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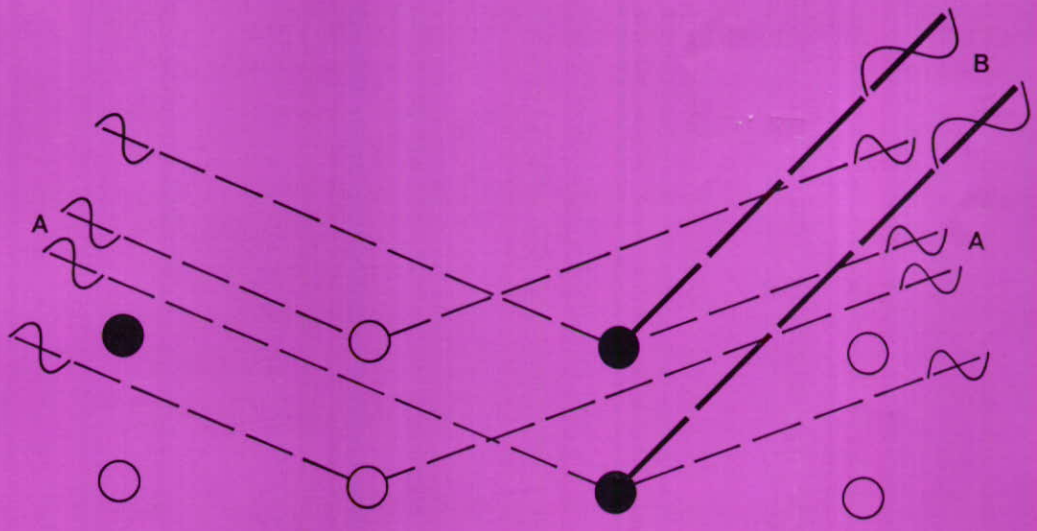

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Cover Schematic diagram showing conventional Rayleigh scattering (A) by non resonant atoms in a crystal (open circles) and both Rayleigh (A) and resonance scattering (B) by resonant atoms (full circles). *Specific Radiation Crystallography.*

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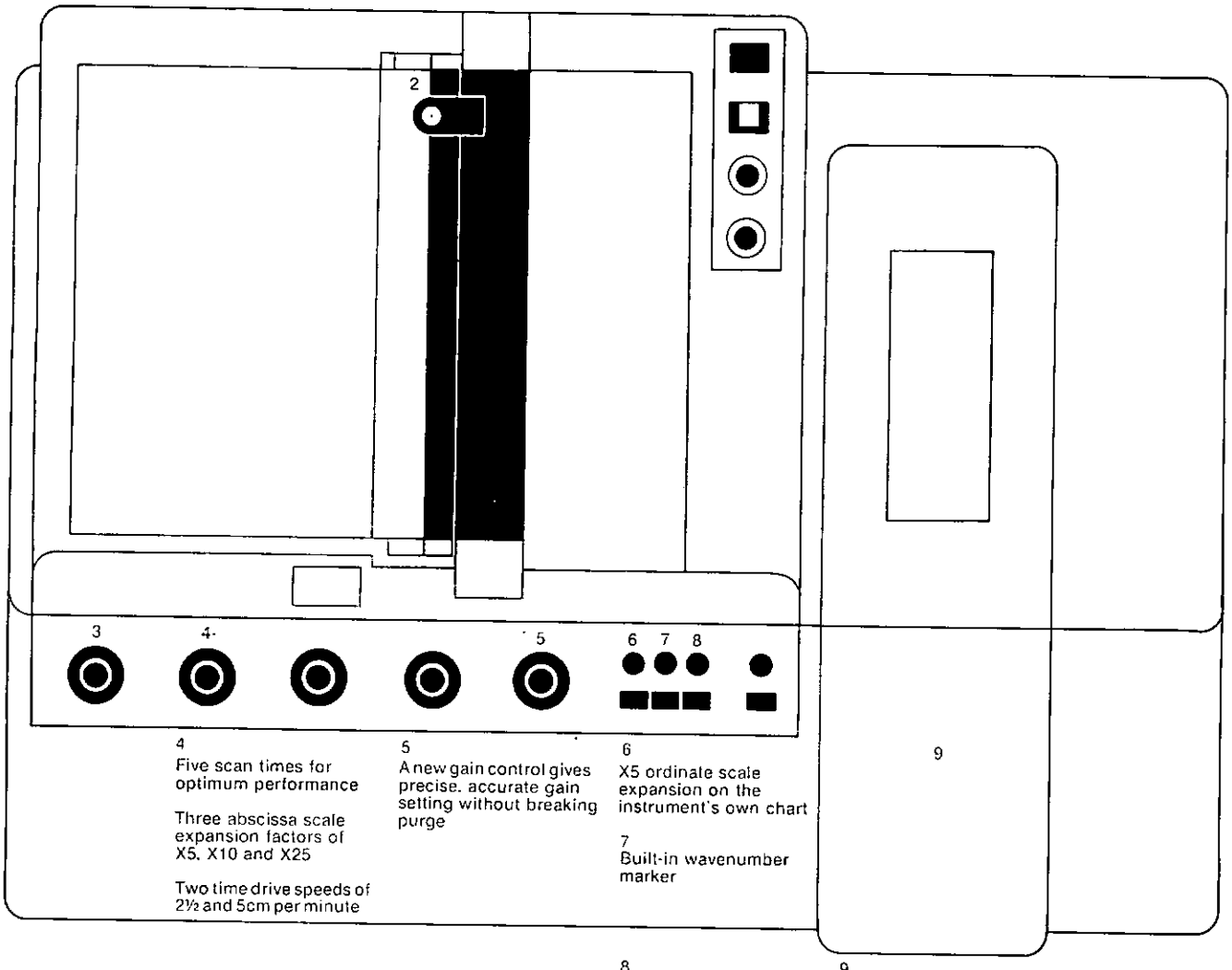

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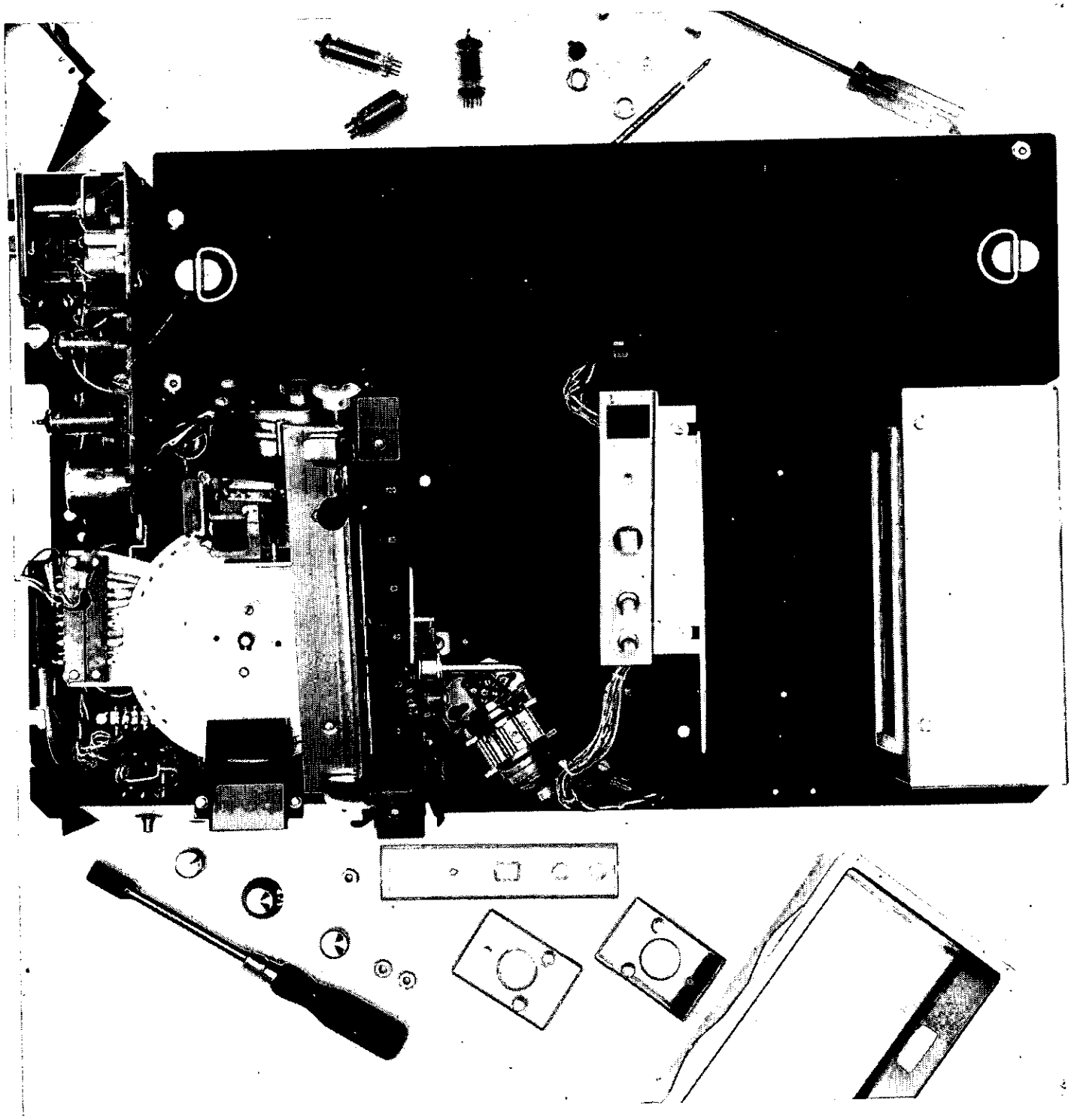

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Editorial

The new format partly dictated by metrication is with us. The paper size A4 is derived from the basic metric sheet A0. A0, 841 x 1189 mm., has an area of one square metre; this is based on the ratio of 1 to $\sqrt{2}$, enabling a range of smaller paper sizes of identical proportions to be obtained by successively halving the sheets. Thus A0 halved gives A1. Any standard sized sheet can be obtained by cutting a large sheet with no waste.

We have used a heavier quality paper and a new typeface to give greater clarity. Redesign of the title page provides for information for members, particularly the names and addresses of Branch Editors whose responsibility it is to provide news and a considerable proportion of the articles from their branch membership.

The decisions affecting typography and layout depend on a number of factors, including fashion. Fashion is a very real thing, affecting all aspects of life including typography and layout. These must be agreeable and effective, but within the limits of the material supplied, the intention of its message, the facilities of the printer and typesetter and the economics of the job. Thus a larger page means more space, but this is not necessarily used to cram more in; more importantly it gives scope for improved layout and attractive legibility.

The present emphasis on the need for communication is not just between scientist and non-scientist, but also between one scientist and another. Specialisation can remove a chemist from contact with other specialised areas of chemistry. The Journal provides a medium of communication between members, Council and members, authors and readers, advertisers and customers.

We hope that the changed format will contribute to improved communication for Institute members.

Specific Radiation Crystallography (SRC)

By J. F. Duncan, A. G. Freeman and J. H. Johnston

Conventional X-ray diffraction techniques have for a long time been one of the major methods used in the study of structural aspects of solids. This method only distinguishes between atoms in different sets of equivalent positions in the structure. Therefore it cannot satisfactorily be used to investigate the details of structures in which partial or complete replacement of a set of crystallographically equivalent atoms by one or more impurity atoms has taken place. This type of substitution is important in determining the role of trace elements in mineral and solid state systems, and possibly also in biochemically significant molecules.

We have been working on new methods which enable the siting of specific atoms to be determined. The first two use Mossbauer methods; one is based on measuring the peak area ratio of the absorption lines in the Mossbauer spectrum and the other on Mossbauer nuclear diffraction effects. The third method, applicable to all elements of higher atomic number than fluorine, involves the interference between the conventionally diffracted X-rays and the X-rays reasonantly scattered by trace elements in the sample.

Mossbauer Methods

Mossbauer spectroscopy is similar to all other forms of spectroscopy in having a radiation source, a sample (absorber or scatterer) and a detector.[1] Absorption occurs by nuclear excitation of the Mossbauer atoms of the sample when the γ-ray energy of the source is adjusted by Doppler movement (about 0.011 cals/mole per cm/sec velocity for ^{57}Fe) until it exactly corresponds with the nuclear absorption levels of the sample. Although there are about 30 Mossbauer nuclei we are concerned here only with ^{57}Fe, the most commonly used.

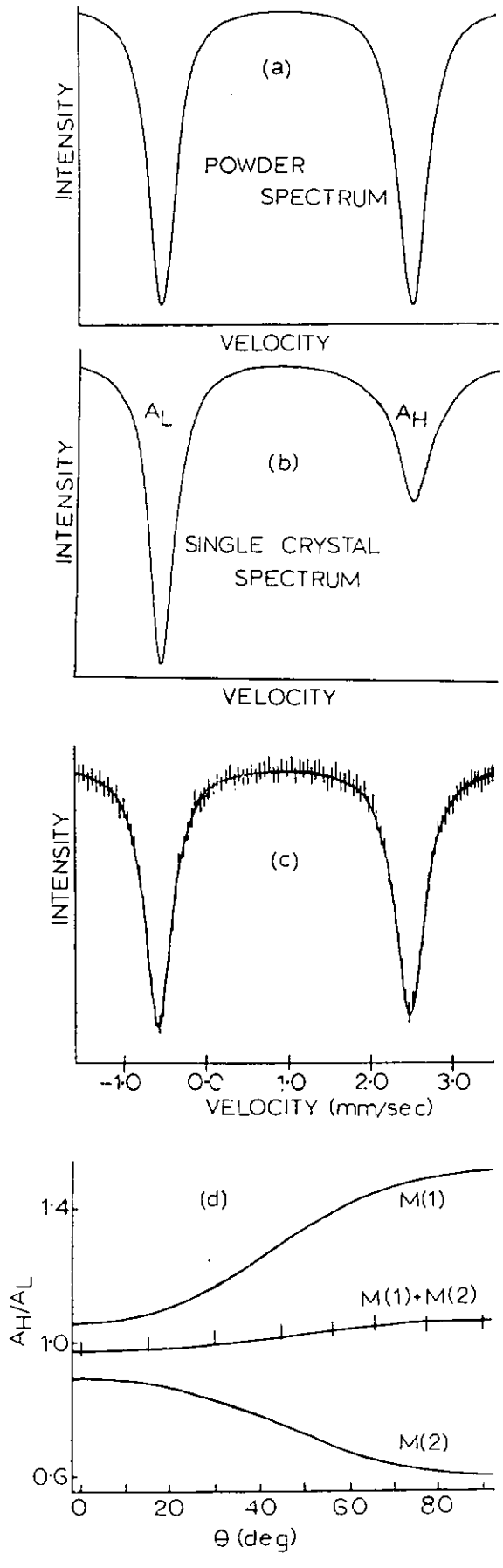
1. Quadrupole peak area ratio (QPAR) method

A typical quadrupole-split Mossbauer spectrum for ^{57}Fe is shown in Fig. 1a. The splitting into two peaks arises from the interaction of the quadrupole moment of the Mossbauer nucleus with the surrounding asymmetric electric field gradient (EFG) at the nucleus. Such an asymmetry may be due to the distortions of the electronic environment around the nucleus as a result of bonding and/or the different types and geometry of the surrounding ligands. This is usually different for each different type of site within a crystal lattice.

For a powder sample these peaks are of equal area (intensity) as shown in Fig. 1a. However, for a single crystal sample this is not the case. The ratio of the area A_H of the high energy peak to A_L that of low energy peak depends on the sample orientation with respect to the incoming γ-ray (see for example, Fig. 1b). The ratio of A_H/A_L is dependent on the absorption probabilities of these peaks and if more than one site is present in the lattice this ratio is also dependent on the percentage of a particular type of site occupied by the Mossbauer atoms.[2]

Slices of known orientation are cut from single crystals and their Mossbauer absorption spectra determined. The site positions of, percentage occupancy by, and sign and direction of the EFG of the Mossbauer atoms, can be estimated by comparing experimental values of A_H/A_L with those theoretically calculated using a non linear least squares refinement procedure. The EFG sign and

Chemistry Department, Victoria University of Wellington, New Zealand



1a. A typical quadrupole split Fe^{2+} Mossbauer absorption spectrum for a powdered sample.

b. A similar Fe^{2+} Mossbauer absorption spectrum for a particular orientation of a single crystal sample.

direction so determined yields information about the bond type and bond direction, but more importantly, the site positions and percentage occupancy are obtained, even when the iron is in minor to trace amounts.

Since the experimental value of A_H/A_L depends on sample thickness, the conditions under which the experimental and theoretical values of A_H/A_L can be validly compared must first be determined.[3]

This technique is particularly useful in crystals which contain two or more different Mossbauer sites giving rise to very closely overlapping peaks which cannot be resolved in the powder spectrum—as is necessary for site identification by the method of Bancroft, Burns and Maddock.[4]

We have successfully applied our new technique to olivine $(Mg.Fe)_2SiO_4$[2] and cordierite $Al_3(MgFe)_2[Si_5AlO_{18}]$[5]. In olivine there are two very similar octahedral sites; M(1) and M(2), which both the iron and magnesium ions can occupy[6]. This gives rise to very closely overlapping peaks in the powder Mossbauer spectrum. However, by analysing the overall experimental peak area ratio as described above we have shown that the iron is equally distributed between these two sites[2]. Fig. 1c shows an experimental Mossbauer spectrum for a single crystal sample of olivine oriented with the γ-ray direction perpendicular to the (100) crystallographic plane. Fig. 1d shows theoretical curves of A_H/A_L as a function of θ (the angle between the γ-ray direction and the *a* crystallographic axis when the γ-ray direction is parallel to the (001) plane) for the cases in which the iron is assumed to be all in the M(1) site; all in the M(2) site; or equally distributed between the M(1) and M(2) sites. The experimental data fit the curve for the last situation very closely.

In cordierite Fe^{2+} can replace the magnesium ions in the octahedral sites[7], or occupy either or both of the two channel sites in the structure. Also Fe^{3+} ions can replace Al^{3+} ions in one of the two tetrahedral sites[8] (see Fig. 2a). Using the QPAR method on the experimental spectra (one of which is shown in Fig. 2b) 79% of the total iron content is found to be Fe^{2+} in octahedral sites; 20% is Fe^{2+} in the large channel sites; and 1% is Fe^{3+} in the T_1 tetrahedral sites.[5] The total iron content of this sample is only 0.9% by weight.

Also from the directions of the EFG of these ions, we have been able to determine the principal bonding directions for the iron in these octahedral

c. An experimental and computer fitted Mossbauer absorption spectrum for a single crystal sample of olivine oriented with the γ-ray direction perpendicular to the (100) crystallographic plane.

d. Theoretical curves of A_H/A_L as a function of the angle θ (see text) for: M(1); all the iron in the M(1) site: M(2); all in the M(2) site: M(1) + M(2); evenly distributed between the M(1) and M(2) sites. The bars represent the experimental values with errors included.

and channel sites. It emerges that these are such as to provide an explanation of the pronounced pleochroic effects in this mineral.

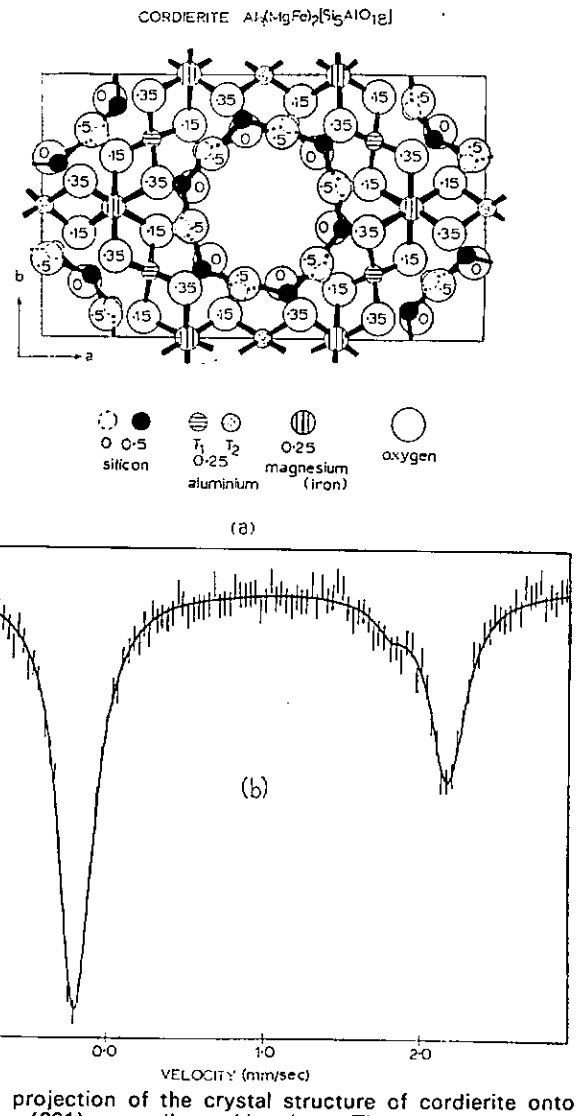
2. Mossbauer Nuclear Diffraction (MND) Method

Since the energy of the γ-radiation corresponding to the Mossbauer transition is of the same order as that of X-rays used in conventional X-ray diffraction, γ-rays may be diffracted in the same way. Both X-rays and γ-rays are scattered (diffracted) by the electrons of the atoms in the lattice. This Rayleigh scattering is insensitive to small changes in energy (velocity) of the source. However, in addition, the γ-rays may be scattered by Mossbauer nuclei when the source is moved to achieve resonance. This resulting scattering is sensitive both in phase and amplitude to small changes in the velocity of the source, from which the phase of the scattering may be determined (see below).

In a γ-ray diffraction pattern of a crystal containing a proportion of Mossbauer atoms, in which the Bragg angle is scanned, peaks are obtained according to the well-known Bragg equation. Black with coworkers[9,10] have developed the theory for this γ-ray scattering in some detail but we will only mention the significant aspects here. Non-Mossbauer atoms show only Rayleigh type scattering of the incident γ-radiation (A in figure on front cover). However, Mossbauer atoms give rise to both Rayleigh (R) and nuclear scattering (N) (B in figure on front cover). In addition, these two scattered beams can interfere (RN) as there is a definite phase relation between them.[9] Thus, the angular γ-ray diffraction spectrum is different for the cases in which the source is moving either on (R + N + RN detected) or off resonance (R only detected). This effect is shown in the (200) diffraction spectrum of pyrite FeS_2 (see Fig. 3a(i)).

After obtaining the angular position of the Bragg maximum for a certain peak reflection we fix the system on this and study the intensity of the scattered beam as a function of the source velocity—i.e. we determine the Mossbauer spectrum (R+N+RN) at a particular Bragg angle. Such a spectrum for the (200) reflection of pyrite is shown in Fig. 3a(ii). In order to understand the difference between the scattered and absorption spectrum for this reflection let us consider the effect of the individual components in the scattering process.

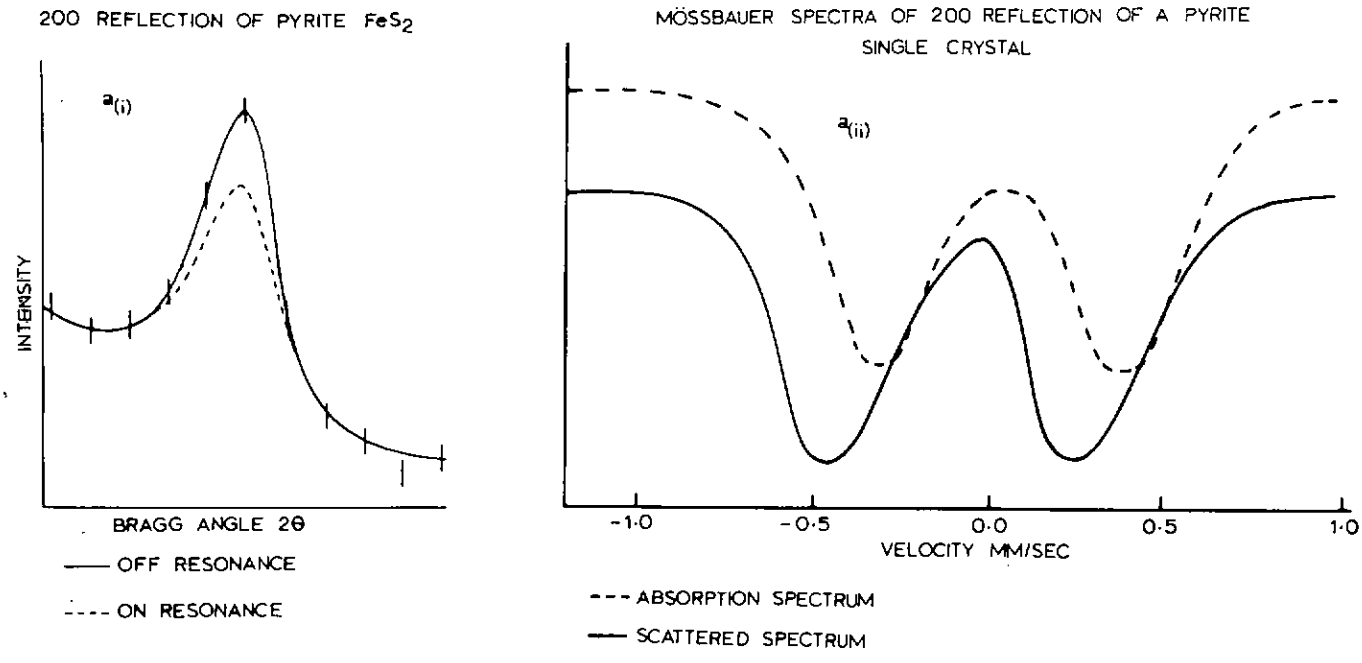
The Rayleigh (R) scattering component (Fig. 3c) which is normally independent of source velocity shows an absorption because the Rayleigh scattering decreases as a result of increased absorption of the γ-radiation at the Mossbauer resonance velocity. Conversely the nuclear scattering (N) (Fig. 3b) increases at the resonance velocity. The interference (RN) term (Fig. 3d) shows a change in sign as the velocity scans through the resonance value. If the nuclear scattering from a Mossbauer atom is in phase with the total Rayleigh scattering from all atoms in the lattice, then this interference term is of the form shown in Fig. 3d(i). If the phase

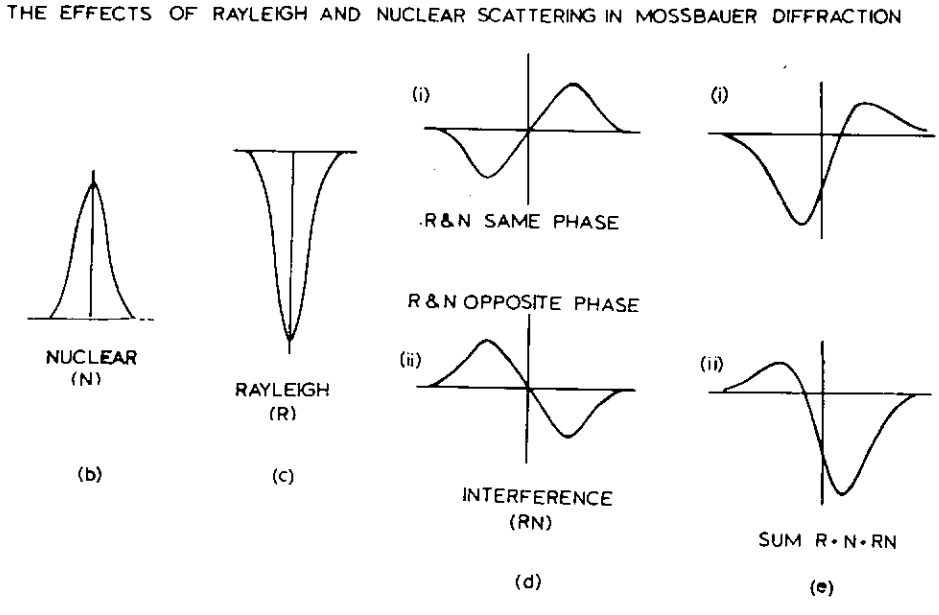


2a. A projection of the crystal structure of cordierite onto the (001) crystallographic plane. The numbers by the respective atoms are the z-fractional co-ordinates of these atoms.

b. An experimental and computer fitted Mossbauer absorption spectrum for a single crystal sample of cordierite with the γ-ray direction parallel to the (010) crytallographic plane and at an angle of 105° from the *a* crystallographic axis.

is opposite, then the net interference term changes sign and the form is as shown in Fig. 3d(ii). These three components add together to give the respective asymmetric peaks shown in Figs. 3e(i) and 3e(ii). These have a positive intensity only when the nuclear scattering is greater than the total Rayleigh scattering. This is generally not the case and is the reason why most previous workers[9,10] have not considered this nuclear diffraction process as an important structural tool. However, even if the absorption component is greater than the scattering component, resulting in a negative overall scattering on resonance, the asymmetry arising from the interference component is still present, and both the sign and the magnitude of the phase of the scattered radiation from the Mossbauer atoms may still be determined. This is not possible in conventional X-ray diffraction methods. Fig. 3a(ii) shows the conventional Mossbauer absorption spectrum and the Mossbauer diffraction spectrum





3a. (i) The experimental angular diffraction spectrum for the (200) reflection of pyrite for the cases in which the source is moving at velocities both on and off the Mossbauer resonance value.
(ii) The experimental absorption and scattered Mossbauer spectra for the (200) reflection of pyrite.

b. The nuclear component of the radiation scattered at the Bragg maximum.

c. The Rayleigh component.

d. The Rayleigh-nuclear interference component when the Rayleigh and nuclear components are of:
(i) the same phase.
(ii) the opposite phase.

e. The resulting sum of the Rayleigh, nuclear and Rayleigh-nuclear interference components when the Rayleigh and nuclear components are of
(i) the same phase.
(ii) the opposite phase.

(R+N+RN) for the (200) reflection of pyrite. In this case the phase of the Rayleigh scattering is the same as that of the nuclear scattering and Rayleigh (R) term is greater than the nuclear (N) term, resulting in overall negative asymmetric peaks.

As a corollary, if the overall crystal structure of a mineral or compound is known, then it is possible to compare the experimentally measured phase angle from the Mossbauer nuclear diffraction spectrum for a certain Bragg reflection with those calculated for a number of different possible Mossbauer sites within the crystal. This will enable positive identification of the Mossbauer atom site. If there are a number of different Mossbauer atom sites then the number of reflections required to solve the problem will be increased accordingly. This method is easiest for centrosymmetric systems in which the phase angle for each set of crystallographically equivalent atoms can only have one of two values, 0° or 180°.

We have again successfully applied this method to cordierite to identify the iron sites, and our results agree with those obtained in the QPAR method previously mentioned. Determination of the percentage occupancy of the sites by this method requires about 10% total iron and was not possible with cordierite.

The major disadvantage of this scattering technique is the very low source intensities obtainable for γ-rays compared with those for X-rays. However, the ability to determine the phase of the iron atoms is a major advantage in the solution of the structure of complex minerals, and biological compounds such as proteins. This can be evaluated by a relatively easy experimental procedure.

3. X-ray Resonance Diffraction (XRRD) Method

Specific radiation detection can in principle be extended to the more general case of X-ray diffraction using a detector which is sensitive to a particular energy of radiation. In this case the source is a conventional X-ray generator and the detector is a high resolution solid state device which distinguishes between the different X-ray resonance energies of specific trace elements and the incident radiation. The method involves a study of the difference between the normally diffracted radiation at the Bragg angle and the resonance radiation of the specific elements concerned. We have observed the effect for the iron atoms in a single crystal of sodium nitroprusside and are using it to study the substitution of iron in cordierite and iron, nickel and chromium in beryl. This method appears to be general and versatile and could open wide possibilities in new developments in structural chemistry.

Conclusions

These new methods of SRC now allow several new types of investigation, depending on the role of trace elements in compounds, to be undertaken. Some examples follow:

(i) Distribution of trace elements in minerals, how they are affected by ore genesis, and the related energetics.

(ii) Cluster formation of trace elements within the body of crystal.

(iii) The siting of impurity ions in semi-conductors.

(iv) The distribution of different valence states between crystallographically equivalent sites in compounds.

(v) The determination of the position of a trace element in a biological molecule, e.g. how much cobalt can substitute for iron in haemoglobin and does it play any significant role?

(vi) The determination of the phase angle for the diffraction of atoms in crystals.

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Acknowledgements

We thank Mr. E. F. Stevens for the drawings.

N.Z. INSTITUTE OF CHEMISTRY

CONFERENCE

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20 - 24 August 1973

The Conference is to be held in Christchurch at the Ilam site of the University of Canterbury.

This year, the theme of the Conference is "The Chemist and New Zealand Resources". The main papers of the general sessions will emphasise new uses, current problems, future developments and the utilisation of our natural resources.

The first day of the Conference will be organised by the Specialist Groups within the N.Z.I.C. together with a meeting for teachers on Chemical Education. The next three days will involve four major symposia covering minerals, wool, timber, and pastoral food products. Visits to local points of interest are to be arranged.

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5 July	*Water Chemistry and Corrosion*	Mr D. J. Ogilvy

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G. A. Wright

Some Newer Concepts in Electrochemical Science

J. O'M. Bockris

The Flinders University of South Australia, Bedford Park, South Australia.

Professor Bockris has made many authoritative contributions to electrochemical science, and his books and papers have had a profound influence in shaping modern electrochemistry. As Guest Lecturer at the NZIC Conference, Wellington, 1972 he gave the Main Lecture on which this review paper is based.

Summary

The New Electrochemistry began in the 1950's with the introduction into Western Electrochemistry of kinetic relations between overpotential and current density. Overpotential represents the shift of the Fermi level in the metal needed to bring about a change in the ratio of the anodic and cathodic current densities from that at equilibrium.

The structure of electrical double layers as Hg has advanced by the understanding of the bonding of ions to Hg, by the introduction of water molecules into the model, and by the establishment of optical methods whereby adsorption on solids can be measured. The activating step in electron transfer arises more from the partaking of the equilibrium thermal states in the reaction and less in electrostatic fluctuations within the solvent.

The evaluation of the detailed sequence of steps in electrode reactions is difficult and can only be accomplished in simple processes. Several new methods (isotope analysis; the dependence of radical coverage on overpotential, and the examination of the effect of rotation rate on ring-disc currents at the same potential) help the situation. The *rate-determining* step can sometimes be identified and is important in electrocatalysis. In this field, volcano relations between rate and substrate bond strength suggest that Pt is difficult to equal: hence the effort has gone to attempting to use very small quantities on other substrates where the rate per atom is greatly increased owing to the existence of spillover effects — one step occurs on the Pt and succeeding steps better on the main substrate.

The electrochemical reduction of oxygen, — a superimportant reaction, — is one in which the mechanism requires more clarification. H_2O_2 only occurs in a parallel path in reduction at Pt in acid, — and if the surface is dirty. However, on Au, it is an intermediate in acid: and it usually is in alkaline solution. Paths in Pt in acid solution involve bonds to the metal. The surface of noble metal electrodes has been shown to contain oxide in the anodic region and not merely adsorbed O.

Electrocrystallisation has received several clarifications recently, in particular the positions on surface at which atoms first undergo charge transfer (planes, not growth steps) and the detailed mechanism of dendrite growth where the essential fact is the emergence from the diffusion layer of the substrate of a pyramidal growth at the summit of which the radius of curvature is less than the diffusion layer thickness of the substrate. Corresponding to these conclusions are a number in mechano-electrochemistry, in which a mechanism for the acceleration of dissolution in straining is found, with an attendant effect on the interpretation of stress condition. H in metals is another area in which electrochemical theory has contributed well to the evaluation of solubility, — therefore permeability, — at local points of stress and enables one to derive a critical potential positive to which no embrittlement can occur.

Ellipsometry has been the key to the measurement of very thin films on surfaces and the understanding of passivation. Transient ellipsometry is the key to the avoidance of the effects of roughening on ellipsometric work.

It is easy to pick the area for the greatest advance in electrochemistry in the next twenty years: it will be in biochemistry where modern electrochemistry has rationalised potentials in terms of electron exchange at interfaces and the semi-conductive properties of substrates. A very speculate approach to some connections between solions and possible electrochemical brain mechanisms exists..

Lastly, the Ecological has become an area of intense effort in Electrochemical Technology. The energy of the future must be in the form of electricity from floating reactors or solar cells. The energy travels cheaper as H_2 than in wires and at the site of use it can be converted back to electricity in fuel cells. A general use of H_2 in energy conversion storage synthesis, water production, — and removal of pollution, — gives rise to the term "The Hydrogen Economy".

Introduction

It is commonplace to say that scientific fields undergo radical renewal over a period of about fifteen to twenty years. The generalization has certainly proved applicable to the field of electrochemistry. Until about 1950, books under this title described mostly the physical chemistry of ions in solution (now 'ionics'), and the electrode process aspect (now 'electrodics') was suppressed to a single fuzzy chapter. The last twenty years have been ones of tremendous development, just in this neglected area of electrode processes. It has arisen from the application of concepts of chemical reaction kinetics, and solid state physics, and the break out from the thermodynamic theory which had previously been mysteriously applied to kinetic electrode processes. But what has made the electrode process area into a really exciting one, and made it worthy of the more generous title, Electrochemical Science, is that it has been shown that electrodic concepts have a ready application to surface problems in engineering, metallurgy, biology, etc. To cap this, serious and well supported predictions of a Doomsday in the middle of the next century (pollution, exhaustion of resources) are upon us, and electrification of most processes in technology is one path among the necessary paths to escape. A corresponding evolution will be necessary in the direction of a great spread of electrochemical technology.

The aim in the present article is to describe a few of the more exciting changes in fundamental electrochemistry during the last few years.

Overpotential

The Faraday Society in 1947 held a meeting entitled "Electrode Processes" and it is possible to know something of the state of the field at that date by a perusal of the papers at the meeting. It is clear that the attitude then was still overwhelmingly thermodynamic. Electrode processes were seen in a thermodynamic way, with a disturbance of this by something called *over*potential. The origin of the latter was sought in some characteristic idiosyncracy of the electrode concerned, typically a gas film blocking the charge transfer between solution and metal.

Between 1947 and 1952 a great transition in realization in electrochemistry occurred in the West, changing to an attitude already current in Russia. The concept became generally accepted that, without overpotential, no electrochemical reaction would occur, — rather a reversal of the preceding view, according to which the main trouble about electrode processes was the *occurrence* of overpotential.

The concepts of the modern view are easily explained. If we regard the current on a surface as consisting of two partial currents, an electron donating one (electrode to solution) and an electron accepting one (solution to electrode), then the equilibrium situation, about which everybody had been writing for so many years, is given by the equation:

$$0 = i_{\rightarrow} - i_{\leftarrow}$$

A critical matter is the position of the Fermi level in the electrode. When a shift from the equilibrium position of the Fermi level occurs, the electron donating part of the current begins to exceed the electron accepting one, and a net current flows. It is the *change* of the Fermi level which is the *over*potential. Thus, the passage of a net current at an electrode is intrinsically connected with overpotential. This concept is the nucleus of New Electrochemistry, and the equation which enshrines it is called the Butler-Volmer equation which can be written in the form:

$$i = i_o \left(e^{-\alpha_c \eta F/RT} - e^{\alpha_a \eta F/RT} \right).$$

where i is current density, i_o that which occurs equally in magnitude but opposite in direction at the reversible (equilibrium) potential; α_c and α_a are near-constants usually between 0.25 and 2 in value; η is the overpotential and F/RT is a well-known parameter. The equation is the electrode-kinetics analogue of the Arrhenius equation in thermal kinetics.

Because overpotential is so important in electrochemistry, it is worth saying a word more about it. It is helpful to explain it in terms of an analogy and one of the best is that of an adjustable sales tax and its relation to income. The purchase price, the E_{rev}, has to have added to it an extra price, the overpotential, before the goods can be bought (i.e., before current can flow). To make the analogy a correct one, the tax would have to be sophisticated and increase with log of the rate of spending.

Analogies are desirable because one of the more unfortunate aspects of overpotential is that it is not widely understood among chemists, even by surface kineticists outside electrochemistry. It is the arbiter of much in electrochemical reactions, and electrochemical reactions seem to play a wide part in nature — one would think the concept would have already reached the high school books. On the contrary, although every chemist knows the exponential relationship between reaction rate and temperature, only a small fraction of them as yet know the analogous relationship between the electrochemical reaction rate and overpotential.[1]

Electrical Double Layer

The structure of the double layer as seen at the beginning of the 50's was due to Stern, and is shown in Fig. 1.

Stern[2] had mentioned in his paper that the position of specifically adsorbed ions may be different from that of the ions not so tightly bound. Grahame's[3] measurements had deepened this picture and there arose, thereby, the concept of an inner Helmholtz plane, as the plane in which such ions lie.

The major developments in concept which occurred since 1950 were in two directions. In one the concept of Lange and Mischenko[4], that there are contributions to the overpotential at the double layer separate from this due to charges, was modelized. The first equational presentation was that of Bockris and Potter[5] who supposed the existence of a water dipole layer which would contribute a potential difference which might depend on pH. MacDonald[6], suggested the incorporation of a water dipole layer into the double layer model, this was taken up by Mott and Watts-Tobin[7] who derived equations for the potential dependence of the dipole layer at the electrode, assuming zero interaction between the dipoles.

Bockris, Devanathan and Muller[8]* worked this model out in a different way, and the important aspects of their contribution were that they stressed the contribution of water dipoles to all aspects of electrode behaviour, e.g., the current-potential relation, organic adsorption, and so on. Accounting for the repulsion term reduced to more manageable portions the large potential difference which would have arisen from Mott and Watts-Tobin version of this model, which was in several ways inconsistent with observations.

The structure of the double layer as seen in 1963 was summarised by BDM (see Fig. 2). It has not conceptually changed since that time. Other authors, Damaskin[9], Levine[10], Parsons[11], have accepted essentially the addition of the dipole component of the model originating from Stern, which arose in the above sequence of contributions. The detailed model for water on the electrode is not established (BDM used a crude two-state model). It is possible for example that the water molecules may be in some kind of associated form on the surface — research needs to be in this direction.

A development of interest concerns the nature of the specific adsorption forces. These had been regarded in the past vaguely as chemical. However, the specific adsorption of tetra alkyl ammonium ions seems to be inconsistent with this. Anderson and Bockris[12] made a calculation of the interaction of anions with mercury electrode surfaces, and showed that the assumption that the dispersive interaction of the ions with the mercury surface was consistent with the degree of contact adsorption and the radius among the anions. There seems no need to assume chemical bonding.

One of the more diagnostic ways whereby one may test the consistency of a model for the electrical double layer is to calculate the adsorption isotherm. Three attempts to do this were published during the 1960's, the first by Bell, Levine and Calvert[13]; the second by Bockris, Devanathan and Muller[8]; and the third by MacDonald and Barlow[14, 15].

In spite of superficial differences, the model which underlies these three isotherms is much the same. One difference arises: that of BDM images the ions only into the metal, and neglects multiple imaging in the solution. The multiple imaging which the other two isotherms embody is certainly an overestimate, because it assumes that there is perfect dielectric imaging in the solution; this needs a sharp dielectric discontinuity, which probably does not exist at the boundary between the outer Helmholtz plane and the Gouy layer. The actual dielectric situation will be that the dielectric constant changes over some 5-10A out into the solution, and the boundary will be disturbed on a molecular scale by thermal motion. It is not easy to make the correct allowance for imaging and it may be that the approximation which neglects it is a better one. This seems to be indicated by some calculations due to Wroblowa and Muller[16], who contrasted the numerical sequences of the BDM model with that of Bell, Levine and Calvert [13] and found the latter to be grossly discrepant with experiment in four properties.

* Abbreviated to BDM for this article.

A distinction between the two isotherms became recently available from the work of Bonciocat, Bockris and Sen[17], who showed that the differentiation of the first of the single imaging isotherms of BDM predicts the shape of the capacitance-potential curve, whilst that of Levine et al[13], and of MacDonald and Barlow[14,15] did not.

Thus the situation with regard to the structure of the electrical double layer has been substantially advanced since the term of Stern. Much remains to be done. The structure of the water molecules on the surface must be researched. The interaction between adsorbed organic molecules and the water molecules must be taken into account in a third approximation of the BDM model. The greater consistency of the single imaging model with experiment is insufficient to resolve satisfactorily the single imaging verus multiple imaging problem. But the most important lack in double layer studies comes from the little knowledge of double layers at solids. Here a large field of research awaits good experimental determinations.

A start on such work has been made by Genshaw and Chiu[18], and developed by Paik and Bockris[19, 20]. It uses ellipsometry which measures the change of refractive index of the double layer during adsorption. This may be related with little ambiguity to the coverage of the electrode with ions. It can be shown that artifacts due to the potential dependence of the refractive index can be avoided if measurements are made of several sequences[24, 25]. Fredlein, Damjanovic and Bockris[21] have shown that the frequency of oscillations of a plate placed in a solution reflects the surface tensions of the metal-solution interface. They have shown that sufficiently precise control of the electrode surfaces allows the capacity to be measured with sufficient significances (i.e., absences of spurious roughness effects), so that we can apply the well-known relation:[22]

$$C = \frac{\partial^2 \gamma}{\partial \Delta \phi^2}$$

to the determination of γ, and hence, eventually, to adsorption. Such methods, as did the method of Grahame[3], involve obtaining the potential of zero charge in the solution concerned, and making one measurement of adsorption by another method; these seem less applicable than the ellipsometric approach.

Elucidation of Reaction Mechanisms

The interest in electrochemical reaction mechanisms arises partly from an attempt to relate catalytic results to rate-determining reactions.

At an early stage in the development of electrode kinetics it was thought that the gradients of the change of overpotential of log of current density would be a mechanism-indicative parameter. However, this parameter turns out to be only occasionally specifically diagnostic (Damjanovic[23]). Greater pessimism in the matter of coming to a clear conclusion on reaction mechanisms has been expressed by Despic[24], but it is not justified so long as it is recognised that there is no set and definite method whereby the rate-determining step of an electrochemical or chemical reaction may be determined; nor, often, great certainty of the uniqueness of the result obtained. Thus, Despic took computer studies of the number of possibilities of reaction mechanisms associated with certain formalised reaction sequences. The result was that the possibilities are stupendous in number. However, they are reduced to a practically small number by three factors.

(i) Chemical intuition (or formally rough estimates ($\pm \frac{1}{2}$ ev) of the heats of activation associated with various paths) throws out a great number of possibilities, which a computer might choose. (It chooses only on the basis of permutation and combination of the symbols in the chemical reaction.)

(ii) Many possibilities are eliminated by the observed α values. If a rate-determining charge transfer occurs after one more fast electron transfer has occurred, this parameter is lower than that often observed.

(iii) Lastly, it is unlikely that a unique determination can be made of a full mechanism in the sense of knowing each consecutive step, except for simple reactions, such as the hydrogen evolution reaction. But, what can often be done with little ambiguity, is to find the rate-determining step.

The rationale of mechanism determination is too long to give here (cf. Bockris and Srinivasan[25]); among examples of mechanism determination are, however, use of the dependence of radical concentration on potential which may distinguish between alternative possibilities in rate-determining steps[26], the use of isotope factors[25-29], the use of the rotating disk with ring[30-33].

Electrocatalysis

The dependence of the electrochemical reaction upon potential has given rise among non-electrochemists to a misunderstanding of what is meant by electrocatalysis: it is not the effect of the electrode potential upon the reaction rate (pedagogically, this could be called a primary electrocatalytic effect). All the interest centres on variation of the factor before the overpotential containing the term in the equation

$$i = i_o e^{\alpha \eta F/RT}.$$

Electrocatalysis in fact is catalysis in electrode reactions. We take the exchange current density as a measure of the electrocatalytic properties of a substrate.

Thus, if we consider a certain reaction, e.g., the oxygen evolution reaction, then tabulate the exchange current density as a function of the substrate at the same temperature, we are exhibiting the electro catalytic situation for this reaction. (See Fig. 3[34].)

Platinum is the best electrocatalyst for several electrode reactions, i.e., it is used in the important reduction of oxygen and oxidation of hydrocarbons in acid solution. The reason for the dominance of platinum is interpretable in terms which relate to the fact that many electrocatalytic situations obey a volcano type[29, 35] when rates are plotted as functions of a bonding parameter of the substrate. As the bond strength gets larger, the coverage of the electrode with radicals tends to increase, and thus the reaction rate; but at sufficiently high bondings, the particles are adsorbed with too great a bond strength to allow their easy catalytic removal.

Among the noble metals, platinum occupies a mid-way position in respect to heats of sublimation, i.e., bond strength. Hence, its excellent capacity as a catalyst.* Another aspect of platinum is its nobility. If an electrode is insufficiently noble, even if its catalytic power is a splendid one, it will dissolve on use. Thus, attempts to make a cheap catalyst "like platinum" would demand a substrate as noble as platinum, with bonding properties to oxygen about the same as that possessed by platinum. Looked at in this way, a substrate having properties as satisfactory as platinum becomes difficult to conceive, although it is perhaps possible in terms of conducting oxides.

The hunt for the cheap catalyst has changed its direction since 1970. The economic criterion is watts per sq. cm. per dollar of catalyst. If the platinum loading can be reduced sufficiently, platinum would become economic and the amount per year sufficiently small to be supplied.

In this respect work which shows how to position platinum in such a way that its use in porous electrodes is optimised is important.[37] However, of more importance would be work which showed that by producing the platinum in sufficiently small particle size or perhaps of a certain shape, the number of atoms per gram of platinum used as surface atoms could be increased; and perhaps the rate constant per atom augmented.

* A simplistic analysis of factors in electrocatalysis was published by Bocciarelli[36]. It assumed that the thermionic work function was of primary importance in determining the reaction rate. However, it has been shown[25] that the metal-metal junction in electrochemical cells cancels out the primary fact of thermionic work functions.

In this respect the recent work of McHardy[38] needs attention. He has shown that a few ppm of platinum in tungsten bronzes* give rise to catalytic effects which render the surface of the bronzes roughly equivalent to one which can be obtained with bulk platinum. The economic importance of this work seems substantial, but only if it can be proved that the catalysis can last through many months of use.†

A contribution from McHardy are investigations with an ion-probe technique with mass spectrography, which showed that the platinum deposits on the bronze surface were associated with alumina, presumably from the crucible. Another contribution showed that rate of reaction on the bronze varied with the third power of the platinum concentration.

Rationalisation of this has been investigated by McHardy. The surface platinum is 10^3 times more active than bulk Pt. The relation between the rate per unit area of the whole surface and the amount of Pt on it cannot be rationalized in any way except by means of a "spillover" mechanism. The O_2 undergoes a first step on the several consecutive reactions on the Pt surface. However, it goes faster with respect to the overall reaction if the radicals produced by the first step diffuse away onto the substrate of bronze and continue to react there. The mechanism leads to a rationalization not only of the current-platinum concentration, but also of the fact that the presence of platinum does enhance the dissolution of sodium.

The Oxygen Reduction Reaction

The central importance of the electrochemical reduction of oxygen:

$$O_2 + 4H^+ + 4e \rightarrow H_2O$$

arises from its being the origin of a major contribution to energy loss in fuel cells; and to the probable presence of this reaction as a part of biological energy conversion.

What is the rate-determining step of this reaction? Most of the work of the "fuel cell age" (1958-68) in seeking improved catalysts for oxygen reduction was carried out without knowledge of this rate-determining step, and therefore was largely inspired groping (as indeed has been most successful catalyst work).

The mechanism of the oxygen reduction reaction is interesting because there seem to be two path possibilities. In the one, metal-oxygen bonds are formed; in the other, hydrogen peroxide is an intermediate.

Thus, in alkaline solutions, a path which did not at all involve the adsorption of O_2 might be:

$$O_2 + e \rightarrow O_2^-$$
$$O_2^- + H^+ \rightarrow HO_2$$
$$HO_2 + e \rightarrow HO_2^-$$
$$HO_2^- + H^+ \rightarrow H_2O_2$$
$$H_2O_2 + e \rightarrow OH + OH^-$$
$$OH + e \rightarrow OH^-$$
$$^2(HO^- + H^+) \rightarrow 2H_2O$$

However,

$$S + O_2 + H^+ + e \rightarrow SO_2H$$
$$SO_2H + H^+ + e \rightarrow SO + H_2O$$
$$SO + H^+ + e \rightarrow SOH$$
$$SOH + H^+ + e \rightarrow S + H_2O$$

involves the substrate, S.

There are several ways in which one can distinguish between the two paths. Vesselowski[40] determined the reaction in the surface oxide, by introducing O^{18} onto the surface of the electrode, then evolved oxygen upon this surface. Presence of O^{18} in the evolving O_2 molecules would prove the oxide path. In the examples used by Vesselowski the result was positive.

Damjanovic and Genshaw[32] used a rotating disc electrode, with ring, extensively in the determination of the way in which hydrogen peroxide took part in the reduction of oxygen; a complex pattern of behaviour was shown.

In the reduction of O_2 at Pt, H_2O_2 only appears in so far as the surface is dirty (site blocking). It occurs by a separate parallel reaction and H_2O_2 is not further reduced to water.[41]

On the other hand, on Au in acid solution (at below 0.3v), the O_2 reduction reaction proceeds along a single reaction path with H_2O_2 as a reaction intermediate, which further reduces atom increasing rate as the potential becomes more cathodic.[42]

It is remarkable that so little work has been done on the detailed determination of the rate-determining step for oxygen reduction. Some work has been carried out by Damjanovic, Dey and Bockris.[43] The rate-determining step in the reduction of O_2 on Pt in acid seems to be (on bare Pt)

$$O_2 + H^+ + e \rightarrow OH_{ads} + O_{ads}.$$

It is difficult to make any generalizations concerning the rate depending step in O_2 reduction which apply to all noble metals. The mechanisms seem disappointingly different. They do seem to point to the catalytic importance of the metal-oxygen bond which again rationalises the situation with regard to platinum and its predominance as a good catalyst for oxygen*, for the bond is intermediate in strength among the noble metals.

One of the difficulties of work with platinum in oxygen evolution and reduction is that the nature of the oxide surface changes in the vicinity of 0.9v (with respect to a hydrogen electrode in the same solution), viz., slightly cathodic to the region of potential at which the reduction of oxygen occurs. At some positive potentials the surfaces are covered by an oxide film, whereas at more negative potentials the metal is free from oxide, although it contains adsorbed oxygen.[44] The evaluation of the characteristics of the surface of platinum as a function of potential is a good example of what may be done with ellipsometric analysis; it shows also the difficulty of interpreting reactions in catalysis without corresponding optical monitoring of the nature of the catalyst surface. Figure 4 shows ellipsometric results of Paik and Bockris[19] concerning platinum oxides: whilst the thickness increases at potentials positive to about 0.9v, the optical parameters of the oxide remain constant; thus a single oxide is growing.

Electrocrystallisation

Research on electrocrystallisation is in two parts. One studies atomic reaction paths for movement of ions from the solution to points on the electrode surfaces, followed by migration on growth sites. The other is the building of ions into various types of crystals once the ions have become atoms upon the surface, although they seem to form a kind of dipole on the surface, with an electron in the metal. The first problem was solved in the 50's; the second problem has received little attention. Although one or two special problems have been solved (in particular the theory of dendritic growth[45, 46]), most crystallization kinetics remain without even consistent systematization of facts.

Concerning the first problem, the results show that, at least on the metals examined, the ions first deposit on crystal planes, migrate across these to growth sites and incorporate into the crystal. At low current densities, the *surface* diffusion to growth sites is the rate-determining step, whereas when the overpotential is out of the reversible region, the rate-determining reaction starts to be charge transfer.

An alternative proposition was made by Harrison and Thirsk. The mechanism of Mehl and Bockris is shown in Fig. 5[47] and that of Harrison and Thirsk in Fig. 6. It is easy to distinguish between these two mechanisms be-

* These were originally thought by Damjanovic, Sepa and Bockris[39] to be themselves catalysts. Although they do have a weak catalytic power for oxygen reduction, if no other models are incorporated in them, the catalysis is not as good as that of platinum.

† Pulsing appears to restore electrodes which are becoming de-activated. Does it replate the material which has dissolved?

* Note, however, that this is not so in alkaline solution, where gold appears to be the best catalyst.

cause in that due to Harrison and Thirsk the velocity of the deposition reaction, the discharge step, would increase with the number of steps per square centimetre of surface. A critical examination to prove this point has been carried out by Razmuney and Bockris[48]. The result of the experiment showed that at crystals which contained configurations in which the number of steps per square centimetre varied seven times, the discharge rate hardly varied. In that case, the mechanism for the electrode reaction is not that of Harrison and Thirsk.

There is a general reason why discharge at steps would be less likely than that onto planes. It has to do with the distortion [49] which occurs in the solvation shell of ions when they discharge. The ion can reach the transition state with less distortion if it discharges onto a plane rather than at an edge. Therefore the former reaction is likely to be more rapid than the latter (i.e. the heat of activation will be lower). The calculations which involve this conclusion are, however, crude indeed and it was necessary to demonstrate the effect experimentally.

The likely surface diffusion path for metal deposition, at least near the reversible potential for several metals, is increased by reasonable results for the concentration of surface adions. (Cf. Table 2.)[47]

Table 2

Values of Surface Adion Concentration of Ag Electrode from Various Workers

	$C°_{ad}$ (moles am^{-2})
Mehl and Bockris	90×10^{-11}
Gerischer	15×10^{-11}
Lorenz	3×10^{-11}
Despic & Bockris:	
(a) Nonactivated	3×10^{-11}
(b) Activated	160×10^{-11}

Although the problem of a phenomenological theory for electro-crystallization has proved difficult (even on single crystals), the velocity of the growth of dendrites has been solved by Barton and Bockris[45], with significant additions by Diggle, Despic and Bockris.[46] At first pyramids grow upon the electrode surface by the rotating spiral mechanism. The pyramid may be regarded as growing up within the diffuse layer characteristic of the surrounding substrate. As it grows, the distance between the end of the diffusion layer and the pyramidal tip grows less and the rate of deposition to the tip, still controlled by linear diffusion, grows more. However, it can be shown that as the pyramid grows the tip sharpens, i.e., the radius of curvature decreases. There is a limiting condition at which the dendrite tip attains a radius of curvature which would bring it below that necessary for the beginning of spherical diffusion. The limiting current becomes controlled no longer by the thickness of the diffusion layer, but by the radius of curvature of the dendrite tip.

Hence when this spherical diffusion begins, the limiting current is greater than for the diffusional case, and the place where the tip of a growing pyramid attains a radius below that of δ, becomes then a seat of much more rapid growth. A thin crystal is formed which shoots out into the solution.

Much else can be said about the theory of this mechanism, e.g., there is a tip sharpening mechanism (so that when the tip radius is reduced to a size of the order of about 100Å, a Kelvin effect occurs in the free energy of the atoms in the tip, their dissolution tendency increases, i.e., the deposition rate at constant overpotential is reduced and the tip returned to the stable tip size). It is possible to interpret not only the fact that there is a latency time for the development of dendrites after switching on a current (it is the time for the pyramid to grow to critical dimensions), but also a critical overpotential below which a dendrite will not grow. (For the shaping properties of the pyramid are dependent on the potential.) Dendritic side arms can also be interpreted, and the shape of the growth velocity-potential relation theoretically deduced in quantitative agreement with experiment.

Mechano-electrochemistry

One of the more important aspects of the contributions of electrochemistry to engineering is the interpretation of stress corrosion cracking. It was once thought that the stress which developed at certain points in metals gave rise to changes in the reversible electrode potential, and that this affected the corrosion at points of stress. However this effect is negligible. Stress corrosion cracking is associated with the effect of stress upon some aspects of the electrode reactions occurring. Local stress may break a protective passive film; this type of dependence has been shown by Raicheff & Despic[50].

One aspect of corrosion cracking is the dependence of the velocity of dissolution of metals, unencumbered by films or by complexities of hydrogen co-deposition, upon stress. Qualitatively such effects were chosen by Gerischer[51] and quantitatively by Hoar[52]. However, these workers did not produce a theoretical model, and a detailed study leading to such a model was first carried out by Damjanovic, Raicheff and Bockris[53]. They based their work upon an essential result due to Hoar, viz. that it is the rate of stressing which is the important aspect. They discovered that the velocity of dissolution of the metal increases greatly (10 - 100 times) beyond a certain critical rate of stress.

An essential result is shown in Fig. 7[54] where the increase of current due to the application of strain at a given rate is found. The current reaction forms a plateau when the strain is sufficiently large. These plateau values of the current density depend on the rate of straining. As the rate of strain increases, an increasing number of particularly active sites per unit area and time come into the solution. The current needed, before the limiting value (all new sites used up) is reached, can increase (Fig. 8[54]). The number of slip planes which have high index faces is important. If new planes contacting the solution during straining (i.e., the slip planes) do not have a high index, the phenomenon is not observed. There is some evidence that the planes with a high index have an i_o larger than that of lower indices.

Such results may have significance in stress corrosion when the current density needed is greater than that which would seem to be available at the given overpotential (without accounting for the rate of straining on i_o).

Hydrogen in Metals

It has been known for many years that hydrogen enters under certain critical conditions into the lattice of some metals, and causes duress in their strength, with dramatic engineering consequences. The amount of damage carried out by such hydrogen is dependent *inter alia* upon the solubility of the hydrogen in the metal. This itself is dependent upon the local stress, the equation being:

$$S = S_o e^{\bar{V}\sigma/RT}$$

One important parameter which must be determined if the hydrogen damage problems are to be understood is the partial molar volume of hydrogen in the metal concerned. The first workers to do this were Beck, Bockris, Nanis and MacBreen[55]; they used an electrochemical method, the essence of which is shown in Fig. 9. Hydrogen is introduced at the cathodic side of a membrane, allowed to diffuse through the membrane, and removed anodically in a separate circuit using the membrane as a bi-electrode. The difference is that the measurement of the permeation then becomes electrical, i.e. can be sensitively carried out. It is of course necessary to devise a machine which subjects the membrane to tensile and compressive stress, after which a variation of the permeability of hydrogen with stress at once gives a partial molar volume, according to the equation:

$$\frac{\partial \ln P_1/P_2}{\partial} = \frac{\bar{V}}{3RT}.$$

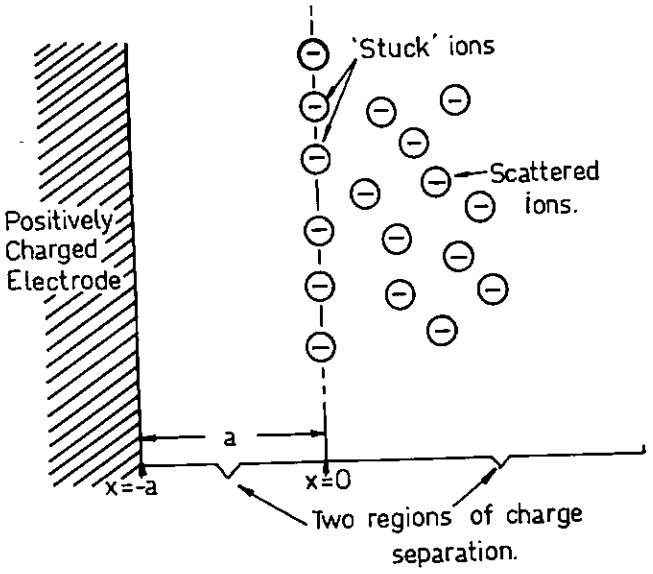


Fig. 1

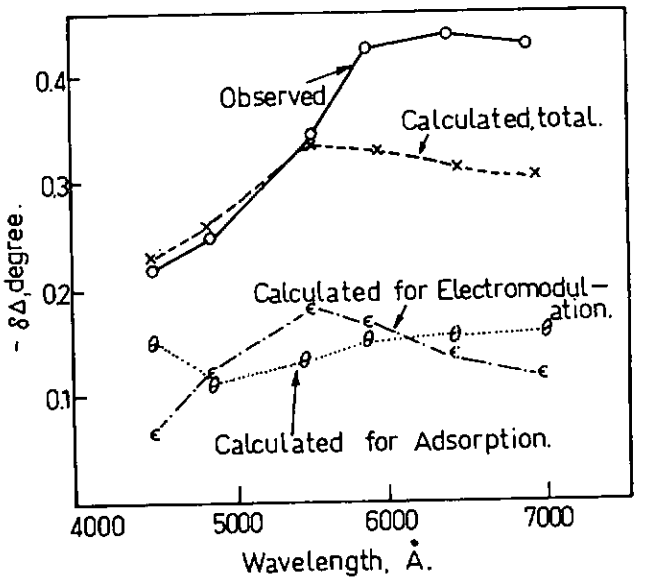


Fig. 4

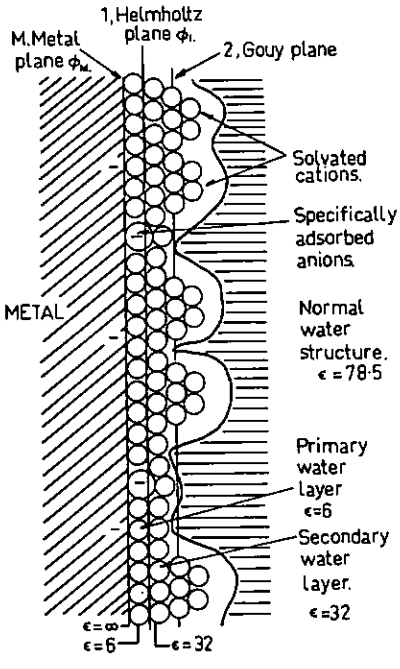


Fig. 2

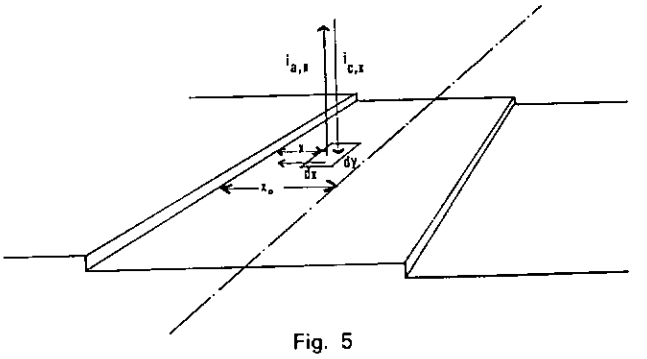


Fig. 5

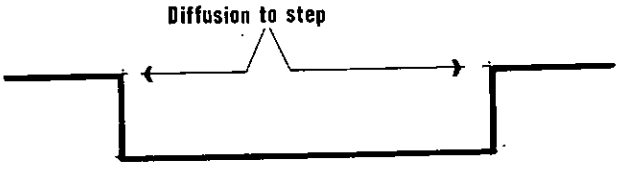


Fig. 6

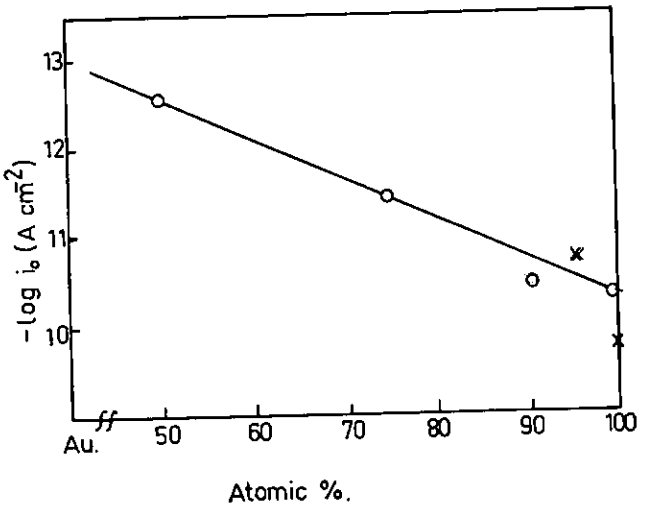


Fig. 3

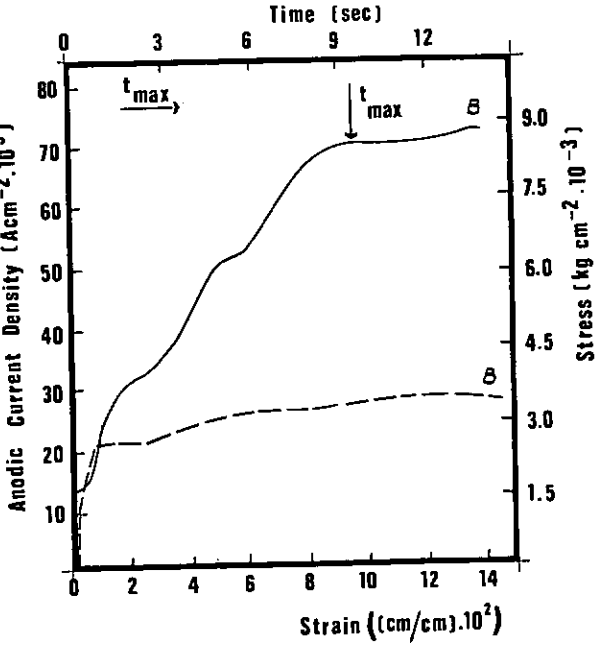


Fig. 7

It may be that here the electrochemical content was only that of an experimental technique. However, the functions of hydrogen in metals and the damage which results are subject to basic electrochemical factors. This is because the rate of permeation of hydrogen into a metal depends upon the concentration and activity of the hydrogen on the surface of the metal. Thus the rate of permeation is affected by which mechanism of hydrogen evolution is taking place on the metal (one in which the steady state of H on the surface is small; or the other large). Correspondingly, the amount by which the permeability of stressed areas increases (for permeability is proportional to solubility) is dependent upon the partial molar volume of hydrogen in the metal.

Very interesting results are obtained if one examines the permeation of hydrogen through a metal membrane as a function of time[56]. It is found that behaviour with respect to time, in particular the ability to reverse the result, is a function of time[56]. Below some critical over-potential, the result can be reversed, one could go up and down the permeation time line as many times as one wishes: the metal is undamaged. However, when the overpotential exceeds a certain amount, dependent upon the substrate, there is a fall of the permeation rate compared with a situation expected by extrapolation at lower overpotentials; the permeation-time relation becomes non-reversible; the metal is damaged. Fig 10.

It is possible to deduce a critical overpotential at which this damage can begin. If one knows the mechanism of the hydrogen evolution reaction, it is possible to relate the equivalent pressure inside voids within the metal to the overpotential. Knowing this pressure inside the voids, it is possible for one to relate the pressure at which spreading of the voids will occur to the mechanical properties of the metal, e.g. Young's modulus, and the shape of the crack. Knowing the mechanism of the hydrogen evolution reaction and the mechanical properties of the metal, one can show the overpotential at which the spreading of cracks occurs. Thus, an electrochemical condition for the stability of metals to hydrogen is available.

Such work relates directly to spontaneous corrosion, so long as hydrogen evolution is the cathodic reaction, and it should be possible to estimate the region of danger by calculating the critical overpotential needed for cracking a certain metal, relating this to the mixed potential at which the metal corrodes.

Thin Films on Metals

Civilisation depends upon the protective nature of very thin films on metals, for only the noble metals are stable in natural environments and the rest would decap to oxides of low strength if they were not protected by oxide layers. These oxide layers are however very thin, often $<<50$Å, and until the mid-1960's, their detection and examination by electromagnetic radiation was uncertain.

Ellipsometry has made the difference to the study of these situations. The major advantage of the technique for electrochemical problems is that it is not foiled by the adsorption of the incident radiation in the solution, as would be, say, an electron beam in an attempt to apply LEED to electrochemical systems.

What one does in ellipsometry is to irradiate a surface with elliptically polarised light, knowing certain parameters Δ and Ψ before and after the light strikes the surface. Briefly, Δ measures the change in amplitude. Thus parameters Δ and Ψ can be related to the film parameters; t the film thickness in n_∞ the film's refractive index; and κ the film's adsorption coefficient. Up to 1971 ellipsometry was a laborious technique for it involved not only the optical dimensions, but also some auxiliary measurement (coulometry of the surface usually) to bring in a third piece of information, so that the two experimental parameters Δ and Ψ, plus the auxiliary parameter, could be used to solve equations with three unknowns. In 1971 Paik and Bockris [19, 20] showed that the expression of the intensity of reflection involved also the same t, n_∞ and κ, as did the expressions for Δ and Ψ. Therefore, parallel measurements on the same surface under the same conditions of the intensity of the reflected wave allow us to evaluate all three ellipsometric parameters.

An example of the application of ellipsometry is the evaluation of the passive situation of iron in solutions of pH 8.4[57]. Fig 11 shows the parameters of the iron before and after passivation. The interpretation is that as the current climbs towards the peak, islets of oxide develop near the iron surface; by the time the peak has been reached they nearly fill the surface[58]. The islets are crystalline. However, Mossbauer spectroscopy [59] on the passive layer shows that part of it is amorphous. It follows that the final composition of the passive layer seems to be formed not only by the growth and coagulation of the oxide islets, but also perhaps by the very high current density of the dissolution of iron in the free areas between the islet, this perhaps results in a dissolution-precipitation contribution (which would tend to give an amorphous layer) finally blocks dissolution. Work by Bockris, Bhimisano Rao and Reddy [60] seems to show that in the case of nickel at pH 3.4 the major mechanism is dissolution-precipitation. Some doubt was expressed in this work when it was shown that ellipsometric parameters could be affected by roughening[57], if the measurements were not carried out quickly enough (within seconds). Furthermore, a sign was incorrect in the analysis of the dependence of the growth on time. The mechanism for nickel is hence ambiguous. However it has been shown by Reddy[61] that the sign used in the original paper is still valid and consistent with a dissolution-precipitation interpretation of the results. A number of numerical crosschecks on the nickel results seem to support the correctness of the original model.

Transient ellipsometry is the ultimate technique in electrode-surface measurements. The development of ellipsometric spectroscopy also promises much (Cf. Kruger and McBee[62]).

Bio-electrochemistry

In biological systems electrical potential differences are found at all membrane-solution interfaces. Since the beginning of the century such potential differences have been interpreted blandly in terms of the Nernst equation[63]; (a) because the knowledge of electrode kinetics was absent, or not widespread; and (b) because an electrode kinetic interpretation upon more molecular lines seemed to require "electrodes", and the presence of electronically conducting analogues of electrodes could not be seen in most biological systems. The work of Rosenberg[64] and others has cleared away this difficulty, and we know now that many biological materials exhibit semi-conduction. The way has been cleared to an electrodic interpretation of many biological phenomena. The present situation has been summarised by Drazic[65].

Qualitatively, a thumbnail sketch of the direction of development can be given. Essentially, some biological systems can be seen as containing electrochemical circuits equivalent to microfuel cells. A hint of the existence of electrochemical energy conversion arises if one attempts to interpret, though in an all-too-general way, the high efficiency (40-50%) of biological energy conversion[66]. This clearly cannot involve a heat engine, nor photovoltaics. Electrochemical cells would give very high efficiencies were they to be in some sense responsible for conversion of the chemical energy of the oxidation of organic molecules to mechanical work.

Del Ducca and Fuscoe[67] were the first to suggest a specific model for this and it is shown in Fig. 12.

Freeman Cope[68] was the first to draw a diagram with the same type of suggestion, the fuel cell-like function of a biological cell, but with some experimental evidence. Lazzaro Mandel[69] was the first to give specific evidence that the relation of the rate of certain biological reactions

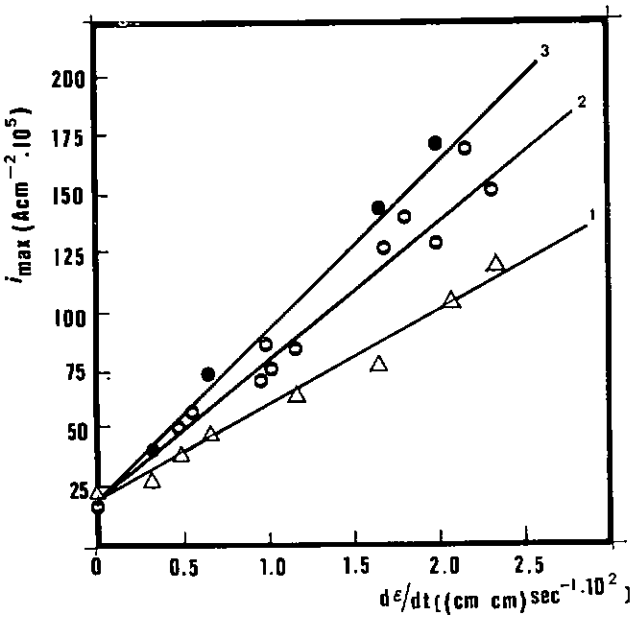


Fig. 8

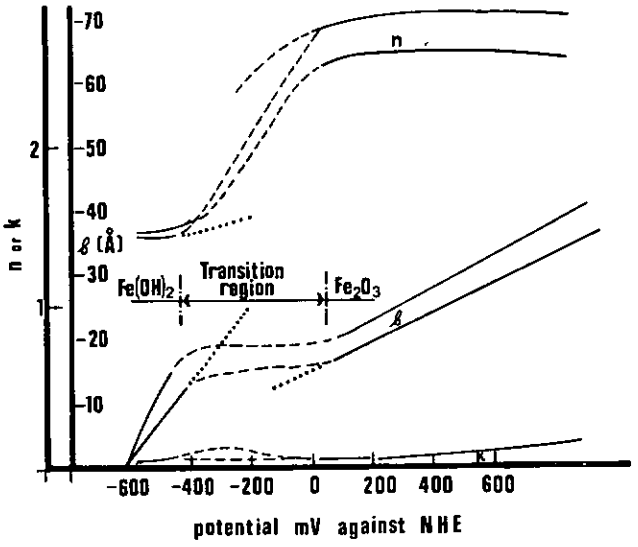
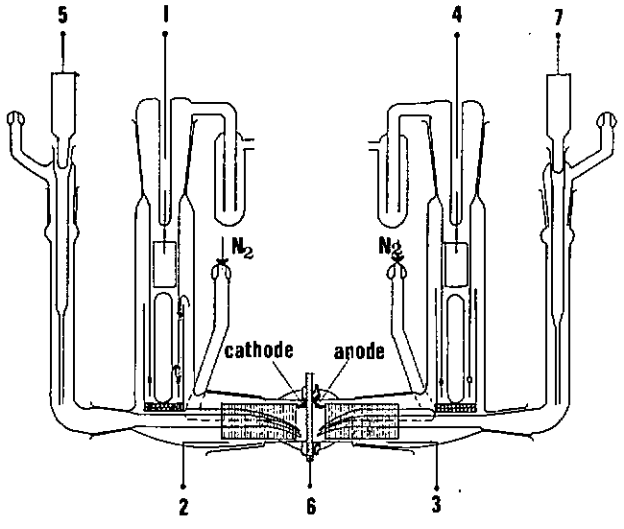


Fig. 11



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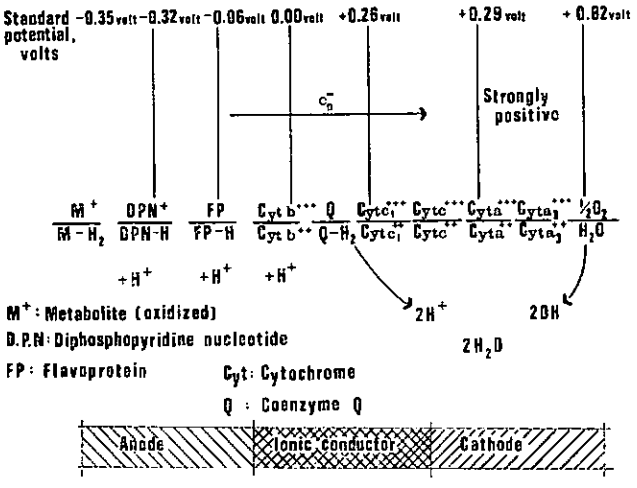

Fig. 12

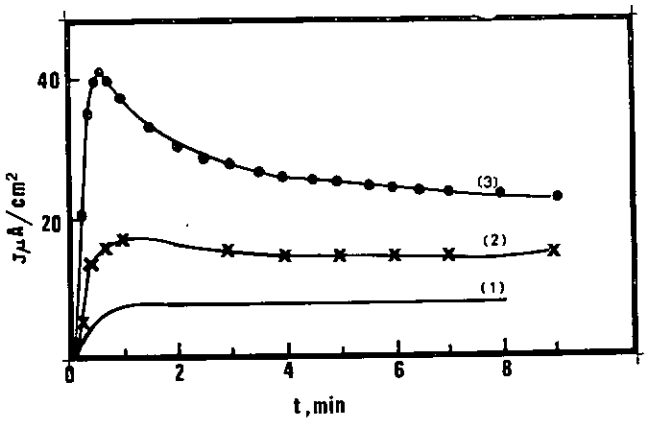

Fig. 10

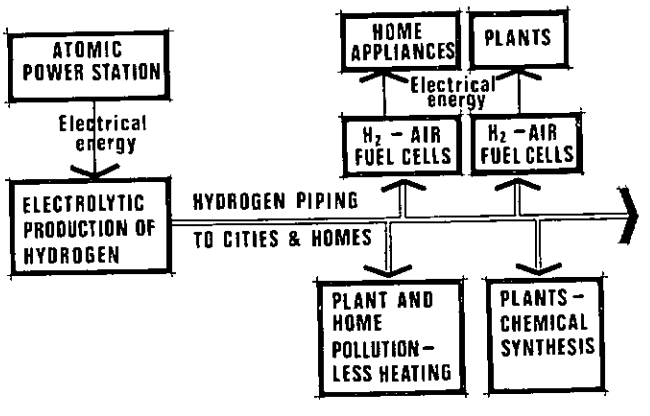

Fig. 13

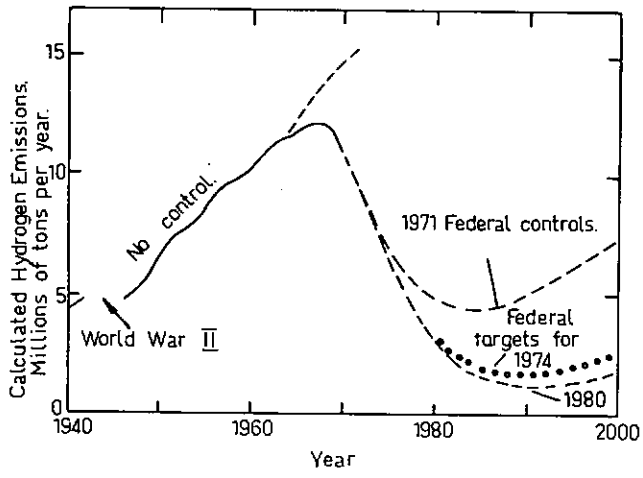

Fig. 14

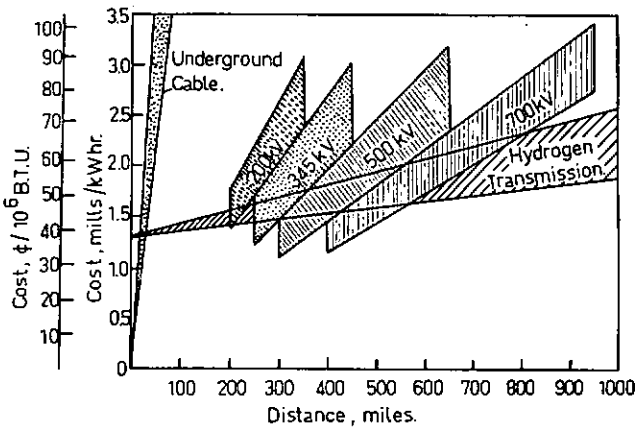

Fig. 15

to potentials across membranes was characteristic of interfacial electrochemical charge transfer.

These works were drawn together by Bockris[70] who suggested that the prevalence of electrical potential differences in biological situations and the specific results of Cope and Mandel implied that interfacial charge transfer was frequently a rate-determining step in biologically important reactions. Some biochemical reactions may not be thermal reactions, in which the main points is collision between the particles and reaction in this way, but rather electrochemical cells in which the reactants do not necessarily meet, but communicate by means of exchange of charge with a common substrate.

Recently Bockris and Drazic[63] have made speculative suggestions which attempt to relate the function of some solions (electrochemical devices in which current is controlled in a specific way by diffusion and very sensitive to change of size of the passage between the two electrodes) which can be used as integrators and differentiators, and mechanisms in the brain. One may speculate that computer-like mechanisms in brains may utilise, in the absence of electromagnetic systems, such electrochemical elements.

The Electrochemistry of Cleaner Environments

It has for many years not been good for the reputation of the scientist to make predictions of doom by pointing to increasing pollution, exhaustion of resources, failing energy reserves, etc. However, Doomsday discussions have now been given respectability by work published by Meadows et al[71]. The essence of the work is the use of computers to calculate the feedback effects of various postulated scenarios of government control, devotion of substantial parts of the gross national product to anti-pollution research, etc. The general result is that using present technology around A.D. 2050 (± 30 years) will be seen, whatever scenario is chosen, very dramatic happenings — sudden intolerable rise in pollution, sudden great reduction in population, etc., which can be reasonably described as a breakdown of the technological society.

However, there is a brighter side to the work of Meadows et al[71]. If the world population can be stabilized by about 2000 A.D. — if completely clean abundant energy can be achieved — and if recycling of all metals, and much else, can be achieved — then the Doomsday conclusions can probably be avoided.*

The significance of electrochemical technology in this context is the following: At present, only 7% of our energy is through the medium of electricity, the rest is fossil fuels. The continued burning of fossil fuels will indeed lead to the kind of disaster indicated by Meadows et al[71], there is no way by which pollutants can be removed from effluents 100%, and the maximum particle removal, say 95-99%, means that the net pollutant ingress would rise again (from c. A.D. 1990) towards the amounts experienced in the absence of controls. (See Figs. 13[72] and 14[71]).

However, in the new sources of energy (atomic, solar, geothermal), the medium of all energy will originate from electricity. Electrochemical processes will replace most chemical processes. The latter were polluting, and, although they can be made cleaner, it is doubtful whether their economics, even when cleaned, will be comparable with the economics of intrinsically clean electrochemical processes, using very cheap electricity which must arise from abundant atomic energy.

Another aspect of the wide role which electrochemistry will play in the post industrial society arises from the concept of the Hydrogen Economy. To obtain very cheap electricity (e.g., one-fifth the present cost), reactors must be very large indeed (10,000 MW). Their thermal pollution could not be withstood on land. They must float. This means that they may often be a long way from the centres in which the power will be used. Transfer of electricity over such long distances, say 1,000 miles by a grid system, would make it expensive. This is not so if it is ferried about as hydrogen in pipes (Fig. 15). The hydrogen would be produced from the almost cost-free electricity produced at the reactor site. It would be reproduced by fuel cells at the receptor site. The advantage would not only be the production of cheap electricity, but the presence of pure water. Domestic drinking and cooking water will come with the electricity supply.

The Hydrogen Economy is being extensively examined, and in many senses appears to offer the basis of an Ultimate Economy, i.e., one which, in terms of the energy available from it, or the pollution which it would build up, would be viable as far ahead as we can at present conceive.

Conclusion

What impresses about the field of Electrochemical Science is its breadth and its relevance to the near future. There appears to be at present three great areas of interest in electrochemistry, research into which would form part of the basis of a viable future.

(1) The development of surface aspects of materials science, and therefore material stability.
(2) The development of a non-pollutive technology.
(3) The development of bio-electrochemistry.

All these areas are associated with one concentral concept, the dependence of the electron flow rate upon the displacement of the Fermi level in the metal from that at which there is no current, i.e., the overpotential.

* However, it is not yet clear whether the steady state concentration of recycling metals (etc.) will be able to support the present world population.

ANNOTATIONS TO FIGURES:

Fig. 1. Stern Model with a layer of (—1) excess charge stuck to the electrode and the remainder scattered in cloud fashion. The locus of centres of the stuck ions is at a distance 'a' from the electrode (Note: only the excess charges are shown in the diagram and the water molecules are omitted. The latter sit on the electrode and separate it from ions).

Fig. 2. Solvent adsorption model of the double layer according to Bockris, Devanathan and Muller.

Fig. 3. Extrapolated value of log (Exchange Current Density) for oxygen reduction on Au-Pt and Au-Pd alloys as a function of alloy composition.

Fig. 4. Observed and calculated change in relative phase retardation, $S\Delta$ of polarised light with wavelength accompanying a potential change of 0.5v (versus NHE) of gold electrode in 0.1N Br^- solution.

Fig. 5. The model of an electrode surface for consideration of current distribution. (↓) cathodic current. (↑) anodic current. (←) surface diffusion flux.

Fig. 6. Model with rate-determining diffusion to a step.

Fig. 7. Anodic c.d. – strain and stress – strain (broken lines) relationships for iron "B" in deaerated 0.11N H_2SO_4 solution at E = –0.290V (NHE) and strain rate of 0.01/(cm/cm sec^{-1})/.B–breaking point.

Fig. 8. "Maximum" anodic c.d. (i_{max}) – strain rate ($d\epsilon/dt$) relationships for iron "A" – 1, iron "B" – 2, and iron "C" – in dearated 0.1N H_2SO_4 solution. Initial c.d. 15.10^{-5} Acm^{-2}.

Fig. 9. The cell used for the determination of hydrogen permeation rate.

Fig. 10. H_2 permeation transients for Armco Fe (thickness L = 0.77 mm) in presence of 0.1N H_2SO_4 for increasing cathodic current densities at 25°C. (i) i_c = 0.4mA/cm^2; (2) 0.8mA/cm^2; (3) 4.3mA/cm^2.

Fig. 11. The solution of the ellipsometric results, using coulometry and assuming $Fe(OH)_2$ below this peak and Fe_2O_3 above it.

Fig. 12. Analogy of biological oxidation of a metabolite to a conventional electrochemical oxidation reaction.

Fig. 13. The Hydrogen Economy.

Fig. 14. Estimated effect of federal controls in the U.S.A. on hydrocarbon emission from passenger vehicles. A rising trend is expected after 1985 because of increasing number of cars.

Fig. 15. Relative costs of energy transmission by electricity cables and by hydrogen pipeline.

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BRANCH NEWS

Auckland

The Auckland Branch has encouraged some local members to investigate the local disposal of noxious chemicals. One outcome of this has been the establishment of a disposal service organisation based at Rocklabs Ltd., Parnell. More details will be announced later.

The Auckland Branch offered its services to the Police and the Commission of Enquiry into the spillage of a dangerous chemical which led to the "Parnell Civil Emergency". Several members were involved in the course of their employment.

The Branch has donated $10 to the George Holmes Memorial Fund.

Mr. H. C. Green has been recommended as official observer to the Centennial Conference of the Society of Analytical Chemistry to be held in the Imperial College, London from July 16 - 19 1974.

The committee is discussing reciprocal membership with the Oil and Colour Chemists Association.

Professor R. J. H. Clark, University College, London, visited Auckland recently and gave a lecture at the University on "Advances in Raman Spectroscopy". Professor Clark is a graduate of Canterbury University.

A joint symposium on Food Chemistry with the Institute of Food Technology is planned for Wednesday May 9th at Danish House.

Personal

Dr. W. R. Roper returned recently from leave at Bristol University where he researched on organo-metallic compounds.

Mr. B. N. Hannan is spending one year as a tutor, touring the Mediterranean on a luxury yacht!

Mrs. Mary Mullens has left U.E.B. Industries to become a technician in the Chemistry Department, Auckland University.

Mr. N. Lodge has returned from the U.K. where he successfully completed a one year course at the University of Reading leading to the degree of M.Sc. (food science).

Manawatu

The March meeting of the branch was addressed by Professor J. K. Syers, Soil Science, Massey University, on 'Recent Research into the Chemistry of Phosphate in Soils'.

Massey University

Recent visitors to the Department of Chemistry, Biochemistry and Biophysics have included Dr. D. Williams, Cambridge University, Dr. R. J. Clark, University College London and Dr. H. Mohler, Research Biochemist from Roche Products Laboratories, Basle.

Dr. D. R. K. Harding has arrived to take up a post-doctoral fellowship in the Department of Chemistry, Biochemistry and Biophysics. He is to work with Professor R. Hodges on the organic chemistry of polypeptides. Dr. Harding is an honours graduate from the University of Canterbury and gained his Ph.D. from the University of Western Ontario.

Dr. K. W. Jolley has returned from leave spent at the University of Liverpool and Jeol Laboratories, London. He was investigating recent developments in Fourier Transform Nuclear Magnetic Resonance.

Applied Biochemistry Division D.S.I.R.

Dr. L. Kennedy has been appointed to work on the enzymology of regulation of carbohydrate metabolism in plants and in bacterial systems. Dr. Kennedy graduated Ph.D. in biochemistry from Otago University and spent two years doing post doctoral work on the microbial metabolism of polysaccharides in the Biochemistry Department, University of California, Davis.

Dr. L. N. Nixon has been appointed to work on the characterisation of mutton flavour volatiles using gas chromatographic and mass spectrographic techniques. Dr. Nixon graduated Ph.D. in organic chemistry from Otago University and spent two years doing post doctoral work on the chemistry of biosynthesis of pyrroles and porphyrins in Professor Battesby's Department in the University of Cambridge.

Dr. J. W. Lyttelton is spending six months at the Plant Industries Division, C.S.I.R.O., Canberra. There he is continuing studies of the reactions of isolated chloroplasts in relation to limitations to the photosynthetic effciency of plants.

Dr. G. B. Russell is spending 15 months at the Unit of Invertebrate Chemistry and Physiology, University of Sussex, Brighton, working on the chemistry of insect hormones, in relation to previous studies he has made of phytoecdysones in New Zealand trees and ferns.

Dr. G. W. Butler recently attended a meeting in London concerned with chronic cyanide toxicity arising from the use of the tropical crop cassava, organised by the International Development and Research Centre.

Wellington

Chemistry Division, D.S.I.R.

Dr. A. F. Wilson, Technical Superintendent at the N.Z.F.P. Mill, Kinleith, delivered a seminar in February which was entitled "New Developments in the Forest Industry". This well-attended lecture gave an insight into both the advantages and shortcomings of the present pulping process and suggested lines of research which might lead to better utilisation of the raw material.

Mr. S. S. K. Tan, who gained his Bachelor of Food Technology from Massey University, has joined the Food Laboratory.

Mr. G. J. Soteros, who recently completed papers for his M.Sc. at Victoria University, has joined the Water Laboratory.

Mr. R. A. Palmer, a student bursar, has joined the Physical Chemistry section where he will be involved in E.S.R. and Mossbauer studies. Mr. Palmer recently completed studies for his M.Sc. under the supervision of Dr. E. Sinn at Victoria University.

Mr. R. J. Armstrong has resigned from the Toxicology Section. He hopes to continue the same line of work in the U.K.

The Dominion Analyst, Mr. I. R. C. McDonald, attended the 3rd Australian National Symposium of Forensic Sciences which was held in Sydney in February While in Australia Mr. McDonald made a visit to the Division of Analytical Laboratories' New South Wales State Laboratory, studied the operations of the Breathalyser system in N.S.W. and was involved for two days with State analysts and police in a discussion on illicit drugs. He was also called to Canberra to discuss the incidence of mercury in New Zealand fish exports to Australia.

Soil Bureau, D.S.I.R.

Dr. B. K. G. Theng was recently awarded a Senior Fellowship by the Alexander von Humboldt Foundation of the German Federal Republic. Dr. Theng and his family left Wellington in February to spend approximately fifteen months in the University of Bonn.

Victoria University of Wellington

S. R. McConnell has been awarded the McKee Trust Post-graduate Scholarship, and A. D. Woolhouse the 1971 Hilder Memorial Prize which is awarded by the New Zealand Institute of Medical Laboratory Technology.

Canterbury

The February meeting of the Branch was held at the Medical Centre of Christchurch Public Hospital. A buffet meal for members and their wives was followed by a tour of the Clinical Biochemistry Department.

This year's "Chemistry in Action" lecture to 6th and 7th form students was given by Professor G. N. Malcolm and entitled "Macromolecules in Physical Chemistry and Molecular Biology".

The Branch prize for second year chemistry for 1972 has been awarded to Mr. J. A. N. Chambers.

Lincoln College

Professor B. Howard has returned from sabbatical leave. He spent six months with the Rowett Research Institute in Aberdeen before going to the Department of Bacteriology, University of California at Davis where he investigated different aspects of rumen bacteria.

Dr. R. Bicherstaffe has been appointed to the staff of the Biochemistry Department. He comes from the Unilever Research Laboratories in Bedford, England.

Mrs. G. M. Reid and Mr. D. C. Edmeades have been appointed Teaching Fellows in the Department of Soil Science.

Canterbury University

Dr. P. G. Hodgson has taken up an appointment as visiting lecturer for 1973. He will be working on single crystal E.S.R. studies of coboglobin.

Professor R. O. C. Norman will be at Canterbury for about 6 weeks in July and September as an Erskine Fellow.

The Chemistry Department is mounting Open Day displays on May 2-5 as part of the University of Canterbury centenary celebrations.

Professor L. F. Phillips has been awarded a Corday-Morgan Medal and Prize for 1971 by the Chemical Society.

Christchurch Hospital

Miss M. Taylor and Miss M. Sheat have joined the Clinical Biochemistry Department.

Industry

Miss R. Dorrington, a graduate of Massey University, has joined the staff of the TVL Biochemical Laboratory at Prebbleton.

Otago

Issues in Regional Development

The first local branch meeting for the year was held jointly with the local branch of the Royal Society of New Zealand. Three members of the National Development Council, who are also all Fellows of the Institute, spoke on the following topics:

Sir Malcolm Burns, "Beech Forests".

Dr. H. C. Holland, "Industrial Development and Conservation".

Professor J. F. Duncan, "Power, Politics and People".

The meeting gave local members the opportunity to discuss aspects of the Regional Development Seminar, held in Dunedin on 14th and 15th March, with members of the N.D.C. About 160 people attended.

Chemsitry Department, O.U.

Dr. R. F. Smith has returned after a year's sabbatical leave which he spent at Imperial College working on topics in electrochemistry with Professor M. Spiro. The latter was Mellor Visiting Professor at Otago in 1970.

Professor Loren Hepler of the University of Lethbridge, Canada, is currently Mellor Visiting Professor. He is at present giving a series of lectures on various aspects of the application of thermodynamics to chemical problems.

Drs. B. M. Peake and C. G. Pope attended the Second Australian Summer School in Theoretical Chemistry, held at the Research School of Chemistry, Australian National University, Canberra, during the two week period 4th - 16th February.

Pharmacy News

Dr. H. W. Puffer, formerly a Lecturer in Pharmacy at Otago University, while returning to Los Angeles from a marine toxin expedition on the research vessel Alpha-Helix in waters near New Guinea, called on former colleagues at Otago in a brief but most welcome visit in January 1972.

Visitors

Dr. R. J. H. Clark, Reader in Inorganic Chemistry, University College, London, visited the Chemistry Department on the 13th and 14th March. He gave two lectures, the first on the Raman Spectra of Molecular Halides in the Vapour and Condensed Phases, and the second covered certain aspects of the history of titanium chemistry.

Professor J. F. Duncan, Head of the Department of Chemistry, Victoria University of Wellington conducted a seminar on "Recent Developments in Mössbauer Crystallography" on the 15th March.

Book Review

Industrial Chemistry — Organic (2nd Edition), by D. M. Samuel. Published by The Royal Institute of Chemistry (Monographs for Teachers No. 11), London, 1972. 142 pages. Price £1.50 (£1.12½ to C.S. members).

The products of the organic chemical industry are buttresses to the structure of modern life, without which most of our creature comforts and a good deal of its essential fabric would crumble. Mr. Samuel's little book deals systematically with industrial organic chemistry from its precursors and their sources to its products and their uses, and makes frequent, useful comparisons between competitive, obsolescent and obsolete processes. The bulk of today's industrial organic products are most economically manufactured from petroleum feedstocks, and since the present state of the industry is the concern of Mr. Samuel's book, little space has been devoted to other renewable raw materials, the organic organics. The massive contribution of petrochemicals, some 90% of total organics produced by industry and amounting to about 25 million tons per annum in Western Europe alone, makes it imperative that the common schoolboy should be disabused of such beliefs as that potassium cyanide is made from horses hoofs and wood-ash, or even that ethyl alcohol is usually prepared by the fermentation of sugars. These and more complex molecules are more frequently manufactured directly from hydrocarbons, air and water under controlled conditions in processes of charming stoichiometric simplicity, but which are no doubt extremely tedious mechanistically. I find the work informative and interesting, the text well supplemented by a large number of flowsheets and illustrations together with a useful appendix of current (1972) prices of many commercial organic materials. The book suffers perhaps from its lack of a subject index and cannot therefore be classified as a pocket reference work. It is however what the author intended it to be, a readable and educational monograph.

Alan Metcalfe.

Copies of this Monograph are available from the Registrar — $3 per copy.

Invitations

Australia

The next conference of the Organic Division of the Royal Australian Chemical Institute will be held at the holiday resort of Cowes, Phillip Island, Victoria (80 miles from Melbourne) from February 18-21, 1974. Members of the N.Z.I.C. are cordially invited to participate in this conference. Invited speakers include R. W. Taft, University of California, and J. E. Baldwin, Massachusetts Institute of Technology. Apart from the presentation of invited lectures and research papers, the organisers hope that the relaxed atmosphere of Cowes will prove conducive to informal meetings and discussions.

Anyone interested in attending this conference should write for further information to Dr. L. W. Deady, Chemistry Department, La Trobe University, Bundoora, Vic. 3083, Australia.

Poland

From 17 to 22 September 1973, the United Nations Educational, Scientific and Cultural Organisation (UNESCO) will convene in Wroclaw, Poland, an *International Congress on the Improvement of Chemical Education*, in collaboration with the Committee on the Teaching of Chemistry of the International Union of Pure and Applied Chemistry (IUPAC), and the Polish National Commission for UNESCO. The conference will be sponsored in Poland by the Polish Academy of Sciences and by the Ministry of Science, Higher Education and Technology, and will be held at the Institute of Chemistry University of Wroclaw. Participants will be accommodated in the hotels and student hostels in Wroclaw.

This Congress is part of an ongoing programme for the improvement of chemical education which, in the past, has included the collaboration of UNESCO and IUPAC in the publication of a survey of chemical education at university level, a publication on evaluation in chemistry, and conferences in various countries on chemical education.

Aims of Congress

In addition to the exchange of ideas and information among those directly involved, the principal aims of the Congress will be:

1. To identify and analyse the present problems and recent trends (especially over the last four years) in chemical education, at all levels; within and outside the formal educational system.
2. In the light of this analysis, to outline a proposed four-year co-operative plan of action — among international, regional and national organisations — for the further improvement of chemical education.
3. As a means of disseminating widely the analysis of the problems and the proposed solutions, to prepare material for Volume IV of "New Trends in Chemistry Teaching".

Topics of Trend Papers

The main work of the Congress will be centred around the discussion and refinement of papers, circulated in advance of the Congress.

The areas in which such trend papers will be prepared have tentatively been identified as the following:

1. Factors influencing chemical education:
   The public image of chemistry and society's needs; the evolving needs of other professions; the changing needs and views of industry; evolution in the nature and structure of chemistry; the changing characteristics of students; new understanding of the psychological processes of learning chemistry; new and more detailed learning objectives in chemistry; variations in methods of teaching chemistry, including the role of laboratory work; the enhanced potentialities of new educational technology.
2. New approaches to the process of designing and evaluating chemistry courses and programmes.
3. Improved techniques of assessing student achievement.
4. Trends in training and retraining chemistry teachers.
5. National chemical education improvement — varying approaches.
6. International co-operation in chemical education improvement.

All participants will attend in a personal capacity. Attendance will be limited to about 250-300. Those wishing to receive an invitation should apply to the Division of Science Teaching, UNESCO 7, Place de Fontenoy, 75700 Paris, immediately.

The final versions of the trend papers, along with the recommended co-operative action programme, will become Volume IV in the series of UNESCO publications on "New Trends in Chemistry Teaching".

Conditions covering award of Institute Prizes

1. THE I.C.I. PRIZE

This prize of $100.00 and a medallion has been donated by I.C.I. (New Zealand) Ltd. The conditions of the award are as follows:

1. The prize shall be awarded to a member of the Institute who, in the opinion of the Council, has made some contribution to some branch of chemical science, this contribution to be judged by research work published or accepted for publication during the five years immediately preceding 30 April in the year of the award.
2. Applications by members, or nominations, which may be submitted by Branch Committees or by individual members, must be accompanied by copies of papers presented in support of the entry. The Council itself may nominate candidates for the award.
3. A nomination or application, once made, shall stand for five years, but material which fails to satisfy clause 1 shall automatically be deleted, and additional material may be presented at any time.
4. If in the opinion of the Council there is no candidate of sufficient merit, the Council may refrain from making the award.
5. The prize shall be presented at the annual conference of the Institute or at a meeting of the Branch to which the prize-winner belongs.
6. A member to whom the prize has been awarded shall not be eligible for re-nomination.

2. THE CHEMICAL ESSAY PRIZE

The New Zealand Institute of Chemistry shall offer annually a prize for an essay or review on a chemical topic. The conditions of the award are as follows:

1. The prize shall be open to anyone who has not attained the age of 25 years before April 30 in the year of the contest, whether a member of the Institute or not.

   (Note: Entries from students will be welcomed).
2. The entry shall be not longer than 5,000 words.
3. The entry shall be in a form suitable for publication and the Institute shall have the right to publish the winning entry.
4. Applications, in completed form, must be received by the General Secretary, P.O. Box 250, Wellington, not later than 30 April in the year of the contest.
5. The entries shall be judged by a Committee of examiners set up by Council for the purpose. The President of the Institute and the Editor of the Journal shall be ex officio members of this Committee.
6. The award shall be made by the Council after consideration of the report of the Committee of examiners, and the presentation of the prize shall be made, whenever possible, at the annual conference of the Institute.
7. No award shall be made if, in the opinion of the Committee of examiners, there is no entry of a sufficiently high standard of merit.
8. The value of the prize shall be such sum as the Council may from time to time determine, and the prize shall be spent on books or instruments to the satisfaction of the Council.

   (Note: The value of the prize is at present $50).

3. Sponsorship for the Morcom-Green Edwards Prize has been withdrawn.

FINAL REPORTS FROM IUPAC

The following Final (Definitive) Reports have been published in *Pure and Applied Chemistry* during 1972.

Reprints of Reports marked * may be purchased from the IUPAC Secretariat, Bank Court Chambers, 2-3 Pound Way, Cowley Centre, Oxford OX4, 3YF, U.K.

A Guide to Procedures for the Publication of Thermodynamic Data (Commission on Thermodynamics and Thermochemistry): 29 (1-3), 395-408.

Erreurs en Microanalyse organique elementaire (Commission des Methodes microchimiques et d'Analyse des Traces)—I: 29 (1-3), 409-492; —II: 29 (4), 629-686; —III: 30 (1-2), 301-334.

Catalogue of Physicochemical Standard Substances (Commission on Physicochemical Measurements and Standards): 29 (44), 597-616.

Recommendations on Ion Exchange Nomenclature (Commission on Analytical Nomenclature): 29 (4), 617-624.

Recommendations for the Presentation of NMR Data for Publication in Chemical Journals (Commission on Molecular Structure and Spectroscopy): 29 (4), 625-628.

Atomic Weights of the Elements 1971 (Commission on Atomic Weights): 30 (3-4), 637-650.

* Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis—I: General Atomic Emission Spectroscopy (Commission on Spectrochemical and other Optical Procedures for Analysis): 30 (3-4), 651-680. Price US $1.20 (£0.40).

Nomenclature of Inorganic Boron Compounds (Commission on Nomenclature of Inorganic Chemistry): 30 (3-4), 681-710.

* Definitive Rules for Nomenclature of Steroids (Commission on Nomenclature of Organic Chemistry and IUPAC-IUB Commission on Biochemical Nomenclature): 31 (1-2), 283-322. Price US $1.50 (£0.50).

Analysis of Interlaboratory Measurements on the Vapor Pressure of Gold [31 (3), 371-394] and of Cadmium and Silver [31 (3), 395-432] (Commission on High Temperature and Refractory Materials).

* Definitions, Terminology, and Symbols in Colloid and Surface Chemistry—I (Commission on Colloid and Surface Chemistry): 31 (4), 577-638. Price US $2.25 (£0.75).

A One-letter Notation for Amino Acid Sequences (IUPAC-IUB Commission on Biochemical Nomenclature): 31 (4), 639-646.

Definitive Rules for Naming Synthetic Modifications of Natural Peptides (IUPAC-IUB Commission on Biochemical Nomenclature): 31 (4), 647-654.

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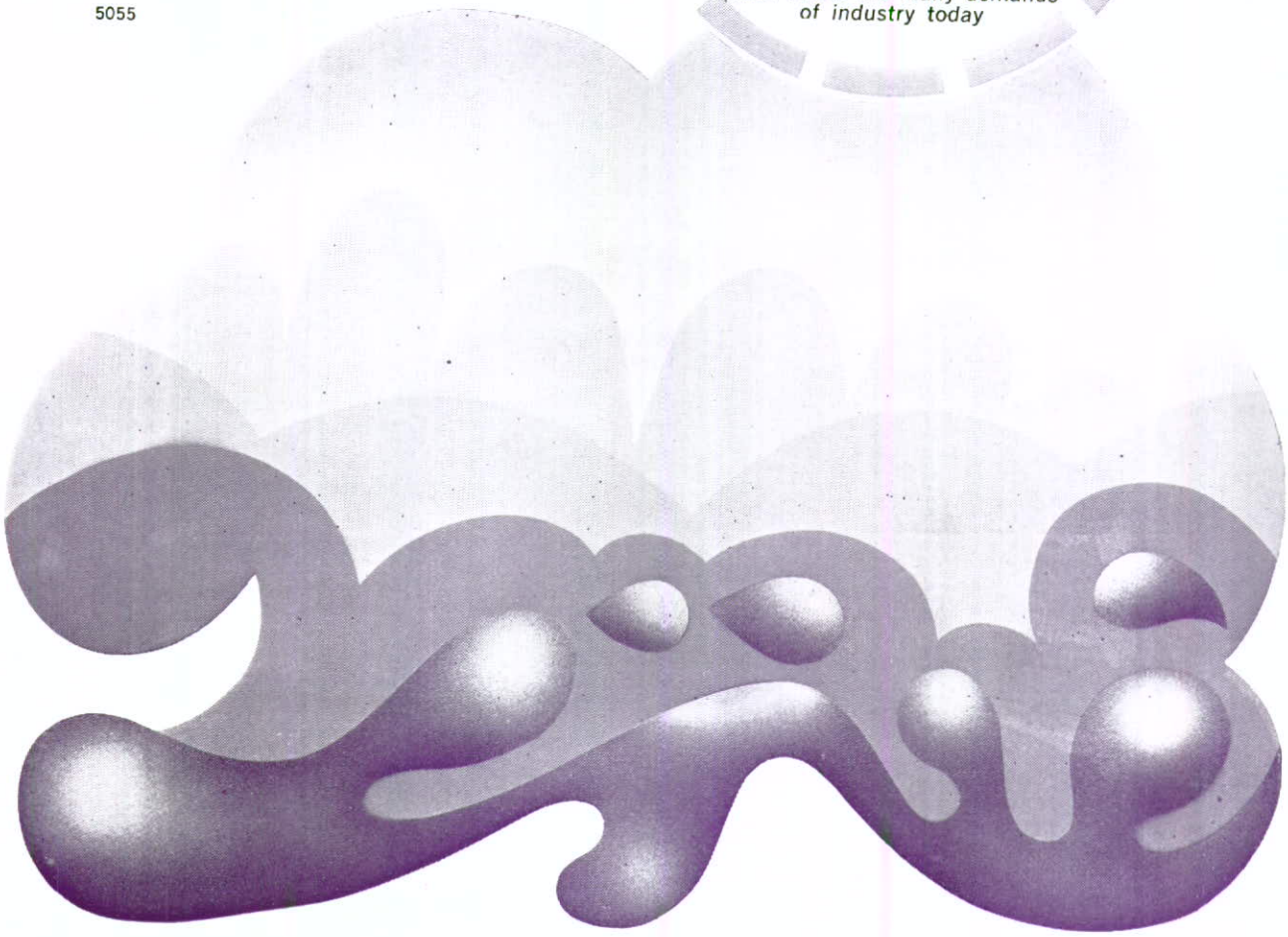

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Mr Ivan S. Hart

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ROYAL SOCIETY OF NEW ZEALAND SCIENTIFIC CALENDAR

APRIL 1st, 1973 — MARCH, 1974

INTERNATIONAL MEETINGS

Date	*Sponsors*	*Place*	*Subject*
August 13th - 18th	The Royal Society of New Zealand and the International Union of Biological Sciences	Massey University, Palmerston North	"Mechanics of Regulation of Plant Growth"
December 2nd - 10th	International Association of Plant Physiologists International Union of Quaternary Research (INQUA) and Royal Society of New Zealand	University of Canterbury Christchurch	IX INQUA Congress

CONFERENCES

April 10th - 13th	N.Z. Farm Forestry Association	Rotorua	
May 8th - 10th	N.Z. Institute of Foresters (A.G.M.)	Auckland	"Marketing of Forest Produce"
May 8th - 10th	The Entomological Society of New Zealand	Victoria University of Wellington	
May 9th - 10th	Quantitive Biology Group	Gracefield, Lower Hutt	
May 14th - 18th	N.Z. Archaeological Association	University of Canterbury, Ilam, Christchurch	Biennial Conference
May 15th - 19th	N.Z. Institute of Architects	Victoria University of Wellington	
May 21st - 25th	Agricultural Pest Destruction Council	University of Waikato, Hamilton	
May 21st - 25th	N.Z. Society of Pathologists	Auckland	
May 23rd	N.Z. Institute of Food Science and Technology	Massey University, Palmerston North	
May 24th - 27th	N.Z. Dental Association	Wairakei	
June 11th - 15th	Medical Association of N.Z.	Rotorua	
July 6th - 8th	Geological Society of New Zealand	University of Auckland	
August	N.Z. Association of Economists	University of Canterbury	
August 7th - 9th	N.Z. Weed and Pest Control Conference	Logan Park, Auckland	
August 15th - 27th	N.Z. Marine Sciences Society	Wellington	
August 20th - 24th	N.Z. Institute of Agricultural Sciences	University of Waikato, Hamilton	
August 20th - 24th	N.Z. Institute of Chemistry	Christchurch	
August 21st - 23rd	N.Z. Microbiological Society	Lincoln College	Annual Scientific Meeting
August 23rd - 25th	N.Z. Institute of Medical Laboratory Technology	Christchurch	
	N.Z. Ecological Society	Invercargill	
August 29th - 31st	N.Z. Electronics Institute	University of Canterbury, Ilam, Christchurch	
August 30th - 31st	N.Z. Association of Clinical Biochemists	Auckland	
September 20th - 22nd	N.Z. Dental Association (Regional)	Queenstown	
October 26-28	N.Z. Society of Radiographers	Waikato Hospital, Hamilton	
November 6th - 8th	N.Z. Grasslands Association	Te Kuiti	
November 30th - December 2nd	The Royal Astronomical Society of N.Z.	Massey University, Palmerston North	
December 10th - 14th	Physics Dept., University of Canterbury	University of Canterbury, Christchurch	"Science of Materials"
February 7th - 11th, 1974	N.Z. Veterinary Association	Nelson	

SYMPOSIA

May 14th - 15th	N.Z. Institution of Engineers	Victoria University of Wellington	"Energy Conservation in Buildings"
May 14th - 16th	N.Z. Geochemical Group	Cawthron Institute, Nelson	
July 4th	N.Z. Institute of Chemistry, Wellington Branch	Institute of Nuclear Sciences, Lower Hutt	"Resources of the Sea"
August 10th	N.Z. Institution of Engineers	Annex to Building Centre, Auckland	"Tall Buildings"
August 16th - 18th	N.Z. Institution of Engineers	Wellington	"Increasing Efficiency in the Building Industry"
August 21st - 23rd	University of Auckland, Centre for Continuing Education	Auckland	"Acoustics"
November 27th-29th	N.Z. Hydrological Society	Lincoln College, Christchurch	Annual Symposium

LECTURES

Date	*Lecture*	*Place*	*Lecturer*	*Subject*	*Sponsor*
May 2nd		Wellington	Mr. G. A. Eiby	"The World of Nicholas Copernicus" (Quincentenary of birth of Copernicus"	R.S.N.Z. Wellington Branch and The Royal Astronomical Society of New Zealand
May 16th		Victoria University of Wellington	Professor Kenzo Tange Professor of City and Architectural planning, Tokyo University		N.Z. Institute of Architects
July 25th	Hudson Memorial Lecture	Dominion Museum, Wellington	Professor H. W. Wellman	"Sea Floor Spreading and the Changing Shape of New Zealand"	R.S.N.Z. Wellington Branch
August 29th	Slade Memorial Lecture	School of Engineering, University of Canterbury, Ilam			N.Z. Electronics Institute
August 20th - 24th	Packer Memorial Lecture	University of Canterbury			N.Z. Institute of Chemistry (Annual Conference)
October 3rd	Miller Memorial Lecture	Victoria University of Wellington	Professor J. K. Syers	"Phosphate Chemistry in Soils, Sedimental Waters"	N.Z. Institute of Chemistry Wellington Branch

VISITING LECTURERS FROM OVERSEAS

Name		*Lectures*
Professor R. V. Jones	Professor of Natural Philosophy (physics), Aberdeen University, U.K.	Distinguished Visitor, Canterbury University Centenary. In N.Z. March 15th—end of May
Professor A. W. Fairhall	University of Washington, U.S.A.	April 4th, N.Z. Institute of Chemistry, Wellington Branch
Professor Gilbert S. Ross	Department of Neurology, State University of New York	April 18th, Seminar, Wellington Postgraduate Medical Society
Professor R. Belcher	University of Birmingham, U.K.	May 2nd N.Z. Institute of Chemistry, Wellington Branch
Professor Kenzo Tange	Professor of City and Agricultural planning, Tokyo University	May 16th, Conference, N.Z. Institute of Architects
Professor W. R. Pitney	St. George Hospital, Kogarah, N.S.W.	May 21st - 25th, Conference, N.Z. Society of Pathologists
Professor L. C. Woods	Oxford University, U.K.	June 11th - 15th, Mathematics Department, University of Auckland
Professor R. L. Wain	Wye College, U.K.	In N.Z. July 3rd—end of August — July 26, The R.S.N.Z. Nelson Branch "Chemical Pollution of the Atmosphere"
Professor C. Henry Kemp	Department of Paediatrics, University of Colerado, U.S.A.	October 3rd - 6th, Seminar, Paediatric Course, Otago Postgraduate Medical Committee

SEMINARS

Date	*Place*	*Theme*	*Sponsors*
April—October as below	Medical Centre, Wellington Hospital	"The Scientific Basis of Medicine"	Wellington Postgraduate Medical Society
April 18th	Lecturer: Professor Gilbert S. Ross, Dept of Neurology, State University of New York	"What is Pain? 25 years of Thoughts and Investigation"	
June 27th	Lecturer: Professor J. D. K. North, University of Auckland School of Medicine	"The Impact of Basic Science of Immunology on Clinical Medicine"	
August 29th	Not finalised		
October 17th	Not finalised		
May 21st - 25th	Massey University, Palmerston North	Technology Week	Faculty of Food Science and Biotechnology, Massey University
August 10th	Building Centre, Auckland	"The Planning and Design of Tall Buildings"	N.Z. Institute of Architects, N.Z. Institution of Engineers, University of Auckland, Department of Continuing Education
	University of Otago, Dunedin	Paediatric Course	Otago Postgraduate Medical Committee Faculty of Medicine

SCIENCE FAIRS AND EXHIBITIONS

Date	*Place*	*Sponsors*	
August 17th - 26th	Auckland	Auckland Institute and Museum	Schools Science Exhibition
September 10th - 30th	Otago Museum, Dunedin	R.S.N.Z. Otago Branch	Science Fair
September 3rd - 7th	Wellington	R.S.N.Z. Wellington Branch	Science Fair

Information received to February 15th.

PUBLICATIONS OF THE ROYAL SOCIETY OF NEW ZEALAND

(FORMERLY THE NEW ZEALAND INSTITUTE)

The following publications may be obtained from the General Secretary, The Royal Society of New Zealand, P.O. Box 12249, Wellington (Office: 6 Halswell Street, Thorndon).

TRANSACTIONS. Volumes 1-53 (2-6, 8, and 43 out of print), $2.00 each; Vols. 54-79, $4.00 each; Vols. 80-88, $6.00 each. NEW SERIES: Zoology—Vols. 1-10, Botany—Vols. 1-3, Geology—Vols. 1-6, General—Vols. 1, 2; Biological Sciences—Vols. 11,12, Earth Sciences —Vols. 7, 8. $6.00 each.

JOURNAL. A quarterly *Journal of the Royal Society of N.Z.* has been established to succeed the *Transactions*. Vol. I (1971)—$18.00 per annual volume ($10.00 to members of affiliated societies).

PROCEEDINGS. Incorporated with *Transactions* to 1960. Annually from Vol. 89 (1961), $2.00 each.

BULLETIN NO. 1. New Genera and Species of Coleoptera. By MAJOR BROUN. Complete, $4.00; Parts 1-8, 50 cents each.

BULLETIN NO. 2. Revision of N.Z. Byrrhidae. By MAJOR BROUN, 20 cents.

BULLETIN NO. 3. Studies in the Bryology of N.Z. By H. N. DIXON. Complete sets (1-6) to approved institutions only, $3.00; Parts 1-4, 50 cents each.

BULLETIN NO. 4. Address by H.R.H. the Duke of Edinburgh to Scientists in New Zealand. Free on request.

BULLETIN NO. 5. Handbook of N.Z. Mosses. By G. O. K. SAINSBURY. Offset reprint 1972 $5.00.

BULLETIN NO. 6. Mosquitoes and Freshwater Ecology of the South Pacific. By M. LAIRD, $3.00.

BULLETIN NO. 7. An Index to the Collembola, three Volumes. By J. T. SALMON, $6.00.

BULLETIN NO. 8. Cook Bicentenary Expendition in the South-west Pacific. Compiled by RONALD FRAZER. 141 pp. 1971, $4.00.

BULLETIN NO. 9. Recent Crusta. Movements. Papers presented at the International Symposium on Recent Crustal Movements and Associated Seismicity, Wellington, N.Z., 10-18 February 1970, Edited by B. W. COLLINS and RONALD FRAZER. 247 pp. 1971. $8.00.

BULLETIN NO. 10. Swimming Crabs, by W. STEPHENSON, $2.00.

IN PREPARATION—

BULLETIN NO. 11. South East Solomons Cultural History—a Survey of Results.

FUTURE PUBLICATIONS

BULLETIN NO. 12. Proceedings of International Plant Physiology Symposium on Mechanisms of Repuletions of Plant Growths—August 1973.

BULLETIN NO. 13. Proceedings IX INQUA Congress, December 1973.

MAORI ART By A. HAMILTON (limited number available to institutions only). Bound, $80.00, Unbound, $60.00.

MANUAL OF N.Z. COLEOPTERA. By MAJOR BROUN. Parts, 5, 6, 7, 50 cents. Parts 1, 2, 3, and 4 out of print.

MANGAREVA DICTIONARY. By E. TREGEAR, 20 cents.

OMEGA NAVIGATION SYSTEM Report of ad hoc Committee, 50 cents.

CORONARY HEART DISEASE Report of ad Hoc Committee, $3.00.

PROCEEDINGS OF 8th INTERNATIONAL RADIOCARBON DATING CONFERENCE $8.00.

Special rates are available to members who purchase through their member bodies.

All prices quoted are New Zealand Currency.

This Newsletter has been complied for your information and interest by members of the Member Bodies' Committee. Suggestions for later numbers will be welcome; please send to the General Secretary, Royal Society of New Zealand, Box 12249, Wellington.

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Newsletter

THE ROYAL SOCIETY OF NEW ZEALAND

No. 15 1973

MEMBER BODIES

Name of Society	Date of Affiliation	Secretary's Name and Address
Auckland Institute	June 10, 1868	Mr E. G. Turbott, Auckland Institute and Museum, Private Bag, Auckland.
Wellington Branch of the Royal Society of N.Z.	June 10, 1868	Dr D. C. Thompson, Box 3085, Wellington.
Canterbury Branch of the Royal Society of N.Z.	October 22, 1868	Mr E. R. Mangin, Lincoln College, Canterbury.
Otago Branch of the Royal Society of N.Z.	October 18, 1869	Mr W. J. Brockie, Geography Department, University of Otago, Box 56, Dunedin.
Hawke's Bay Branch of the Royal Society of N.Z.	March 31, 1875	Mrs J. Winkley, The Museum, Napier.
Nelson Branch of the Royal Society of N.Z.	December 20, 1883	Mr W. Bowers, P.O. Box 233, Nelson.
Waikato Branch of the Royal Society of N.Z.	June 18, 1954	Miss D. Gregan, Box 908, Hamilton.
Rotorua Branch of the Royal Society of N.Z.	November 16, 1954	Dr D. J. Mead, Forest Research Institute, Rotorua.
Geological Society of N.Z.	May 19, 1961	Dr R. A. Cooper, N.Z. Geological Survey,, Box 30368, Lower Hutt.
N.Z. Institute of Chemistry	June 25, 1964	Dr W. E. Harvey, Box 250, Wellington.
N.Z. Ecological Society	November 26, 1964	Dr M. R. Rudge, Box 1887, Wellington.
N.Z. Society of Soil Science	May 19, 1965	Mr L. G. Blakemore, c/o Soil Bureau, Private Bag, Lower Hutt.
Manawatu Branch of the Royal Society of N.Z.	November 25, 1965	Mr B. D. W. Jarvis, Department of Microbiology, Massey University.
N.Z. Institute of Agricultural Sciences	November 25, 1965	Mr D. K. Yerex, Box 11175, Wellington.
The Institute of Physics (N.Z. Branch)	May 19, 1966	Dr G. F. Stuart, Physics and Engineering Laboratory, Private Bag, Lower Hutt.
New Zealand Hydrological Society.	June 23, 1966	Mr J. Simmen, c/o Department of Earth Sciences, University of Waikato, Private Bag, Hamilton.
Royal Astronomical Society of New Zealand	December 15, 1966	Mr P. D. Cain, Box 3181, Wellington.
New Zealand Archaeological Association	October 26, 1967	Mr M. Trotter, Box 24059, Linwood East, Christchurch.
New Zealand Microbiological Society	February 15, 1968	Dr M. J. Baxter, Animal Health Department, Massey University, Palmerston North.
The Institute of Fuel (N.Z. Group)	February 15, 1968	Dr J. B. Stott, University of Canterbury, Private Bag, Christchurch.
The Nutrition Society of N.Z.	May 30, 1968	Dr T. G. Ludwig, Dental Research Unit, Medical Research Council, Box 3155, Wellington.
Entomological Society of N.Z.	August 29, 1968	Mrs S. Miller, 4 Maymorn Road, Te Marua, Upper Hutt.
Ornithological Society of N.Z.	August 29, 1968	Mr B. A. Ellis, 44 Braithwaite Street, Wellington, 5.
N.Z. Psychological Society	November 27, 1968	Mr B. E. Jones, Psychological Service, Department of Education, Box 50196, Porirua.
N.Z. Geographical Society	February 19, 1969	Dr J. E. Hay, Department of Geography, University of Canterbury, Private Bag, Christchurch.
New Zealand Marine Sciences Society	August 28, 1969	Dr D. Burns, N.Z. Oceanographic Institute, Box 8009, Wellington.
Royal Aeronautical Society (New Zealand Division)	August 28, 1969	Mr R. L. Williams, c/o N.Z. NAC, Box 96, Wellington.
New Zealand Society of Dairy Science and Technology	October 14, 1971	Mr N. F. Sage, Box 459, Hamilton.
New Zealand Institute of Food Science and Technology	April 20, 1972	Mr S. L. Oldfield, Biotechnology Department, Massey University.
New Zealand Veterinary Association	April 20, 1972	Mr L. J. Thompson, Box 106, Hamilton.
Operational Research Society of N.Z.	October 20, 1972	Mr B. K. Campbell, Applied Mathematics Division, Box 196, Wellington.
N.Z. Computer Society, Inc.	November 23, 1972	Mrs B. J. Macnab, P.O. Box 6338, Auckland.