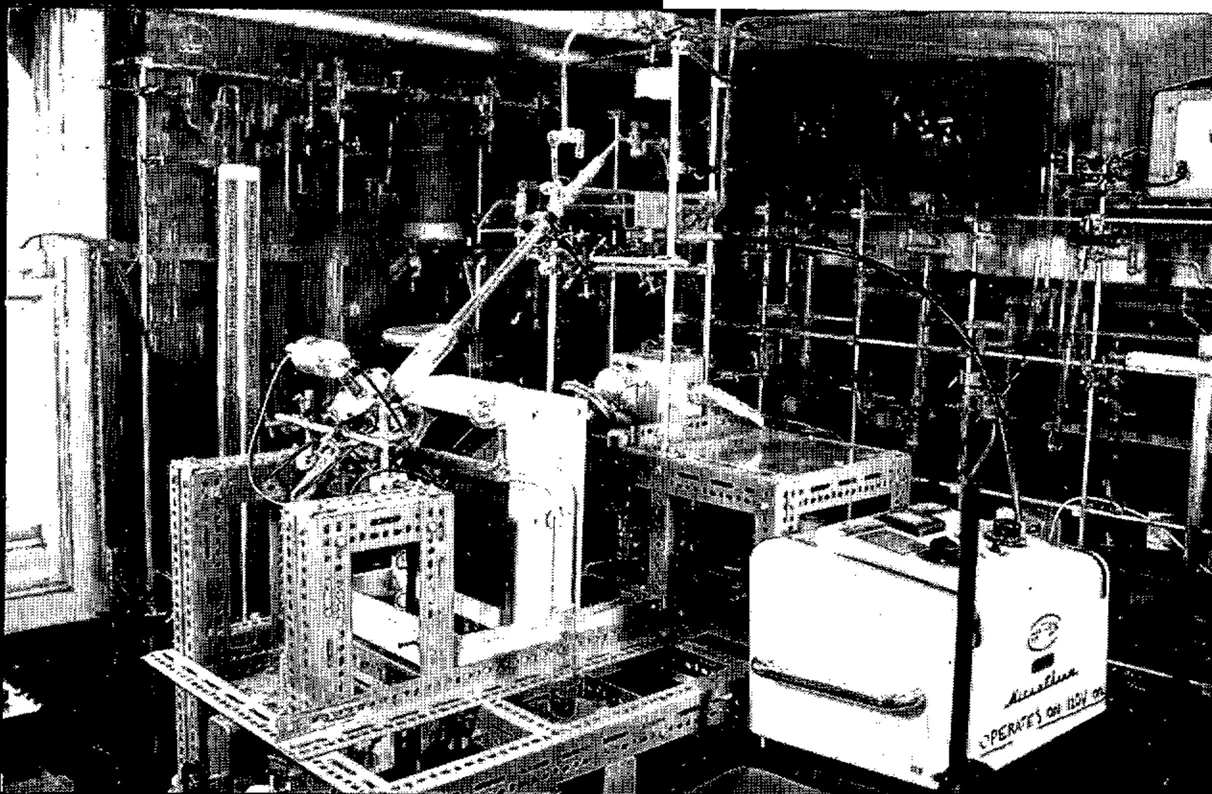
CHEMISTRY IN NEW ZEALAND

JOURNAL OF
THE NEW ZEALAND
INSTITUTE
OF CHEMISTRY



Vol. 32, No. 3, June, 1968

SHELL OIL NEW ZEALAND LIMITED

Staff appointments

At the end of this year Shell will be offering employment to men (or women) with degrees in Chemistry, Civil or Mechanical Engineering, Agricultural Science and Commerce. There may be also a few opportunities for graduates in other subjects, e.g. Economics, Law or Arts.

POSITIONS AVAILABLE

Most of the graduates will initially be stationed in Wellington. Each man is appointed as soon as possible to a position best suited to his qualifications, talents and interests and he is asked to follow a planned programme to enable him to use all his knowledge and ability at an early opportunity. The work is accepted as qualifying for corporate membership of professional Institutions or Societies.

Chemists will begin in the Central Laboratory on product development and testing, technical service, and the supervision of quality control, and may also be employed in chemicals marketing.

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ADVANCEMENT

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Shell Oil New Zealand Limited is staffed by New Zealanders, of whom the most able may be eligible for promotion to senior positions overseas. With individual recognition, supervision and guidance each graduate is encouraged to progress towards the most senior position he is capable of filling. His own efforts towards self development may be aided in several ways, including overseas training for the most promising men.

SALARIES

Young graduates have a special salary scale and it is Shell's policy to offer salaries and conditions of employment (including retirement benefits) at least comparable to those offered by other large firms.

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ENQUIRIES

More detailed information is available in the booklet "A guide to graduate employment with Shell Oil New Zealand Limited" Copies of this booklet are available from the University.

Interviews can be arranged to suit any students who may be interested.

Enquiries may be addressed to:
The Staff Manager, Shell Oil New Zealand Limited,
Shell House, The Terrace, PO Box 2091, Wellington. Telephone 45-060.

or Shell House, Albert Street, PO Box 1084, Auckland. Telephone 32-240

or St. Elmo Courts, Hereford Street, PO Box 2095, Christchurch. Telephone 62-939.

CHEMISTRY IN NEW ZEALAND

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Mass spectrometer used by Professor Phillips in his study of 'fast reactions'. Photo R. H. Nokes

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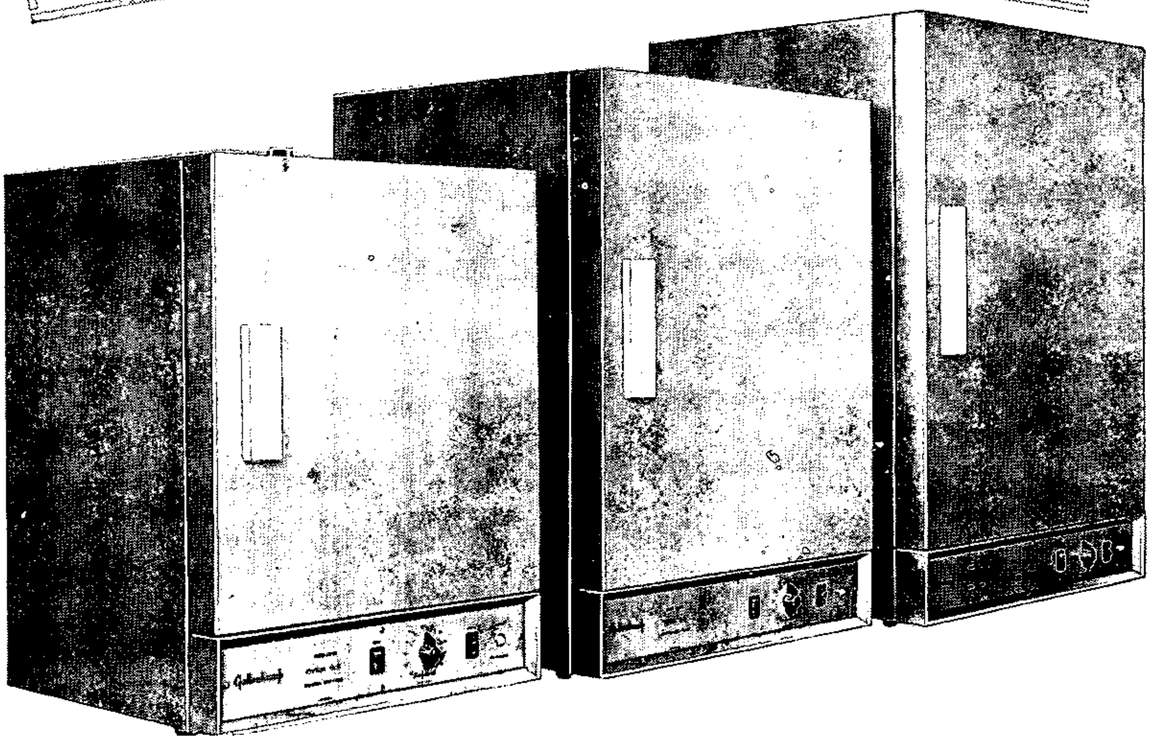
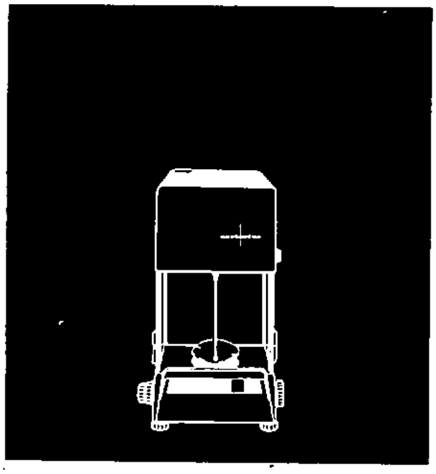
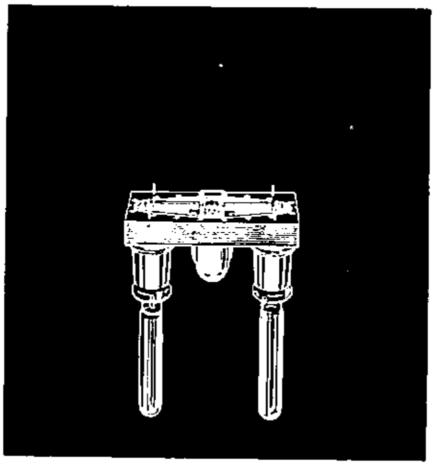


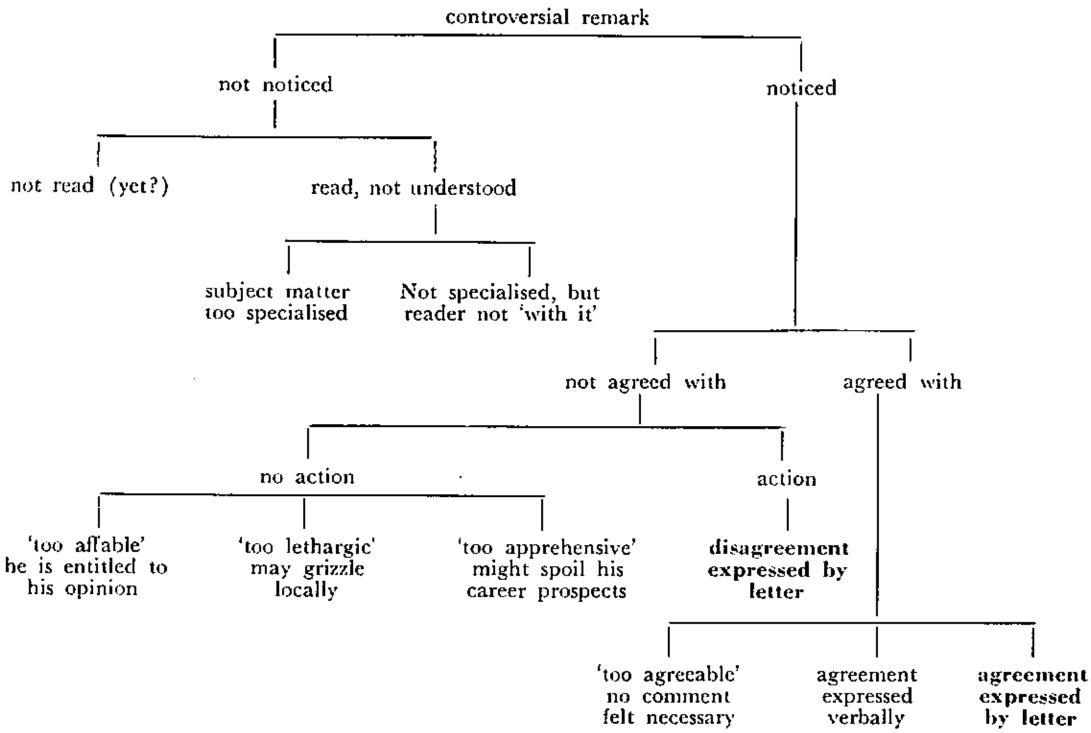




Editorial . . .

WHAT PRICE CONTROVERSY?

SEVERAL contributors have expressed disappointment at the apparent lack of reaction to controversial points in their articles. Assuming that the points made were indeed controversial, one naturally asks why there was no reaction. The following diagram sets out some of the possibilities:



We can see that the reactions which contributors hope for (shown in bold type) are only two of a number of possibilities. One of the other possibilities calls for closer scrutiny. Is it a fact that some chemists are unwilling to express a differing opinion because they are afraid that they will thereby jeopardise their career prospects? This actually has been suggested to us.

In 'Chemistry in Britain' we often read letters written in quite vigorous terms expressing disagreement with articles or policies. Presumably in Britain there is no fear that one's progress up the professional ladder will be thwarted for so doing. (Unless, of course, such letters are written by people who have already suffered this and therefore no longer need to be deterred by such a threat.)

Could it be that the climate of opinion in our small and relatively affluent economy breeds a lethargy towards constructive criticism? It would be a terrible thing if chemists in New Zealand were so cramped by their country's small economy that they were unable to function honestly as scientists.

If this is a real problem here, does it give another reason for going overseas to escape such 'scientific claustrophobia'?

ELEMENTARY PARTICLES *

L. F. Phillips
Chemistry Department, University of Canterbury

ELEMENTARY particles have always been of great interest to chemists; soon after the discovery and characterisation of the *electron* in the 1890's Thomson suggested that valency was associated with electrons and proposed that electrostatic attraction resulting from the transfer of electrons from one atom to another might be responsible.

The *proton* was discovered at about the same time, in the "positive canal rays" from a discharge through hydrogen. It was shown to be analogous to the electron in that it was a smallest unit of positive electricity and to be identical with a hydrogen atom from which an electron had been removed.

Several other developments vital to chemists came at this time: Rutherford's discovery of the nucleus in 1911 was followed by Bohr's theory of the hydrogen atom (1913), Moseley's demonstration of the significance of atomic number (1913) and the Lewis-Kossel theory of the stable electron octet (1916). At this time there were believed to be just two elementary particles, the electron and the proton.

The existence of a heavy neutral particle, the neutron, was freely predicted, e.g. by Rutherford, in the early 20's. Bothe and Becker in 1930 actually detected neutrons but were unable to prove that they were not just very penetrating gamma rays, and it was Chadwick in 1932 who finally demonstrated the occurrence of reactions such as

$$He^4_2 + Be^9_4 \rightarrow C^{12}_6 + n^1_0$$

when light elements such as Li, Be, B were bombarded with α-particles.

So far we have been dealing with particles that most chemists regard as old and familiar friends. Two others in this category were predicted theoretically at the end of the 1920's, namely the *positron* (actually an anti-particle) and the *neutrino*. The positron was observed more or less by accident (by Anderson in 1932) in the products of bombardment of atoms by cosmic rays. (Then, as now, cosmic rays were the source of the most highly energetic bombarding particles.) The neutrino, on the other hand, was not really an experimental fact until Cowan and Reines in 1959 observed the capture of antineutrinos by $\bar{\nu}$ protons

$$\bar{\nu} + p \rightarrow n + e^+$$

followed prompty by $e^+ + e^- \rightarrow 2\gamma$ when they subjected a large cadmium-filled liquid scintillation counter to the intense antineutrino flux from a nuclear reactor.

A reaction involving neutrinos themselves

$$Cl^{37} + \nu \rightarrow A^{37} + e^-$$

had almost certainly been observed by Davis in 1955, but the small number of Ar^{37} counts, 0.37 ± 3.4 per day, due to the relative rarity of neutrinos in the flux from nuclear reactors, was not considered sufficient proof at the time because of possible uncorrected effects of the cosmic background. (The reaction with Cl^{37} is now employed in "neutrino telescopes" which normally operate in the lower levels of deep mines in order to be away from cosmic rays.)

It is interesting to contrast the means by which these last two particles were predicted. Pauli originally postulated the existence of the neutrino in 1930 in order to avoid having to discard two well-established conservation laws—those of energy and angular momen-

* Branch Chairman's Address, Canterbury Branch, 1967.

tum. The first law was apparently violated in β decay, since there was observed to be a continuous range of energies in the electrons ejected from β-active nuclei. The process is in fact

$$n \rightarrow p + e^- + \nu$$

where the difference between the energy of the reaction and the energy carried by the electron is the energy carried by the undetected neutrino. All of these particles have spin $\frac{1}{2}$ (in units of $h/2\pi$); writing the spins as arrows, the reaction is able to be expressed as

$$(n)\uparrow \rightarrow (p)\uparrow + (e^-)\uparrow + (\nu)\downarrow$$

and the total angular momentum is seen to be conserved. The invention of a new particle to avoid violating a conservation law is one important general procedure.

Pauli's suggestion about the neutrino met with a lot of opposition at first; this lessened after the discovery of the neutron in 1932 when it was realized that a (protons + neutrons) theory of the nucleus would solve a number of outstanding problems, and once a heavy neutral particle had been observed it was not too hard to believe in the existence of a light neutral particle.

For the positron, Dirac in 1928 solved an equation which he obtained by making the Schroedinger equation conform to the requirements of special relativity. This equation is essentially

$$(p^2 + m^2c^2)\psi = o$$

where:
p = momentum
m = rest mass
c = velocity of light
ψ = wave function

which has as acceptable solutions for the energy

$$(E^2 - m^2c^4 - c^2\hbar^2k^2)^2 = 0$$

(where $\hbar$ = h/2)

The interesting feature of this result is that E can be positive or negative, since it occurs as E^2 inside the bracket. Now if the negative energy levels were actually available, all electrons would go into them as a first preference and no free electrons with positive energy would ever be observed—contrary to fact. Dirac therefore postulated that the sea of negative energy states is normally filled to the brim and only manifests its presence when there is a bubble, i.e. an unfilled level. Such a bubble behaves as an electron in every respect except charge, i.e. it behaves as a positron.

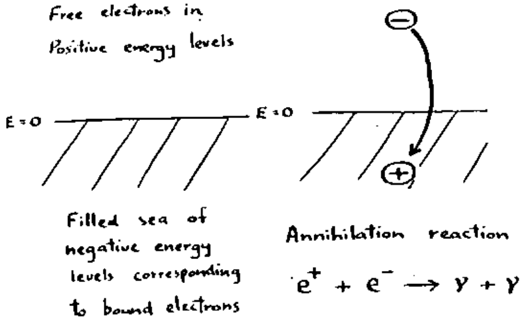


Fig. 1

The annihilation reaction

$$e^+ + e^- \rightarrow 2\gamma$$

is then to be regarded as a spectroscopic transition in which an e^- falls into a vacant level in the sea. (*Two* γ photons (spin = 1) are required for spin conservation.) (Fig. 1).

This gives us a second general method of inventing new particles—i.e. postulating antiparticles for ones already known. (Some particles turn out to be their own antiparticles!)

There is still one more kind of particle that most people have heard of, the *meson*. It was predicted by Yukawa in 1935 in order to explain the strong, short-range forces which hold atomic nuclei together.

Consider the types of forces, or "interactions", which are known:

1. Gravitational, extremely weak (10^{-39}), long range.
2. Electromagnetic, moderately strong (10^{-2}), long range.
3. Weak interactions (10^{-14}), short range, responsible for β decay.
4. Strong interactions (10^0), short range, hold nuclei together.

The best current picture of "action at a distance" through empty space or an intervening medium is that it occurs through an interchange of energy-carrying particles. For example, in the electromagnetic (coulomb) interaction between two electrons the electromagnetic field between the particles is always quantized into photons, and we can represent the interaction as the exchange of a virtual photon (one having no permanent existence) (see fig. 2).

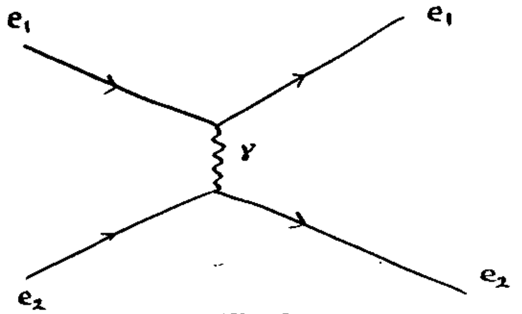


Fig. 2

Similarly the gravitational field can be regarded as quantized into gravitons, and this type of interaction is visualised as in Fig. 3.

Now if the virtual particle has a finite rest mass, its creation violates the law of joint conservation of mass and energy. But according to the uncertainty principle

$$\Delta p.\Delta x \sim \Delta E.\Delta t \sim h/2\pi$$

we are allowed to violate conservation of energy by an amount ΔE for a time of the order $\Delta t = h/2\pi\Delta E$. The maximum distance any particle can travel in this time is $c.\Delta t = R$, which is necessarily the maximum range of the force concerned. Putting $\Delta E = mc^2$, we find $R = h/2\pi mc$.

The gravitational and electromagnetic forces have unrestricted ranges, so the rest masses of the graviton and photon must be zero. The range of strong nuclear forces, on the other hand, is known to be only about 10^{-13} cm; when the numbers are put in this corresponds to a mass about 200 times that of an electron. (This is a third general method of deducing the existence of a new particle, i.e. by quantizing a force field.)

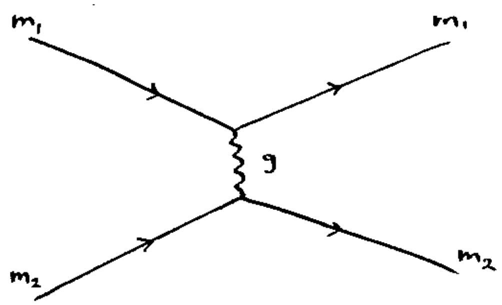


Fig. 3

Mesons were searched for and about 1936 copious showers of negatively charged particles of the correct mass were found in the debris of cosmic rays. These particles, the μ^-, were believed for the next 10 years to be Yukawa's mesons. (The war was at least partly to blame for this lapse). However, their interaction with atomic nuclei was not nearly great enough for them to be the particles responsible for nuclear forces.

In 1947 Bethe and Marshak proposed that the μ^- was actually a decay product of Yukawa's meson, and the latter, the π meson, was observed soon after by Powell and Occhialini. The π mesons were found to be of three kinds: π^+, π^- and π°. The last decays by electromagnetic interactions to 2γ in about 10^{-16} sec. The first two, if they avoid an encounter with a nucleus, decay by weak interaction to products which usually include some μ^- in about 10^{-8} sec.

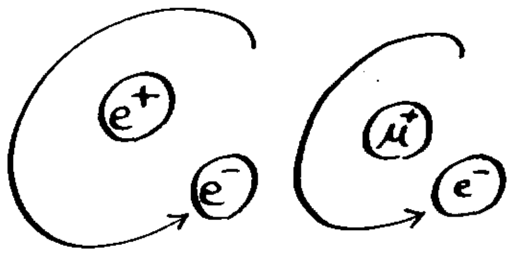
The μ^- is something of a mystery; it is not really a meson—apart from its mass it is not distinguishable from an electron, and it is always classified with the leptons, or light particles.

We have now obtained the following elementary particles from which to build the universe:

Particle		Rest Mass (MeV)	Spin	Decay mode	Lifetime, sec.
Graviton:	g	0	2	stable	
Photon:	γ	0	1	stable	
Leptons: (light)	e^-, e^+	0.510976	$\frac{1}{2}$	stable	
	μ^-, μ^+	105.70	$\frac{1}{2}$	$(e^- + \nu + \bar{\nu})$	2.212×10^{-6}
	$\nu, \bar{\nu}$	0	$\frac{1}{2}$	stable	
Mesons: (medium)	π^+, π^-	139.63	0	$(\mu^+ + \nu$ etc$)$	2.56×10^{-8}
	π^0	135.04	0	2γ	$< 4 \times 10^{-16}$
Baryons: (heavy)	p	938.213	$\frac{1}{2}$	stable	
	n	939.506	$\frac{1}{2}$	$(p + e^- + \nu)$	1.04×10^3

This is a good time to bring in some chemistry.

It is actually possible to do some very interesting chemistry with these new particles, provided we work quickly. It is usual to start with one of the elements positronium or muonium (fig. 4).



Positronium Atom *Muonium Atom*

Fig. 4

Both of these are very similar to hydrogen spectroscopically and, although their lifetimes are short (ca. 10^{-5} sec.), it has been possible to observe reactions such as

$$Mu + O_2 \rightarrow OMu + O$$

which is analogous to $H + O_2 \rightarrow OH + O$.

The 13 elementary particles of the last table would be enough for many people; however, physicists have continued to invent new ones, and at the moment the tally is between 100 and 200. Two effects have served to swell this total. These are:

(1) When two particles, e.g. π^+ and p, are allowed to collide, at a certain collision energy the cross section for collision may go through a sharp maximum. At this energy a temporary sticky-collision, or "resonance particle", is formed—often of a very short lifetime and correspondingly uncertain energy, i.e. mass. Physicists have, in general, labelled these resonances as new particles. If chemists did the same thing we should have to regard O_3 and O_2 as different elements!

(2) If two particles collide with sufficient energy one of them may become excited, the excitation energy being large enough to add an appreciable amount to the particle's mass. In the process some of the internal quantum numbers of the particle are usually changed. The new entity thus obtained is also often considered to be enough of a new particle to warrant a note in Physics Review Letters. In chemistry the analogous procedure would be to regard electronically excited atoms as

Table of quantum numbers for describing quantities which are conserved during strong interactions

Symbol	*Name*	*Range of values*	*Examples*
A	Atomic mass No. = Baryon No.	0, ±1, ±2 . . .	He^4_2, A = 4 n } nucleon p } N , A = 1 π^- , A = 0 $\bar{p}$; A = −1
Q	Electric charge in units of the charge on a proton. $\bar{Q}$ = mean electric charge for an isotopic spin multiplet.	0, ±1, ±2 . .	n , Q = 0 } nucleon p , Q = 1 } N , $\bar{Q} = \frac{1}{2}$ π^-, Q = −1 } π°, Q = 0 } π, $\bar{Q} = 0$ π^+, Q = 1 }
I	Isotopic spin; gives multiplicity M of state in which particles differ only in electrical charge (M = 2I + 1).	0, ½, 1, 3/2 . . .	N , I = ½ (n, p) π , I = 1 (π^-, π_0, π^+) Λ , I = 0 (Λ) Δ , I = 3/2 (Δ^-, Δ°, Δ^+, Δ^{++})
γ	Hypercharge = $2\bar{Q}$ (Related to strangeness by S = γ — A)	−2, −1, 0, 1	N , γ = 1 (S = 0) π , γ = 0 (S = 0) Λ , γ = 0 (S = −1) Ω , γ = −2 (S = −3)
J	Spin angular momentum in units of $h/2\pi$.	0, ½, 1, 3/2 . . .	N , J = ½ π , J = 0 η , J = 0 Δ , J = 3/2
P	Parity = Symmetry w with respect to inversion of wave function in a centre of symmetry.	±1	N, P = +1 π, P = − 1 (most mesons −1, most baryons +1)
G	An intrinsic property for mesons with $\gamma = 0$ only, (i.e. mesons lacking in strangeness)	−1, +1	π, G = −1

being different elements from the same atoms in their ground states.

However, even when all the resonances and recurrences, i.e. excited states of particles, are allowed for, there are still very many interesting new particles and new quantum numbers to describe them—too many to put into this lecture (see the table above). In the last few years a great deal of attention has been given to the symmetry properties of groups of similar particles, e.g. the baryons, and to methods of deducing the existence of new particles from various symmetry schemes (equivalent to various forms of conservation laws) e.g. those called SU(3) or the "eightfold way". More recently the aim has been to explain the overall symmetry properties by schemes in which the strongly-interacting particles are constructed from various mixtures of sub-particles (known as *quarks*) having charges of $\frac{1}{3}$ or $\frac{2}{3}$ of an electronic unit. The search for quarks is now on and, presumably if it is successful, the next job will be to find sub-sub particles in order to explain the properties of the quarks.

Suggested further reading: Articles which appear every 3 or 4 months in "Physics Today"; the recent article by Gell-Mann and others in "Scientific American" (date of issue February 1964).

THE GROWTH OF BIOCHEMISTRY IN NEW ZEALAND

*N. L. Edson, B.Med.Sc., M.B., Ch.B., Ph.D.(Cantab.), F.R.S.N.Z.**
University of Otago

NEW ZEALAND was slow to appreciate the value of academic biochemistry. Chemists, trained in the classical way, were expected to use their talents successfully in all the problems of agriculture and veterinary science and a chemist who handled biological material was often called a "biochemist" although he had received no academic training in the subject. This may help to explain why New Zealand made such a small contribution to the field of experimental biology.

Biochemistry seldom developed as a discipline *sui generis* anywhere. It usually found its inspiration in medicine, veterinary science, or agriculture. This happened in New Zealand where biochemistry was taught for many years at the Otago Medical School under the title of physiological chemistry and at the former Massey College under the name of agricultural biochemistry.

It was my privilege to be the first—and, I believe, the last—occupant of a chair of biochemistry in the University of New Zealand. The chair was created in 1949, although the department began its existence five years earlier within the Physiological Department of the Medical School.

After the demise of the federal University of New Zealand and its replacement by six independent universities, departments of biochemistry multiplied within the new system. A chair of biochemistry was established in the Chemistry Department at Victoria University. This was followed by the establishment of chairs at Canterbury University (Lincoln College), at Massey University and finally at Auckland University. Thus New Zealand is now well provided with schools of biochemistry, each destined to develop along its own lines. Parallel developments in the science faculties of the universities have led to the growth of important biochemical sections, e.g., Professor Matthew's work on nucleic acids in the Molecular Biology Department at Auckland University where there is an association with microbiology.

Outside the universities there have been important contributions to fundamental biochemistry from institutions such as the Meat Research Institute, the Plant Chemistry and Plant Pathology Divisions of the Department of Scientific and Industrial Research, the Fats Research Laboratory of the same Government agency and from the Agricultural Department's research centres at Ruakura and elsewhere.

It seems clear that the main function of the university biochemical departments will be the teaching of a well rounded core of theoretical biochemistry, but it is most desirable that each department should develop

* Professor Edson recently retired from the Chair of Biochemistry, University of Otago.

its own specialized programme of teaching and research in some field that will benefit New Zealand. This has happened already, e.g., Professor Smith's school of detoxication studies, especially those concerned with insect pesticides, and Professor Howard's interest in the micro-organisms of the rumen.

Despite any suggestion arising from its unfortunate name, biochemistry is not an appendage to chemistry. On the contrary, it is a biological subject that places its emphasis on *living* organisms, not on abstract systems. In Otago it has been insisted that a student aiming at a full knowledge of the subject and ultimately at a research career must have a sound education in fundamental physics and biology and advanced training in chemistry up to a third-year course; courses in physiology and microbiology are required and some further study of mathematics is highly desirable. Such a broad background to a biochemical education is by no means excessive. It must ensure that the student of biochemistry has acquired a clear insight into the fundamental importance of physics and chemistry in biology.

In brief, the student of biochemistry must appreciate that the structural chemistry of carbohydrates, lipids, proteins, nucleic acids and porphyrins is the fundamental basis of his work. Equally important is the ultrastructure of living cells. Here, there is room for co-operation between chemical, biological and biochemical departments. The undergraduate needs a clear understanding of free energy changes in biochemical processes; sources of free energy, its storage and release; photosynthesis and nitrogen fixation. And these questions should be preceded by a thorough knowledge of enzymes, their active centres and kinetics, mechanisms of enzyme reactions and the behaviour of multi-enzyme systems. This core of theory must be supplemented by study of cell replication, the genetic code, induction and repression of enzymes and the theory of control in metabolism by genetic influence, allosteric proteins, kinetic adjustments and by hormones.

These questions must be considered in the context of living cells, microbial, plant and animal, in relation to their ultrastructure and to the environment.

Moreover, biochemistry should not be taught in an academic vacuum. From time to time the relevant problems of the real world arise and applied biochemistry should be rich enough in knowledge and wisdom to make a useful contribution to solution of the problems of the every-day world.

With the establishment of several departments of academic biochemistry the stage is set for considerable growth of the subject in New Zealand, leading to a substantially larger output of graduates to work for the ultimate benefit of the primary industries of the country and of medicine.

At Otago in 1945 the first stage of biochemistry was opened with six students. Today there are approximately ninety students in this class. The increase in the numbers of science students at all levels has compelled a reorganization of biochemistry which has outgrown its original accommodation in the Medical School. A new building to accommodate over 300 science students and research workers has been planned on a site in Castle Street opposite the University Clock Tower. Here the school of biochemistry will find itself in the Science Block close to other schools of science. Biochemistry will then come under the administration of the Science Faculty instead of the Medical Faculty. It is proposed that 2nd year medical students will still receive an elementary scientific course in the Biochemistry Department but subsequently they will receive instruction in clinical biochemistry throughout the rest of the medical course. To this end, a department of Clinical Biochemistry has been established under Professor Sneyd who specializes in the biochemistry of hormone action. The Biochemistry Department of the future will devote most of its efforts to the instruction of science students. It is likely that this cleavage of interests will benefit both sections of students. Indeed, an earlier specialization led to the appointment of Associate-Professor Cousins to the Dental Faculty for the purpose of originating a special course in biochemistry for dental students. In this case the scheme has ben a thorough-going success and similar developments may prove to be beneficial in some of the other universities.

The consequence of all current developments will be a bright future for biochemistry in New Zealand. In a foreseeable time there should be no shortage of young biochemists for recruitment into industry and the research institutions of the country.

As to the subject itself, the major growing points appear to be in genetics, in the control of metabolic sequences, in the correlation between cell structure and biochemical function and in the question of cell differentiation. It may be presumptuous to predict that the emphasis of the future will cause enzyme kinetics and the mechanism of enzyme action to withdraw from biochemistry into pure chemistry and that a reconstellation of subjects may even promote the disappearance of contemporary biochemistry and its withdrawal into a comprehensive discipline now emerging under the name of cytology. If so, biochemistry will merge with physiology at the level of the single cell. Moreover, it seems certain that zoologists and botanists will pay increasing attention to biochemical functions and that their departments will be colonized by groups of biochemical research workers.

The secondary schools should not be omitted from our calculations because there is evidence of increasing concern with biochemical functions in school biology. This may mean that a larger number of first-year students will enter the University with a preformed interest in biochemistry.

It would be hard to deny that living organisms are composed of molecules or that most of the vital phenomena depend on molecular reactions. Accordingly, it is obvious that an understanding of life must come down to a molecular level. Under these circumstances it is not surprising that biochemistry has invaded all branches of biology.

New Zealand is now making up for its tardiness in accepting the existence of academic biochemistry. The foundations of academic work are firmly laid in several educational centres and so we can expect accelerated, diverse developments to follow. We can also expect a freer interchange of personnel between the University institutions *per se* and between the Government laboratories and the Universities. My worthy successor, Dr. George Petersen, has been a member of the Plant Chemistry Division's staff. It will be his task to lead the impending developments at Otago.

In departing from the biochemical scene, I look forward to a period of exciting advances in the subject and especially to a leap forward in its usefulness and vitality within New Zealand. I do this in complete confidence that there is a fine generation of younger biochemists who will lead us into new fields and new appraisals and create the necessary developments. In this connexion it is interesting to look back at an article written in 1954 (Edson, N. L. The Teaching of Biochemistry. Journal of the N.Z.I.C., *20*, 16).

The Registrar again has copies of the Monographs for Teachers, Numbers 1-14 in stock. The following is a full list of titles and prices. This batch was received after devaluation and prices are slightly increased.

1. Principles of Electrolysis. C. W. Davies ... 38c
2. Principles of Oxidation and Reduction. A. G. Sharpe 38c
3. Principles of the Extraction of Metals. D. J. G. Ives 64c
4. Principles of Metallic Corrosion. J. P. Chilton 64c
5. Principles of Chemical Equilibrium. P. G. Ashmore 48c
6. Principles of Titrimetric Analysis. E. E. Aynsley and A. B. Littlewood ... 48c
7. Principles of Catalysis. G. C. Bond 64c
8. Principles of Atomic Orbitals. N. N. Greenwood 64c
9. Principles of Reaction Kinetics. P. G. Ashmore 80c
10. Industrial Chemistry — Inorganic. D. M. Samuel 80c
11. Industrial Chemistry — Organic. D. M. Samuel 64c
12. Elements of Chemical Thermodynamics. E. A. Guggenheim 75c
13. Principles of Osmotic Phenomena. J. F. Thain 86c
14. Principles of the Colloidal State. G. D. Parfitt 64c

AUTOMATION AND CHEMISTRY

W. Whittlestone

Ruakura Animal Research Station, Hamilton

THIS is not a scientific paper on automation. Rather it is an essay aiming at giving a background to the concept of automation for readers with a chemical training. A few references will be given at the end to papers which illustrate the techniques and instruments which are now available for automating some laboratory operations.

As man has increased his control over nature, there has been an increasing level of sophistication in the way in which he has turned the forces of the natural world to his own use. First there was the evolution of ingenious tools which made it easier for primitive man to manipulate the world round about him. With the development of sources of power, mechanisation became possible. In effect, this is a means by which man uses mechanical devices to amplify his manipulative ability. A small force applied to the control lever of a crane enables one man to handle many tons; and the crane is designed with control motors and the like to make it possible for man's intelligence to guide a series of operations requiring enormous force. In other examples, of which there are many thousands, an ingenious piece of machinery enables a single operator to carry out a whole range of complex and precise manipulations on, for example, a metal casting. Another example is the automatic loom which, guided by suitable punched cards carries out a repetitive weaving operation with great skill and precision. However, in none of these instances does the machine think for itself. It can continue to repeat a series of complex processes, but if a fault develops it may perform the most ludicrous operations.

Automation is the next development in the progress from a hand tool to the highly mechanised factory. In a sense we may regard automation as an amplification of man's intelligence, parallel with the amplification of his strength which power tools have made possible. In fact, one of the reasons for the rapid development of automation in some industries is that there is an acute shortage of highly skilled labour, and it has become essential to replace with a machine man's skill and ability to think. The dairy industry offers a number of examples of this sort of problem. Many of the operations in a cheese factory are unpleasant because of conditions of high humidity and temperature combined with manual exertion. Cheese making is a skilled operation requiring judgment and intelligence but it is very difficult to attract suitable personnel into an industry whose basic operations tend to be unpleasant. This has stimulated the mechanisation research programme of the Dairy Research Institute, and already very substantial advances have been made in the elimination of the unpleasant operations from cheese making. The next phase will be the automating of these complex mechanical operations so that judgement as well as physical labour will be eliminated from the process. Another reason for the introduction of automation in industry is the fact that often it is possible to produce a better product when the factory has suitable automatic control. This is particularly true in the food handling industry and a splendid example of it is the Automated Butter Factory at Morrinsville. One of the crucial problems in food manufacture is the maintenance of a high level of hygiene. It is almost impossible to obtain this with a large number of operatives, personal hygiene being a very variable element. Furthermore, in the handling of a sensitive product such as milk or cream highly efficient "in-place" cleaning is essential. However, to "in-place" clean a complex factory using manual control opens up the possibilities for the contamination of the product and the damaging of equipment. An automated cleaning operation however, can undertake exceedingly complex cleaning cycles without any danger whatever of having the detergent become mixed with the product or have the wrong detergents mixed together. Such a process has a central control unit which, in effect, thinks for itself and when instructed to carry out a cleaning operation ensures that the right solutions are pumped through the right pipes, that only empty vats are washed and the whole system is rinsed and ready for operation without any danger of contamination to the product. There are many industries in which automation is essential because of the need for extremely high speed in dealing with imbalances in the system, e.g. a modern oil refinery. There are many other high speed chemical processes where instantaneous control is required if the system is not to become hopelessly unstable. Another example which needs fast control and is also inherently exceedingly dangerous is the nuclear energy industry. Here the basic reactor is dangerous to life when in operation, and control of the neutron flux within the reactor requires extremely rapid responses by the control system. Another industry which depends to a very large degree on automation is the electronics industry. The manufacture of components such as resistors and transistors can be made almost completely automatic and thus the main labour cost in the manufacture of a resistor may well lie in the testing operation. However, by the use of computers it is possible to automate completely the testing of transistors, resistors, semi-conductor devices and the like.

It has been said that the three basic components of automation are communication, computation and control. Communication starts at a transducer. This is usually a device which produces an output in the form of an electrical voltage. One of the commonest is the strain gauge. This is used to indicate the weight of containers, the pressure in a system, the rate of flow of a gas or a liquid and sometimes the amount of movement of a component. The electrical resistance thermometer, the thermistor and thermo-couple are good examples of transducers which can be connected to produce a voltage which is a function of temperature. The conductivity cell is in effect a transducer producing a resistance change which can be converted into voltage and is a function of electrolyte concentration. The glass electrode may be thought of as a transducer relating the pH of a solution to voltage, while platinum electrode systems may be used to measure the redox potential. Similarly sodium ion concentration can be measured and converted to voltage. A slightly more sophisticated type of transducer is one which can measure the dielectric constant of a solid or a solution. Yet another type of transducer is the photocell which exists in many forms. This may be used to measure the optical density of a liquid or the density of a smoke.

In the second stage of an automated process the output from a series of transducers is fed into a central computation system. The computer mechanism carrying out the computations may be an analogue device or it may be digital. Analogue computers have the great advantage of extreme speed of operation but are limited in accuracy. However, for many control purposes they are adequate. They are based on the use of electrical circuits which can bring about such operations as the addition, subtraction, multiplication, division, differentiation or integration of quantities which can be represented as voltages. The building block of such a system is the operational amplifier. This is usually an amplifier of extremely high gain which is fitted into feed back circuits capable of bringing about the required manipulations. The output from the final operational amplifier in a computing system is fed to a power amplifier which in turn drives some type of prime mover able to manipulate valves and so change pressures, temperatures, concentrations and the like when used as a controller.

With the development of increasing speed of operation in digital computers, this type of system is used increasingly for control purposes. With the advent of integrated circuits of great reliability and small size together with higher frequencies of operation, the digital system with its much higher accuracy has now most of the advantages of the earlier analogue systems together with much greater versatility and accuracy. To operate a digital system from a transducer requires some sort of analogue to digital converter. An example of this is the digital volt meter which is capable of producing a binary number from any voltage fed into it. The shaft encoder is another example. This device converts any rotation of a shaft into a binary number which may be read by tiny photo transistors. Thus, the output from a pressure gauge, a pH meter, a conductometer or a thermocouple may be converted into a digital number capable of being read by a computer.

Perhaps one of the most useful pieces of "fallout" which has been associated with the development of automation has been the development of Boolian algebra and the science of cybernetics. Boolian algebra is named after George Boole who attempted to reduce logic to a calculus. His effort was basically an intellectual exercise, but by an extraordinary coincidence it proved to be a most valuable system for the development of the theory of switching and is in fact a logical approach to the development of complex relay systems. From the nature of this type of algebra the binary system was essential, so again it fitted into the requirements of the modern computer. For those who would like a painless introduction to Boolian algebra I would recommend a paper by H. R. Henley in 'Wireless World' of January 1965, entitled 'Logic Without Tears'. This develops the concepts of Boolian algebra as applied in the electronic control field. It is a most valuable discipline and once its principals have been grasped it takes much of the pain out of the problem of devising automatic control systems. The development of the science of cybernetics, so named by Norbet Weiner in his book of this name published in 1947, is even more exciting. This has brought together such widely separated concepts as feed-back control in engineering, information theory, thermodynamics and neurology. In the past we depended on human judgement once we moved from simple, causally related systems to complex systems which are basically probabilistic. The science of cybernetics is literally taking the guess work out of complex systems, and by providing models for the operational research worker has made it feasible to use computers to cope with situations quite beyond human intelligence. The introduction of operational systems into very large factories has amplified the intelligence of management and has laid the foundation for a systematic approach to problems so complex that in the past they have been regarded as quite beyond logical control. As indicated earlier the industrial revolution was based on power amplification while automation is based on the amplification of intelligence.

The control processes in an automatic factory are much simpler than measurement and computation. Very often they consist of motorised valves. Such devices can be used to regulate temperatures, pressures, flow rates, concentrations etc. Sometimes the control is based on the regulation of the electrical current. This is commonly used for temperature control and in any process using electrolysis. Another type of control is that of motor speed, and very ingenious systems are now available which make it possible to convert an electrical voltage into a precise rate of rotation. This type of control is important in steel mills, paper-making machines and the like.

One of the concepts basic to all automated processes is that of negative feed-back. Any self-regulating system, whether it be a simple thermostat or a complete biological organism, is dependent on feed back loops. In the case of a thermostat using a bimetallic switch as the regulator there is no proportional control and feed-back is of the crudest type, simply turning off the heater when the device is too warm and turning it on again when the temperature falls below the set point. More sophisticated controls bring about a variation in the heating current which is proportional to the error. This eliminates the inevitable swing in temperature which simple on-off control brings out. Both systems however involve negative feed-back. That is, the signal from the thermometer operates in a direction opposite to the trend; if the temperature is rising the controller tends to lower it, and conversely if the temperature falls the controller raises it. Another example of this sort of control is the regulation of electrolyte strength by the use of a conductivity cell. The resistance of a cell is compared with a standard and if it falls the amount of electrolyte added is reduced. If the resistance rises or the conductivity falls the amount of electrolyte is increased. A nice example of a sophisticated feed-back system is the automatic control of the calorific value of the gas produced by the Hurll P3 catalytic cracker. In this process, briefly, a catalytic chamber is heated by the burning of oil feed-stock. When the correct tempertaure is reached automatic controls bring about a steam purge followed by a cracking cycle during which the feed-stock is fed into the hot catalyst bed, together with steam and a small amount of air. During the cracking cycle the temperature of the catalyst drops and as soon as a predetermined value is reached the control system switches to a steam purge followed by the initial heating process again. The complete cycle is automatic. The gas emerging from the system is checked in a calorimeter for its heating value and the information from this measurement is fed back to a controller which regulates the amount of steam and air added during the cracking cycle. Thus the calorific value of the gas is held constant by a rather complicated negative feed-back system. Another sophisticated feed-back loop is that which maintains the neutron flux density in a reactor. The signal from the flux measuring device is fed to a motor system through suitable amplification and this in turn withdraws or projects control rods of high neutron absorption capability into the reactor. Thus the "runaway" of this dangerous device is made almost impossible.

New Zealand is not often thought of as a country advanced in the application of automation. However, a visit to the Morrinsville Co-operative Dairy Company will be most enlightening to many city bred New Zealanders. This company has the world's largest butter churns in operation. The loading and unloading of these devices is totally mechanised and the bulk packing of the butter is carried out in an automatic unit. This makes it possible for one operator to supervise the packing of the entire output of a factory producing at the moment about 10,00 tons of butter per annum. Perhaps the most interesting facet of this factory is the automated in-place cleaning system. This is controlled by an optical card reader on which the programme is set out in the form of clear strips on a blackened plastic card. This central controlling unit looks after the selection of cream tanks, and the processing of the cream by two treatment units which incorporate the automatic neutralisation of acidity. It supervises the intake of new cream and the discharge of processed cream in a pre-arranged order. As tanks become available for cleaning, completely automatic in-place cleaning is carried out without any loss of time, an important point in maintaining a high level of hygiene. The panel also controls such matters as steam pressure, oil feed to boilers and the like. This factory will not only produce the highest quality butter in the world because of its exceptional standards of hygiene but it will do it without the arduous labour associated with the normal butter making process, and will require a very small staff of technical operators whose jobs are very attractive indeed. In the near future we may well see a similar development in the cheese-making industry, thanks to the effort of the New Zealand Dairy Research Institute.

I would like finally to take a look at a few devices which offer possibilities for the automation of certain types of process in the laboratory. Most chemists are familiar with the Auto-analyser. This is not quite an automated process. It is rather a sophisticated example of mechanisation. However, before the true automation of laboratory work can be developed it is essential to develop to a maximum the mechanisation of laboratory operations. For this reason, transducers responding to chemical changes are essential.

Newsletter

THE ROYAL SOCIETY OF NEW ZEALAND

SUCCESSOR TO THE NEW ZEALAND INSTITUTE 1867-1933

No. 4 MAY 1968

ANNUAL MEETINGS AND CONFERENCES OF SCIENTIFIC SOCIETIES

May 14-15 -	- N.Z. Genetical Society, Annual Meeting, Christchurch.
May 16 -	- Geological Society of N.Z., Annual General Meeting, Wellington.
May 18 -	- Ornithological Society, Annual General Meeting, Wellington.
June 1-3 -	- N.Z. Archaeological Society Conference and Annual General Meeting, Wanganui.
August 15 -	- N.Z. Ecological Society Annual Meeting, Auckland.
August 19-24 -	- N.Z. Institute of Chemistry Annual Conference, Auckland.
August 20-22 -	- N.Z. Institute of Agricultural Sciences, Annual Conference, Christchurch.
November 23 -	- Royal Astronomical Society of N.Z., Annual General Meeting, Oamaru.
November 28-29	- N.Z. Hydrological Society, Annual General Meeting in Wellington and Symposium on Floods and Droughts.

This is all the information to hand so far. Member Bodies are asked to send such information to the General Secretary, Royal Society of New Zealand, as soon as possible, in order to produce as complete a calendar as possible.

SIR ERNEST MARSDEN

Although physically confined to a wheelchair he is very interested in everything scientific and manages to attend some meetings. He is always delighted to have visitors for a little chat.

THE NEW ZEALAND GEOPHYSICS PRIZE

In October 1967 the Astronomy and Geophysics Section of the Wellington Branch of the Royal Society of New Zealand established a prize to be known as "The New Zealand Geophysics Prize".

The prize will be awarded by the Committee of the Section to the author or co-authors of the most meritorious contribution to the study of Geophysics

either (a) carried out in New Zealand

or (b) carried out by a New Zealander temporarily overseas

or (c) pertaining to the New Zealand region

and published in the previous two calendar years.

The prize will normally be awarded annually, but no award shall be made if in the opinion of the Committee no suitable contribution has been published. Except in special circumstances an award shall not be made more than once to the same author.

The prize will consist of suitably inscribed books purchased with the interest received from a sum of $500 invested for this purpose.

The members of the Prize Committee, to whom submissions may be made this year, are:

Dr E. I. Robertson, Assistant Director-General, D.S.I.R. (Convener)
Professor F. F. Evison, Victoria University of Wellington
Dr J. F. Gabites, Director, N.Z. Meteorological Service.

The prize committee will make recommendations to the Committee of the Astronomy and Geophysics Section by 1 July.

THE NEW ZEALAND SOCIETY FOR EARTHQUAKE ENGINEERING

The Council of the N.Z. Institution of Engineers agreed to the formation of a society with the object of advancing the science of earthquake engineering. The Society was formed on 8 April 1968 with Mr W. P. Edwards, Engineering Consultant, as Chairman. There will be collaboration with the New Zealand National Committee for Earthquake Engineering and through it with the International Association.

Earthquake engineering relies upon contributions from many disciplines and the society will provide opportunity for free exchange of ideas. Membership will not be restricted to members of the N.Z. Institution of Engineers, although the Society is affiliated to that body. The Society will be in the hands of engineers, scientists, architects and insurance people, from all of whom membership is solicited.

One of the principal activities will be dissemination of the most recent information by the publication of a bi-monthly bulletin, free to members. The bulletin will feature original articles from overseas authorities as well as from local authors, emphasising the practical aspects of earthquake engineering and related topics in architecture. The first issue is scheduled for June 1968.

The Society proposes to operate a technical advice service for members and local authorities and others.

Numerous bodies in New Zealand have conducted seminars on topics related to earthquake engineering. One object of the Society will be to participate in and co-ordinate these activities where possible.

Substantial financial assistance from the Earthquake and War Damage Commission has been assured. Nevertheless, the strength and vigour of the Society will depend on a large active membership and all people interested in earthquakes and earthquake phenomena are urged to join. Apply to the Secretary, Box 5036, Wellington.

THE ROYAL ASTRONOMICAL SOCIETY OF NEW ZEALAND

The New Zealand Astronomical Society Inc. was founded in November 1920 and assumed its present title on receiving a Royal Charter in 1946. Its aims are to encourage interest in astronomy and to facilitate mutual assistance among observers.

It has a *membership* of 277, of which twenty are affiliated societies.

Meetings are held in the Carter Observatory, Wellington, at 7.30 p.m. on the first Wednesday of each month from March to November. Annual General Meetings are commonly held in centres other than Wellington, late in November.

The Society publishes a quarterly journal, "Southern Stars", and issues a monthly news sheet to members.

There are a number of *specialist sections*. The most active is the Variable Star Section, the members of which reported over 26,000 observations during the year ending 30 September last. These are published in the Section's circulars.

From time to time the Society organises lecture tours of the country by distinguished overseas astronomers. It awards annually the Murray Geddes Memorial Prize in recognition of notable astronomical work carried out in New Zealand.

NEW MEMBER BODIES

The New Zealand Microbiological Society
The Institute of Fuel (New Zealand Group).

This Newsletter has been compiled for your information and interest by members of the Member Bodies' Committee. Suggestions for later numbers will be welcome; please send to the General Secretary, Royal Society of New Zealand, Box 196, Wellington.

DAVID F. JONES LTD.

The measurement of potential by electrode systems is well known, and by applying this to a feed-back system the potentiostat has been developed, a tool which has tremendous value in the study of corrosion. The system holds the potential of the metal under study constant with respect to a given solution, thus making possible the measurement of current without the alteration of the electrode potential. Without the potentiostat, both current and potential will change at the same time, so producing a rather confusing picture.

Another type of transducer which has quite an important place in chemistry is a galvanic cell which produces a current proportional to the oxygen concentration of the solution in which it is immersed. It consists of a silver/porous lead cell with potassium bicarbonate as an electrolyte contained within a polythene membrane. The oxygen diffusing through the polythene permits the cell reaction resulting in the oxidation of the lead to take place, thus producing a current proportional to oxygen concentration. A thermistor placed within the cell automatically corrects for temperature effects, thus making it possible to read off directly on a galvanometer the oxygen level of e.g. river water. Another nice example of automatic analysis is that of iodo-aminoacids. This is based on the degradation of the original mixture with an enzyme, followed by column chromatography using gradient elution, the output being finally fed through an Auto-analyser after the addition of colour reagent. Thus the whole process of degradation, separation and elution is carried out automatically. In any discussion on the mechanising of laboratory processes the coulometric titrimeter must be mentioned. Such an instrument eliminates the need for standard solutions. It is possible to measure an electric current with extreme precision. Using a precisely known resistance and comparing the voltage drop across it with a standard cell, it is possible to pass an electrolytic current through a solution with appropriate electrodes and so to produce a reagent at a rate which is exactly known, e.g. iodine may be generated at a platinum electrode from a potassium iodide solution and, for example, by so arranging the current the amount of iodine generated may be standardised at one part per million per second. By back titrating after the addition of an excess of thiosulphate, the timer reading is directly related to the iodine concentration. By using a 2% sodium sulphate solution in an external coulometric cell, it is possible to carry out an acid or an alkali titration automatically using a standard glass electrode pH meter as the controller. When one considers the time involved in making up standard solutions, or the cost involved when one buys them ready made, it can be seen that the coulometric titrimeter has many advantages.

Reference has been made to the operational amplifier. This is a high gain DC amplifier which may be capable of quite a high frequency response. A typical amplifier will have a gain of one to two million. With the gain reduced to one, by a large amount of feed back, such an amplifier has an enormous input impedance and a substantial power output. By suitably arranging the feed back circuits it may differentiate, integrate, add, multiply or produce complex functions of the input voltage. C. F. Morrison of the Department of Chemistry of Washington State University has described a generalised instrument based on operational amplifiers which can do quite a range of laboratory jobs. It is not appropriate in an article such as this to describe technical detail. However, some idea of the value of this instrument may be gained from the following list of capabilities. It has a programme plug board which makes it possible to hook it up in a conformation suitable for the application in mind. For example, it would operate as a potentiometric titrator. In one version this is digital and so is capable of feeding a signal into a digitally operated printometer, thus automatically printing out the results of a titration. The output in another form may be fed to a strip chart recorder. Another circuit conformation turns the device into a polarograph. In this case the output goes to a standard potentiometric recorder. By slight modification the output may be displayed on a cathode ray oscilloscope. Again the device can be used for the study of conductance variations in solution and one neat application is as a conductimetric titrator. It may also be hooked up to operate as an automatic colorimeter for the study of reactions involving colour changes.

The mechanisation of many laboratory operations is now quite commonplace and many mechanised analytical systems may be bought off the shelf. With the availability of small, reliable computors, in the not too distant future one may safely predict that the automation of many analytical procedures will become a matter of course, and many of the routine jobs now employing the valuable time of skilled chemists will be carried out by automated units capable of thinking for themselves.

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This is intended to give a small sample from an enormous literature showing the trends which are developing in chemistry.

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CURRENT CHEMISTRY

REACTIONS AND PROPERTIES OF RADICALS AT LOW TEMPERATURES

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THE interaction of high energy radiation with solids, including both ionic solids and organic glassy solids, causes colouration. The ionic systems have been intensively studied with considerable success by optical, electrical conductivity and electron paramagnetic reasonance measurements. The accumulated evidence suggests that the colouration effects are due to formation of defect centres consisting of various combinations of lattice vacancies, electrons and interstitials.

In recent years systematic studies of non-ionic or glassy ionic systems have been undertaken. Most of these studies have been made on material held at low temperatures, either 77K or 4K. Interpretation of these results is more difficult than for the ionic solids because of the molecular nature of the compounds and the random structure of the glassy material. However, radicals and ions appear to be the most prevalent species.

The mechanism of the interaction of high energy radiation with molecular systems may be regarded as the production of one primary ion pair per photon. This occurs by the 'stripping' of an electron from the molecule by a Compton scattering process. In general, a photon of energy of 1 MeV will produce a primary energetic electron with about 500 KeV. The primary electron will lose its excess energy by inelastic collusion with the consequent production of about 3000 secondary ion pairs per photon. Although there is a tendency for these events to occur in 'tracks', the separation between them is such that they may be regarded as independent.

In liquid systems, recombination of the ion pairs occurs within 10^{-18} seconds, leading to the formation of excited states with the consequent formation of radicals which can further react to form stable products. The nature and distribution of these products is used to deduce the course of the previous events.

In the organic glassy systems it is possible to freeze out many of the secondary reactions and examine the reactions of the radicals and trapped ions in more detail.

Of particular interest are the species observed in non-polar organic glasses such as 3 methyl pentane and 2 methyl butane. In these systems it has been possible to identify centres due to radicals of the parent hydrocarbon and trapped electrons. No direct evidence for cations of the hydrocarbon has been obtained, although their existence can be deduced by the use of glassy systems containing small quantities of solutes which have lower ionization potential than the solvent hydrocarbon. Energy is deposited uniformly throughout the system with the formation of hydrocarbon cations from the solvent. By energy migration process the solute cations are formed in high yield

$$RH^+ + \text{Solute} \rightarrow RH + (\text{Solute})^+$$

The process of energy migration is not completely understood and is under investigation in other laboratories—nor is the mechanism whereby the solvent cations react with themselves to produce stable species.

When electron scavenging solutes are present, no trapped electrons are observed. Instead, products from the reactions of the solute with the electrons are detected. These may be anions produced by electron capture such as CCl_4^- proposed to explain the results observed at 20 K in 3 methyl pentane, containing carbon tetrachloride or radicals produced by associative electron attachment. For example $CH_3I + e \rightarrow CH_3 + I^-$ as observed in 3 methyl pentane glasses containing methyl iodide near 77 K.

The subsequent reactions of these species at various temperatures are of interest. It has been found that the radicals from the solute such as CH_3 react by an apparent first order process which has required some ingenuity in interpretation.

In the absence of high energy sources experiments are now being carried out on systems of hydrocarbons with alkyl halide solutes in which electrons are produced in situ by photo-ionization of an added solute, tetra methyl phenylene diamine (TMPD). Such a system has the advantage that no solvent cations are produced and that the reactions of the desired radical can be studied without other radiation damage effects.

Experiments are being carried out to determine the nature and yield of the stable products formed by the reactions of the radicals generated in order to determine the mechanism of the solid state processes.

Preliminary experiments have shown that the rate of radical disappearance varies rapidly with temperature in the range 60–100 K, indicating that the role of viscosity of the solute plays an important part in the processes. A programme has been initiated to obtain a measure of the relative diffusion coefficients of small molecules such as O_2 and small alkyl halides in hydrocarbon solvents at low temperature by examining the quenching of phosphorescence of anthracene and other molecules. Diffusion coefficients measured in this way should correlate better with the radical reaction data than macroscopic viscosity measurements just completed in other laboratories.

These problems are of a purely academic nature but may lead to a better understanding of the mechanisms of reactions and energy transfer in the organic solid state.

NATURAL GAS FROM KAPUNI

R. Worley, M.C., A.M.I.C.E.
(General Manager, Auckland Gas Company Ltd.)

This account of Kapuni Gas is abridged from a paper given to the Auckland Branch of the New Zealand Institution of Engineers on 24 April, 1968.

THE Kapuni Natural Gas and Condensate Field was discovered by an oil consortium comprising Shell-B.P.-Todd(Europa) in 1959, and its economic importance was proved by the drilling of three additional wells during the following two years. For a number of reasons the commercial development of the field is only now about to begin.

The flow from the Kapuni wells contains about 40% carbon dioxide which will have to be separated out and discarded. Of the remainder, about two-thirds is raw Natural Gas containing methane, ethane and some propane and butane, and one-third is Oil Condensate suitable for treatment at the Whangarei refinery for motor spirit production. Unfortunately, this condensate cannot be made available economically without an assured market for a substantial flow of gas. Two propositions were early considered: petrochemical and fertiliser usage was not found to be justified, and the use of the gas for base load electricity generation was rejected as being wasteful of a valuable indigenous fuel. Thorough surveys showed that the greatest national benefit would be secured by using the gas as gas, and in November 1967 the Natural Gas Corporation Act was passed. The Government, having previously completed negotiations with the Oil Consortium, was now in a position to arrange piping of gas to nine North Island Gas Undertakings for industrial and domestic users. Recent progress has been rapid and by October 1969 gas is expected to be coming into use in Wellington and Auckland and the intervening cities along the route of the pipe line.

Chemists will be interested in the comparison of Kapuni gas with Coal gas shown in Table I. The characteristics of the Kapuni gas show it to be from one of the best natural gas fields in the world, its desirable properties including non-toxicity, complete freedom from sulphur, and high calorific value. The Table indicates appreciable amounts of propane and butane and it is possible that these gases, at present imported from overseas, will become available from Kapuni for use as bottled gas.

Modification of equipment to make the best use of Kapuni gas when it arrives is already in progress. Obviously the process of conversion will be expensive, but it seems certain that the costs will be more than justified by the great benefits which will accrue to industry, commerce and domestic consumers by the availability of this cheap, versatile, efficient, non-toxic fuel.

Table I

Kapuni Gas	
Methane	80.18%
Ethane	10.12
Propane	4.26
Carbon dioxide	2.54
Nitrogen	1.53
n-Butane	0.51
Pentane	0.12
Hexanes	0.02
Water vapour	0.01
Specific gravity	0.699
Calorific value	1,150 B.T.U. per cu. ft.
Auckland Coal Gas	
Hydrogen	42.3%
Carbon monoxide	23.9
Methane plus paraffins	16.8
Nitrogen	10.1
Carbon dioxide	4.3
Unsaturated hydrocarbons	1.7
Oxygen	0.9
Specific gravity	0.58
Calorific value	450 B.T.U. per cu. ft.

INSTITUTE OF CHEMISTRY CONFERENCE 1968

Thinking of coming to the Auckland Conference? Dates are Monday 19 to Saturday 24 August. The following notes are intended to supplement the information which you will have already reecived by personal circular.

SESSIONS

Analytical Workshop: An opportunity to try out in practice some of the newer methods in analytical chemistry. Instrumental techniques in operation will be gas chromatography, Auto-analysis, atomic absorption, U-V and I-R spectroscopy. A useful range of electrochemical methods will include polarography, chronopotentiometry, Karl Fischer titration, chloride determination using polarised silver electrodes and the analytical use of potentiostats and operational amplifiers. Radiochemical experiments will demonstrate how isotopes of low activity can be used with advantage in the conventional chemistry laboratory. Note: not all the equipment will be highly elaborate—as much emphasis will be given to simple and cheap methods as to those requiring expensive "hardware".

Lab. sessions: Wednesday afternoon and Thursday morning.

Chairman: Mr. J. K. Johannesson (Auckland Technical Institute) assisted by Dr. F. J. B. Aggett (University of Auckland), Dr. D. F. Nelson (D.S.I.R., Chemistry Division) and Mr. C. Small (Green Lane Hospital). *If there are any other analytical methods you would like to see included or if you wish to contribute apparatus to the Workshop, please write to Mr. Johannesson, A.T.I., P.O. Box 5044, Auckland.*

Biochemistry: Symposia on Structure and Function of Membranes and on the Metabolism and Action of Hormones are being organised by the Manawatu Branch. For latest details you should contact Dr. J. C. Hawke (Massey University) or Mr. J. T. France (Professorial Unit, National Women's Hospital).

Sessions: Tuesday afternoon and Wednesday morning.

Chairmen: Professor G. T. Mills (University of Auckland) and Professor D. G. Bonham (O. & G. School, University of Auckland).
Papers: Session 1—Mechanisms of ionic accumulation across membranes, Dr. P. Wiggins (University of Auckland); Electron microscopy and the elucidation of membrane structure, Dr. S. Bullivant (University of Auckland); Membrane of the red blood cell, Mrs. C. Winterbourn (Massey University); A biochemical interpretation of transport mechanisms, Dr. R. C. Lawrence (N.Z. Dairy Research Institute, Palmerston North).

Session 2—Insulin, Professor J. G. T. Sneyd (Otago Medical School); Regulation and peripheral action of growth hormone, Dr. D. J. Scott (Auckland Hospital); Steroidal hormones in pregnancy, Mr. J. T. France (O. & G. School, University of Auckland).

The Chemist and Management: Four speakers will cover the experience of chemists in management in different industries. It is particularly hoped to include a speaker from a government department to represent the chemist managing research and a talk from a young chemistry graduate with limited experience in an industrial laboratory who can present the picture from the laboratory looking out.

Discussion will be encouraged on such questions as:

Is a chemical training a good basis for management generally?

Is a chemical background an advantage in industrial or commercial activities, where there is a greater or lesser degree of chemical content?

Are the logical processes of thought, which the study of sciences in general and chemistry in particular should develop, advantageous in management?

How best can a chemist supplement his basic scientific training to make himself a better manager?

Session: Tuesday afternoon.

Chairman: Dr. J. S. Watt (Fletcher Industries).

Geochemistry and Mineral Resources:

A number of invited speakers will participate. Dr. B. G. Weissberg (Chemistry Division, D.S.I.R.) will discuss the chemistry of formation of ore bodies. Dr. A. J. Ellis (Chemistry Division, D.S.I.R.) will discuss geochemical method of prospecting. Dr. R. R. Brooks (Massey University) with Dr. N. E. Whitehead as co-author will give a paper on the biogeochemical search for uranium in New Zealand. Professor M. Kennedy (University of Canterbury) will discuss the bacterial leaching of copper ore. Mr. I. R. McDonald (Chemistry Division, D.S.I.R.) will discuss the utilisation of New Zealand clay as a paper filler.

Session: Wednesday morning.

Chairman: Dr. I. K. Walker (Chemistry Division, D.S.I.R.).

Liaison between Government, Industry and Tertiary Education:

Industry and research organisations depend for their supply of professional chemists on the universities, and for their technicians on the technical institutes. The objectives of the teaching institutions and the needs of the employer organisations will be discussed.

Speakers who have so far agreed to participate are Professor H. N. Parton, Mellor Professor of Chemistry, University of Otago; Dr. W. M. McGillivray, Director, Dairy Research Institute; and Mr. R. A. Keir, Principal, Auckland Technical Institute. It is planned to have a fourth speaker who will speak from the viewpoint of the industrial employer.

Session: Friday morning.

Chairman: Professor A. L. Titchener (University of Auckland).

Chemical Engineering: Papers will include one on Automatic Control of Process Industries; Mr. W. E. Russell (N.Z. Farmers' Fertiliser Co.) on New Developments in the Fertiliser Industry; Dr. P. L. Spedding (University of Auckland) on the Fuel Cell.

Session: Friday afternoon.

Chairman: Mr. G. Maskill-Smith (N.Z. Wallboards Ltd.).

Student Papers: This session is being planned as a new feature of Conference in which a group of selected Ph.D. students representing Chemistry Departments throughout the country will meet to explain the aims and purpose of their research in a general chemical context and to present their results. The number of papers will be small and a high standard of both content and presentation is expected. With this in view the Institute is offering a prize for the best paper as judged during the session.

Session: Thursday morning.

Chairman: Professor P. B. D. de la Mare (University of Auckland).

ADDRESSES

Tuesday morning: "Industrial Chemistry"—speaker to be announced.

Wednesday morning: The Mineral Resources of New Zealand, Dr. R. W. Willett, Assistant Director-General, D.S.I.R.

Wednesday evening: The Easterfield Address.

Thursday morning: "New Dimensions in Analytical Chemistry"—Dr. Lloyd Smythe, Atomic Energy Authority, Lucas Heights, Sydney.

Friday morning: "Liaison betwen Government, Industry and Tertiary Education"—Hon. R. D. Muldoon, Minister of Finance.

LOCAL VISITS

Arrangements have been made for members and their wives to visit one of the following establishments on the Thursday afternoon.

(a) Crown Lynn Potteries Ltd.
(b) Manukau Purification Works.
(c) Pacific Steel Ltd.
(d) Fibremakers N.Z. Ltd.
(e) Postgraduate School of Obstetrics and Gynaecology.

If you would like us to arrange any other visits, please contact Mr. G. R. White, Chemistry Department, University of Auckland.

TOURS

Two tours have been arranged—

(a) N.Z. Forest Products Ltd., Kinleith (Pre-conference tour, Monday 21st).

(b) Glassworks and Oil Refinery, Whangarei (Post-conference tour, Saturday 24th).

NEW BUILDINGS

Recent progress on new buildings in Auckland has been rapid.—*Come and see for yourself.*

Finally, *if you have any suggestions or enquiries re Conference, or if you have not received the circulars, we should like to hear from you.* The Conference Chairman is Mr. K. E. Seal (Amalgamated Brick and Pipe Co.) and Secretary is Mr. K. M. Gawne, 5 Janet Street, Pakuranga.

SEE YOU AT CONFERENCE

BRANCH NOTES

Auckland

University. The University Chemistry Department held a highly successful Open Day on Saturday 4th May with more than 1500 visitors. Tours of the teaching laboratories, computer and photographers' suites, the cobalt source and the workshop were arranged. Research areas on view included radiochemistry, solvent extraction, infrared and Raman spectroscopy, electrochemistry, surface chemistry, X-ray crystallography, cancer chemotherapy and organic use of I.R., U.V., and O.R.D. techniques. The specialised exhibits were counterbalanced by glass blowing demonstrations and a continuous film show.

Chemistry Teaching. Some twenty-five school and university teachers from all parts of the country and representatives of the Department of Education convened at Lopdell House from 1st to 5th April. The meeting was arranged to consolidate the new Scholarship and Bursary Chemistry prescription by preparing a working guide which will be made available to sixth form teachers.

Branch Meeting. Professor McGlashan spoke to the Branch in April on "Understanding Entropy Changes".

Personal. Dr. J. B. Macaskill has joined the physical chemistry section of the Fertiliser Manufacturers' Research Association. He will be initially engaged in vapour pressure measurements on the HF-fluosilicic acid system as part of an effluent study, and in X-ray work.

Manawatu

Massey University

Dr. L. F. Blackwell recently accepted a position as lecturer in physical-organic chemistry in the Department of Chemistry and Biochemistry at Massey University. His interests lie in the field of kinetic isotope effects.

Dr. G. N. Malcolm, Associate Professor of Chemistry at Otago University has been appointed to the Chair of Physical Chemistry at Massey University. He is to take up his appointment towards the end of the year.

Mr. G. B. Latimer has resigned from the Food Technology Department of Massey University to take up a post with the N.Z. Dairy Board.

From the beginning of this year the Department of Food Technology has been split into two departments; the Department of Food Technology headed by Professor J. K. Scott, and the smaller Department of Biotechnology headed by Professor R. L. Earle. The degree offered is Bachelor of Technology, with options for Food Technology or Biotechnology.

Plant Chemistry Division

Dr. G. W. Butler, Director of the Plant Chemistry Division of D.S.I.R. Palmerston North, travelled to the Division of Tropical Pastures C.S.I.R.O., Brisbane, Queensland in April for further investigations into the selenium metabolism in plants.

Dr. J. K. Heyes from the Department of Botany, Edinburgh University, is at present visiting the Plant Chemistry Division, D.S.I.R., Palmerston North, to further his studies on RNA metabolism in plants.

Dr. B. D. E. Gaillard has recently left the Plant Chemistry Division, D.S.I.R., Palmerston North, to return to the Laboratory of Animal Physiology, Wageningen, The Netherlands. Dr. J. Zwartz is shortly to return to Wageningen also.

Dr. E. Wong of the Plant Chemistry Division, D.S.I.R., has been awarded an Alexander von Humboldt Research Fellowship from West Germany. He will spend 12 months working at the Plant Biochemistry Department, University of Freiburg. While overseas, Dr. Wong will attend the IUPAC 5th International Symposium on the Chemistry of Natural Products in London.

Dr. J. MacRae has recently been appointed from the Department of Agricultural Biochemistry of the University of Newcastle-on-Tyne, to a position in the Plant Chemistry Division, D.S.I.R., Palmerston North.

Dr. A. R. Cashmore of the Plant Chemistry Division, D.S.I.R., Palmerston North, was awarded a Walter Mulholland Fellowship, and recently left for Cambridge University, England, with the intention of travelling overland from Madras. Mrs. P. K. Cashmore, who was on the staff of the Protein Section of the N.Z. Dairy Research Institute accompanied him.

Dairy Research Institute

Dr. R. M. Dolby, Chief Chemist of the N.Z. Dairy Research Institute, recently returned from a tour of the United States of America, England and Europe.

Mr. C. R. Southward, a casein chemist of the Chemistry Department of the N.Z. Dairy Research Institute, recently spent some time near San Francisco, California, gaining an insight into the problems of using casein in human foodstuffs.

During the 36th Annual Factory Managers' Week run by the N.Z. Dairy Research Institute, a new Processing Hall, containing a variety of equipment (including a mechanised cheesemaking machine) was opened by Sir Andrew Linton, Chairman of the N.Z. Dairy Board.

Wellington

Victoria University

Dr. A. F. M. Barton, Lecturer in Physical Chemistry, has been a Southampton Research Fellow. Dr. Barton graduated from the University of Auckland and has had experience in high temperature and pressure work.

Dr. B. Halton is expected to arrive later in the year to take up a lectureship in organic chemistry. Dr. Halton graduated from the University of Southampton and has worked on small ring compounds.

Dr. A. M. Taylor, Senior Lecturer in Geochemistry, is a former Otago graduate. He gained his doctorate at Pennsylvania State University and has since held appointments with Union Carbide Corporation and C.S.I.R.O.

Chemistry Division

Mr. W. R. Braithwate has joined the Metallurgy Section to work on problems of corrosion. Mr. Braithwaite was formerly Head of the Corrosion Department in the Central Research and Engineering Division of British Insulated Callender's Cables in London.

Dr. K. S. Raxworthy is working in the Spectrographic Section. He recently completed his doctorate at Canterbury working on gas radical reactions under Professor Phillips.

Mr. R. J. Weston, a graduate from Auckland, is working in the Organic Section.

Dr. A. J. Ellis attended the 2nd Australian Electrochemistry Conference held in Adelaide in February.

Miss de Castro is working at Chemistry Division on the Colombo Plan scheme. She is a chemist from the Government Vulcanology Service in the Philippines.

Otago

University of Otago

Dr. G. B. Petersen, previously of Plant Chemistry Division, D.S.I.R., has arrived to take up the Chair of Biochemistry.

Dr. G. N. Malcolm has been appointed to the new Chair of Physical Chemistry in the Department of Chemistry and Biochemistry, Massey University. Dr. Malcolm, who is the present Chairman of the Otago Branch, will take up his new position early in 1969.

Professor M. H. Panckhurst is on leave at the University of Oregon.

Dr. I. D. Watson is working at Imperial College, University of London.

Professor H. N. Parton, a former President of N.Z.I.C., has been appointed Pro-Vice Chancellor of Otago University.

Professor R. E. Corbett has been elected Dean of the Faculty of Science.

Professor M. L. McGlashan, Visiting Mellor Professor to Otago University, has returned to the University of Exeter. During his stay in Dunedin he conducted numerous seminars on topics of Physical Chemistry, and spoke to the local branch on "Quantities and Units; The Spelling and Grammar of Physics and Chemistry."

Dr. J. C. Dacre has returned to Dunedin from the United States where he has been working in the School of Public Health, University of California, Berkeley, and also at the National Communicable Diseases Centre, Atlanta, Georgia.

Lectures to Sixth Formers

The first lecture for 1968 was given recently by Dr. R. M. Carr. An audience of over 200 heard his address on 'Chemical Architecture'.

Book Reviews

Advances in Magnetic Resonance. Volume 1. Edited by J. S. Waugh. Published by Academic Press, New York, 1965. 413 pages. Price US$15.

This book is the first of a series of publications of review articles on magnetic resonance aimed at the research worker. The scope of the planned volumes ranges from electron spin resonance, nuclear magnetic resonance and quadrupole spectroscopy to related areas such as molecular beam, optical pumping and microwave spectroscopy. The first volume contains six review articles, "The Theory of Relaxation Processes" by A. G. Redfield, "Chemical Rate Processes and Magnetic Resonance" by C. S. Johnson, Jr., Nuclear Magnetic Resonance of Paramagnetic Molecules" by D. R. Eaton and W. D. Phillips, "Theory of Nuclear Spin-Spin Coupling" by M. Barfield and D. M. Grant, "Geminal and Vicinal Proton-Proton Coupling Constants in Organic Compounds" by A. A. Bothner-By, and "Electron Spin Resonance of Radical Ions" by K. W. Bowers.

It is most pleasing to see Redfield's theory of relaxation published in this volume. However, I would have preferred to see a few examples worked out in detail to illustrate the handling of the equations of motion. Chapter 2 outlines the phenomenological and the density matrix approaches to relation processes and successfully summarises what information can be gleaned from a study of chemical rate processes by electron spin resonance and nuclear magnetic resonance spectroscopy. The chapter on NMR of paramagnetic molecules clearly points out the wide application of nmr spectroscopy as a trial in determining the electronic configuration of the unpaired electron in a paramagnetic transition metal ion complexes or free radicals. The fourth chapter on nuclear spin-spin coupling constants discusses the various theoretical approaches making comparisons with experimental results.

The last two chapters are compilations of experimental data which have been carefully prepared and presented with extensive references. I am sure that the effort in carrying out this task is well justified as it will save many hours for the research worker who requires such NMR couplings and ESR data of free radicals. The ESR data review only includes organic radical ions.

I am sure that this volume will be most valuable to all workers in the field of magnetic resonance and I hope additional volumes of the same standard will appear in the not too distant future.

R. M. GOLDING.

The Petroleum Chemicals Industry. Third Edition, 1967, by R. F. Goldstein and A. L. Waddams. Published by E. and F. N. Spon Ltd., London. (General and Industrial Chemistry Series). 509 pages. Price U.K. £6.

The objective of this monograph is to set down the major routes to the important petroleum chemicals and to explain their end uses.

The rapid, world-wide growth of petroleum chemicals has been triggered by the increasing demands of three growing industries—nitrogen fertilisers, high polymers and manmade fibres, and by the discovery of new processes or the need of new raw materials for synthetic rubbers and biodegradable synthetic detergents. These industries remain outside the normal scope of this book, but processes discovered or developed to supply them can be credited with much of their growth in the last decade.

Changes in the direction of development of the petroleum chemicals industry have accelerated in the last ten years. The first change is from what was practically an American monopoly until the end of the second world war to the now world-wide coverage of this industry.

The second change is the use of heat, air and water only as the means of processing petroleum hydrocarbons. Where chemicals are used, the trend is that they should either form an integral part of the final product e.g. in vinyl chloride, or they should be used in modest amounts for recovery and recycling.

The three main sources of synthetic organic chemicals are coal, oil and vegetable products. Each source has its own peculiar advantages; but the indications are that a country with free access to oil will have a large and growing share of the field; compared with coal, oil has the advantage that it already is combined with hydrogen. Compared with vegetable products it is more readily transportable, and a given weight of oil will give a higher yield of synthetic chemical than the same weight of vegetable product.

The monograph gives a brief summary of the history of the petroleum chemicals industry, source materials, hydrocarbons in crude petroleum or by-products of refining process, and separation of hydrocarbons. Several chapters are devoted to the chemistry of paraffins, manufacture of olefins and chemical developments based on them, manufacture of diolefins, naphthenes, aromatics and acetylene. A large section covers the manufacture and reactions of the principal classes of petroleum chemicals. A summary of chemical byproducts (usually non hydrocarbon) arising from refinery operations is given and the final chapter deals with the economics of the petroleum chemical industry —the effect of locality on choice of raw material and route and the main end uses. Finally, appendices list the boiling points of the simpler hydrocarbons, give general information and charts, statistics of world petroleum production and consumption and of manufacture of synthetic organic chemicals of non coal tar origin in the U.S.A. and U.K.

This book is a valuable source of reference on petroleum chemicals to manufacturers and users alike. It is logically arranged and easy to read.

W. Jeune.

Catalytic Hydrogenation over Platinum Metals, by Paul N. Rylander. Academic Press. New York and London, 1965. 550 pages. $22.50.

As the author himself remarks, practical problems associated with the catalytic hydrogenation of organic compounds are most readily solved by using an empirical approach and an extensive knowledge of the literature. Emphasis has been placed in this book on the presentation of available information on the behaviour of functional groups and their interaction during hydrogenation, and the effects of reaction conditions, the form and composition of catalyst materials (based on the elements Ru, Rh, Pd, Os, Ir, and Pt) upon the course of hydrogenation reactions.

The complexity of heterogeneous reactions of the type with which the book is concerned prohibit detailed mechanistic interpretation, but some discussion by Rylander of the role of the catalyst and an outline of the geometrical and electronic factors in catalysis would have perhaps enabled the practical chemist to make a more educated guess at the type of catalyst and experimental conditions likely to prove most rewarding.

The task of collecting, correlating and cataloguing available data has been performed admirably, and will relieve the chemist, interested in either the theory or applications of catalytic hydrogenation, of much of the burden of literature survey.

A. Metcalfe.

The Thermal Properties of Transition Metal Ammine Complexes, by W. W. Wendlandt and J. P. Smith. Elsevier Publishing Co., Amsterdam/London/New York, 1967. 235 pages. Price $10 (NZ).

This book includes the results of various investigations on the solid state thermal dissociation of transition metal ammine complexes. Only those compounds that contain metal to nitrogen bonds with the ligand are included.

It is a work for the specialist although inorganic chemists in general will find it interesting reading.

A major problem that is clearly presented is the difficulty of comparing experimental results from different laboratories when slightly differing experimental conditions are used to study identical compounds. As a consequence, a major portion of the data presented comes from the authors' laboratories.

After a brief introduction, a chapter outlining the various modern thermo-analytical techniques is presented. These include differential thermal analysis, thermomagnetic techniques, high temperature reflectance and infrared spectroscopy, gas evolution-mass spectrometric analysis and thermodilatometric analysis. Then follow ten chapters giving results of dehydration and deammination temperatures and thermal decomposition stoichiometries with examples from cobalt, chromium, copper, nickel, zinc, cadmium and platinum complexes. Good author and subject indices follow a final chapter on miscellaneous metal ammines.

The book is neither free from misprints (pp. 51, 162, 175, 190) nor from errors of fact (the $[Cr(NH_3)_3(H_2O)_3]^{3+}$ ion on p. 104 is red, not blue), but few books are.

This book is not a comprehensive review, but it does have its place in presenting the problems and techniques available to workers contemplating or at present investigating the thermal properties of inorganic complexes.

D. A. House.

R.I.C. Monograph for Teachers No. 14. "Principles of the Colloidal State" by Dr. G. D. Parfitt. 64 cents.

While the colloidal state is not included in school general science or chemistry examination prescriptions, this topic is usually treated in biology when the properties of protoplasm are considered.

In this Monograph, after a brief but useful introduction in which he outlines the scope of the subject and its everyday applications, the author divides his attention between lyophobic sols and lyophilic sols in the ratio of about three to one.

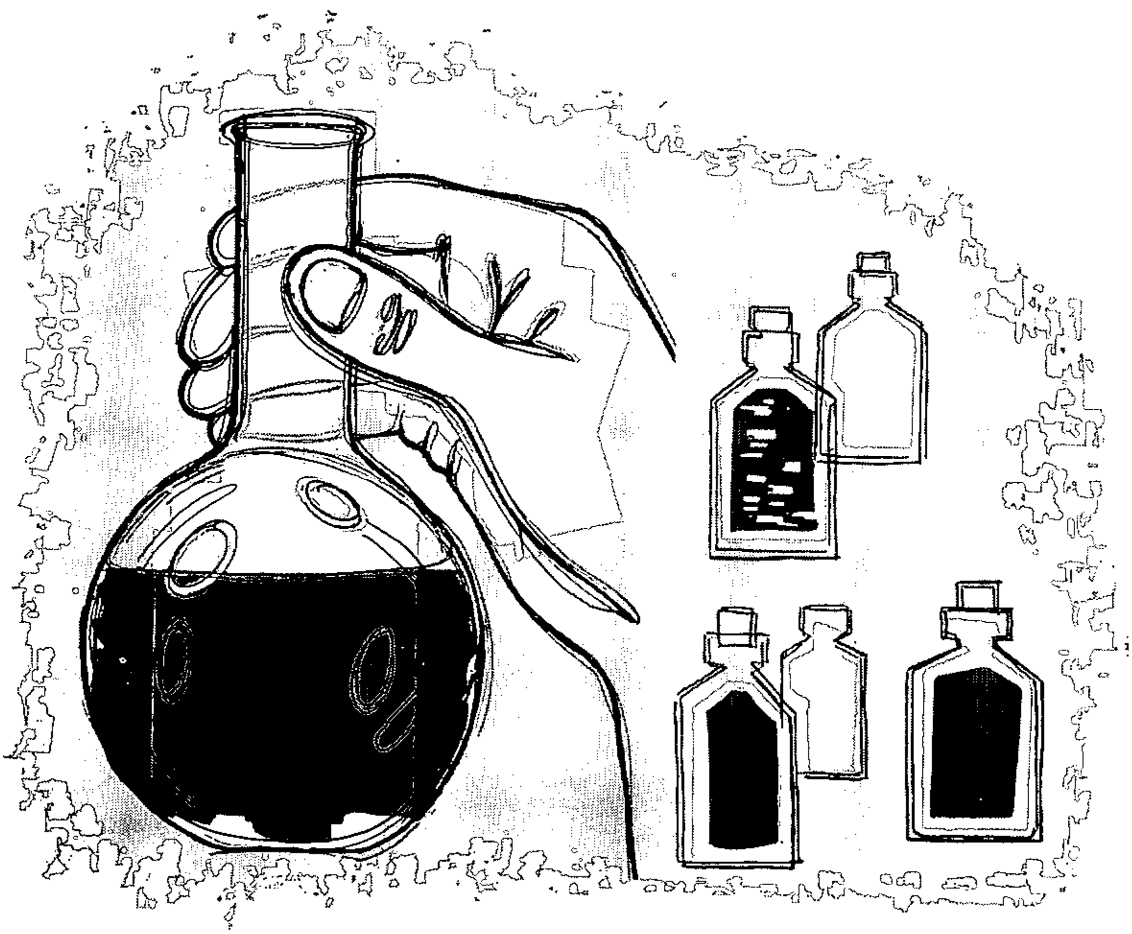
Sections are devoted to the stability, electrical charge, sedimentation, colligative properties and preparation of sols.

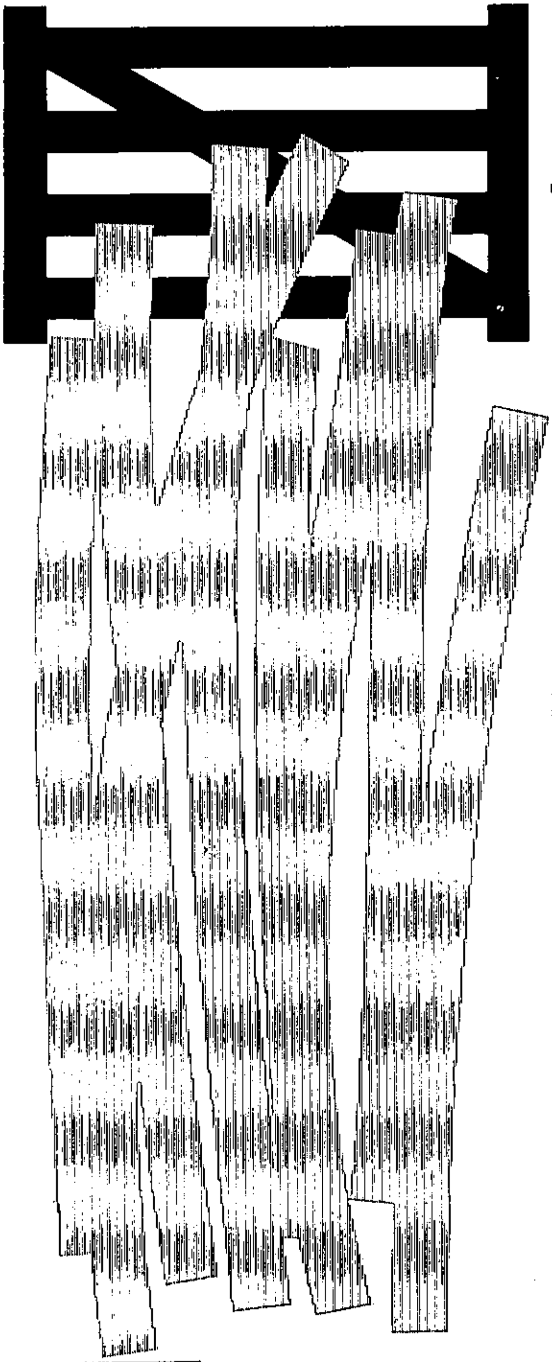
Minor topics of interest are the determination of Avogadro's Number from Brownian Movement, a discussion of the behaviour of the surfaces of oxides in contact with water, salting out and the grouping of detergent molecules into aggregates (micelles).

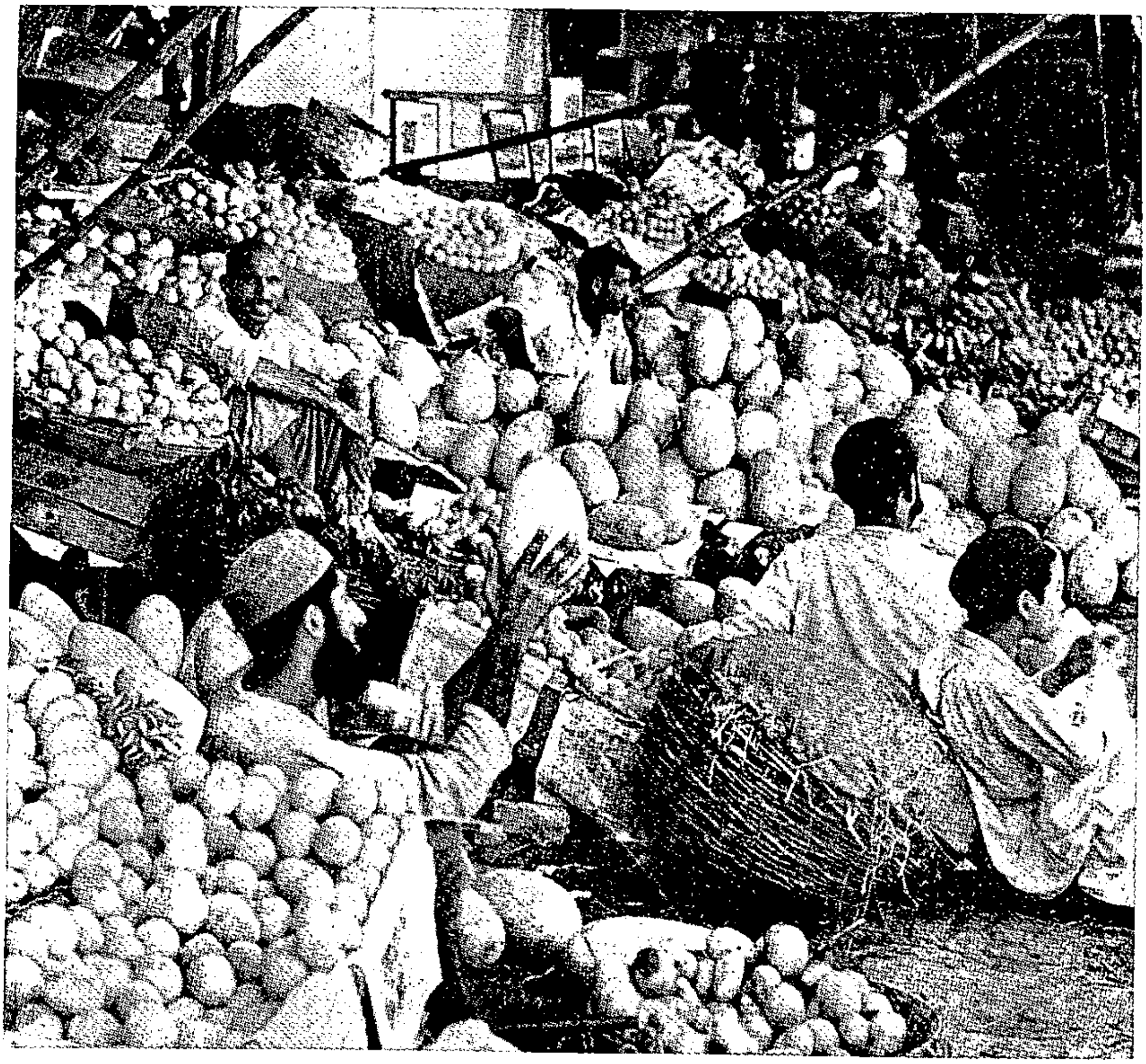
The Monograph is rounded off with a list of a dozen suggestions for further reading.

A. F. Baker.

Copies will be available from the Registrar shortly.







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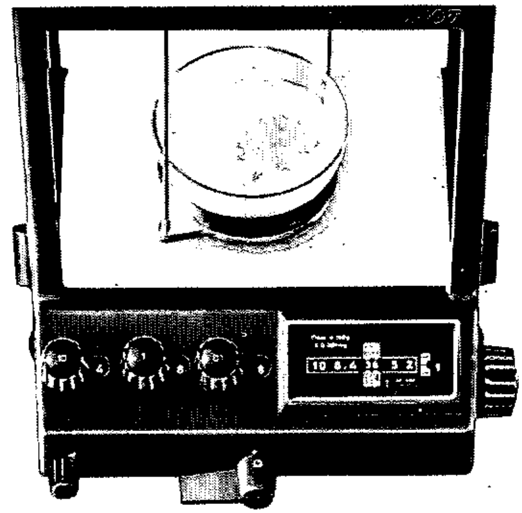

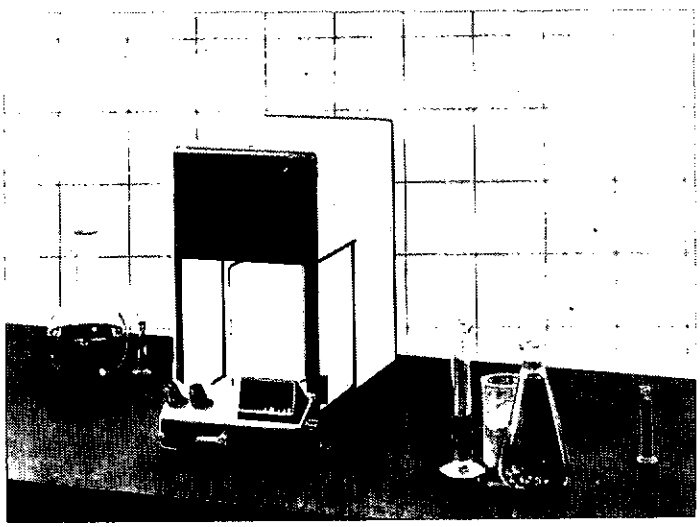

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