Vol. 55 No. 4 October 1991

# 4 Chemistry



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# EDITORIAL

As this edition of "Chemistry in New Zealand" goes to press, change continues apace in the New Zealand economy and for all those engaged in science based occupations. Changes are occuring in ways never envisaged in the public, private and educational sectors. The members of the boards of the new Crown Research Institutes will have been selected and the most recent way of managing Public Sector science will have began, engendering even more change than so far experienced. In the private sector those once large in science based activities have quietly and with little publicity faded away. The once largest industrial R & D laboratory in New Zealand will shortly finally close its doors and the people and specialized equipment be dispersed. ICI has withdrawn from the funding of the annual ICI prize, something not expected from an international giant. Those who remain in industrial jobs have fewer resources and often no mandate to explore new ways of meeting the challenges of modern global marketplace. In education as a nation we have abandoned the time proven principal that is is wise for society to willingly support the education of the talented young, whatever their personal backgrounds and then expect to be well rewarded later by the fruits of successful careers. Instead we have adopted the opposite stance of expecting payment now for an education, making a higher education as difficult as possible and giving little thought to the future needs of society by supporting talented people. Career development and a reasonable security of tenure, both vital components of an academic, scientific or industrial working life have been seriously jeapordised by the growing habit of limited tenure appointments in all kinds of science based occupations.

Against such a background it is not surprising that the membership of NZIC continues to slowly decline as those with chemistry qualifications either leave their jobs or are scattered widely both geographically or administratively in organizations which use some form of chemistry skill only as one of several means to achieving complex and usually solely commercial goals. In such an environment people are more likely to join interest groups associated with their employment sector than a national professional group.

To overcome this tendency NZIC Council has resolved to increase measures to ensure that members of NZIC are kept fully aware of Institue news and initiatives by means of this magazine and by way of short newsletters to Branch Committees from the Secretariat. It has been resolved that "Chemistry in New Zealand" will continue to be published in this or similar format to publically present the views of the Institute. It should be in the interests of every chemist in New Zealand to be a member of NZIC. Unless membership does increase and there is an

Editorial	55
Personal Chair for Brian Halton	56
Penny Brother's Proposals for Specialist Groups Adopted	57
23rd International Chemical Olympiad. Robert Maclagan Reports	58
Microwave Digestion	60
Science & Technology in Australia Prof. Frank Larkin's Keyndote Address	61
Soil-Water Chemistry and Mineral Stability  Harry Percival's Presidential Address	66
Letter to the Editor. Will the sea level rise?	71
Product News	72

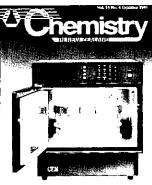
enthusiam for joint action on a whole range of issues it will be difficult to sustain the Journal and in the long term, the Institute.

The address to the 1991 conference by Professor F.P. Larking, Professor of Chemistry at the University of Melbourne provides some interesting relevant and stimulating views on what is happening in Australia. New Zealand could well learn much from following some of these initiatives.

R. B. Hall Editor

Special feature for next issue:

High Pressure Liquid Chromatography H.P.L.C.



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**Editorial:** Technical and scientific articles should be submitted to the editor no later than 1st of the month of publication. The editor will always welcome commercial and industrial news on product design, development and testing, processing techniques, company and personal news etc.

# PERSONAL CHAIR for DR. BRIAN HALTON AT VICTORIA UNIVERSITY

The appointment of Dr. Brian Halton to a personal chair in acknowledgement of outstanding scientific research has recently been announced by the Vice-Chancellor, Professor Les Holbrow of Victoria University.

Professor Halton has attracted international attention with research into synthetic organic compounds which are highly strained in their structure and have high internal energies.

Such compounds often have only a fleeting existence during chemical reactions and only rarely can they be directly observed, so their properties have to be deduced from the results of the reactions.

But the research has resulted in new insights into molecular architecture and is also producing interesting new compounds that could have commercial applications. "We are studying the fundametal properties of these compounds. Now it's up to other people to utilise the properties we've described," Professor Halton said.

Dr. Halton obtained his PhD at Southampton University and following post-doctoral work in Florida, joined the staff at Victoria in 1968. He was appointed a reader in 1977 and in 1987 the University awarded him the comparatively rare degree of DSc for his published research on strained organic molecules.

He is a Fellow of the NZ institute of Chemistry and was its president in 1986-87. He has received several awards for excellence in research, including the research medal of the NZ Association of Scientists, and has lectured widely by invitation at overseas universities.

Recently Professor Halton has been investigating an exciting new range of highly fluorescent compounds discovered accidentally during research at Victoria by a Chinese doctoral student, Mr. QiLu, who was studying hydrocarbons with unusual structures.

The fluorescence of the new compounds is spectacular; a test tube containing a dilute solution of the materials can light up a room when held over an ultraviolet sun-lamp. They, or related compounds, may have commercial uses in the laser industry and the University has taken out a provisional patent on them.

In addition to his direct research, Professor Halton has made notable contributions to the review literature on organic chemistry, and is series editor for two specialist serials.

# **CONFERENCES**

12th Australian Symposium on Analytical Chemistry incorporating 3rd Environmental Chemistry Conference

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# THE ROYAL SOCIETY OF CHEMISTRY

# Research Funding Available

### **RESEARCH FUND 1992**

The RSC Research Fund exists to assist members in their research by the provision of grants of up to £500, for example for the

purchase of chemicals, equipment or for running expenses of chemical education research.

If you work in a university, polytechnic, college or school anywhere in the world and your work is held up for lack of moderate funding, the Research Fund may be able to help you.

A limited number of grants, each of approximately £500g, will be awarded for 1992. Applications from members of The Royal Society of Chemistry will be considered on merit, but account will be taken of any other source of financial aid available to applicants.

Funds are limited, so preference will be given to those working in less well-endowed institutions; applications from those in UK universities will receive particular scutiny. Council is especially anxious to see inventive applications of a 'pump priming' nature and is prepared to consider applications from those working in chemical education as well as chemistry research.

Members in developing countries should note particularly that additional funds have been made available for 1992 by the Society's International Committee, to provide grants for successful applicants from such countries. Preference will be given to those able to cite collaborative research projects with UK institutions.

Application forms, together with the regulations governing the Fund, may be obtained from Mrs. D. Howes, The Royal Society of Chemistry, Burlington House, London W1V OBN. The closing date for applications is 1 November 1991, but submissions sent well in advance of this date would be much appreciated.

# VISITS TO DEVELOPING COUNTRIES

The Society, through its International Committee, has established a scheme of awards to enable members of the Royal Society of Chemistry to visit chemical establishments in developing countries. The visits must clearly be of benefit to the county concerned and the visitor would be expected to give lectures and engage in other forms of information exchange. The grants will complement, where appropriate, those for visits to Commonwealth countries available from the Corday-Morgan Memorial Fund.

The intention is to help applicants to make stopovers in or diversions to a developing country while travelling for other purposes. Support for travel within a developing country may be given when appropriate. Applicants must be members of the Society and the funding would cover the additional travel costs together with appropriate subsistence, up to a maximum of £500.

Applications should be submitted on the official form and will normally be considered within one month of receipt.

Application forms are available from the International Committee Awards, c/o The local Affairs Officer, Royal Society of Chemistry, Burlington House, Piccadilly, London W1V OBN.

# The Corday-Morgan Memorial Fund

The RSC Corday-Morgan Memorial Fund exists to assist members of any established Chemical Society/Institute in the Commonwealth to visit chemical establishments in another Commonwealth country. There is no restriction on age but the visits must be clearly of benefit to the country concerned. The intention is to help applicants to make stopovers in, or diversions to such countries while travelling for other purposes and it is hoped that lectures will be given during a visit.

The grants will complement, where appropriate, those for visits to developing countries available from the International Committee's fund, and funding would cover the additional travel costs involved, together with appropriate subsistence.

The maximum award to any individual is normally £500 and persons eligible must be citizens of, and domiciled in, any Commonwealth county. Applicants must be travelling to another country (not necessarily in the Commonwealth) and would normally stop en route to visit a third country which must be in the Commonwealth.

Applications should be submitted on the official form and will normally be considered within one month of receipt.

An application form for support from the fund is available on request from the Corday-Morgan Memorial Fund, c/o The Local Affairs Officer, Royal Society of Chemistry, Burlington House, Piccadilly, London W1V OBN.

# **PEOPLE**

# SCIENCE AWARDS OF THE ROYAL SOCIETY OF NEW ZEALAND

Dr. J.M. Coxon of the University of Canterbury has been elected to a Fellowship of the Royal Society of New Zealand for destinguished research on the reaction mechanisms of organic molecules of a wide range of types, including photochemical, thermal and chemically induced process.

# SPECIALIST GROUPS OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

At the August Council meeting the matters raised by Penny Brothers in the following paper were fully endorsed for adoption.

Specialist Groups play an important role in terms of both scientific activities and professional education of NZIC members through meetings, conferences, workshops and courses.

The multidisciplinary nature of some Specialist Groups means that they will always have some members who are not eligible for full NZIC membership. While NZIC does not want to discourage the participation of these people in Specialist Group activities, Specialist Group members should be members of NZIC if they are eligible.

The following scheme provides greater recognition of Specialist Groups by Council, in particular in terms of some financial support by way of a capitation grant. In return the scheme should provide some incentive for Specialist Groups to encourage their members to join NZIC.

### 1. Council

Each year Council will appoint one of its members as a Specialist Group liaison person. This person will represent Specialist Group views on Council. The liaison person should make direct contact with each Specialist Group secretary or chairperson during the year. In addition, Specialist Group officers should have a standing invitation to attend any Council meeting as observers.

# 2. Capitation

Each Specialist Group will receive an annual capitation grant based on the number of its members who are also NZIC members (possibly excluding student or retired members). This grant could be tied to the per capita amount calculated for the Branch grants. For example, the census of Specialist Group members prepared by Alan Turner (28 March 1990) shows 650 Specialist Group members who are NZIC members. At \$4 per head this would amount to \$2,600 in Specialist Group grants each year.

Some controls would be necessary. A Specialist Group might be required to have a minimum number (25) members to be eligible for a grant. Initially, Specialist Groups could be required to submit a summary of their activities for the last three years in order to demonstrate a viable level of activity.

Each Specialist Group could choose whether to have the grant forwarded to its treasurer as a lump sum, or to have the Secrtariat hold the Grant on its behalf. Currently, the Secretariat offers some services gratis to Specialist Groups. These include provision of mailing labels, stationary, stamps and reimbursement for photocopying charges. Many Specialist Groups do not take advantage of these services. With the provision of a capitation grant each Specialist Group would then be responsible for meeting its own costs, although some may choose to continue to use the services of the Secretariat and this would be debited to an account maintained by the Secretariat.

Each Specialist Group might have a different use for its grant. The very active groups would find it helpful in meeting running costs like newsletters and meeting. Smaller groups, or those with widely scattered members might wish to let the grant accrue for a period of time and then use it towards holding a conference or workshop, or apply it towards sponsoring an overseas speaker to an NZIC conference. Since the size, level of activity, and goals of each Specialist Group is different it is important not to restrict the way the funds are used.

(Alternative: The funds could be held by the Secretariat as a matter of course. A Specialist Group could either: use Secretariat services and have its account debited; request reimbursement of funds spent; or request funds to use for a particular purpose. Accumulated Specialist Group funds not used with five years would revert to NZIC. This alternative would give tighter controls and would prevent automatically disbursing funds to inactive Specialist Groups.)

### 3. Subscription Invoices

The annual subscription notice sent to each NZIC member should list the Specialist Groups to which the member belongs, in addition to a list of all the active Specialist Groups. The NZIC member must renew Specialist Group membership each year by opting to remain on a Specialist Group mailing list. In addition, this will be the means by which an NZIC member can join a Specialist Group, by choosing to receive a Group's newsletter. Since Specialist Group membership and hence the capitation grant will result simply from an NZIC member choosing to be on the mailing list, limits can be set by allowing each NZIC member to choose only two Specialist Groups as part of the NZIC subscription. Members wishing to belong to more than two Specialist Groups will pay a small charge for each extra one (say \$5, enough to cover capitation). After the subscription exercise the Secretariat will provide an up-to-date membership list to each Specialist Group secretary.

# 4. Annual Reports

Specialist Groups must each year provide the following to Council: an Annual Report of their activities, a financial statement (unless its finances have been handled exclusively by the Secretariat) and a membership list (since this may contain non-NZIC members who will not be included on the list held by the Secretariat). This reporting will allow monitoring of the level of activity and use of the capitation grant and will also ensure that once a year the Specialist Group membership lists held by the NZIC Secretariat and each Specialist Group secretary are reconciled. As a public relations exercise the Secretariat may wish to continue the practice of making mailing labels available since this is a relatively inexpensive exercise which would avoid duplication of effort by the Secretariat and Specialist Group secretaries.

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#### 5. Secretariat

The relationship between the NZIC Secrtariat and Specialist Groups has been partially covered in the proceeding sections. The secretariat will continue in its present function of making Council agendas, minutes and other information available to Specialist Groups. Other services could be offered by the Secretariat including conference or workshop administration, and duplication and mailing of newsletters.

6. Conference Support

An important aspect of Specialist Group activities is organisation of conferences (which may be at times other than the NZIC conference), workshops, or courses. Specialist Groups may apply to Council for funds to assist in such activities. An application must give the nature of the meeting(conference, workshop, or course), the date and venue, a preliminary budget and an estimate of the number of registrants. Council will make a commitment to fund all well supported applications with a reasonable level of seed money (ca.\$1000).

In return, Council agrees to underwrite losses. As a safeguard, the budget submitted with the application should indicate that the meeting is planned to at least "break even" (and preferably budget for a profit), and that an attempt will be made to recoup the "seed money" which would be repaid to Council. If a profit results, Council would be entitled to a share negotiated on the basis of Council's underwriting role and the level of initial Council support. Participants who are not NZIC members (or members of a society with a reciprocal agreement) must be charged a higher registration fee. Council may request a progress report closer to the meeting date to review financial arrangements and progress with registrations. After the meeting a report together with a financial statement should be submitted to Council.

In addition, the Secretariat may be able to make a registration package available to conference organisers, or to negotiate with a Specialist Group to take part of the conference organisation.

7. As a matter of urgency, the Secretariat and Specialist Group secretaries should act to reconcile membership lists. This would then be revised annually as outlined above.

# Report of New Zealand Observer to 23rd International Chemical Olympiad, 7-15 July, 1991, Lodz, Poland

by Robert Maclagan

# Description of the Olympiad Experience

Arriving Amsterdam's Schiphol airport to fly to Warsaw, I was relieved to meet up with the Netherlands team and the IUPAC observer. Communication from Poland had consisted of just one letter, inviting us to send an Observer. At Warsaw, we were met by I.Ch.O. committee members and we proceeded by bus, train and tram to the dormitory at the University of Lodz. I was paired with another Observer from Mexico which allowed us to compare impressions of the Olympiad, and plans to send a team to next year's Olympiad. That evening there was opportunity to meet some of the other Leaders and Observers and some of the team members, including two members of the Australian team who attend my old school.

Next morning the Olympiad Opening Ceremony was held. This was an impressive event, with many of the teams in uniform, a string quartet performing, and speeches of welcome from a deputy minister, the city president, and various university officials.

Following the ceremony the Jury (consisting of the Leaders) inspected the laboratories to ensure that safety regulations were observed, and the apparatus provided was appropriate. Following lunch the Leaders, and most of the Observers, were separated from the students to begin the Jury deliberations. We travelled by

bus to the Hotel Podklasztorże at Sulejow, built on the site of a 12th century Cistercian monastery.

The first task was to approve the two laboratory tasks and then prepare an official English version which was supposed to be the basis of the translations into other languages. The discussions were in English, but unfortunately the English comprehension of the Polish organisers was sometimes not up to following the debate. The English speaking teams (Australia, Britain, Canada, U.S.A. and Singapore) had the advantage of being able to work as a group. The task was slowed by the availability of only a limited number of computers and a slow photocopier. However, by 4:30 a.m. the final English copies of the Practical Exam were copied and ready to be couriered back to Lodz. This task was apparently completed earlier than in some recent Olympiads. The two tasks were the determination of Ka for a weak acid using a pH meter, and the determination of the formation canstants for two ammonia complexes electrochemically.



Australian IChO leaders with IChO President.

While the students spent 5 hours in the laboratory, the Leaders were taken to visit the monastery of the Black Madonna at Czestochowa, an important place for both Polish Catholicism and Polish nationalism. On our way, one of the buses suffered the not infrequent occurence of a blow out of one of its tyres, which meant that we arrived later than expected. That evening the Jury deliberated on the marking scheme for the practical exercises. When the marking scheme was decided copies of the students answer sheets were distributed for the Leaders to mark. The Australian team leaders kindly allowed me to join them in the marking process. 40% of the total mark is from the practical exam. With good preparation, a student's practical marks are often higher than the theoretical exam marks. For example, one of the Australian students achieved full marks in the practical exam.

Next, day while the students were taken on an excursion, the Jury began the long task of preparing the theoretical exam. In a departure from usual practice, the Polish organisers gave the jury a choice of two alternative questions for each of the six questions in the exam. One member of the Jury described them as going from "fiendish to very fiendish". Once the six questions were decided the jury split into six groups to refine each question. This often involved shortening the question by removing parts of the original question or rewording the question to make it more comprehensible. I ended up working with the Polish originator of the most theoretical question in the exam, a question claimed by some of the Jury to be more Physics than Chemistry. Our task was over relatively quickly, but some groups took a couple of hours. The revised questions were then examined by the whole Jury and then an official English version was prepared. Again it was a pleasure to share in the great camaraderie of the English speaking Leaders. The questions covered inorganic, physical organic, theoretical, environmental and industrial chemistry. This time the questions were typed in, printed and through the photocopier by a very civilised hour.

During this time I was able to join in the tradition of exchange of gifts amongst the Leaders. Forwarned by my daughter's Maths Olympiad experience, I had come with packaged drink mats bearing the New Zealand flag. Naturally a lesson on the difference between the New Zealand and Australian flags followed.

Next morning we returned to Lodz to await the student's papers. It was only after a reception by the President of the city of Lodz, himself a Chemist, that we got the copies of the students papers. Again I was able to share in the marking of the Australian team. Next day was spent discussing each students answers with the Polish committee members who had made up the questions.

At the end of the discussion an agreed mark was decided and forms initialised. The President of the Olympiad, Professor Zygmunt Kozlowski ended up with 236 questions to mark overnight. He was tired. Undoubtably the Australians were helped by the arrival of one of the team's two grandchildren from Brisbane just before the discussions of their answers to his questions. This process of deciding the marks is one where tactics could mean the difference between one medal and another, a very strong reason for having some continuity amongst future New Zealand Leaders. The hard work over, an excursion next day took us to Chopin's birthplace.

That evening the Jury met to decide the medal cutoffs. The marks were presented in an encoded form which prevented the identification of team scores in the time available. This year the code was 24n14. The top 8-12% receive Gold medals, then the next 18-22% receive Silver medals, and the next 20-32% receive Bronze medals. The cutoffs this year were 87.25% for Gold, 77% for Silver and 61.5% for Bronze. The Australians were very pleased for they had a very high Silver and two Bronze medals.

At this final Jury session details of the 1992 Olympiad were given. The theme of the preparatory questions — the "syllabus" — will be the Chimistry of the Earth. The Olympiad will be held in Pittsburgh, Pennsylvania and the closing ceremonies in Washington, D.C.

Next morning the closing ceremony was held. Those who did not win medals were presented with certificates in alphabetical order. The Jury had agreed that the team members would not be told the medal awards beforehand. Some tears were evident when it was realised the the dream of a medal would not be realised. Next came the Bronze medal winners, again in alphabetical order. The Silver medals were presented in ascending numerical order as were the Gold medals. Fianlly the top the Gold medals were presented. It was not a surprise that the top two were to Chinese students.

Following the closing ceremony I was fortunate to be able to join with two of the Canadian leaders to see parts of the city of Lodz, including the old Jewish Cemetery, the sites of two concentration camps (for Poles), the neighborhood of an old textile factory and the city Art Gallery. This gave me some feeling for the Polish experience which otherwise I would not have had. Next morning we travelled by bus to Warsaw where I stayed overnight before starting on my 46-hour journey home.

### Recommendations

- New Zealand should aim to participate in future Olympiads. Because the cost of sending a team will never be cheaper, I strongly recommend we accept the expected invitation to go to Pittsburgh in 1992.
- 2. The council of the NZIC should make a small financial contribution to the costs of the Olympiad team travel and selection process. The funding of a team will be an uphill battle in the current environment but we should aim high. It would be inappropriate for the NZIC to fund this project at the expense of other chemical education projects.
- Members of the NZIC should encourage their firms and organizations to make a financial contribution.
- 4. The Leaders should initially be University teachers. The choice of leaders varies from country to country. The Canadian leaders were all academics. The British were both school teachers (but one had a Ph.D.). The Americans had another teacher with a Ph.D. and a former academic now working in government research laboratory. The Australian leaders were an academic and an undergraduate who had tutored the team. Eventually we should aim to include high school teachers and even former team members (as was the case of France). The Maths Olympiad leaders have been University teachers, with a school teacher travelling as a Manager/Observer. All the expenses of an Observer must be paid, including travel acoomodation in the host country. It would be desirable to have an Observer, but until funding is secure it would be a luxury.
- 5. The Leaders should rotate off the travelling party. This allows the trainers to be rewarded and a large number of teachers to have an Olympiad experience. This is the usual practice. Some countries, eg. Sweden have had the same Leaders for a number of years. Their long experience is invaluable in Jury sessions. We do not need to follow that practice. The ideal would be a

- Observer/Junior Leader/Senior Leader rotation, but I suspect we can only afford a Junior Leader/Senior Leader rotation.
- 6. The team of 4 should be chosen after a training camp of one week in the May vacation. About 20 students should be selected to attend the training camp. While the date of the training/selection camp varies, most countries adopt this procedure. As well as testing the student's chemical prowess, it allows the section committee to test the students social maturity. A number of teams reported that this was an important consideration in selecting the team members. It should not be as important next year in the U.S. where a minimum drinking age of 21 is strictly policed.
- 7. New Zealand should send some students every year to an Olympiad. It may not be impossible to fund a team of four students and two leaders every year. However, as the Olympiad rules could change from year to year, it is important to have a Leader/Observer at each year's Jury sessions. If we cannot send a full team, I would suggest a team of two students and one leader could be considered. This was the composition of the Slovenian team this year.

### Progress towards a 1992 Team

As well as my observation of the 1991 Olympiad, two major steps have been taken towards sending a team to the 1992 Chemical Olympiad:

- 1) A team of trainers in each University has been obtained. A contact in every local science teachers association has been sought.
- 2) An examination open to "exceptional" 1991 Form 6 students will be sat on Thursday, October 31, 1991 to select a training team of about 20 students.

### Acknowledgements

I wish to acknowledge the financial support of the N.Z.I.C., the Chemical Education Trust and the Chemistry Department, University of Canterbury which allowed me to observe the 1991 Olympiad. Financial support for the Chemical Olympiad project has also been received from Rohm and Haas NZ Ltd. I wish to thank the Australian Leaders, Dr. Alan Arnold and Mr. David Atkins for allowing me to act as a third Australian Leader and learn the tricks of the trade. I would also wish to thank the IUPAC Observer, Dr. Hans Bouma for his support and advice on my Observer's role.

# FROM THE POLICY AND PUBLIC AFFAIRS COMMITTEE

# DIRECTIONS FOR NEW ZEALAND RESEARCH

Discussion Document, Ministry of Research, Science & Technology September 1991

We responded:

- The field set out in this document is far too wide and general to enable NZIC to offer any useful contribution to its present format.
  - NZIC would however, wish to have opportunity to comment on topics relevant to chemistry, ad and when these emerge.
- NZIC is concerned that no clear criteria have yet been defined, by which relative research priorities may be objectively evaluated against potential benefits. Basis for a more quantitive approach has been submitted.
- NZIC considers the attraction, training and retention of sufficient numbers and calibre of skilled, experienced scientists to be the most important issue currently facing in New Zealand science.

# ROYAL SOCIETY OF NEW ZEALAND ACT 1965 Consultative Document for Ministerial Review, October

We are currently considering this paper, with the view to make a submission.

## **Establishment of Crown Research Institutes**

We are endeavouring to maintain contact with the Implementation Committee and have offered to help with aspects relating to chemistry.

Convenor Public Affairs Committee, September 1991

# INDUSTRY LEADER IN CHEMICAL INFORMATION COOPERATE TO PROVIDE UNPRECEDENTED DATA ACCESS TO SCIENTISTS.

Molecular Design Limited and Chemical Abstracts Service (CAS) have announced a cooperative agreement that will significantly advance the access to, integration of, and communication of scientific information, on a worldwide basis.

Under the Molecular Design Limited and CAS agreement, scientists will be able to use a single system--ISIS TM, the new Integrated Scientific Information System from Molecular Design Limited--to access, review, store, and communicate scientific data. ISIS will offer broad access to public databases through STN International as well as in-house databases to give scientists chemical structures, related text, and analytical and test data contained in relational database systems.

"The past ten years have seen steady improvements in our ability to place scientific information in the scientist's hands economically and efficiently. This agreement is a leap forward. It increases not only the pool of available information but also the usability of that information," explains Jim Seals, director of marketing and corporate development for CAS. "By combining the richness of STN data with the chemical-information-management expertise of Molecular Design Limited, we can give scientists unparalleled access to the wealth of personal, corporate, and public data stored in multiple organizations and locations."

According to Steven Goldby, president and CEO of Molecular Design Limited, "This agreement marks an important phase in the efforts by Molecular Design Limited to provide integrated information systems to our users. A year ago, the technology required to bring together the data from serval sources did not exist. With ISIS, we can now give scientists an easily acessible, coherent view of all their scientific information, whether the source is in-house or online, in the same building, or on another continent. The full potential of this powerful system is realized through our agreement with CAS. With access to STN data, we will give scientists a single window to all of their chemical information needs."

The impetus behind this agreement was to solve the problems inherent in accessing and integrating data from different sources. Currently, gathering information from in-house and public databases requires knowledge of the different software packages used to access each database. Once all the necessary information was found, the scientist has had no easy way to integrate the data from these various sources and communicate them to others.

STN is operated jointly by CAS in North America, by Fiz Karlsruhe in Europe, and by the Japan Infomation Center of Science and Technology in Japan. A network of more than 100 databases, STN International offers information on a broad range of scientific fields, including engineering, thermodynamics, materials science, physics, biotechnology, and chemistry. Founded in 1907, CAS, a division of the American Chemical Society, is the publisher of Chemical Abstracts. Committed to providing scientific information to the world, CAS offers printed products to provide current awareness in specialized areas (CA Selects and Chemical Industry Notes), and special services to make the search for information and retrieval of documents quick and convenient (CAS Search Service and CAS Document Delivery Service). CAS also produces the CA File, the CAS REGISTRY File, CASREACT, CIN, and MARPAT.

Since 1978, Molecular Design Limited products have defined the scientific-information-management standard for a worldwide roster of respected pharmaceutical and chemical companies. Its suite of desktop, mainframe, and networked- host-computer software gives scientists local and remote access to the wealth of proprietary information stored in molecule, reaction, and relational databases. Comprehensive commercial databases for in-house use are provided by Molecular Design Limited to expand an organization's existing information to include published molecule and reaction data covering several decades of chemical research. Molecular Design Limited is a wholly owned subsidiary of the Maxwell/Macmillan Group.

STN International and CAS are registered trademarks of Chemical Abstracts Service. ISIS is a registered trademark of Molecular Design Limited.

# PROLABO'S APPROACH TO MICROWAVE DIGESTION BY MEANS OF OPEN FOCUSED CAVITY SYSTEM:

When most Chemists think of Microwave Digestion, what comes to mind is an oven equipped to deal with the special problems involved in handling and dissolution of chemicals.

However, in 1982, the chemists at Rhone Poulenc decided that they would design a new Microwave Digestion System specifically for themselves and other chemists. The results of their work was the Microdigest: a Microwave Digestion System without an oven. This system, manufactured by Prolabo, is shown schematically in Figure 1.

It consists of a Magnetron to generate microwaves, a Waveguide to direct and focus the microwave and a cavity to contain the sample.

The open approach to Microwave Digestion fulfills a number of important criteria.

### SAFETY:

A system that operates at atmospheric pressure.

### Reproducibility:

Precise control of the calories going into a sample.

### Flexibility:

The ability to use any type of reagent (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HF, HClO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub>). At any stage during the digestion.

# Universality:

A wide array of applications can be run on the one system. Food, Tissue, and Biologicals. Both Kjeldahl and Trace Metals. The open vessel allows fumes to be vented while the refluxing action (illustrated in figure 1) ensures volatiles loss is eliminated. Being able to vent fumes also means large samples can be Digested: Up to 5g in the Microdigest and as much as 10 to 20g in the new Maxidigest System.

### Automation:

The Prolabo System can offer automation without the need for External Robotics. In the case of the A300/A301, a load and leave it approach can be adopted.

A carousel for sequential loading and digesting of up to 16 samples, and a reagent addition system that permits automated addition of up to four reagents. Coupled with the capability to use 16 individual digestion parameters, or the same digestion parameters for each flask, ensure flexible and total unattended microwave digestion is now a reality.

The Prolabo range of microwave digesters include the A300/A301 automated systems. M300/M301 manual and semi automated digester, maxidigest for large samples up to 20g and the floyd closed vessel system.

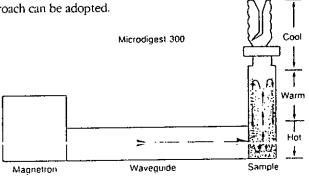


Figure 1. Schematic diagram of waveguide design for focused microwave digestion.

# SCIENCE AND TECHNOLOGY POLICIES IN AUSTRALIA: PLANNING FOR THE FUTURE

Professor Frank P. Larking, FTS

Deputy Vice-Chancellor (Research) and Professor of Chemistry The University of Melbourne

Past-President, Federation of Australian Scientific and Technological Societies

Presented at New Zealand Institute of Chemistry 1991 Jubilee Conference, University of Canterbury, Christchurch, New Zealand 27 August 1991

In the mid-1980's Australia lost its way, from both a science and technology perspective and from an economic standpoint. The entrepreneurs, with their take-over share deals and assets stripping of once solid and conservatively managed Australian companies, were hailed as national heroes and role models for our youth. The banks fuelled the process with careless lending policies. Money was readily available with little security required, especially if one was prepared to speculate in millions. We did not invest to create real wealth.

Tertiary courses in business management, accounting and law, enjoyed unprecedented demand with the image of providing a fast-track to smart cars, large houses, yachts and the high life, well before one was 30 years of age. By contrast, entrance scores for students enrolling in science, engineering and education reached a low ebb.

In Australia we neglected the fundamentals of developing our wealth-generating industries as an economic imperative, and of promoting the recruitment of a fair share of our very best students to the science and technology professions to underpin our prosperity. Governments failed to show leadership and vision through this period. We are fortunate that our best known company, BHP, survived takeover attempts which almost certainly would have resulted in its dismembering. Today, our economic recovery depends on companies such as BHP and a few other technologically sound companies with long-term stategies that are economically competitive in the international marketplace.

The consequences of our excesses are clear. External debt in Australia now exceeds \$135 billion, more than \$7500 for every Australian. Our debt has been increasing at the rate of \$1.2 billion per month. The debt represents more than 35% of our annual GDP, with interest costs to service the debt in excess of 25% of all of our export income. We must face the harsh facts that our exports are still predominantly in the non-manufactured sector and that their export value, as a percentage of GDP, has not increased for 30 years. In 1960, Australia ranked third among leading nations in terms of GDP per capita. In 1990, by this measure of our standard of living, Australia had slipped to ninth place. Over the same period New Zealand declined from third to eleventh position (Figure 1).(1)

The path to economic recovery in Australia will be long and difficult. Part of the solution, if we are to preserve our quality of life, must be strengthening our science and technology base. Today, I wish to address some of the issues and recent developments in Australia, but first a comment about the Federation of Australian Scientific and Technological Societies, FASTS.

# FEDERATION OF AUSTRALIAN SCIENTIFIC AND TECHNOLOGICAL SOCIETIES

It was in response to a growing concern that the importance of science and technology in Australia was not being adequately recognised by the Government and the community that the Federation of Australian Scientific and Technological Societies was established in late-1985. I was delighted to learn that here in New Zealand a similar Federation of Scientific and Technological Societies has recently been formed. In Australia, the Federation of Australian Scientific and Technological Societies, abbrevaiated as FASTS, has rapidly consolidated its position as the major lobby group for science and technology. The umbrella organisation encompasses over 70 member societies representing, through these bodies, approximately 60,000 professionals. Scientific society members are working in science, technology and engineering through industry, medical research centres, State and Federal Government laboratories, Government departments and the education sector from primary through to the tertiary level. Much of FASTS endeavours have been predicated on the conviction that a strong science and technology base is fundamental to the economic prosperity of Australia.

The objectives of FASTS are:

- (a) to promote discussion within the scientific and technological community, leading to policy formulation in the national interest:
- (b) to enhance communications between the scientific and technological community and governments, industry and commerce; and
- (c) to promote understanding among the Australian public of the work done within the scientific and technological community and its importance to the nation.

There are five Standing Committees which monitor progress and develop policy initiatives in special areas. The Committees are concerned with:

- science and technology policy of Federal and State Governments;
- science and mathematics in schools interfacing with tertiary education;

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- tertiary education interfacing with employment;
- industrial research and development policy; and
- Government, science and technology agencies.

FASTS has now established a wide network throughout Australia and is consulted by the Federal Government and its agencies on policy matters related to science and technology. The media has also provided wide coverage to many of the issues that FASTS has highlighted. I believe that we would not have achieved the level of awareness of science and technology issues and made the progress to which I shall refer, without the stimulus provided by the Federation.

In 1988, as a consequence of the continuing concern expressed about the state of science and research in Australia, the Government established a number of reviews. There have been several positive outcomes since that time which have been embraced as Government policy.

# SCIENCE COUNCIL

In may 1989, the Prime Minister announced the establishment of a Science Council as a forum for the exposure of science and technology issues of national importance. The Council is chaired by the Prime Minister and includes other senior ministers with strong protfolio interests in science and technology, along with key representatives of the scientific community and leaders of industry. While the Council meets infrequently, it has been effective since its establishment and has focussed attention on a number of issues of critical importance. The establishment of the Council has been widely welcomed by a concerned community. There is evidence that it has had a significant impact on policy formulation in Canberra.

Linked to the Council is a Coordination Committee on Science and Technology with a membership of senior representatives from all Government departments with a significant science and technology portfolio interest, along with representatives of major government research and funding agencies. Policy planners in several departments now have an improved framework to consider science and technology issues which require high level coordination.

In addition, Professor Ralph Slatyer was appointed as the Chief Scientific Advisor to the Prime Minister and Cabinet. He is a distinguished biologist and enjoys the confidence of much of the scientific community as well as of Government and opposition members.

An important new development has been the publication of a Federal Budget Paper devoted to Science and Technology which highlights the Government's commitment to this area through policy initiatives. This paper, and other statistical reports produced through the Department of Industry, Technology and Commerce, have provided valuable infomation for an informed debate.

The Australian Science and Technology Council, ASTEC, has been retained but its impact on policy setting has diminished.

### COOPERATIVE RESEARCH CENTRES

As part of the 1990 election campaign, the Prime Minister announced the establishment of up to 50 Cooperative Research Centres, earlier promoted through the Science Council and the Office of the Chief Scientist. The first 15 of these Centres have already been established and consideration for a further 20 is currently in progress. A total of \$100 million of new money is being provided for these Centres.

It is clear that the Government has expectations that the Centres will result in real economic gains for the nation. Universities and Government research agencies, through these Cooperative Research Centres, are expected to provide a knowledge base for new innovations. The industry partners are the ones that must provide the development capital leading to commercialisation.

In the past, many promising R&D initiatives have not come to fruition in Australia becouse of the lack of venture capital for the development and commercialisation of promising research. This is a serious deficiency which has not been overcome by the establishment of our Cooperative Research Centres. I have a concern that if the Cooperative Research Centres are not successful, then they will be viewed as failing because of the lack of university and government agency research, whereas the most likely cause will be the lack of a satisfactory industrial infrastructure to develop and market the technology internation-

ally. The Federal Government has not yet grasped the importance of developing a National Science and Technology Strategy within which the role of industrial RD&D is central.

### **CSIRO**

The Commonwealth Scientific and Industrial Research Organisation is Australia's premium research body. For more than fifty years it has been the cornerstone for Australia's national R&D effort, especially related to the agricultural and mining resource industries.

The Federal Government commitment to CSIRO research has declined very significantly with the decrease in direct Government funding in real terms from 1983 to 1990 being in excess of 26%. The Chief Executive Officer of CSIRO, Dr. John Stocker, has recently estimated that CSIRO needs at least an additional \$20 million per year to refurbish outmoded buildings and replenish other resources. There has been a requirement for CSIRO to increase its percentage of funding from external sources to at least 30% of its total annual budget. The policy has had positive outcomes through increased links between CRISO and industry and a reappraisal of priorites for research.

My criticism, however, has been directed at the substitution policy of replacing Government funding by industry funding. A sounder policy is one where Government funding is preserved and there is an incremental increase due to a greater industry contribution to an already low level of total R&D within Australia.

A vigorous campaign has been waged by the CSIRO Officers Association centred around declining morale, uncompetitive salaries, decreased direct funding and declining research infrastructure within the organisation. There have been some positive outcomes from the campaign. The recurrent appropriation funding has increased in real terms since 1988-89 to \$400 million in 1990-91. The capital component<sup>(2)</sup> has continued to decrease, however, hence the concern over infrastructure. Recently new salary awards have been determined for CSIRO scientists which place them in a more competitive financial position relative to their industry counterparts and certainly well ahead of University academic staff.

Unlike developments in New Zealand, the Australian Government appears committed to the retention of CSIRO as a single entity. There is an agenda being shaped, however, through its involvement with the Cooperative Research Centres, which will irreversibly change the role CSIRO makes to Australian science.

Many of us would share John Stocker's concern that the New Zealand Government was short-sighted in the dismemberment of DSIR. One can only hope that the new corporate structure of Crown Research Institutes will be effective and maintain balanced research priorities, addressing long-term issues of national strategic, social and economic importance, as well as supporting research for short term commercial gain.

The Federal Government in Australia has pursued a limited objective of corporatisation with the replacement of our Rural Industry Research Councils by corporations that are commercially oriented and substantially independent of Government. The limited experience so far indicates that the change has not been beneficial for research, especially in areas of national strategic significance. I doubt that Australia has a strong enough industrial base committed to research and development as part of its culture to entrust coporations to underpin our core export industries without Government intervention.

### HIGHER EDUCATION SECTOR

It can be readily established that successive Australian Governments have not given higher education the priority it needed to accommodate the growth in student numbers, while preserving quality of education. In 1980-81, the Australian Federal Government devoted some 4.6% of budget outlays to higher eduction. By 1989-90 the commitment had been reduced to only 3.5% of budget outlay. The decrease of 1.1% for higher education represents a funding shortfall of some \$956 million in 1989-90 dollars. During the period we have experienced a substantial growth in the number of students in higher education 34%, resulting from higher retention rates to year 12 at the secondary school level from 36% in 1983 to more than 65% in 1991. If a constant level of funding per student had been maintained thoughout the decade, the higher education budget would be around \$1360 million, in 1989-90 dollars, more than the present

funding level. One consequence of this lack of financial commitment has been a serious decline in the competitiveness of university science and technology activities, both at the teaching and research levels, when measured against international norms.

What ASTEC has described as "the very fabric of our public research system" — the serviced laboratories, specialist library books and journals, computer resources, animal houses, technical workshops, and major equipment items — is being seriously eroded by the lack of appreciation by Australian research policy planners of the real costs of research. There is an urgent need in Australia to rebuild our research infrastructure to remain competitive at an international level. The replacement of outmoded buildings and equipment in universities requires the commitment of at least an additional \$100 million per annum to these items.

One of our major concerns is that the lack of infrastructure resources will result in a decrease in the quality of our postgraduate education and the quality of our research output. Ultimately, our international economic competitiveness suffers if we are not pursuing first-rate scientific research.

I consider that the research infrastructure question is the major research problem still confronting higher education institutions in Australia today. Our ability to recruit enough talented people to replace academic staff retiring in the 1990s and our capacity to accommodate the growth in student numbers are also unsolved resource problems.

### AUSTRALIAN RESEARCH COUNCIL

In 1988, the Australian Research Council replaced the Australian Research Grants Committee. A turbulent period has followed as the ARC redefined its mission. The ARC is the central body funding non-medical research in the higher education sector. The funding available to the Council to promote research in higher education institutions has risen very significantly from \$79.5 million in 1988, to \$208 million in 1992 (1989 dollars). This growth has been welcomed since a number of serious deficiencies in the system have been able to be addressed. The most notable are:

- an expanded ARC grants scheme for small and large projects;
- an increased number of postgraduate research awards at more ralistic stipend (currently in the range A\$13,504 to A\$17,427);
- a career fellowship scheme from the postdoctoral to the professorial level;
- new Special Research Centres and Key Centres of Teaching and Reasearch.

While these initiatives are welcomed, they have been achieved at a high price for the pre-1987 universities. The abolition of the binary divide, to create a Unified National System for tertiary education with some 35 universities instead of the previous 19, has resulted in a greatly increased demand for grants and a significant raising of research expectations. Unfortunately, only about 25% of initial grant applications to the ARC are now funded.

Other costs to the pre-1987 universities include:

- A net loss of university discetionary research funding for the five-year period 1988-92 of not less than \$125 million. This money, known as 'ARC Clawback', has been used, along with some new money, to fund the expanded ARC. Politically this was necessary for a Government intent on equity without providing sufficient funding to accommodate the research expectations of staff from the college sector as they were transformed into university academics. As noted earlier, the consequences for universities, especially on research infrastructure, have been devastating.
- Inadequate discretionary funds for research promotion. This
  has severely restricted the ability of universities to directly
  influence their own research mission.
- Inability to adequately nurture young staff and to promote new research initiatives in unfashionable areas.
- Inability of institutions, especially in the science and technology disciplines, to accept postgraduate research students if the academic supervisor does not have available external research funding.

### INDUSTRIAL RESEARCH AND DEVELOPMENT

The total research and development effort in Australia was 1.24% of GDP in 1989-90. The business enterprise component was 0.53% of GDP. Our total R&D effort is well below that of our

principal trading partners. Even allowing for structural differences it should be at least 2% of GDP. The Government portion of total R&D expenditure is about average compared with our trading partners. It is, however, almost twice that of the private sector, whereas in most industrialised countries the public sector R&D level is only approximately half the private sector level.

The Australian business R&D expenditure, at 0.52%, is well behind that of Germany at 2.1% of GDP, Japan 2% and the USA 2% by a factor of four. Denmark at 0.79%, Italy at 0.75%, Canada at 0.74% and Ireland 0.52%, also outrank Australia.<sup>(3)</sup> In the present economic climate, there is growing evidence that business R&D, in real terms, is declining in Australia. This is a cause for much concern. It is interesting that there is a general trend relating business R&D activity to the standard of living as measured by per capita GDP.

I note that the New Zealand commitment to R&D for 1989/90 was <1% of GDP, with the business R&D contribution being 0.31% of GDP. The New Zealand performance is lower than that of Australia and also declining. Based upon the latest comparative figures available, for 1987, New Zealand ranked 17th out of 23 OECD countries in investment for research and development. (4)

I consider that it is imperative for the Australian Government to take stronger action to boost the level of industrial R&D in Australia. Tax concessions and other initiatives have not provided sufficient incentive. It is timely for more direct legislative measures to be taken. Australia cannot expect to economically produce more value- added maufactured goods unless we harness the inventiveness and ingenuity of Australians through higher levels of industial development, building upon a sound research base.

A recent study by the Industrial R&D Board in Australia<sup>(5)</sup> has clearly demonstrated the rewards to be gained from pursuing R&D activities. The study found that returns on R&D investment by major Australian firms ranged from 2.5 to 10 times by way of sales. It was also reported in the study that companies investing a threshold of about 3% of sales revenue in R&D, regardless of the industry, achieved growth factors faster than lower R&D investing competitors.

The nurturing of value-adding industries is vital to our export performance. Technology-dependent products will not be competitive in the marketplace without the development of advanced manufacturing underpinned by sound R&D programs.

The aluminium industry in Australia provides an excellent example of the impact of technology on export performance. (It is now the second largest export earner for Australia and the fifth largest for New Zealand.) In 1980, the value of exports of the Australian aluminium industry (bauxite, alumina, aluminium and semi-fabricated products) was \$1209 million, of which \$101 million, or 8.4% by value, was aluminium and its products. In 1989, the total value of our exports by the aluminium industry had risen to \$5142 million, a 325% increase, of which \$2492 million (48.5% by value), was in processed aluminium and its products.<sup>(6)</sup>

The value-adding ratio from bauxite (\$22 per tonne) to aluminium (\$2500 per tonne) was a factor of 28, since 4 tonnes of bauxite is required to produce 1 tonne of aluminium. The value-adding ratio from bauxite to a semi-fabricated aluminium product is estimated to be of the order of a factor of 40.6 While a number of other factors beyond R&D are also vital to achieve this value-added gain, the competitive technology which can only emerge through leading edge R&D is critical to achieve the outcome.

I have consistently supported a FASTS call for a national industry R&D strategy.

### NATIONAL INDUSTRY R&D STRATEGY

A policy developed as part of a national industry R&D strategy should include the following cornerstones.

- A clear target of industrial R&D of at least 1% of GDP to be reached by 1995, should be set by the Government. This 1% target is double our present industry expenditure but is still significantly less than the expenditure by many of our trading partners, including Japan, Sweden, USA, UK, Belgium and Germany. It should be matched by a further 1% for Government sponsored R&D.
- 2. All companies should be required to contribute to R&D at a level of at least 1% of sales to assist in the achieving of this

target. A company could choose to either directly undertake the R&D or to contribute to an industry sector research fund. A levy precedent is well established in the primary industry sector and should be extended to both the manufacturing and tertiary industry sectors. For example, the Australian high technology trade deficit is currently projected to be \$10 billion by 1994. Banks and insurance companies are major users of information technology through office machines and electronics, computers, data base, and the like. If at least 1% of sales was spent on R&D by this sector in Australia then with information technology imports as high as \$10,000 million, \$100 million would be available for R&D to overcome the trade imbalance. A similar analysis could be applied to many other sectors including petroleum products, paper products and chemicals. In the latter area, Australia currently imports about \$4 billion worth of chemicals per year.

 The annual reports of all companies should include a declaration of the percentage of turnover spent on R&D. This requirement is already the case in some countries. If implemented in Australia it would help to promote discussion on the importance of undertaking industrial R&D.

In the United States, for example, Chemistry and Engineering news publishes annually R&D figures for all major chemical companies as a percentage of sales. It is difficult to obtain comparable data for chemical companies operating in Australia. The best estimate that I have been able to make indicates that, on average, a US chemical company spends more than five times the amount on R&D than that expended by their Australian counterpart.

It is evident to me that our chemical industry cannot expect to remain internationally competitive unless it is prepared to invest in harnessing the inventiveness of Australian chemists.

### POLICY INITIATIVES FOR THE FUTURE

The poloicy initiatives which I consider Australia should by taking to secure its economic future can be categorised under three headings:

- Strengthening our skills base through education and training;
- Developing wealth-generating industries:
- Enhancing our international competitiveness.

### Skills Base

It is imperative that we preserve the quality of our education system at the primary, secondary and tertiary levels. There has clearly been a neglect of the fundamentals with respect to science and mathematics in schools. We have failed to attract enough of our talented graduates to return to the school environment, to stimulate and nurture students with promise to pursue careers in science and technology. The Minister for Employment, Education and Training, Mr. John Dawkins, has recently proposed that mathematics and science should be compulsory for all year 11 and 12 students. An intergovernmental committee is scheduled to report on the proposal by the end of the year. In Victoria, more than 90% of all year 11 students are taking mathematics and more than 60% at least one science subject. It is not sufficient to simply participate, however, the content and the standard of the tuition must also be preserved.

At the tertiary level we have reduced the resources available to preserve the quality of education which is so vital to our future as part of a global economy. Furthermore, too few of our very best students are studying science and technology oriented courses. These are areas which I believe must be more vigorously addressed. I note the New Zealand has a similar problem, with fewer graduates being produced each year for veterinary science, horticulture, agriculture and forestry combined, than for law.

Salaries of academics have declined alarmingly in the last 20 years relative to community norms. For example, in 1970 a lecturer at the minimum point on the scale received a salary equal to 1.36 x average weekly earnings (AWE). By 1990 this had declined to 1.12 x AWE. The trend is the same for our academic leaders with a professorial salary declining from 3.62 x AWE to 2.29 x AWE in 1990. Recently there has been an acknowledgement of the decline with modest academic salary increases, but the promising step has not been sufficient to restore the competitive position required to attract enough high quality people to an education profession.

It is also a priority to attract more women into science and technology professions. Compulsory mathematics and science at school will help. The growth in female enrolments is really quite encouraging. In Engineering at the University of Melbourne, female enrolments have reached some 20% of the cohort in 1991, with the enrolments in Chemical Engineering exceeding 40%. For many scientific disciplines the number of female enrolments is close to that for their male counterparts. These are promising trends which need to be nurtured. There is still, however, a significant descrepancy at the postgraduate

### **Wealth Generating Industries**

It is no longer possible for a small country to have a diverse manufacturing base and still remain internationally competitive, the economy of scale and the need for leading edge innovation has fostered concentration. It is important that Australia identify niche industries related to its basic strengths. Our strengths lie in the upgrading of our natural resources and in the exploitation of our knowledge based industries. Areas such as mineral beneficiation and refining, scientific and medical instruments, computer software and food science are all areas where Australia could seek to establish niche industries. The level of commitment to industrial R&D to which I have referred earlier will clearly be critical if we are to place ourselves strategically on the world stage.

It is also important that there be better career rewards for the wealth creator, including the educators. For too long our priorities as a society have been distorted. Higher rewards accrue to the money managers rather than to the wealth creator. There is evidence that there is growing awareness of this fundamental flaw in our society.

### **International Competiveness**

Our policies must be oriented towards establishing international worldwide networks to markey our products. No longer is it sufficient to limit one's horizons to the Australasian market. Penetration of international markets cannot be achieved unless companies adopt a worldwide perspective. The importance of humanity and social science courses in higher education to support this sector should not be underestimated. Expertise in Asian language, good management practices and a sound knowledge of the social and cultural values of our trading partners can be vital to developing trading links.

Financial factors such as interest rates, exchange rates, work practices and wages, are also central to the implementation of a competitive strategy. Finally, I consider that it is imperative that the science business interface be strengthened through more science literate managers being educated to influence the direction of our major companies.

The obstacles that we face to the success in creating what Australia's Prime Minister has described as a ¢clever country¢, but which I would prefer to call a technologically smart society, include thelack of a positive community attitude to a balanced development, an inadequate national R&D infrastructure, insufficient capital for long-term development, and too limited an internation outlook.

### THE ROLE FOR CHEMISTRY

One may reasonable ask "Is there a role for chemistry in an economic revival strategy?" We frequently proclaim that chemistry is a central science. Without chemistry one cannot obtain solutions to many problems which confront the management of, for exaple, the environment, resource upgrading, medical science or primary industries. Chemistry is central to preserviang our quality of life. It is clear that the climate is right for us to do more to attract the attention of our politicians and the community to the importance of our profession. In Australia, 1992 will be the 75th year since the foundation of the Royal Australian Chemical Institute. We are currently planning a series of major activities to highlight the importance of chemistry to society.

I have been particularly pleased to see the initiatives being taken by the Royal Society of Chemistry in Great Britain. I believe we could all learn a great deal from the promotion and education campaign that they are currently conducting.

The Royal Australian Chemical Institute is taking an increasing interest in the future direction for chemistry for Australia's well-being. Shortly it is anticipated that the Institute will commission a wide-ranging Strategic Review of Chemical Research in Australia. We anticipate that the Review will operate within a 15-year timeframe and appraise activity within the industrial, the Government research organisations, and the higher education sector with regard to the breadth, quality and relevance of the chemical research being undertaken.

It would be appropriate for the RACI and the New Zealand Institute of Chemistry to explore ways in which we could cooperatively promote the benefits of chemistry. I see it as an important contribution that we could make to the planning for the economic, social and cultural futures of our two countries.

#### CONCLUSION

We still have some way to go in Australia to recognise education innovation and hard work as the cornerstones of national prosperity. If we can more positively influence community attitudes then the politicians will surely follow. There are encouraging signs that we are starting on the long and difficult reconstruction to a stronger value adding manufacturing base. We will need to be driven by the desire for import replacement and the requirement of adding value to our products prior to export.

The challenge for leadership in Australia or New Zealand is to have a clear vision of the outcomes that we want to achieve for the benefit of society. I am clear that to preserve our quality of life, to protect the environment and to enhance our international competitiveness we must be a technologically smart society. Strong science and technology programs are vital for a strong economy. The challenge for all of us is to convince the decision-makers that our vision is meritorious.

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# WHAT'S HAPPENING IN THE INSTITUTE?

The August meeting of Council is now over and you will soon be briefed by your Branch Delegate. One point that did arise was the perceived need to increase communication between Council and all the members of the Institute. Whilst the Journal does fulfill this need, there are many occasions when the information is out of date due to the time lag inherent in a bi-monthly publication.

To speed up communications, it is proposed to produce a one page flyer each month. This will be sent to each Branch for incorporation into their Newsletters advertising forthcoming Branch meetings. It is envisaged that it can be copied directly onto the back of the normal Branch notice.

It is hoped that the flyer will be produced within the first three working days of each month (not January!). It will then be sent to the Branch Chairperson and/or Secretary. It would probably speed up the process if a copy was sent directly to the member of the Branch Committee who compiles the Branch newsletter. To this end we would appreciate receiving the name (and corresponding address) of the compiler of the notices for your Branch.

# **COUNCIL NEWS**

The pre conference meeting of Council in Christchurch was the first time that there had been a face to face gathering of the members. The earlier Teleconference was very successful in that all business matters were properly attended to and there was a sustantial saving in travel costs and Council members were not away from their normal work for as long, as if they had travelled. It was agreed however, that Council should meet physically at least once per year.

### 1991 PRIZE WINNERS

ICI Prize — Professor A.D. Buckingham (Otago University) Shell Industrial Prize — Drs. Bibby, Milestone, Parker and Tapp (DSIR Chemistry)

Education Prize — Mr. D. Schollum (Orewa College)

#### PRIZES DISCONTINUED

No award for the NZIC Essay Prize was made this year and the prize is now discontinued. NZIC will make an award at the National Science Fair to replace the essay prize.

It is with regret that Council have been advised that ICI (New Zealand) Ltd are no longer able to support the annual ICI Prize which is consequently discontinued.

# **INSTITUTE HONOURS**

Mr. Raymond Hopgood (Auckland Branch) has been elected to Honorary Fellowship.

Over many years Ray Hopgood has made substantial contributions to the Institute, having been Chairman of the Auckland Branch (1973), a member of the Hazardous Chemical Committee (1985-1988). He has been (and still is) a very active long time supporter of the Institute since his election as M.NZIC in 1962, not only putting great energy into the hazardous chemicals and memership committees, but also helping with short courses, advising committees and generally being there to offer a unique perspective on the issues facing the Institute. Ray recently retired from a long, varied and worthy life in industrial chemisty, starting with the Fletcher group of companies and ending with Chemiplas NZ Limited.

### ANNUAL CONFERENCE

There will be no national NZIC conference in 1992 but there will be, in Auckland in 1993. Because of the introduction of Semester Systems in the universities, the timing of holiday periods and the timing of other conferences in Australia, choosing dates for conferences is proving to be difficult. Ideally firm dates for conferences should be set two to three years in advance to allow for proper planning of venues, arranging programmes and assembling and organising committee.

# CHEMICAL OLYMPIAD

The 1991 Chemical Olympiad was attended by Dr. RSAR Maclagan as observer. His report is included elsewhere in the issue. Council has resoved to assist with sending a New Zealand team to the 1992 Chemical Olympiad in Pittsburgh U.S.A. by providing \$2000.

Personal Branch and business enterprize donations are solicited to allow New Zealand to be represented at this important and challenging event.

# **OFFICERS FOR 1991-1992**

President - Mr. D.S. Winter (Otago)

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*Erratum:* In the Mellor Lecture: Fats a Neglected Chapter in Nutrition pages 42-44 the Greek letter phi  $\Phi$  was wrongly used to designate alpha linolenic acid which should have been printed as  $\alpha$ -linolenic acid as shown in Figure 3.

# SOIL WATER CHEMISTRY AND MINERAL STABILITY IN SOILS

# A PHYSICAL CHEMISTRY APPROACH

# PRESIDENTS ADDRESS TO NZIC BRANCHES 1991

by Harry Percival
DSIR Land Resources Lower Hutt

### Weathering of rocks into soil minerals

Soil is a complex mixture of inorganic and organic compounds containing, for example, mineral materials, organic matter, water and air. Figure 1 illustrates the development of well developed soil from fresh rock over time. The mineral materials component is a loose mass of broken and chemically weathered rock and of interest here is its interaction with soil water which contains a variety of chemical elements in solution (such as potassium, calcium, chloride, sulphate *et al*).

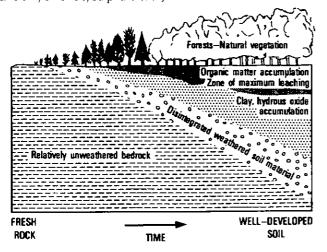


Figure 1: Soil profile developed from weathering (in place) of rock [adapted from Brady (1984)].

The weathering of rocks to form soil is essentially a combination of the mechanical process of disintegration where rocks and minerals are reduced in size and the chemical process of decomposition of minerals within rocks that are caused by hydrolysis, i.e. reaction of minerals with water, and other chemical effects such as oxidation. Soluble components from minerals with water, and other chemical effects such as oxidation. Soluble components from minerals are released into the reacting waters and new minerals are synthesised or are left as resistant end products. The overall scheme of weathering processes under conditions common in humid temperate regions like New Zealand are illustrated in Figue 2. It illustrates

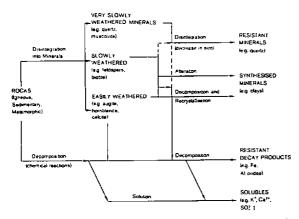


Figure 2: Weathering pathways under acidic conditions [after Brudy (1984)] (solid lines represent major pathways, broken lines minor pathways).

that the inorganic fraction of the soil comprises the residual weathering products of rocks and minerals as the more soluble components are leached away by water.

Why should rocks weather as they do to form soils? Chemical weathering of rocks occur because the rocks which emerge at the surface of the earth, after having been formed at different temperatures and pressures within the earth, are not in chemical equilibrium with present surface conditions, i.e. primary rockforming minerals are usually unstable in the presence of water at ambient temperatures and one atmosphere pressure. These primary minerals weather to secondary minerals of greater stability under earth-surface conditions, viz clays and associated minerals. Figure 3 lists the more important original or primary minerals and the secondary minerals derived from them. The production of new minerals by chemical weathering depends on the nature of the primary minerals present in the rocks and their chemical environment as represented in Figure 4.

ORIGINAL MINERALS Quartz SiO,		SECONDARY MINERAL Clay minerals Al Silicates	
Microcline		Gibbsite	Al(OH) <sub>3</sub>
Orthoclase	KAISi <sub>3</sub> O <sub>8</sub> *	Haematite	Fe <sub>2</sub> O <sub>3</sub>
Na plagiociase	NaAlSi <sub>3</sub> O <sub>6</sub> *	Limonite	Fe <sub>2</sub> O <sub>3</sub> .3H <sub>2</sub> O
Ca plagiociase	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>3</sub>	Calcite	CaCO <sub>3</sub>
Muscovite	KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	Dolomite	CaCO <sub>3</sub> .MgCO <sub>3</sub>
Biotîte	KAlMg,Fe),Si,O <sub>10</sub> (OH),	Gypsum	CaSO, 2H,O
Homblende	Ca <sub>2</sub> Al <sub>2</sub> Mg <sub>2</sub> Fe <sub>3</sub> Si <sub>6</sub> O <sub>22</sub> (OH) <sub>2</sub>	Apatite	Ca <sub>5</sub> (PO) <sub>3</sub> -(Cl,F)
Augite	Ca2(At,Fe)4(Mg,Fe)4Si4O24		
*Formula also tha	at for Volcanic K or Na-Glass		

Figure 3: The more important original (primary) and secondary minerals in soils [adapted from Brady (1984)].

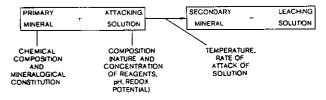


Figure 4: Schematic representation of chemical weathering [after Pedro and Siefferman (1979)].

# Interactions between minerals and aqueous solutions — application of stability diagrams

Chemical weathering environments of waters in contact with minerals can be represented by their chemical composition such as concentrations of cations (e.g.K<sup>+</sup>, Ca<sup>2+</sup>), anions (e.g.Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), aluminium ions, soluble silicon, and pH. It can be shown that minerals which are the least stable. Therefore knowing the chemical composition of waters in contact with minerals (say, the soil waters in between soil particles or interstitial waters in rocks) provides a tool for predicting the stable mineral or minerals in a given environment when mineral solubilities are known. We can identify those minerals which will precipitate or persist in a given soil/rock system or those that will dissolve or cannot persist.

If we wish to determine the relative stabilities of minerals under specific weathering environments (i.e. related to specific composition of contact waters) then a very good way of doing this is to construct stability diagrams showing the solubility relationships of the minerals in question. We do this by graphing equations describing the most suitable solubility reactions for the minerals in an equeous (weathering) environment under

equilibrium conditions. We must also know the equilibrium constants of the solubility reactions.

SiO<sub>2</sub> + 2H<sub>2</sub>O (quartz)

KAlSi<sub>3</sub>O<sub>4</sub> + 4H<sup>+</sup> + 4H<sub>2</sub>O 
(microcline)

K<sup>+</sup> + Al<sup>3+</sup> + 3H<sub>4</sub>SiO<sub>4</sub><sup>0</sup>

M<sub>4</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> + 6H<sup>+</sup>
(kaolinite)

Al(OH)<sub>3</sub> + 3H<sup>+</sup>
(gibbsite)

Al<sup>3+</sup> + 3H<sub>2</sub>O

Figure 5: Equilibria: minerals-aqueous solution.

Figure 5 shows the solubility reactions for four selected minerals-quartz, and microcline (examples of primary minerals), kaolinite and gibbsite (examples of secondary minerals). These reactions are written in a form where all the constituent elements (Si, Al, K) in the minerals are in soluble form in the solubility reaction products. Soluble silicon is represented by the neutral species,  $H_4 {\rm SiO_4}^0$ . The equilibrium constant relation that applies to the equilibrium reactions in Figure 5 is illustrated with kaolinite in Figure 6 [(kaolinite) and ( $H_2 {\rm O}$ ) have unit activities].

 $K^{0} = \frac{\text{Product of Activities of Reaction Products}}{\text{Product of Activities of Reactants}}$   $K^{0} \text{ (kaolinite)} = \frac{(Al^{3+})^{2}(H_{4}SiO_{4}^{0})^{2}(H_{2}O)}{(\text{kaolinite}) \text{ (H}^{*})^{5}}$   $\log K^{0} \text{ (kaolinite)} = 2 \log (Al^{3+}) + 2 \log (H_{4}SiO_{4}^{0}) + 6 \text{ pH}$ 

Figure 6: Equilibrium constant relation for mineral dissolution reactions.

Figure 7 shows the results for all the minerals considered here. The log values of the chemical species on the right-hand side of the equation are logs of the thermodynamic activities of the named species. Thermodynamic activities are the "effective" concentrations in solution of the species, and are related to their actual concentrations. Algebraic rearrangement of the equilibrium constant equations into the linear equation form shown in Figure 8 allows us to represent the solubility reactions graphically by plotting the (log Al³+ +3 pH) variable against log  $H_4 SiO_4^0$  for given values of log  $K^+$  and pH, and the known values of log  $K^0$ . Such plots form a stability diagram (or solution composition diagram) in which the stabilities of minerals can be compared under given environmental conditions.

We can being with the stability diagram in Figure 9 showing a selection of primary minerals and compare their solubility relationships with each other and with gibbsite, a 'reference' secondary mineral often formed at the end of the weathering

Quartz  $\log K^0 = \log H_4 SiO_4^0$ Microcline  $\log K^0 = \log K^* + \log Al^{3*} + 3 \log H_4 SiO_4^0 + 4 pH$ Kaolinite  $\log K^0 = 2 \log Al^{3*} + 2 \log H_4 SiO_4^0 + 6 pH$ Gibbsite  $\log K^0 = \log Al^{3*} + 3 pH$ 

Figure 7: Equilibrium relations for mineral-solution interactions.

Quartz\*  $\log H_4 SiO_4^0 = \log K^0$ Microcline  $\log Al^{2*} + 3 \text{ pH} = -3 \log H_4 SiO_4^0 - \log K^* - \text{pH} + \log K^0$ Kaolinite  $\log Al^{2*} + 3 \text{ pH} = -\log H_4 SiO_4^0 + 0.5 \log K^0$ Gibbsite  $\log Al^{2*} + 3 \text{ pH} = \log K^0$ \*line vertical to x-axis at value of  $\log K^0$ .

Figure 8: Line equations for (log Al³+  $\pm$  3 pH) vs log  $H_4SiO_4^0$  stability diagrams.

# **CHEMISTRY IN NEW ZEALAND**

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sequence for soil minerals. This stability diagram has been drawn for the conditions: 25 °C, 1 atmosphere pressure, pH=7 and log K+ = -3 (i.e. K+ activity =  $10^{-3}$  M, a common value in soil waters) with log K0 values taken from Lindsay (1979). Two of the minerals for which solubility line equations were developed (in Figure 8) are included — microcline and gibbsite. The other minerals are muscovite and K-glass (derived from volcanic ash) — the fomulae of which are given in Figure 3. With other specified environmental conditions the solubility can shift position in the diagram and also relative to each other.

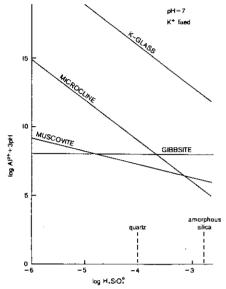


Figure 9: Stability of representative primary minerals compared to that of gibbsite.

Considerable information can be extracted from this type of stability diagram. In such diagrams each line represents the equilibrium solubility of a mineral, as shown, and the most stable mineral at a given soluble silicon activity is the one whose line at that point is the lowest in the diagram. This is the least soluble mineral at that point. Other minerals whose solubility lines lie progressively higher in the digram at that point are less and less stable. Therefore, we obtain a hierarchy of stability. Under the aqueous conditions specified for this diagram the order of stability of the minerals shown will vary with activity of the soluble silicon. At low silicon activities the order of decreasing stability is gibbsite, muscovite, microcline, and K-glass; while at high silicon activities the order changes to microcline, muscovite, gibbsite, K-glass. At in-between silicon activities muscovite is the most stable mineral. K-glass is clearly the least stable of the group of minerals shown at all silicon activities and would be the most weatherable mineral under the specified aqueous conditions.

Where solubility lines cross in the stability diagram both minerals represented by those lines can coexist, i.e. the crossing points represent the situation where both minerals are in equilibrium with each other as well as with the contacting water. Again, the most stable mineral 'pairings' are those at the lowest points in the digram viz. muscovite/gibbsite at a low silicon activity and muscovite/microcline at a high silicon activity. The microcline/gibbsite pair are less stable than muscovite at the silicon activity represented by the crossing point.

What else can the stability diagram tell us? If we take, for example, a soil water composition whose pH, Al<sup>3+</sup>, and soluble silicon level is such as to place it in the diagram below the solubility line of a particular mineral then the soil water is undersaturated with respect to that mineral, i.e. the mineral will tend to dissolve. Alternatively, a composition position above a solubility line of a particular mineral means that the soil water is supersaturated with respect to that mineral, i.e. the mineral will tend to precipitate. This all means that the minerals in contact with the soil water will tend to be those that are the least soluble (most stable) at the given soil water composition.

It is not uncommon to find minerals present in a soil that are (thermodynamically) unstable under the prevailing soil water composition. These minerals are termed 'metastable' minerals and will ultimately convert to stable minerals appropriate to the soil water composition. However, the conversion rate may be very slow.

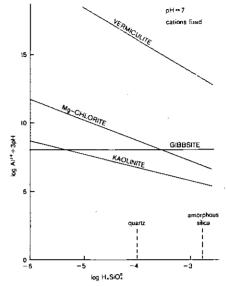


Figure 10: Stability relations of representative secondary minerals.

We have had a look at a stability diagram containing mainly primary minerals. Figure 10 shows the corresponding diagram for a set of secondary minerals (formed under earth surface conditions as against crustal conditions for pimary mineral), with gibbsite again acting as a 'reference' mineral. This stability diagram has been constructed for conditions similar to that for the primary mineral example shown earlier, i.e. for pH=7 and fixed levels of activities for the cations associated with  $Mg_5Al_2Si_3O_{10}(OH)_8$ vermiculite. Mg-chlorite, and  $[\mathrm{Mg_{2.71}Fe(II)_{0.02}Fe(III)_{0.46}Ca_{0.06}K_{0.1}]Si_{2.91}Al_{1.14}O_{10}(OH)_2.\ \log\ K^0}$ values were again taken from Lindsay (1979). The diagram shows that at low soluble silicon activities the order of decreasing stability is gibbsite, kaolinite, Mg-chlorite, and vermiculite; while at high silicon activities the order changes to kaolinite, Mgchlorite, gibbsite, and vermiculite. Vermiculite is always the least stable of these minerals under the specified aqueous conditions. Vermiculite is actually not uncommon in soils, but it exists as a metastable phase. In general the tendency in most aqueous environments in soil systems is for primary minerals to give way to secondary minerals of greater stability (however, 'metastable' intermediate minerals may be found on the way). Stability diagrams of the type shown makes one appreciate that a variety of minerals can be formed in soils in response to a variety of soil water environments and that the chemical weathering environment can be quantified.

# Relative stabilities of some aluminosilicates important in NZ soils

Now that I have briefly discussed the stability sequences of primary and secondary minerals in general I want to concentrate for a short time on a suite of aluminosilicate clay minerals that are significant in many New Zealand soils. There are the minerals kaolinite, halloysite, imogolite, and allophane. The equilibrium solubility reactions are shown in Figure 11. The derived equations for plotting the solubility lines in a stability diagram are shown in Figure 12 obtained by following the equilibrium constant relation procedure described earlier. Figure 13 shows

Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> (kaolinite, halloysite)	+ 6 H <sup>+</sup> ~ 2 Al <sup>3+</sup> + 2 H <sub>4</sub> SiO <sub>4</sub> <sup>0</sup> + H <sub>2</sub> O
Al <sub>2</sub> SiO <sub>3</sub> (OH) <sub>4</sub> (imogolite)	+ 6 H <sup>-</sup> ~ 2 Al <sup>3+</sup> + H <sub>4</sub> SiO <sub>4</sub> <sup>0</sup> + H <sub>2</sub> O
Al <sub>4</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>10</sub> (allophane)	+ 12 H <sup>+</sup> + 4 Al <sup>3+</sup> + 2 H <sub>4</sub> SiO <sub>4</sub> <sup>0</sup> + 7 H <sub>2</sub> O

Figure 11: Equilibria: minerals-aqueous solution (for some minerals significant in New Zealand soils).

Kaolinite, Halloysite	$\log Al^{3+} + 3 pH =$	- log H <sub>4</sub> SiO <sub>4</sub> ° + 0.5 log K°
Imogolite	log Al <sup>3+</sup> + 3 pH =	- 0.5 log H <sub>4</sub> SiO, 0 + 0.5 log K <sup>0</sup>
Allophane	$\log Al^{3+} + 3 pH =$	- 0.5 log H <sub>4</sub> SiO <sub>4</sub> + 0.25 log K <sup>0</sup>

Figure 12: Stability line equations for teh minerals in Figure 11.

the stability diagram containing the solubility lines for kaolinite, halloysite, and imogolite compared to that of gibbsite. [The log  $K^o$  values (25°C, 1 bar pressure) used for this stability diagram were 8.04 (gibbsite), 6.68 (kaolinite), 8.86 (halloysite), 12.08 (imogolite), -4.00 (quartz), and -2.71 (amorphous silica), taken from the author's unpublished review of equilibrium constants which is currently being updated for publication]. There are currently no reliable solubility data available for allophane so no solubility line is drawn for that mineral. I will discuss allophane again shortly.

This stability diagram holds for any pH value (in the normal range of 4-9 for soils). It shows that over a very wide range of soluble silicon activities kaolinite is always the least soluble, and therefore most stable, mineral relative to halloysite and imogolite (and to gibbsite except at very low silicon activities). Therefore the tendency will be for halloysite and imogolite to dissolve and for kaolinite to be precipitated. The presence of halloysite an imogolite in soils suggests that the kinetics of precipitation of these minerals is much more rapid than that of kaolinite or gibbsite otherwise halloysite or imogolite would never form in soils. Therefore both halloysite and imogolite can be regarded as fast-forming 'metastable' minerals.

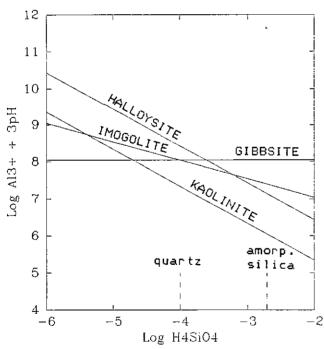


Figure 13: Stability relations of some minerals significant in New Zealand soils.

The stability diagram shows that, in the absence of kaolinite, imogolite is more stable than halloysite at silicon activities of less than about 15 ppm (at ≤3ppm silicon gibbsite becomes the most stable). This implies that under environmental conditions in soils where soluble silicon is removed from soils by moderately intense leaching halloysite could (theoretically) dissolve and imogolite be percipitated. I will show the practical consequences of this stability shift shortly.

Where does allophane fit into the stability sequence of the aluminosilicate clay minerals being discussed? Allophane is known to have a variable composition, in particular variable Si/Al ratios in its structure so that, for example, allophanes possessing ratios of 1/2 and 1/1 are both known. The 1/2 allophane is the most common type of allophane in New Zealand soils. A 1/2 allophane has the same Si/Al ratio as imogolite (and indeed this

allophane is usually referred to as proto-imogolite allophane because of its close structural and chemical formula relationship) while a 1/1 allophane has the same Si/Al ratio as halloysite (and kaolinite). In a stability diagram of the type shown here solubility lines for minerals containing the same Si/Al ratio always lie parallel to one another. Therefore solubility lines for 1/2 allophane and 1/1 allophane would lie parallel to those of imogolite and halloysite respectively. They would lie above or below the solubility lines of these two latter minerals if they were less or more stable respectively. However to fix the positions of the solubility lines of the 1/2 and 1/1 allophanes we would need to know the equilibrium constants of their solubility reactions. To date these have not been experimentally determined, perhaps because of the variable composition of allophanes. However, we can surmise that the 1/2 allophane (proto-imogolite allophane) will probably be very similar in stability to imogolite and to this extent imogolite can act as a 'model' for 1/2 allophane in stability diagrams, in the absence of equilibrium solubility data for allophane.

# A case study of mineralogical change in relation to soil water chemistry

The imogolite 'model' of allophane stability has proved to be useful in interpreting recent field observations of a sequence of soils in which allophane has tended to give way to halloysite as the dominant aluminosilicate clay mineral depending on the drainge conditions for the soils. The mineral stability diagram approach gives us a way of explaining this. The soil profiles (vertical sections of soils) chosen for study were located in the Waikato near Hamilton, viz profiles of Horotiu, Bruntwood, and Te Kowhai soils. These soils are quite close together physically, a matter of tens of metres (rather than hundreds), subject to the same climatic factors and parent rocks but differing in drainage patterns. Figure 14 gives some details about these profiles, concentrating on the subsoil horizons which are low in organic carbon and biological activity and which therefore are dominated by inorganic chemical processes.

Soil	Depth (cm)	Clay Mineralogy includes
Horotiu silt loam	31-130 (5 horizons)	Allophane and kaolin. Dominated by allophane.
Bruntwood silt loam	24-105 (5 horizans)	Allophane and halloysite. Dominated by allophane to 67 cm, thereafter by halloysite
Te Kowhai silt loam	32-128 (8 horizons)	Halloysite. No allophane

Figure 14: Major mineralogical features of soils varying in drainage characteristics.

Soil waters were extracted from the various horizons of field-moist soil samples by the method outlined in Figure 15 viz by centrifuging the samples with a dense water-immiscible organic liquid to displace the aqueous solution from between the soil particles. The aqueous solution forms a layer over the organic liquid, is separated from the organic liquid and then microfiltered to provide a particle-free solution for chemical analysis (Percival, 1990a). Chemical analyses of the soil waters are carried out for the species shown in Figure 16 (ion chromato-

(1)	CENTRIFUGING	3
	Sample:	150 g field-moist soil
	Displacent:	Arklone P (a trifluoroethane) or 1,1,1-trichloroethane
	Containers:	250 ml Polypropylene, or 300 ml stainless steel
	Centrifuge:	11,000 rpm for 30 min
2)	PHASE SEPARA	TION (IPS Whatman Paper)
3)	MICROFILTRATION	
	Membrane:	0.2 μ cellulose nitrate
	Apparatus:	Plastic Millipore

Figure 15: Conditions for soil solution extractions by the immiscible displacement technique.

graphy can also be used to measure the concentrations of the anions listed). The resulting data was processed (Percival, 1990b) using the computer programme GEOCHEM (Sposito and Mattigod, 1980) to calculate the equilibrium distribution of solution species, particularly that of the inorganic aluminium species Al<sup>3+</sup> which is required data for stability diagrams involving aluminosilicate minerals.

Determination	Method
pН	pH meter
Soluble siliça	Spectrophotometry
Cations:	
Na, K, Ca, Mg, Fe, Mn	Atomic Absorption
NH4.	Auto analysis
Al	Spectrophotometry
Anions:	
Cl <sup>-</sup>	Spectrophotometry
F	Spectrophotometry
HCO,	Auto titration
NO <sub>1</sub>	Auto analysis
SO,2-	Auto analysis
PO <sub>4</sub> 3+	Auto analysis

Figure 16: Analysis of soil solution constituents.

The Horotiu silt loam is a well drained soil whereas the Te Kowhai silt loam is poorly drained throughout the profile. Intermediate between these two soils is the Bruntwood silt loam where the upper horizons are well-drained but the lower horizons are poorly drained. In this particular soil sequence allophane (1/2 Si/Ál) is the dominant clay mineral in the well drained protions of the profiles and halloysite is dominant in the poorly drained protions. It turns out that the driving force, if you like, for this distinctive change in aluminosilicate mineralogy is the relative stabilities of allophane and halloysite under the different chemical weathering environments imposed by the different drainage conditions. The drainage conditions have influenced the soil water compositions in contact with the soil minerals, which in turn have caused soil mineral/solution reactions to shift in favour of the more stable mineral in the conditions. This can be illustrated by reference to Figure 17 which shows soil water compositions for the various horizons in the Horotiu, Bruntwood, and Te Kowhai profiles plotted on the soil profiles. So that, when the silicon level is less than about 15 ppm allophane will predominate over halloysite and when

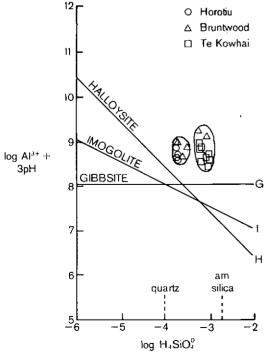


Figure 17: Soil water compositions of Waikato drainage sequence soils compared with solubility lines of the dominant minerals in the soil profiles.

stability diagram containing the minerals, gibbsite, imogolite, and halloysite.

Data falls into two main groups with respective soil water silicon levels of about 6 ppm (mg/l) and about 23 ppm (mg/l). (The log scale in the diagram makes the two groups of points look closer together than in fact they are they are very significantly different groups]. Now the 6 ppm silicon group of points are those representing the well drained horizons of the Horotiu soil profile (all horizons) and the Bruntwood profile (upper horizons) in which soluble silicon has leached out of. Conversely, the 23 ppm silicon group of points are those representing the poorly drained horizons of the Bruntwood profile (lower horizons) and the Te Kowhai profile (all horizons). Thus, the 6 ppm group plot in the area of the stability diagram where imogolite (which can be taken as representing 1/2 allohane) is the more stable of the two minerals imogolite (allophane) and halloysite, whereas the 23 ppm group plot where halloysite is the more stable. This accords well with the mineralogical observations of allophane dominance in the horizons corresponding to the 6 ppm silicon group and halloysite dominance in those horizons corresponding to the 23 ppm group.

What we are seeing here is the dominant alumino-silicate clay mineralgy being controlled by the soil water silicon level, which in turn is being influened by the drainage characteristics of the greater than about 15 ppm the reverse is likely to occur in soils where these minerals are present. This is a good example of the explanatory power of the stability diagram approach to explain observational data on mineralogy and the soil water composition associated with the mineralogy.

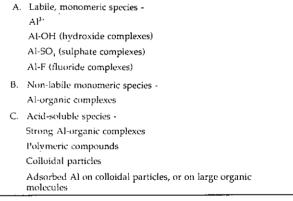


Figure 18: Aluminium species in natural waters.

# The complexity of aluminium chemistry in waters

Before I leave this subject I want to briefly discuss two interesting complicating factor in interpretation exercises of the type I have been describing. This is also an area of current and future research.

In the stability diagrams we have been looking at the aqueous species of aluminium used as the 'reference' is Al<sup>3+</sup>, i.e., the Al<sup>3+</sup> activity must be known or be calculable from measurements of total aluminium to be able to use the diagrams for interpretation of soil water composition. Soil waters will contain some or all of the species of aluminium shown in Figure 18. Not included in Figure 18 are the very slowly acid-soluble species of aluminium in clay particles and very fine sand particles. Al<sup>3+</sup> is always present even if it is only a small proportion of the total aqueous aluminium in the water.

Al<sup>3+</sup> activity can be caluculated from a knowledge of the total aluminium in solution, the pH, total concentrations complexing species of, and the relevant equilibrium constants of the complexing reactions. This can be difficult in practice if there is uncertainty about the actual Al species present and their concentration, particularly the Al-organic complexes which can vary widely. Research is on-going into identifying and measuring these complexes. In addition methods are being developed to measure only specific groups of Al species in the soil water such as the labile, monomeric species (inorganic complexes) or the

# LETTER TO THE EDIT

I have been following the claims about the consequences of the so-called Greenhouse effect. One such claim was that in the event of a one to five degree centigrade temperature increase, the level of the sea would increase to such a height to threaten low lying Pacific Island Nations. Indeed, one popular publication (Greenpeace) mentioned a one to two metre increase in sea height.

In general, the dimensions of all substances increase as the temperature of the substance is increased. This is a well established phenomena and engineers use the known coefficients of linear expansion in designing buildings, bridges etc. Thus I thought it would be easy to establish the validity of popular claims regarding the greenhouse effect.

The coefficient of linear expansion is;

$$\varphi = \frac{\Delta L L}{L_o \Delta t}$$

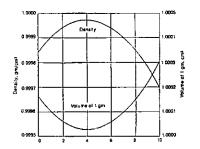
This can be expressed as  $L = L_o (1 + \varphi t)$ t is temperature.

The coefficient and expression for volume is obtained from the the cube of eqn 1 and is;

$$\beta = 3\varphi$$

$$v = v_0 (1 + \beta t) \text{ eqn } 2$$

From this, one can obtain the linear coefficient from the volume coefficient, and given the average depth of the sea, the average height change can be obtained.



My encyclopaedia and the CRC handbook gave me 3780 metres as the average depth of the seas.

All I needed was the coefficient of expansion.

Since the coefficient is the slope of the curve of change in volume vs temperature for a unit volume of water, it seemed a simple task to obtain the coefficient. See graph below.

However, I discovered that water, in the temperature range O C to 4 C, decreases in volume with increasing temperature, unlike most substances. Between O C and 4 C, the coefficient of expansion is negative. A consequence of hydrogen bonding.

Thus, to calculate the expansion, I had to know how much water is below 4 C. Since ice floats freely and permanently at the Poles, it is obvious that some water is close to O C. If half the world's seas were below 4 C, then a 4 C temperature increase would have no effect on sea levels. It is also obvious that deep water, at the bottom of the sea would be at 4 C since at 4 C, water has its greatest density.

The positive coefficient I roughly calculated from the graph below, over the temperature range 4 C to 10 C, as 0.000045. Thus the linear coefficient is one third of this or 0.000015.

Assuming all water is over 4 C, the increase in height is 22.7 centimetres for a 4 C temperature increase.

Assuming half the seas are below 4 C, there is a zero height increase. Between these two height changes must lie the correct value.

This is a far cry from one to two metres.

A further complicating factor is that an increase in temperature would increase the humidity as the warmer air could hold more water. This water would fall as rain and snow over the globe, including the South Pole. But at the South Polar region. snow is trapped on land for huge periods of time, effectively removing water from the seas. This would counter any increase. I cannot easily calculate this as I do not know how much of the world's rain and snow falls over the South Pole. Perhaps some of your readers could calculate this effect.

I cannot off hand see where this simple study is wrong. The coefficient may not be the best and salt water may behave somewhat differently, but I cannot accept one to two metres and the drowning of Pacific Islands because I had a barbeque this summer. Perhaps some of your readers could refine my simple analysis.

Yours sincerely Roger D. Keen

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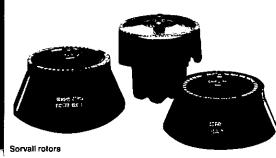
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7 July 1991

# A NEW GENERATION OF PIPETTES FROM EPPENDORF

HIGH ACCURACY AND AUTOCLAVEABLE

EPPENDORF have just released the VARIPETTE 4810 series. The extended range of six Varipette models can pipette liquid volumes from 0.5ul to 2,500ul. There is one single control button for setting the volume, pipetting the sample and ejecting the tip. When the desired volume has been selected, it is locked in place preventing accidental changes. The digital volume readout is always visible during pipetting. Colour coding of the control button matches the colour code of the appropriate pipette tips. (White, yellow, blue or red).

These new pipettes from Eppendorf are comfortable in the hand, with a ribbed pipette body for a secure hold. All pipettes have slim nose cones which fit into most vessels. The 0.5ul pipettes can also use the GELoader tip designed for electrophoresis and DNA work in cuvettes, gel apparatus and 0.5ml tubes. The pipettes have been manufactured from high-quality plastic materials, stainless steel and ceramics to ensure their durability. The 4810 is largely resistant against chemicals. The entire Varipette is autoclaveable at 121 degree C (20 mins.)

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# KJELDAHL DIGESTER

Buchi have recently announced the introduction of their new Kjeldahl Digestion System. The new Digestion Unit B-426/435 along with the programmable Control Unit is the perfect partner to the now well know Buchi Distillation Unit, the B-323.

B-426/435 Kjeldahl Digestion Unit

The new digestors are designed to hold twelve samples, (B-435) and six samples (B-426), to match the capacity of your sample throughout.

An important innovation with the new unit is the combination of digestion vessel holder, aspiration module and rack. This has several advantages. Firstly, it is possible to work outside a fume cupboard without the risk of gas or fume leaks. Secondly, the new compact design allows easy and efficient operation while occupying a minimum of bench space.

The new heating method heats the digestion vessels uniformly from the side, ensuring even boiling characteristics.

Boiling chips are only required when evaporating larger volumes of water (>10ml). Temperature regulation is continuous up to a maximum of 650°C, which can be reached in only 5 minutes. This swift heating time means minimal digestion time. As an example, 1g of organic-biological material would be fully digested in 30-45 minutes.

In addition, Buchi make it easy to coordinate an entire Kjeldahl system since the digestion vessel is standard for all Buchi digestion and distillation units.

### B-436 Control Unit

Remote control of the digestion process via the new Buchi control unit, B-436 allows complete command of the workings of one or two digestion units as well as the B-412 Aspiration and Scrubber unit.

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Programs are safe from loss through power failure: in the event of such an occurrence, the process being run is stopped and the program retained by the Control Unit.

### TRUE "WALKAWAY" CONVENIENCE

Fiske recently introduced the latest addition to its family of Osmometers. Able to process between one and twenty four samples at a time, the Fiske 2400 is completely automatic with stat and batch capabilities.

The Fiske 2400 provides osmolality values by the preferred method of freezing-point depression on samples as small as 5ul. The tests are performed in disposable sample cups with automatic cleaning of the sample probe carried out between each test. The instrument displays each result in turn and these are then recorded on the built-in printer. Further features include microprocessor-controlled calibration and a dry refrigeration bath.



Fiske osmometers are available in New Zealand from Watson Victor Ltd.

### SEVEN NEW ORION METERS

The new range of Orion pH, temperature, mV and concentration meters is now available from Watson Victor Ltd. There are seven new meters to choose from, each cleverly designed, with a particular set of user requirements in mind. All

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A step up, the Model 250A is also designed for field operation and features accurate two-step auto calibration and automatic temperature compensation.

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And for pH analysis in the laboratory, there are four sleek new benchtop meters from Orion. The 420A is a microprocessor controlled meter that gives you the basics for fast, accurate pH measurement.

The Model 520A offers all these features with the option of a combination pH electrode.

For concentration and pH measurement, with the option of a data collection, the 720A is the model to choose.

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The Anton Paar DMA 38 digital density meter from Watson Victor Ltd., provides simple density measurement without a waterbath. The instrument's internal peltier effect thermostat operates from  $15^{\circ}$  to  $45^{\circ}$ , yielding densities precise to  $1 \times 10^{3} \text{ g/cm}^{3}$  in minutes. It can be used with the SP3 sample changer to provide automatic measurement of up to 24 samples without operator attention.

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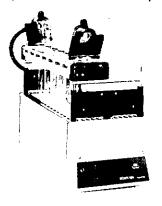
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Brookfield Engineering Laboratories has released the DV-III, a programmable Rheometer ideal for both R & D and quality control applications.

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tion of Casson Yield Value, Brookfield "Thix indes" and Power Law Index. Onscreen and printed plots of % scale versus spindle speed, CPC vs spindle speed, CPS vs shear rate, shear rate vs shear stress and CPS vs Temperature.

DV-III Viscometers are available in IV, RV, HA and HB ranges with standard spindles or cone/plate system, and are compatible with all Brookfield accessories.

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At this year's ACHEMA Exhibition, Sartorius presented a new development: the YDKO1 Specific Gravity Determination Kit, which can be used with many of the laboratory balances made by Goettingenbased manufacturer. Among the compatible balances are the new RC, AC and LC model series, as well as the A series in the field-proven MP8 microprocessor version. The user has the choice of employing this kit with balances of different readability, with 3, 4 or 5 decimal places, all it takes is a simple exchange of the adaptor for the weighing system.

To make the user's work easier, Sartorious engineers designed the kit for high mechanical stability. In this way, the kit can be readily installed on the balance. Easily accessible sample holders of generous size are provided with the kit for measurements in air and in a medium causing buoyancy. The special design of the perforations on the holders prevents air bubbles from adhering to them. The standardized glass plummet, also available in a metrologically verified version, allows simple determination of the density of liquids.

A specially shaped sieve for immersing samples is also included in the kit, for analyzing substances whose density is less than that of the liquid causing buoyancy.

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(Continued from Page 70)

non-labile, monomeric species (organic complexes). The Al<sup>3+</sup> activity calculation is most reliably performed when only the group of labile, monomeric species is measured since the inorganic complexes listed in the slide are fairly well characterised.

### Conclusion

Finally, the stability diagram approach is not only useful in understanding the formation and weathering of the mineral system in soils. It has a wider application because soil mineral equilibria, by controlling the aqueous concentrations of elements, affect all biogeochemical processes. Therefore applications are possible in the important areas of inorganic waste disposal (including nuclear waste), groundwater contamination by toxic elements, plant nutrition, and geochemical modelling in general; all areas in which the identification of solubility-controlling solids is important.

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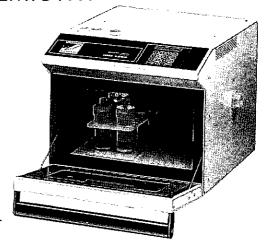
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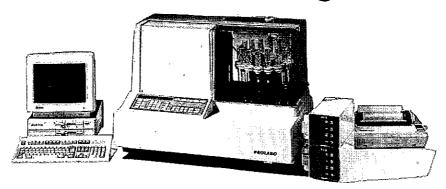
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