Matheson, Senior Lecturer in Physical Chemistry at Victoria University, has recently returned from the U.K. where he spent a sabbatical leave at the University, Reading.

Dr. Francis Young, Chemistry Division, D.S.I.R., is the new Wellington Branch Editor since the departure of Dr. G. R. Burns overseas.

OBITUARY

NESTA MADELINE WOODS

Nesta Madeline Woods died in Auckland on July 25, 1965. Miss Woods was born in Dunedin on February 26, 1896, and was educated at the Union Street School and the Otago Girls' High School. She enrolled as an undergraduate at the University of Otago in 1916 and graduated B.Sc. in 1918 and M.Sc. with second class honours in Physics in 1919. She joined the Health Department as a Bacteriological Trainee in 1920 and passed her qualifying examination as a Bacteriological Assistant in 1923.

In this same year Stanton Hicks (later Sir Stanton Hicks), who was Junior Lecturer in Pathology, obtained a colorimeter and the necessary glassware for estimating blood sugar. With Miss Wood's assistance, a Chemical Pathology (Biochemistry) Laboratory was set up. Her enthusiasm for this new field of diagnostic biochemistry was such that she transferred permanently to the new laboratory, becoming New Zealand's first clinical chemist. She remained working in this field until her retirement on February 19, 1958.

During this time, the few simple colorimetric analyses of those early days developed into the busy complex organization of the modern laboratory. Many people — trainee technicians, laboratory assistants and graduate chemists passed through this laboratory to be trained in the skills of clinical chemistry by a notable, patient teacher and a skilled analyst. Indeed, by Miss Wood's death, not only has New Zealand lost her first clinical chemist, but many chemists have lost a valued friend and colleague.

THE REGISTRY

FELLOWS

Elected March 2, 1966:

PHILLIPS, Leon Francis, M.Sc., Ph.D. (Cantab.), University of Canterbury, Christchurch (Professor of Chemistry).
TOPSOM, Ronald David, M.Sc., Ph.D., F.R.I.C., La Trobe University, Melbourne, Australia (Professor of Chemistry).

ASSOCIATES

BAKER, Richard Thomas, B.Sc., (Hons.) (Notts.), Soils Department, Lincoln College, Lincoln (Assistant Lecturer).
HAGGETT, Theodore Oliver Richards, M.Sc. (Victoria), Dairy Research Institute, Palmerston North (Chemist).
HARVEY, Colin Charles, B.Sc., Rangitoto College, Auckland (Mineralogist).
HODGE, Russell Edward Mason, M.Sc., Rangitoto College, Auckland (Senior Chemistry Master).
KEEY, Roger Brian, B.Sc. (Hons.), Ph.D. (Birm.), Department of Chemical Engineering, University of Canterbury, Christchurch (Senior Lecturer).
LEVER, Michael, M.Sc. (Victoria), Plant Chemistry Division, D.S.I.R., Palmerston North (U.G.C. Post-graduate scholar).
LYON, Ian Charles Thomas, B.Sc., Valley Laboratory Services, Lower Hutt (Chief Chemist).
MIDWINTER, Graeme Geoffrey, M.Sc., Ph.D. (Otago), Department of Biochemistry, Massey University, Palmerston North (Lecturer).
MILLER, Neville Alexander, B.E. (Metallurgy), A.D.S.M., Department of Mechanical Engineering, University of Canterbury, Christchurch (Ph.D. student).
OGILVIE, David James, B.Sc., City Engineer's Department, Palmerston North (Chemist).
RAXWORTHY, Kelvin Stuart, M.Sc. (Canterbury), Chemistry Department, University of Canterbury, Christchurch (Ph.D. student).
SIMS, Ritchie John, B.Sc., Chemistry Department, Auckland University (Temporary Junior Lecturer).
SISSONS, Michael Edward, B.Sc. (Hons.), Ph.D. (Liverpool), A.R.I.C., Northern Roller Milling Co. Ltd., Auckland (Technical Manager).
TURNER, John Charles, B.Sc. (Liverpool), Wallaceville Animal Research Centre, Upper Hutt (Scientist).

FELLOWS

Elected April 27, 1966:

METCALF, Water Sidney, Mus.B., M.Sc., D.Phil., Chemistry Department, University of Canterbury (Reader).
WILLIAMS, Peter Prior, M.Sc., Ph.D. (Cantab.), Chemistry Division, D.S.I.R., Private Bag, Petone (Scientist).

ASSOCIATES

BETTS, Peter Charles, B.Sc., Watkins Gardinol Chemicals, New Plymouth (Technical Sales Officer).
BOND, Michael Anthony, M.Sc., Reckitt & Coleman N.Z. Ltd., Auckland (Production Chemist).
BOULTON, Leslie Howard, M.Sc. (Auckland), 60 Frederick Street, Onehunga (Student Teacher).
CAUGHLEY, Brian Peter, M.Sc., Wellington Polytechnic (Tutor).
DOBSON, Andrew Charles Hugh, B.Sc. (Hons.) (Dublin), G. W. Wilton & Co. Ltd., Auckland (Technical Representative).

DOW, Jocelyn Wendy, B.Sc., Medical School, Dunedin (Research Biochemist).
ELLEN, Christopher Maurice, M.Sc. (Victoria), Pinchin Johnson & Co., Wellington (Industrial Chemist).
ELLIS, Penelope Anne, M.Sc., Polymers N.Z. Pty. Ltd., Auckland (Industrial Chemist).
FORRESTER, Ian Terence, B.Sc. (Hons.) (Canterbury), Biochemistry Department, Lincoln College (Ph.D. Student).
HUGHES, John Theodore, B.Sc. (Lond.), A.R.I.C., Chemistry Division, D.S.I.R., Gracefield (Scientist).
ISDALE, Mrs. Dorothy Helen, M.Sc. (Canterbury), Christchurch Girls' High School, Christchurch (Teacher).
JANSEN, Rudi Bernhard, M.Sc. (Canterbury), Christchurch Boys' High School (Teacher).
JAWORSKI, Frederick William, Waitomo Portland Cement Co. Ltd. (Chief Chemist).
MACKEY, Colin John, M.Sc. (Auckland), Formica N.Z. Ltd., Auckland (Works Chemist).
MARSHALL, Kevin Raymond, B.E.Chem. (Hons.) (Canterbury), M.Sc. (Birm.), Dairy Research Institute, Palmerston North (Chemical Engineer).
NEWSTEAD, David Francis, M.Sc. (Canterbury), Massey University, Palmerston North (Ph.D. Student).
OLDROYD, David Roger, M.A. (Cantab.), Christ's College, Christchurch (Teacher).
OSBORNE, Graham Oliver, B.Sc. (Hons.), Ph.D. (Wales), University of Canterbury, Christchurch (Lecturer).
POOL, Roland Gower, B.Sc., Dunlop N.Z. Ltd., Christchurch (Chemist).
RAETHEL, Henry Alexander, M.Sc. (Victoria), University of Auckland (Temporary Junior Lecturer).
ROUGHAN, Philip Grattan, M.Sc. (Otago), Plant Physiology Division, D.S.I.R., Palmerston North (Scientist).
SYDDALL, Thomas Harold, B.Sc., A. J. Park and Son, Wellington (Registered Patent Attorney).
TAYLOR, Robert William Edgar, Tawa College, Tawa (Head of Science Department).
YOUNG, James Francis, M.Sc., Ph.D. (Lond.), D.I.C., Chemistry Division, D.S.I.R., Gracefield (Scientist).

ABRIDGED MINUTES OF A MEETING OF THE STANDING COMMITTEE OF COUNCIL HELD IN DR. JOHN'S OFFICE, 4th FLOOR, DOMINION FARMERS BUILDING, WELLINGTON, ON MARCH 2, 1966, AT 4 p.m.

Present

Dr. A. T. Johns (President), Professor J. F. Duncan and W. G. Hughson (General Secretary).

The Secretary was asked to send congratulations to T. J. McKee of Lime and Marble, Mapua, Nelson, on the award of C.B.E.

Regret was expressed at the death of three members: Miss Nesta Madeline Woods, Dunedin; Mr. R. N. Woodward, Institute of Nuclear Sciences, Lower Hutt; Mr. Laurence Frederick Addis-Smith, Chemical Laboratory, Johnsonville.

Taxation

A reply had been received from the Minister of Finance, Mr. H. R. Lake. The important section of his letter was as follows:

> "Exemption may be granted when the purposes of an Association or Society is for the general benefit of the community as a whole but this would not extend to an Association or Society which primarily benefitted the members of a trade or association and only indirectly benefitted the community as a whole. . . ."

The Royal Society (of which we are an affiliated member) has been granted immunity in a recent Act and the N.R.A.C. can make a recommendation in this matter so the Secretary was instructed to take the matter up with the Secretary of N.R.A.C. (Mr. Joiner).

Loss of Package

Mr. Hogan reported the loss by a carrier of a package of stationery valued at about £12. It was considered that legal proceedings would be more costly than replacing the stationery.

ABRIDGED MINUTES OF A MEETING OF THE COUNCIL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.), HELD IN THE D.S.I.R. COUNCIL ROOM, SYDNEY STREET, WELLINGTON, ON WEDNESDAY, APRIL 27, 1966, AT 10.30 a.m.

Present

Dr. A. T. Johns (President) in the chair, M. S. Carrie (First Vice-President), Dr. D. R. Llewellyn (Second Vice-President), G. R. White (Auckland), N. H. Law (Waikato), Dr. W. A. McGillivray (Manawatu), Professor J. F. Duncan (Wellington), T. A. Mitchell (Canterbury), Dr. J. C. Dacre (Otago), Miss J. M. Mattingley (Editor), D. J. Hogan (Registrar), W. G. Hughson (Acting Hon. General Secretary).

Mr. White was welcomed as the newly appointed Auckland Delegate and at 1.30 p.m. Mr. I. R. C. McDonald, Chairman of the 1966 Conference Committe attended by invitation to report on Conference arrangements.

The Chairman of the Conference Committee submitted a report and programme summary. This, together with the first Circular already distributed to all members and with further comments by Mr. McDonald regarding guest lecturers, showed that Conference arrangements were well in hand.

Future Conference Policy

The First Vice-President in submitting his report on this matter, emphasised particularly the position of the industrial chemist in relation to the annual Conference.

There were no really new suggestions that have not been made over the past twenty years by Conference committees. Some favoured continuing with annual conferences—others thought biennial or triennial conferences might have advantages. Industrial chemists want an instructional conference whereas Government and University chemists tend to present the results of research.

Industrial chemists are not always free to discuss their work—they frequently have specialist conferences of their own and in many cases the Executives of industry need convincing that the conferences are worth while.

Conferences may be too inward-looking. We should broaden our scope to capture the public imagination and should extend our findings into the economic field.

The most favoured suggestion was that periodically, say every third year, a "bumper" conference should be organised at a particular time and place. There would be a selected theme and papers would be asked for well in advance and would be preprinted and precirculated.

The overall organisation would be in the hands of a National Planning Committee appointed by Council but detailed running of Conference would remain in the hands of a local committee as at present. The Planning Committe would have to operate several years in advance.

RESOLVED (Manawatu/2nd V-P): THAT a National Planning Committee for Conferences be appointed by Council and asked to organise a SPECIAL Conference in Dunedin for 1969.

Conference Roster 1966-1970

1966, Wellington; 1967, Auckland; 1968, Palmerston North; 1969, Dunedin (Special); 1970, Christchurch.

A.N.Z.A.A.S.

N.Z.I.C. will be participating in this Conference which Professor Duncan said had been set down for Christchurch, January 24, 1968.

Journal

The Editor, Miss Mattingley, submitted a long report on the present status of the Journal, and put propositions to Council regarding possible developments at added cost but with standardised format and better service to members.

Dr. McGillivray, a former Editor, supported a standardised format as time-saving—corrections are cheaper. A two-colour cover was also suggested.

RESOLVED (Dunedin/Manawatu): THAT the Editor be given authority to plan for a standard sized Journal as from 1967, and report to next meeting of Council.

Taxation of Journal Advertising

The Registrar said that the Institute would pay about £100 in tax on Journal advertising for the past year.

Mr. J. W. Shanahan, our auditor in Christchurch, has written to the authorities there, the Hon. General Secretary has written to the Minister of Finance in Wellington and the Hon. General Secretary has recently written to the Secretary of N.R.A.C.

The Royal Society, of which we are a member body, has had a sub-committee considering taxation of gift monies etc., and clause 19 of the new Royal Society Act reads "The Society is hereby declared to be exempt from the payment of land tax and income tax".

It is suggested that we first collect information relating to other societies which publish a journal under similar circumstances especially those that may be member-bodies of the Royal Society and that the general situation be discussed with the Royal Society and again with the N.R.A.C.

Royal Society

RESOLVED (1st V-P/2nd V-P): THAT, since by virtue of the number of members, the N.Z.I.C. is entitled to two representatives on the Member Bodies Committee of the Royal Society, we appoint Miss Joan Mattingley (our present representative) and Professor J. Vaughan.

Examinations

RESOLVED (Auckland/Canterbury): THAT Miss J. E. Simpson be awarded the Laboratory Assistant's Certificate.

Examination Fees

The Examinations committee asked Council to consider paying each examiner in the Practical examination a fee of £10 10s. The whole question of examinations paying their way was then considered but it was pointed out that the fee for the candidate had already been fixed at £15.

RESOLVED (2nd V-P/Canterbury): THAT for present commitments the candidate's fee be £15, that future candidates be charged £25 and that each examiner be granted a fee of £8 as from this year.

Prize Entries

There were no entries for the Chemical Essay Prize.

Appointment of Examiners

Examiners were appointed for the Morcom Green-Edwards, and I.C.I. Prizes.

Technicians Certification Authority of New Zealand (T.C.A.)

Profesor A. L. Odell sits on the Authority as a University representative (N.Z.I.C. is not represented on the "Authority"). We have been asked to nominate a representative on the Executive Committee for Science.

RESOLVED (Auckland/Manawatu): THAT Professor A. L. Odell be appointed the N.Z.I.C. representative on the Executive Committe for Science.

Prize for Science Technician

A recommendation from Auckland that Council consider awarding annually a £10 prize to the candidate gaining highest marks in Chemistry in the New Zealand Certificate in Science examination was held over to the next meeting.

Public Relations

Auckland submitted a three-page report at the meeting. This will be taken to Branch committees by delegates and will be considered in detail at next meeting.

Reprints of Lectures

RESOLVED (Canterbury/Editor): THAT Canterbury be granted £10 to assist with the publication of "Chemistry in Action—1965".

Salary Survey Committee

A report received from Dr. Miller showed that there had been a big demand for information but in many cases there were insufficient returns to enable conclusions to be drawn. His committee had been approached to asist in a survey of salaries of technicians. The Secretary was asked to inquire further regarding our involvement.

Apology

The First Vice-President, Max Carrie, has tendered his apologies for absence from the next meeting and from Conference as he leaves in July for U.S.A., Oslo, Warsaw, Munich and Great Britain.

BOOK REVIEWS

Solid Organoalkali Metal Reagents, by AVERY A. MORTON. Published by Gordon and Breach Science Publishers Inc., New York. 1964. 248 pages.

This book sounds as if it is going to be a technical treatise dealing with the preparation and properties of solid organoalkali metal reagents. To some extent this is what it is, and certainly the many listed references give the reader direct access to the practical aspects of the subject. However, a closer look at the book soon reveals that the rather bold sub-title "A New Chemical Theory for Ionic Aggregates", is a more precise description of the contents.

Professor Morton has written this book with one aim—to oust the *anion* from the organic chemist's mechanistic treatment of solid organoalkali metal reactions, and to replace it with a radical pair formed upon the *cation*. The evidence upon which this new approach is based, although circumstantial, is fairly convincing. Unfortunately, the author starts off on the defensive and it is some time before the reader can shake off the initial feeling of being bullied into believing. But by the time the chapter on benzyne is reached the theory is being well presented. In fact the hesitancy that is felt in accepting the postulated benzyne intermediate (a consequence of the anion approach) would probably clinch the deal in favour of the cation, but for the fear of jumping out of the anion frying pan into the cation fire. The choice is too fundamental to be made lightly, but even the unconverted reader will thank Professor Morton for opening his mind on the subject.

In the style of American publications, the book is well laid out and is helped along by an easy style of writing. The new theory was brought into being by the discovery of the alfin catalyst but the book does not begin with a discussion of this reagent. Instead, Professor Morton is content to pass from opening chapters on the theory of solid phase reactions onto chapters dealing with Metalation, Alkylation, the Wurtz Reaction, Benzyne, and Pyrolysis; Chapters 9 and 10 are concerned with alfin catalysts, and the book is completed by discussions on the polymerization of styrene and a number of selected special catalysts.

As an extension of the study of organic reactions in solution, the importance of the carbanion in heterogeneous systems has been strongly emphasized. Professor Morton argues that it has been *over*-emphasized. Whether the reader agrees with this or not, I have no doubt that he will benefit from reading this point of view.

G. J. LEARY.

Conformational Analysis, by E. L. ELIEL, N. L. ALLINGER, S. J. ANGYAL and G. A. MORRISON. Interscience Publishers (a division of John Wiley and Sons Inc.), New York, 1965. XIII + 524 pages. 15.5 × 23.5 cm., £6 15s. ($15).

In the past fifteen years conformational analysis has assumed vital importance in the study of the properties and reactions of organic molecules. This is one of two books published in 1965 on this general field. Hanack's book "Conformation Theory" was published within four months of this text.

The present book is extremely well written and there is little evidence for the uneveness often found in multi-authored texts. It assumes a reasonable sophistication in stereochemistry, but starts from basic principles and could be easily read by a first year graduate student. "Conformational Analysis" is not a text on stereochemistry, a subject covered in Eliel's earlier book "Stereochemistry of Carbon Compounds". The two introductory chapters are followed by a section on Physical Methods in Conformational Analysis showing how conformations have been determined by physical techniques (a topic not dealt with in detail in Hanack's book). This chapter is followed by the application of conformational analysis to ring systems other than cyclohexane in which both carbocyclic and heterocyclic ring systems are considered. The final chapters of the book deal with the application of conformational analysis to Steroids, Triterpenes, Alkaloids and Carbohydrates (168 pages). The carbohydrate section is especially extensive covering 73 pages. The final chapter tidies up the loose ends and deals with conformational energies in some detail.

The diagrams are very clear and there are over 1,400 literature references. Each chapter concludes with a short list of general references to its subject. There is both an author and subject index. The book can be recommended without hesitation to all organic chemists.

R. W. HAY

Chemistry and Beyond, a selection from the writings of the late PROFESSOR F. A. PANETH. Edited by HERBERT DINGLE and G. R. MARTIN, assisted by EVA PANETH. John Wiley and Sons Australasia Pty. Ltd. 1965. 284 pages, 54s.

This volume is essentially a memorial to an outstanding scientist—Friedrich Adolf Paneth—who died in 1958. The intro-

duction of twelve pages gives us a picture of Paneth, the man. There follows a selection from his publications of which 274 are listed in the appendix. Research papers are not included but rather writings of more general interest. The first eleven comprise lectures on the history of chemistry, and tributes paid by Paneth to personalities in the world of chemistry. He remarks in an article, "Thomas Wright of Durham and Immanuel Kant", that "It was one of Kant's deepest convictions throughout the whole of his life that in every science a full understanding needed knowledge of the past". The conviction was surely shared by Paneth. He excels in finding in writings of the past the germ of ideas established today in the light of modern knowledge. Thus of Robert Boyle—"With an insight even more remarkable than that of his successors, Lavoisier, Dalton, and Mendeleef, he thus brought forward more than two hundred years ago a theory for bringing into accord the multiplicity of the chemical elements with the existence of a fundamental substance, a theory which modern science now bases upon an immeasurably richer assembly of facts". Credit is meticulously given, particularly where work had previously been overlooked, and the great (e.g. Lavoisier) occasionally exposed. The remaining sections of the book cover extra-chemical interests—astronomy in articles on Thomas Wright, historical researches on meteorites in the succeeding nine papers, and a miscellaneous group in the final section. A historical research into the *De Alchimia* of Albertus Magnus contains reproductions of the original text of "The Surgery" of Abû 'L Qâsim showing *inter alia* an apparatus for stretching the spine which will be appreciated by anyone who has undergone modern physiotherapy. In "Science and Miracle" Paneth concludes "But inside this world, and during its lifetime, there is no more room for miracles on the macro-scale than in the days of classical physics". "The Salt of the Earth" gives an explanation of a somewhat baffling biblical passage.

I would commend "Chemistry and Beyond". It is a book to be dipped into, to be enjoyed at leisure, eminently readable and with a leaven of humour. Above all, it is indeed a fitting memorial to a remarkable man.

E. B. Davis

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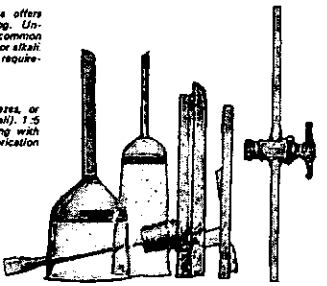

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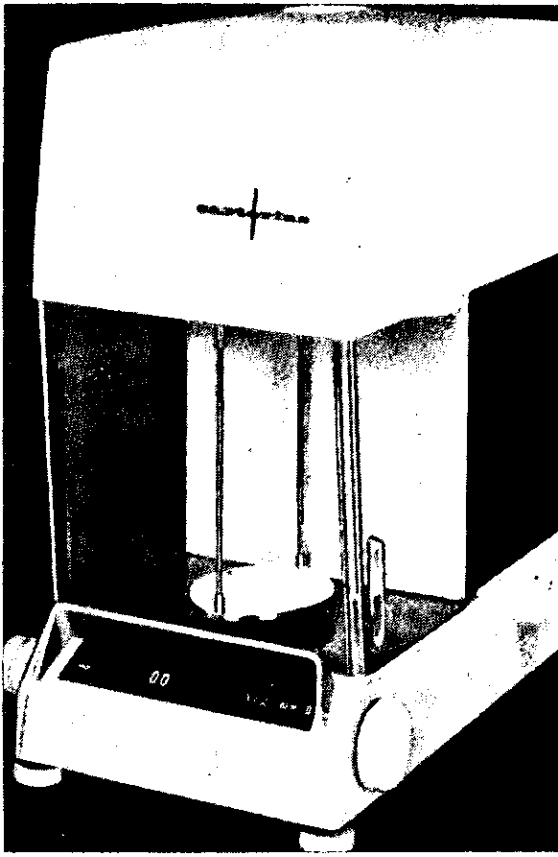

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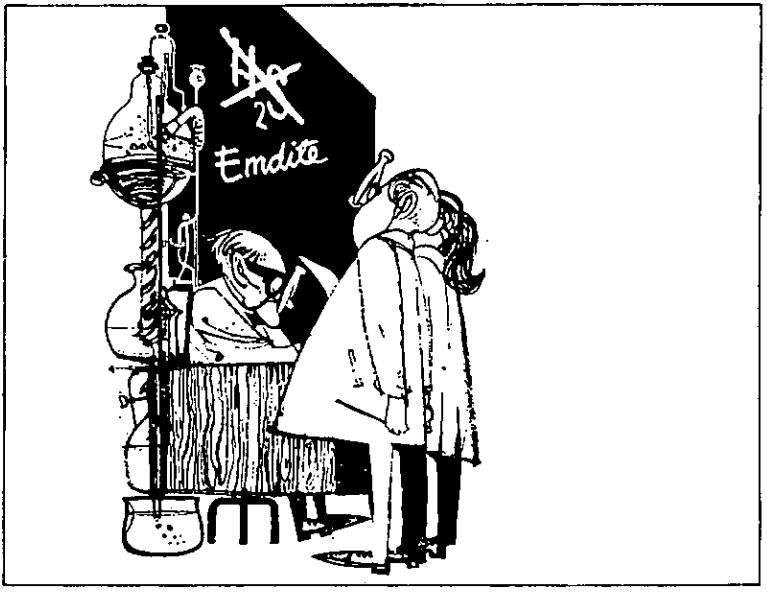

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1. Hart, K.K., Hill, A.G. and Savage, B., J. Roy. Inst. Chem., 1984, 418-23 (reprints are available on request)

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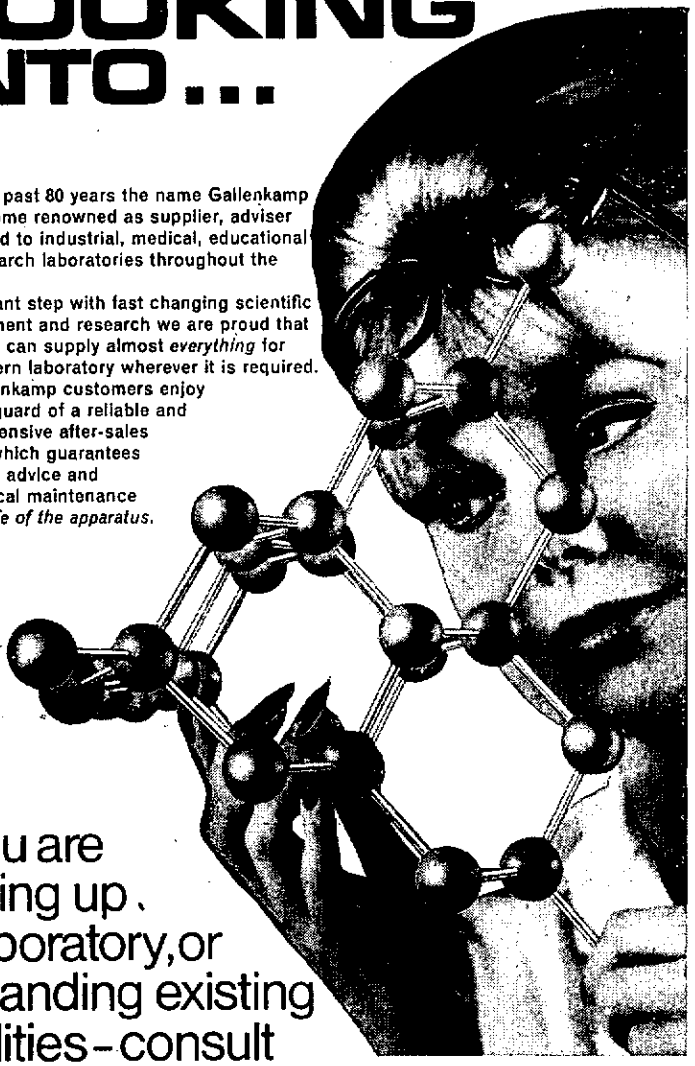

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