# JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

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## THE VOICES OF SCIENCE

In New Zealand's pioneer days scientists, particularly botanists and geologists, played a remarkably active part in the exploration and settling of this country. Among their achievements was the early formation of a national body, the New Zealand Institute, to discuss all aspects of science and to ensure its intelligent application to the problems of a growing colony. In this way they preserved a continuity with those early giants of the Royal Society of London who, by sending Captain James Cook's expedition to this hemisphere to observe the transit of Venus, appended the Southern Cross to the Union Jack.

Until the Institute of Chemistry was formed in 1931 the New Zealand Institute, now known as the Royal Society of New Zealand, remained the only body organized on a national basis to speak of science and for science in our community. The Institute of Chemistry grew from a need for a more specialized professional society. In his Presidential Address published in the October issue, Professor Parton predicts the development of equally strong bodies covering other science disciplines in New Zealand.

Traditionally the Royal Societies, both the parent in London and the scions in younger lands, were composed of men whose demesne was the whole of science. Traditionally, too, the unlettered amateur was admitted equal in status to the formally degreed scientist. *Autre temps, autre moeurs.* Science in all branches is today almost entirely the province of the salaried specialist; while scientific societies, increasing in numbers but decreasing in scope, demand more rigorous professional qualifications for admission.

This schism has undoubtedly resulted in stronger units but it has weakened the corporate structure of science. In a world grown utterly dependent on science, yet deeply suspicious of its activities in certain directions, there are certain basic issues involving intellectual freedom and integrity, as much as practical policy, on which scientists should unite. In 1959 Professor R. S. Allan, President of the Royal Society of New Zealand at the time, made the following statement at the annual meeting of the Council of the Society. "Briefly I will suggest that there is an urgent need in the Dominion for a body competent to provide critical, constructive and independent views on scientific problems in New Zealand and on Government policy where it involves scientific and technological knowledge. I believe that the Royal Society should be this body: that it should function as the voice of scientists in New Zealand." (*Proc. Roy. Soc. N.Z.*, 87, 22, 1959). In his subsequent Presidential Address, an important section of which is summarized in this quotation, Professor Allan advocated the setting up of Sectional Committees of the Society, composed of Fellows in the various disciplines, to fulfil this function.

In fact, is there today any single body in New Zealand which can speak on matters of national concern for all scientists in this country? Our own and similar institutions organized about a single discipline cannot do so. The Royal Society maintains the support of biologists and others who lack a strong professional institute, but has inevitably been weakened by defection of the chemists and the non-interest of the agriculturists. The Association of Scientists, originally founded for this very purpose and because the Royal Society appeared unable to fulfil it, has never attracted adequate adherence of the professional scientists. Both of these bodies are to some degree weakened by inclusion in their membership of many whose interest in science may outrun their knowledge and understanding of it. Furthermore the Royal Society derives part of its strength, for purposes such as publication, from considerable financial support from the Government—the only scientific body which does enjoy such support. No matter how independent its intentions and policy may be, this may well temper its voice on a matter involving political controversy.

An obvious answer to some of these comments is that chemists and other scientific workers should strengthen one of these bodies by joining it and taking an active part in it. Apart from the two disadvantages, already mentioned, in this course—the very general nature of their membership and, in the case of the Royal Society, the possible entanglement of purse strings—many scientists are understandably reluctant to disperse their activity and time over too many organizations.

The recent approach of the Royal Society of New Zealand to this problem has been to set up a series of Committees in various subjects. The members of these committees are, however, chosen as individuals and are not necessarily representative of their professional organizations. Although the Committee on Chemistry consists almost entirely of members of this Institute it may make proposals which do not receive the support of the Institute as a whole. Many members of the Institute who consider the Royal Society on appropriate organisation for expressing opinions on science as a whole in New Zealand nevertheless feel that there should be some safeguards. A safeguard which would give confidence to the Institute would be the knowledge that any pronouncement by the Royal Society on issues involving chemical matters included the opinion of the New Zealand Institute of Chemistry. The same argument applies to co-ordination with other organizations where these exist—for instance, the Veterinary Association and the Institute of Agriculture.

It appears generally recognized that some method is needed for achieving a common policy among scientists on matters of importance to the country and to working scientists. These comments are not offered as a solution to the problem but to direct the attention of Institute members to it. Only if members give thought to the question can the Institute play its part, which should from our numerical strength and knowledge be a major one, in ensuring that statements and recommendations made as representative of science in New Zealand are truly so.

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## THE PRESIDENT

The President for 1961-62 is Dr F. B. Shorland, O.B.E., Director of the Fats Research Laboratory, D.S.I.R., Wellington. Dr Shorland started his career in chemistry as a cadet in the Chemistry Section of the Department of Agriculture in 1927. As a part-time student he completed B.Sc. and won the Sir George Grey Scholarship in 1931. Allowed six months leave from the Department he graduated M.Sc. with First Class Honours in 1932 and was awarded the Jacob Joseph Scholarship. Three years later, with a D.S.I.R. Scholarship and a University Free Passage, he went to Liverpool to study fat chemistry under Professor Hilditch and spent some time in the British Drug Houses and in the Department of

Spectroscopy, Liverpool. He graduated Ph.D. from Liverpool in 1937 and returned to the Agriculture Department Laboratory in Wellington. When the old Chemistry Section was abolished and most of the chemists moved to the Ruakura Animal Research Station in 1945, Dr Shorland transferred to the D.S.I.R. to investigate the composition of New Zealand butterfat and in 1946 became Officer-in-Charge of the newly created Fats Research Laboratory. This Laboratory recently shifted into the old brick building which once housed both the Agriculture and D.S.I.R. laboratories, so that Dr Shorland's present study is the room occupied 35 years ago by his first boss, Mr B. C. Aston.

Dr Shorland's first publication (with J. A. Bruce in 1934) foreshadowed today's industrial exploitation of geothermal steam in New Zealand. Other early work was associated with the Department's studies on bushsickness which preceded the discovery of the essential role of cobalt; but a "hobby" project was the examination of New Zealand fish liver oils for vitamins. This work, in collaboration with the late Dr F. A. Denz, was first published in 1935 and commercial extraction of vitamin-rich oils was carried out on a small scale by Dr Shorland's father in his retirement. These studies proved particularly useful when local sources of A and D were required during the war. Furthermore they directed Dr Shorland's interest to the chemistry of fats and oils of both plants and animals, on which he is now a foremost authority, and most of the 120 papers bearing his name are in this field.

Dr Shorland's achievements have not passed unrecognized. He was invited to deliver the 11th Liversidge Lecture to ANZAAS in Melbourne, was Vice-Chairman of one of the sessions of the IUPAC Congress in Australia last year, and has been invited to be Conference Vice-President of the 1st International Conference of Food Science and Technology to be held in London in September 1962. He has written, by invitation, chapters in several publications including *Chemistry of Fats and other Lipids, Annual Review of Biochemistry, Biochemist's Handbook,* and *Comparative Biochemistry.* In 1950 he was awarded the degree of D.Sc. by Liverpool University, this being only the third award of this degree in the Department of Industrial Chemistry in 25 years. In 1951 he was elected a Fellow of the Royal Society of New Zealand and was awarded the I.C.I. Medal of this Institute. In 1959 his work received wider recognition with conferment of the O.B.E.

Institute members familiar with Dr Shorland's critical and "debunking" approach in technical matters look forward with interest to his guidance of Institute affairs in his period of office.

*Presentation of the Easterfield Medal to Mr T. A. Turney by Dr H. O. Askew.*

## NITROUS ACID AND NITROSATION

T. A. TURNEY

*Chemistry Department, University of Auckland.*

*(Easterfield Lecture, of the New Zealand Section of the Royal Institute of Chemistry, delivered at the 1961 Annual Conference at Auckland.)*

I wish to express my thanks to the New Zealand Section of the Royal Institute of Chemistry for awarding me the Easterfield Medal for 1961, and to thank the Chairman for his kind remarks about my work.

The Chairman mentioned Sir Thomas Easterfield's inaugural address at Victoria University College. Sir Thomas Easterfield obviously had a sense of humour as he records in his reminiscences that following the inaugural lecture he was visited by a man who in his own words "asked me to assist him in a research on making gold from sawdust in which he claimed to have been successful already" (1).

The Easterfield Lecturer is required to give an account of his own researches and I have chosen to speak on nitrous acid and nitrosation. Much of this work has been done in collaboration with research students and I have quite deliberately tended to emphasize our own work and interests. At the same time I have tried to relate these interests to a more comprehensive account of the subject.

I intend to discuss the equilibria present in solutions of nitrous acid in aqueous perchloric acid

$$HONO + H^{+} = NO^{+} + H_2O$$

$$\text{and} \quad 2\ HONO = N_2O_3 + H_2O$$

I then wish to discuss the reactivity of nitrous acid in terms of these species.

The reactions of interest are those of *substitution*

$$X{-}H + HONO = X{-}NO + H_2O$$

where X is usually a C, N or O atom; and of *oxidation*

$$B + HNO + H^{+} = B + {}^{+}NO + H_2O$$

where the base B can take many forms.

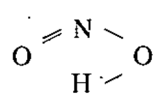
Examples of substitution reactions are for instance the nitrosation of phenols, the diazotization of amines and the formation of nitrites from alcohols. An example of oxidation is the conversion of iodide ions into molecular iodine.

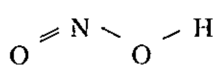
If a mixture of nitric oxide, nitrogen dioxide and water in the gas phase is taken then we get, among a number of equilibria set up, one in which gaseous nitrous acid is formed

$$NO + NO_2 + H_2O = 2\ HONO$$

From the infra-red spectrum of such a mixture it is possible to find the structure of the gaseous nitrous acid molecule.

The spectral evidence suggests that there is a *cis* and a *trans* form




The trans form is three times as abundant as the cis form. There does not seem to be any evidence for a nitro form.

In aqueous solution nitrous acid is best regarded as the hydroxylated form of the nitrosonium ion ( $NO^+$ ) and is formed on acidifying a nitrite. Other bases can replace the hydroxyl to give compounds of the type NOX. An idea of the character of the nitroso group in some of these compounds can be gained by comparison of their nitrosyl stretching frequencies.

| | $\nu$ (cm$^{-1}$) | |
|---|---|---|
| NO Cl $O_4$ (c) | 2329 | $N \equiv O^+$ |
| $Na_2$ (Fe $(CN)_5$ NO) (c) | 1938 | |
| $N_2O_3$ (g) | 1830 | |
| NOCl (g) | 1800 | |
| HONO (g) trans | 1677 | |
| HONO (g) cis | 1618 | —N=O |

There is a gradation from the higher frequencies corresponding to the triple bond of the nitrosonium ion to the lower frequencies typical of the double bond of the covalently bound nitroso group.

These data are the physical basis of a list made by Ingold of reagents in order of decreasing electrophilic reactivity.

$$NO^+, NOCl, N_2O_3, NOOH$$

An interesting point is the very polar nature of the nitrosyl group in nitroprusside (2).

In solution nitrous acid can take part in the general equilibrium

$$HONO + H^+ + X^- = NOX + H_2O$$

where $X^-$ can be $NO_2^-$, $Cl^-$, $Br^-$, $CNS^-$, $NO_3^-$.

I shall consider only two of these equilibria:

$$HONO + H^+ = NO^+ + H_2O$$
$$2\ HONO = N_2O_3 + H_2O$$

Both nitrous acid and the nitrosyl ion are colourless but dinitrogen trioxide is blue in colour and is interesting as it appears to be the only blue nitroso compound where the nitroso group is attached to an element other than carbon.

There were two difficulties in studying these equilibria. The first was to isolate them from one another. The second was decomposition, which occurs by the following path:

$$2N_2O_3 = 2NO + N_2O_4$$
$$N_2O_4 + H_2O = HNO_2 + HNO_3$$

To deal with these difficulties we made a preliminary estimate of the equilibria from thermodynamic arguments using the scheme

$$HONO(aqu) + H^+(aqu) + X^-(aqu) = NOX(g) + H_2O(l)$$
$$\text{and} \quad NOX(g) \rightarrow NOX(aqu)$$

The free energies of the quantities in the first equation were usually known but the second term was more difficult and involved rather uncertain approximations.

However we made an estimate of K for

$HONO(aqu) + H^{+}(aqu) = NO^{+}(aqu) + H_2O\ (l)$ of $7 \times 10^{-5}$

and of K for $2\ HONO(aqu) = N_2O_3(aqu) + H_2O\ (l)$

of $9 \times 10^{-3}$ from which is found

$$N_2O_3/NO^+ = 130.\ HONO/a_{H^+}$$

which shows us that the most favourable conditions of working are to make nitrous acid as low as possible and to measure the ratio $NO^{+}/HONO$ at as high an acidity as possible.

By measurement of the ultraviolet absorption spectrum of nitrite dissolved in 60% perchloric acid we found the spectrum of the nitrosyl ion, and in 10% perchloric acid of nitrous acid. For the equilibrium

$$H^{+} + HONO = NO^{+} + H_2O$$

$$K = (NO^+/HONO)\ (a_w/a_{H^+})$$

and by carrying out experiments in the region 50-53% acid it was possible to get $(NO^{+}/HONO)$. From this ratio we wished to get the value of the activity term in rather concentrated solution and hence K. This is done through acidity functions (3).

As many of you will not be familiar with acidity functions I will digress to discuss these. For an equilibrium

$$BOH + H^{+} = B^{+} + H_2O$$

we write

$$K_{BOH} = (a_{B^+} / a_{BOH})\ (a_w / a_{H^+})$$

for each a of base write $a = cf$

$$= (c_{B^+} f_{B^+} a_w) / (c_{BOH} f_{BOH} a_{H^+})$$

writing $pK_{BOH} = -\log_{10} K_{BOH}$ and re-arranging

we have

$$-pK_{BOH} - \log_{10}(c_{B^+} / c_{BOH}) = -\log_{10}(a_{H^+}\ f_{BOH} / a_w f_{B^+})$$

which we define $= J_o$

$J_0$ is a measure of the activity term and if we take a suitable indicator of known pK we can evaluate it by measuring $c_{B^+} / c_{BOH}$ in a solution of high acidity. It is found generally that $J_0$ is independent of indicator type.

For an equilibrium

$$BOH + H^+ = BOH_2^+$$

we have in similar fashion

$$-pK_{BOH_2^+} - \log_{10}(c_{BOH_2^+} / c_{BOH}) = -\log_{10}(a_{H^+} f_{BOH} / f_{BOH_2^+})$$

for this different indicator type. (4)

It is found for nitrous acid that we get constant values from the $(NO^+/HONO)$ ratio if we use the $J_0$ function indicating the equilibrium

$$H^+ + HONO = NO^+ + H_2O$$

but the alternative possibility

$$H^+ + HONO = H_2NO_2^+$$

using an $H_0$ function does not yield anything like constant values.

We find $(HONO)/(NO^+) = 10^{J_0}\ 10^{8.3}$ for perchloric acid. More recently a value has been found in sulphuric acid $(HONO)/(NO^+) = 10^{J_0}\ 10^{7.9}$ and there are certain difficulties in the calculation of the $(HONO)/(NO^+)$ ratio from the spectral data which would account for the difference. For the equilibrium $2HONO = N_2O_3 + H_2O$ we find that below 46% (w/w) perchloric acid the nitrosyl peak is absent so that all work was carried out below this acidity. Dinitrogen trioxide, which is blue in colour, was always in equilibrium with molecular nitrous acid so that it was necessary to devise methods enabling K to be found without knowledge of the concentration of dinitrogen trioxide. A spectrophotometric and a distribution method were devised.

For the spectrophotometric method we have

$$2\ HONO = N_2O_3 + H_2O$$
$$c_2 \qquad = c_1 \qquad a_w$$
$$c_{NO_2}{}^1 = c_2 + 2c_1$$

measured

$$D = \varepsilon c_1 \text{ (unknown)}$$
$$K = c_1\, a_w / c_2{}^2$$

and these facts together give

$$c_{NO_2}{}^1/D = (1/K\varepsilon)^{1/2}\,(a_w/D)^{1/2} + 2/\varepsilon$$

By estimating the optical density at 6563 Angstrom units and by estimating the nitrite in all forms a plot of $c_{NO_2}{}^1/D$ against $(a_w/D)^{1/2}$ gives a straight line of slope $(1/K\varepsilon)^{1/2}$ and intercept $(2/\varepsilon)$.

Since $\varepsilon$ is about 20, $2/\varepsilon$ is small so that the intercept is not determinable with great accuracy. An alternative procedure using the distribution of dinitrogen trioxide between toluene and water was therefore devised. These two methods combined yielded a value of K of 0.20 ± 0.05 at 20°C (5).

I will consider next the relation of these equilibria to the reactivity of nitrous acid. There are two main paths to consider in aqueous perchloric acid, one via dinitrogen trioxide and the other via the nitrosyl ion ($NO^+$) or the nitrous acidium ion ($H_2NO_2^+$).

The path via dinitrogen trioxide occurs provided the reacting substance is a sufficiently strong base and follows the rate law

$$\text{Rate} = k\ (HONO)^2\ (B) \qquad \text{I}$$

and, if the condition is realized where dinitrogen trioxide is used up as fast as it is formed,

$$\text{Rate} = k^1\ (HONO)^2 \qquad \text{II}$$

Some examples of bases obeying rate law (I) are $CH_3NH_2$; $(Co\ (NH_3)_5\ OH)^{2+}$; $H_2AsO_3^-$; $C_6H_5NH_2$; and aniline shows the limiting form (II).

The other form of the rate law is given by

$$\text{Rate} = k\ (H^+)\ (HONO)\ (B)$$

and same examples of bases obeying this rate law are o—Cl — aniline; $N_3^-$; $I^-$; $HCOO^-$; but under no condition has it been possible to obtain a limiting rate of the form

$$\text{Rate} = k\ (H^+)\ (HONO) \qquad (6)$$

Since no limiting rate of this form is reached it is not possible to decide whether the attacking species is the nitrous acidium ion formed in the reaction

$$H^+ + HONO = H_2NO_2^+$$

or the nitrosonium ion

$$H^+ + HONO = NO^+ + H_2O$$

The next series of experiments were designed to distinguish between these two possibilities. This was done by considering the way in which the rate constant of a reaction varied with acidity. For nitrous acidium ion attack

$$d(\log k_2)/dy = -dH_0/dy$$

while for nitrosonium ion attack

$$d(\log k_2)/dy = -dJ_0/dy$$

where $k_2$ is the second order rate constant, y the percentage acidity and $H_0$ and $J_0$ the appropriate acidity functions.

The reaction chosen for investigation was the reaction of phenol with nitrous acid with the reactants at 0.001N concentrations at 0.6°C. Ninety per cent. of the phenol is converted to nitrosophenol and good second order rate constants, first order in phenol and first order in nitrous acid, were found.

| $HClO_4$% (w/w) | 25 | 30 | 35 | 40 | 45 |
|---|---|---|---|---|---|
| $d(\log k_2)/dy$ | 0.04 | 0.05 | 0.06 | 0.12 | 0.10 |
| $-dJ_0/dy$ | 0.13 | 0.15 | 0.18 | 0.20 | 0.22 |
| $-dH_0/dy$ | 0.06 | 0.07 | 0.08 | 0.10 | 0.11 |

These results support the view that the nitrous acidium ion is the active species.

This conclusion is interesting in view of the fact that the thermodynamic results for the nitrous acid equilibria appear best interpreted as an equilibrium between nitrous acid and the nitrosyl ion. The above result is not entirely unambiguous and we can consider an alternative possibility. Writing POH for phenol then the phenol can be protonated on the oxygen and we might have

$$POH + H^+ = POH_2^+ \text{ (rapid equilibrium) followed by}$$

$$POH_2^+ + HONO \rightarrow \text{product, (rate determining)}$$

We have $H_0 = pK + \log POH/POH_2^+$, and according to this theory

$$\text{Rate} = k\ (POH_2^+)\ (HONO).$$

$$\text{But} \quad \text{Rate} = k(\text{expt})\ (POH)\ (HONO) \text{ experiment}$$

$$\text{and} \quad (POH_2)^+ = (POH)\ 10^{pK-H_0}$$

$$\text{whence } \log k(\text{expt}) = \log k + pK - H_0$$

$$\text{whence } d\log k(\text{expt})/dy = -dH_0/dy$$

This is again consistent with experiment.

It seems that it is not possible to distinguish the pairs $(BH^{+})$ (HONO) and (B) $(H_2NO_2^{+})$ by kinetic arguments but attack by the nitrosyl ion seems excluded (7).

We can exclude the possibility $(BH^{+})$ (HONO) on other grounds. If the attack was on $BH^{+}$ then the substitution should be *meta* whereas it is known to be mainly *para* even under strongly acid conditions as in the Liebermann reaction. We are thus left with the nitrous acidium ion as the most probable attacking species.

To summarize we can say that we have established experimentally the equilibrium constant for the nitrous acid dinitrogen trioxide system and that the mechanisms of a large group of nitrosations are consistent with a scheme in which dinitrogen trioxide is formed in equilibrium concentration.

In the case of the acid catalysed nitrosation the thermodynamic arguments suggest that the important equilibrium is that between nitrous acid and the nitrosyl ion while the kinetic arguments suggest the nitrous acidium ion is the important species.

In conclusion I should like to thank the students who have worked with me on nitrous acid, in particular Mr Morrison and Dr Wright, for their collaboration. I should also like to thank the Research Grants Committee of the New Zealand University for making substantial funds available for research. Finally, I should again like to thank the New Zealand Section of the Royal Institute of Chemistry for the award of the Easterfield Medal.

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## HONORARY FELLOWS

In the October, 1961, issue of the *Journal* we recorded briefly the election at the August Council Meeting of two further Honorary Fellows, Mr R. L. Andrew and Mr A. D. Monro. Notes on the life and work of the new Honorary Fellows are given in the following paragraphs.

Mr Andrew received his early education in chemistry in the School of Mines at Thames and his first years in the old Colonial Laboratory, which he joined in 1906, were devoted to analytical work for the Mines Department and the Geological Survey. As early as 1910, however, he commenced under the newly introduced regulations of the Food and Drugs Act, work which was to provide for many years his main and most satisfying interest. In an article on this subject in *Chemistry in the Development of New Zealand Industry,* published by the Institutes in 1947, Mr Andrew wrote "The analyst in New Zealand has done much to curtail the sale of adulterated foods and drugs but new and difficult problems remain for him to meet". His own pioneer work leading to the introduction of the freezing point test for added water in milk, and the reductase test (methylene blue) for ascertaining the bacteriological condition of milk, was responsible at a comparatively early stage for a great improvement in New Zealand milk supplies and his publications in this field made important contributions to knowledge and practice throughout the world. In later years he campaigned against the exploitation of vitamins and other scientific discoveries in misleading advertising of drugs. The other field with which his name will be long associated is the use of iodized salt to prevent goitre in New Zealand. His studies on the extraction of iodine from natural sources helped to establish the relation between incidence of goitre and the amount of iodine available from local soils and waters. When losses of iodine from iodized salt were recorded he and members of his staff demonstrated that much of the loss was to the container.

For the last six years before his retirement in 1946 Mr Andrew was Director of the Dominion Laboratory. One of his retirement occupations, the documentation of the life and work of William Skey (who described himself in a facetious epitaph as "New Zealand's primal analyst"), was indicated in the article on Skey published in the August, 1961, issue of the *Journal.* We regret to record that Mr Andrew has recently been in hospital in Wellington.

**Mr Monro,** a graduate of Canterbury University College, came to the Chemistry Department of Victoria University College as a Lecturer in 1921 and apart from a year spent in Scotland as an exchange lecturer in 1928 he continued teaching at Victoria until his retirement as Associate Professor in 1960. For many years "Bobby" Monro was the core of activity in the Chemistry wing at Victoria, his Inorganic lectures in the early days of the electronic theory of valency providing a stimulus to critical thought which influenced many of today's senior chemists in New Zealand. His research interests were largely in co-ordination compounds and in problems associated with the use of New Zealand ironsands. Mr and Mrs Monro were outstanding in the hospitality and understanding help in crises which they gave to students, especially those living away from home, and the affection with which they are remembered by many was evident in the presentation made to them by former students and staff in February, 1960.

Both Mr Andrew and Mr Monro were foundation members of the Institute and played important parts in the early stages of its development. Mr Monro was a member of the Publications Committee which inaugurated this Journal in 1936.

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## ROYAL AGRICULTURAL SOCIETY AWARD

### STUDIES ON SOIL ORGANIC MATTER

Two members of the Institute, Professor T. W. Walker and Mr A. F. R. Adams, of Canterbury Agricultural College, jointly received the 1961 special prize for research awarded by the Royal Agricultural Society of New Zealand. The prize is fifty guineas.

The award was based on work published under the general title "Studies on Soil Organic Matter" (Walker and Adams, *Soil Science,* 1958, *85,* 307; 1959, *87,* 1; and Walker, Thapa and Adams, *Soil Science,* 1959, *87,* 135.) A fourth paper (Walker, *J. Brit. Grassl. Soc.,* 1960, *15,* 74) crystallized the results of these studies. This paper shows that a full understanding of the processes involved in soil formation and development can be of great assistance in using the grass-legume associations, which build up organic matter levels and so improve nitrogen status and structure, to achieve high productivity and at the same time maintain or improve soil fertility.

For these studies on organic matter accumulation, consideration was given to the three effective variables in soil development (a) parent material, (b) degree of weathering, (c) degree of leaching—a simplification of the usual five soil-forming factors. This approach had already been used very successfully by other workers to explain observed progressive changes in clay mineralogy and nutrient status that occur during soil development.

The main elements of organic matter are carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorus. For many situations all of these can be derived from the air except phosphorus, which must come from the parent material of the soil. In a natural grassland climate the build-up of organic matter can be explained as follows. In a vegetation-free site on a weathered parent material such as fresh alluvium, all the phosporus will be in an inorganic form. In the virtual absence of nitrogen, legumes can establish and grow well in this environment. This phase is commonly seen in newly-colonized river-beds and road cuttings. Continued legume growth results in addition of organic matter and later, as nitrogen builds up, in invasion by non-legumes. At maturity organic matter levels will be high, limited amounts of inorganic phosphorus are becoming available, insufficient to sustain legumes against competition by grasses, which therefore become dominant. This progression may of course be interrupted through deficiencies of other nutrients.

The expectation that higher levels of organic matter should be found in soils from phosphorus-rich parent materials, which follows from the above hypothesis, was borne out in one of these studies, as shown in the following table.

| *P in parent material* | *Weight of P in profile* | | |
|---|---|---|---|
| | *Total* | *Inorganic* | *Organic matter* |
| (1) Low | Low | Very low | Low |
| (2) High | High | Moderate | High |

Soils in category (1) need added phosphorus for adequate legume growth. In category (2) other nutrients may limit legume growth before phosphorus does.

A further study examined the influence of the degree of weathering and leaching on organic matter accumulation on the same parent material. The organic matter was low in a zone of weak weathering and leaching, passed through a maximum under intermediate conditions and fell again to low levels under strong weathering and leaching. The corresponding changes in inorganic phosphorus were from high through to medium to low. Total phosphorus also decreased, showing clearly a loss of phosphorus from the profile during development. The pattern so established can be used to explain the nutrient needs for higher production from any given situation.

These principles have been illustrated in a study of the build-up of organic matter which followed a development on virgin soils from pumice. The conclusion from this work is that a thorough knowledge of soil-forming processes will enable increased herbage production to be achieved in a logical and scientific manner.

# NEW ZEALAND MEDICINAL PLANTS

The last twenty years have seen a considerable increase of interest in plant constituents which may be of value in medicine, and in New Zealand several members of this Institute have been making systematic studies on indigenous plants. This has lead to a revival of interest among both botanists and chemists in the use of native plant remedies by the Maori. Mr S. G. Brooker and Mr R. C. Cooper have now compiled a list of plants used for medicinal purposes in New Zealand, with a series of introductory discussions relevant to this subject. These have been published as a Handbook of the Auckland War Memorial Museum under the title *New Zealand Medicinal Plants* (paper cover, 46 pages; price to public 15s.).

The introductory sections include notes on the nature and extent of New Zealand flora, plants exploited commercially, chemistry and pharmacology, medicinal plants of the old-time Maori, and the missionaries and medicine. The main section, "Literature on New Zealand Medicinal Plants", covers 25 pages double column in small type. The information is presented by plant families arranged alphabetically, with most references to species including botanical notes, medical uses, pharmacology and chemistry. Reference is made to non-indigenous plants where the chemistry or pharmacology is relevant.

In a small country containing over 2,500 endemic species of plants it is disappointing that the native race appears to have established comparatively few effective remedies of plant origin. Earlier writers, particularly Elsdon Best, have attributed this largely to the Maori belief that a sick person was possessed by spirits commanded by Maikinui, either as a penalty for breach of *tapu* or through the sorcery of an enemy. Exorcism rather than internal medication was therefore logical, and herbal remedies were restricted mainly to treatment of wounds and similar obvious injury. Brooker and Cooper consider, however, that Best underestimated the medicinal use of plants by the early Maori. The matter is confused by the enthusiasm for herbal concoctions following the introduction of European medicines, particularly as an impressive addition to *tohunga* rituals. This probably resulted in more information on toxicity than on therapy.

Apart from the stultifying effect of a demonic theory of disease it may be queried whether the twenty-odd generations of habitation in New Zealand between the coming of the Hawaiiki Fleet and the European invasion would have allowed a very long period for the accumulation of an extensive and effective *materia medica* by the haphazard and empirical trial of a wide variety of plants against diseases which are themselves ill-defined. One wonders, for example, how much persistent trial and fatal error was required to evolve the cooking and steeping process whereby karaka kernels were converted to an important food free from the highly toxic karakin.

In compiling *New Zealand Medicinal Plants* the authors and their helpers have brought together a great deal of information which was hitherto widely scattered and some of which was in danger of being lost. They have succeeded in making a systematic treatment without sacrificing the fascination of the subject. Their work reveals how much is still unknown, despite the work of Briggs and others in recent years, about the chemistry and pharmacology of New Zealand plants.

—N. T. C.

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## BRANCH CHAIRMEN 1961-62

### AUCKLAND BRANCH

The Chairman for this year is again Professor D. R. Llewellyn. Details of his academic career were recorded in the April 1961 issue of the *Journal*.

### WAIKATO BRANCH

Mr R. J. Lancaster, Waikato Branch Chairman for 1961-2, is a member of the *Journal* Committee. He completed M.Sc. at Victoria University College in 1936 and joined the Department of Agriculture Chemical Laboratory in Wellington in 1936, having previously worked for two years with a firm of industrial analysts in Wellington. Between 1938 and 1942 he was located in Christchurch carrying out an extensive programme of analysis of pasture and crops in connection with nutrition problems of sheep in Canterbury. Later he served as a meteorologist with the Royal New Zealand Air Force in the Pacific and on his return was transferred to the newly established Ruakura Animal Research Station at Hamilton. His early work at that Station was in connection with the development of chemical methods of estimating digestibility of pasture and the intake of pasture by grazing cows and he was responsible for the introduction of the faeces nitrogen method of assessing digestibility which is now widely used. For some years Mr Lancaster has been studying physical and chemical factors which influence the quality of silage produced from grass. During a period of study leave in 1959 he spent several months in America and Europe visiting institutions engaged on agricultural nutrition work.

## MANAWATU BRANCH

Dr A. T. Johns is serving as Chairman of the Manawatu Branch for the second time, having held this office in 1953. Details of his education and early experience were recorded in the *Journal* for April 1953, page 49. In the last few years Dr Johns has established an international reputation for the outstanding work carried out under his direction on bloat in cows, a subject which followed naturally from the studies on rumen metabolism, and especially of digestive processes, which he commenced at Cambridge in 1946. Dr Johns is now Director of the Plant Chemistry Division, D.S.I.R., Palmerston North. He studied in the United States under a Dominion Civil Service Fellowship in 1954, attended the ANZAAS Conference at Perth in 1959, and during a visit to the United States, Europe and Russia in 1960 he attended the 8th International Grasslands Congress at Reading.

## WELLINGTON BRANCH

Chairman of the Wellington Branch for the ensuing year is Dr A. J. Ellis. Dr Ellis graduated M.Sc. (1st Class Honours) from Otago University in 1952. After working for three years at the Dominion Laboratory, Wellington, he returned to Dunedin to complete the Ph.D. degree, presenting a thesis on the chemistry of water solutions at high temperatures and pressures. Since 1958 he has been head of the Inorganic Section of Dominion Laboratory with particular research interests in the chemistry of the natural hydrothermal areas of New Zealand, and related laboratory research on the physical chemistry of aqueous electrolyte solutions above 100°. In 1960 Dr Ellis visited research institutions with related interests in U.S.A. and Europe and also geothermal utilization schemes in California, Iceland and Italy. He was elected an Associate of the Institute in 1954 and has served as Secretary and Council Delegate for the Otago Branch and on the Wellington Branch Committee.

## CANTERBURY BRANCH

This year's Branch Chairman, Dr W. S. Metcalf, was born in Otago but attended secondary school in Napier. He graduated M.Sc. with first-class honours from the University of Otago in 1939, and is probably unique among our members in holding also the degree of Mus.B. During his academic career he was awarded the Inglis Prize, George Young Scholarship, Duffus Lubecki Fellowship, and a Post-Graduate Scholarship in Science. He also won the Institute's I.C.I. Prize in 1954. Dr Metcalf's first appointment was as a Junior Lecturer at Otago University in 1940. He joined the chemical staff of the Department of Agriculture in 1943, working first in the Chemical Laboratory in Wellingon and later at Ruakura Animal Research Station, but returned to the academic fold as Senior Lecturer at Victoria University in 1945. Subsequently he spent a period in England and obtained the degree of D.Phil. at Oxford. He is now Senior Lecturer at Canterbury University. Dr Metcalf's research interests have been varied and include U.V. spectra and equilibria of chloroamines; iodine complexes; vitamin A in shark liver oil; the alkaloid perloline from *Lolium perenne;* hormones in cow urine; and particularly fluorescence of organic compounds in gases and solutions. He has published papers in a number of these fields.

## OTAGO BRANCH

Mr J. Robb, Chairman of the Otago Branch for this year, was educated at the Otago Boys' High School and graduated B.Sc. in Mathematics in 1944. On completing Stage 3 Chemistry in 1945 he took up a position as Chemist at the Glendermid Tannery Ltd., Sawyers Bay, Dunedin, and he is still with that firm. After part-time studies at Otago University he graduated M.Sc. in 1955.

Mr Robb was elected an Associate of the Institute in 1949 and has served previously on the Otago Branch Committee.

# BRANCH NEWS AND NOTES

## AUCKLAND BRANCH

Dr R. E. Mathews of the Plant Diseases Division, D.S.I.R., has been appointed Professor of Microbiology at the University of Auckland.

Mr W. Boustridge has been promoted to Production Manager and Works Chemist at British Imperial Paints.

Dr R. C. Cambie has been promoted to Senior Lecturer at the University of Auckland.

## WAIKATO BRANCH

The Branch Secretary, Mr F. D. Dorofaeff, is again in the news. This time we record his marriage to Miss Julie Perrow, also a member of the Branch. Both Dorofaeffs continue to work in the Chemical Laboratory of Rukuhia Soil Research Station, Hamilton.

Dr R. Hodges, M.Sc., Ph.D.(Manchester), recently returned to New Zealand to take up an appointment with the organic chemistry team at Ruakura Animal Research Station. Dr Hodges had previously been carrying out research on natural products, especially terpenes, at Glasgow University.

## MANAWATU BRANCH

Dr P. S. Robertson has recently returned to The Dairy Research Institute after three years at the National Institute for Research in Dairying, Shinfield, Reading, where he worked on tallowy discoloration and bacteriology of cheese.

Mr H. A. L. Morris, formerly Research and Development Manager at Birdseye (N.Z.) Ltd. has joined the Department of Food Technology at Massey College as a Senior Lecturer.

Dr G. Petersen, Plant Chemistry Division, D.S.I.R., is on leave for two years and is working at Oxford in the Department of Professor Sir H. A. Krebs.

Dr M. Howard is working at Plant Chemistry Division for one year on a Senior National Research Scholarship. His main interest is in the metabolism of rumen protozoa.

Dr M. H. Proctor, formerly of the Biochemistry Department, Cambridge University, has joined the staff of Plant Chemistry Division, D.S.I.R.

## WELLINGTON BRANCH

Mr A. H. Swaney, formerly of Ivory Spray Chemicals Ltd., Nelson, is now with Inca Ltd., Christchurch.

Mr S. H. J. Wilson has recently retired from his position at the Institute of Nuclear Science, and is living at his home in York Bay, Wellington.

## OTAGO BRANCH

Dr A. D. Campbell has returned to the Chemistry Department, University of Otago, after a year at Birmingham University on sabbatical leave.

Mr R. M. Carr has left the Chemistry Department, University of Otago, on leave to take up an appointment at Imperial College, London.

# COUNCIL MINUTES

## ABRIDGED MINUTES OF A MEETING OF THE COUNCIL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.) HELD IN WELLINGTON, NOVEMBER 24, 1961.

PRESENT

Dr F. B. Shorland (President, in the Chair), W. G. Hughson, (Vice-President), R. W. Oliff (Auckland proxy), R. J. Lancaster (Waikato), Dr A. T. Johns (Manawatu), Dr A. J. Ellis (Wellington), D. J. Hogan (Canterbury proxy, Registrar), Dr W. G. Hanger (Otago), N. T. Clare (Editor), and Dr W. E. Harvey (Hon. General Secretary).

APPOINTMENT OF OFFICERS AND SUB-COMMITTEES:

Officers and subcommittees of the Council for the ensuing year were appointed or re-appointed. *The full list of officers and sub-committees was published in the December Journal.*

TRUST FUND:

*Resolved*: That Dr F. B. Shorland be appointed a Trustee. (Sir Theodore Rigg and Mr J. C. Andrews remain in office until September, 1962).

THANKS TO RETIRING OFFICERS:

*Resolved* that letters of thanks be sent to Mr J. L. Mandeno and Dr R. Gardner who have retired as Employment Officer and the Institute's representative on the Science Technicians Committee of the Technicians Certification Authority respectively.

HONORARIA:

*Resolved* that the Honorarium for the Hon. Gen. Secretary be £50.
*Resolved* that the Honorarium for the Editor be £35.
be £35.

CONFERENCE 1961:

The final report from the 1961 Conference Committee was received and revealed a profit of £4 9s. 11d.

*Resolved* that the Conference Committee be thanked for their efforts and that the profit from the Conference be credited to the Overseas Visitors Fund.

CONFERENCE 1962:

The 1962 Conference will be held at Lincoln on August 15-17, 1962 (Wednesday-Friday). The Royal Society Congress will be held from August 13-17 and the R.S. have agreed to schedule their chemistry lectures so far as possible for August 13 and 14. The President of the Institute will be Chairman of the Chemistry section of the Congress.

*Resolved* that the sum of £20 be advanced to the Conference Committee.

EXAMINATIONS COMMITTEE:

*L.A.C. Examiners*: *Resolved* that L.A.C. Examiners receive £2 2s. 0d. per subject.

SALARY SURVEY:

Preliminary results from the recent salary survey were tabled.

*Resolved* that 300 reprints of the Salary Survey report be printed.

It was agreed that copies of the report should be distributed to Members of Parliament, the Public Service Commission, Secretary and Assistant Secretaries of D.S.I.R. and Agriculture, Council of D.S.I.R., Heads of Government laboratories and the Royal Commission on the Public Service.

OVERSEAS VISITORS:

Dr W. A. Waters, F.R.S., will be visiting Australia early in 1962 and it was agreed that the Secretary should write to Dr Waters to see if he would extend his tour to include New Zealand.
(Negotiations are nearly complete and Dr and Mrs Waters will be in New Zealand from approximately April 1-14, 1962).

CHEMISTRY IN ACTION:

*Resolved* that the Canterbury Branch be paid £8 0s. 0d. towards the cost of *Chemistry in Action.*

MEMBERSHIP SUBSCRIPTIONS:

There appears to be no great measure of agreement on this subject, it being generally felt that it could not be disassociated from the question of election to the Fellowship.

FELLOWSHIP:

The Canterbury Branch submitted a report (originally submitted in 1959) dealing with election to the Fellowship and in particular comparing the requirement for Fellowship under the N.Z.I.C. and the R.I.C. Rules.

*Resolved* that the Canterbury Branch report on the Fellowship be adopted.

*Resolved* that Mr S. G. Brooker be asked to consider drafting rules for the election to Fellowship which incorporate the spirit of the Canterbury report.

It was agreed that if possible this Rule should be introduced as soon as possible, if convenient before the re-drafting of all the Rules is completed.

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

A letter from the General Secretary of the A.N.Z.A.A.S. suggested that the N.Z.I.C. could contribute to the continuance of A.N.Z.A.A.S. by seeking affiliation and by encouraging our members to become members of A.N.Z.A.A.S.

It was agreed that the Secretary write to A.N.Z.A.A.S. seeking more details of what is involved in carrying out the above suggestions.

BRANCH GRANTS:

*Resolved* that Branch grants for the present financial year be £20 0s. 0d.

ROYAL SOCIETY OF NEW ZEALAND:

It was agreed that much good may come from some informal discussion with officers of the R.S.N.Z. and the President and Secretary agreed to proceed with these talks.

# THE REGISTRY

## Fellows

(Elected November 24, 1961)

BATT, Richard Dean, M.Sc., Ph.D., D. Phil., F.R.I.C., Biochemistry Department, Medical School, Dunedin (Associate Professor).

FASTIER, Frederick Noel, M.Sc., D.Phil., F.R.I.C., Pharmacology Department, Medical School, Dunedin (Associate Professor).

WHITE, Edwin Percy, M.Sc., D.Sc., Ruakura Animal Research Station, (Senior Principal Scientific Officer).

## Associates

(Elected November 24, 1961)

HUGILL, Archie James, B.Sc., Ph.D.(Birm.), Scott and Bowne Ltd., Auckland (Production Manager).

McCURDY, Alan Underwood, B.A., B.Sc., Aranui High School Shortland Street, Christchurch (Head of Science Department).

SINHA, Anandi Prassad, M.Sc. (India), Massey Agricultural College, Palmerston North.

THOMAS, Brian Russell, M.Sc., Ph.D.(Lond.), Dominion Laboratory, D.S.I.R., Wellington (Senior Scientific Officer).

## Leave of Absence

CARR, R. M. (For two years).

PETERSEN, G. B. (For two years).

## Resignation

JOHANNESSON, J. K.

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# SECOND CONGRESS OF MAN-MADE FIBRES

The Second Congress of Man-made Fibres will be held in London, May 1-4, 1962. It will be organized under the sponsorship of the Comite International de la Rayonne et des Fibres Synthetiques, the headquarters of which are in Paris where the first Congress was held in 1954. The London Congress, meeting in the Royal Albert Hall, will seek to give a clear picture of the present state of the industry, its aims and position within the textile industry, its economic and social impact, and especially the technical developments in the eight years since the first Congress.

Man-made fibres is the generic term to describe all fibres other than those of natural origin such as wool, cotton, silk and flax. Some have cellulose as raw material, the rest, produced from chemicals, are known as synthetic fibres. Man-made fibres now account for 22% of all textile fibres produced in the world, having doubled their relative share of the world production compared with immediately before the Second World War. At the present rate of increase of production (between 6% and 7% per year) the output will be nearly doubled in the next 10 years. Of the total of 3,300,000 tons produced in 1960, synthetic fibres represent about one fourth in weight and very nearly one half in value.

## OBITUARY

### N. A. MARRIS

The death has occurred of Norman Andrew Marris, M.Sc., B.Com., F.N.Z.I.C., who retired recently from the position of Officer-in-Charge, Information Bureau, Department of Scientific and Industrial Research.

Mr Marris was educated at Nelson College and Canterbury University where he took his Master of Science degree with Honours in Chemistry. He joined the Dominion Laboratory as an Assistant Analyst in 1928. In 1935 he was promoted to the position of Analyst and became Gas Examiner under the Board of Trade Regulations. In the same year, he completed his B.Com. degree. In 1940 he joined the Head Office of the Department as a Professional Officer, and in 1943 became a Senior Executive Officer.

When, in 1944, the New Zealand Government opened a Scientific Liaison Office in Washington, Mr Marris was appointed as the first Scientific Liaison Officer. He remained in this position for three years during which he did very valuable work for New Zealand. His courtesy, friendliness, and diplomacy made him particularly suited for this work.

He returned to New Zealand in 1947 and was shortly afterwards appointed Officer-in-Charge, Information Bureau. In this position he had the task of co-ordinating the diverse functions of the various sections of the Bureau. Mr Marris was also in charge of the Scientific Liaison Service of the Department, and for many years was New Zealand Liaison Officer for the Commonwealth Agricultural Bureaux.

Mr Marris' death, soon after his retirement through ill health, will be deeply regretted by all those with whom he came in contact including many members of the Institute, of which Mr Marris was a Foundation Member. He was elected a Fellow of the Institute in 1940.

Mr Marris is survived by his wife, a son, Mr David Marris of Hamilton, and a daughter, Mrs Lyndsay Gullen of Timaru.

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## 1961 CONFERENCE REPORT

The Report of the 1961 Conference Committee records a total of 181 registrations for the Conference held last August in Auckland. There were 152 full members, 15 students and 14 members of the Committee. On the Thursday morning 140 members took part in the three excursions—to Onehunga Woollen Mills and the Auckland Metropolitan Drainage Board; Carbonic Ice Company and Chelsea Sugar Refinery; Astley's Tanneries and Crown Lynn Potteries. For the Post-Conference Tour to Forest Products Pulp Mill at Kinleith and the hydrothermal area at Wairakei there were 24 members. This excursion was a very full day's programme, starting from Auckland early in the morning with breakfast at Te Kauwhata, lunch at Kinleith provided by Forest Products and dinner at Putaruru.

## CORRECTION

In the list of Branch Delegates in the December issue the Delegate for Canterbury was incorrectly recorded. The Canterbury Delegate on the Council for this year is Mr R. W. Cawley.

# BOOK REVIEWS

*X-RAY ANALYSIS OF ORGANIC STRUCTURES*, by S. C. Nyburg. Academic Press, 1961. 434 pp. Price 93s.

The author's purpose in writing this book is clearly stated in the preface. "X-ray structure analysis is essentially a branch of physics and one which involves an appreciable amount of mathematics. Thus it is difficult for the chemist, and in particular, the organic chemist and biochemist to understand how X-ray structure analyses are carried out—to assess the reliability of published results or to appreciate fully the powers and limitations of the method. Accordingly there appears to be a need for a book which firstly presents the X-ray structural method with the minimum of formal mathematics and secondly which gives an adequate survey of the organic and biological material which have so far been examined."

In supplying these two needs the author has effectively written two books, either of which can be enjoyed independently. The first six chapters present the X-ray method with the absolute minimum of mathematics in the simplest form. The account is particularly rich in the procedural details which are so often lacking in text books on this subject, and is quite comprehensive. The reader is given a clear and realistic picture both of the underlying principles of the method and of the actual operations performed by the investigator. The reader with little previous knowledge will find this the finest introduction that has been written. The organic chemist whose interest is only casual should be warned however that, although this treatment is within his grasp, X-ray crystallography is a complex subject and its mastery will require some determination.

The last three chapters describe the results of various X-ray studies which have been made on organic and biologically important compounds. The difference between this and other previous compilations is that the results are discussed from the viewpoint of the chemist rather than the crystallographer. The various types of molecules are well classified, and the organic chemist can quickly discover just what X-ray studies have established in, for example, the alkaloid field, or the theoretical chemist can lay his hand easily on the bond length data in certain molecular types. Where relevant, the accuracy of the various results is indicated. This section of the book alone will make it invaluable to the majority of chemists for nowhere else will they find such a lucid, pointed summary of so much structural information. It is only to be regretted that a work of this type is of necessity out of date before it is even published, and it is to be hoped that Dr. Nyburg or some other will publish sequels written in the same manner.

—D.H.

*NEUERE METHODEN DER PRAPARATIVEN ORGANISCHEN CHEMIE*, edited by Wilhelm Foerst. Published by Verlag Chemie, GmbH, Weinheim. Volume II, 1960, 272 pages; volume III, 1961, 326 pages. Price: with cardboard covers each 14.50 DM; bound 18.00 DM. (In German).

Volume I of this series was published during the last war, was reproduced in the United States, and is now out of print.

Volumes II and III have paper covers giving books of limited durability. The paper is of moderate quality but print and formulae are clear and easy to read. The two volumes contain 25 review articles on organic reactions, selected not on any system, but because of the interest and importance attached to the reactions. Most of the sections are taken from review articles of *Angewandte Chemie* brought up to early 1960 by addenda.

The emphasis is on a general survey of the selected reaction with a hundred or so references to the literature. There is not an extensive discussion of reaction mechanisms, nor as much practical recipe and detail as one might have expected. Articles are generally shorter than those of the Organic Reactions series, and there is little duplication of subject matter.

The volumes serve for advanced students, and for those engaged more particularly in synthetic organic chemistry. It is refreshing when so many books are at a price level prohibitive to individual chemists, or to smaller libraries, to find an excellent value provided by these volumes. Titles of articles follow.

Vol. II. Syntheses with acetoacetaldehyde; preparation of peptides and ureas using reactive amides or imides; preparation of long-chain carboxylic acids from 1,3-cyclohexanediones; cyclopentanone -*o*- carboxylic ester ketene in preparative organic chemistry; preparative and analytical importance of phosphines and related compounds; reduction of carbonyl compounds by complex hydrides; alkylation of aromatic amines; chemical syntheses of intermediates of sugar metabolism; amidomethylations; selective catalytic oxidation with noble-metal catalysts; alkylation of phenols with olefines; continuous production of phenylsodium; newer investigations on oxidations with lead tetraacetate.

Vol. III. Reactions of sulphur with aryl-aliphatic and aliphatic compounds; introduction of substituents into the pyridine ring; olefination of carbonyls using triphenylphosphinemethylenes (Wittig reaction); n-bromosuccinimide, properties and mode of reaction; the acyl-lactone rearrangement; syntheses with acid amides; syntheses with chloramine; preparation of esters, amides and anhydrides of phosphoric acid; aromatic compounds from pyrylium salts; production of the acetylenic bond; syntheses employing diazoketones.

—E.P.W.

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# CHEMICAL AND PETROLEUM ENGINEERING EXHIBITION

The 2nd Chemical and Petroleum Engineering Exhibition will be held in London from June 20 to 30, 1962, and the 4th Congress of the Federation of European Petroleum Equipment Manufacturers will also meet in London from June 25 to 28. The exhibition will be the largest display of chemical plant and petroleum treatment equipment ever held in Europe, with 400 to 500 exhibitors. It will be sponsored jointly by the British Chemical Plant Manufacturers' Association and the Council of British Manufacturers of Petroleum Equipment. Further information on this exhibition may be obtained from: Engineering in Britain, 34 Victoria Street, London, S.W.1.

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