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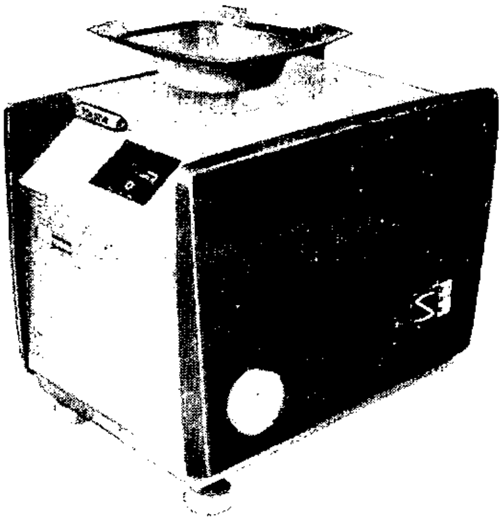

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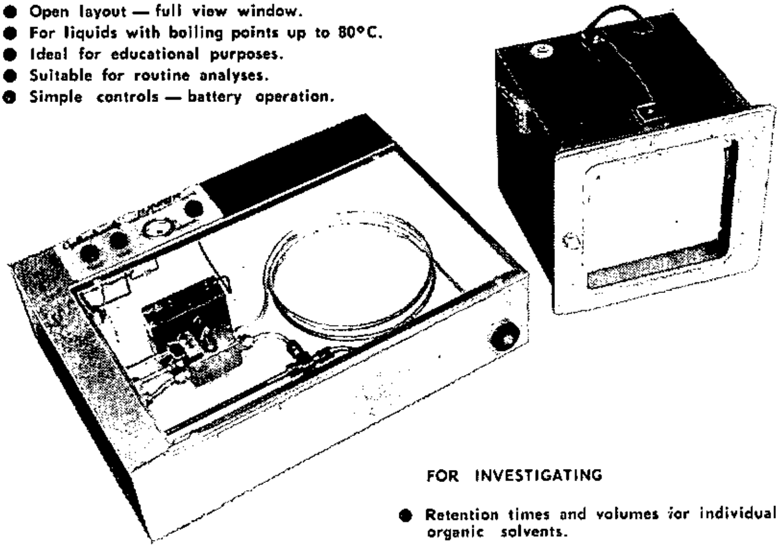

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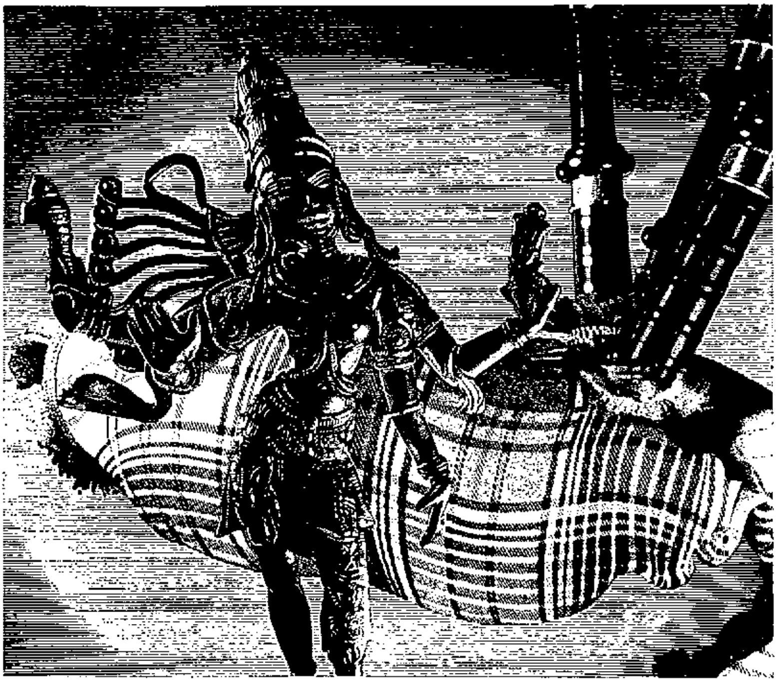

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JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

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L'ENVOI

In writing previous editorials, the retiring editor adopted a custom he once thought silly — the use of the "editorial we". The less egotistic sound of the plural had its uses, although there were sometimes difficulties when "we" could be interpreted as "the Institute". The time has come to revert to the first person singular; for with the completion of this isue, the twenty-sixth since editorial responsibility was handed to the Waikato Branch, the *Journal* passes to new management.

In the last five years I have learnt a lot about chemists and chemistry in New Zealand, made many new friends and learnt to know old ones beter. (If I have made enemies they are in hiding still.) I hope the benefit has been two-way, and that the *Journal* and the Institute have at least not suffered in the process.

I am indebted to many for their advice and help: but I thank especially the Editorial Committee, Dr Davies, Mr Lancaster and Mr McNaught, who never failed to do the chores imposed on them; the Branch Editors who maintained the "gossip pages" and suggested papers; the Registrar, for copy and reminders about essential business; Mr Wilson and Miss Brown of Editorial Services for their interest in and sympathetic handling of the production and their alertness in correcting the errors of the amateur editor (including, at least once, my spelling); and my wife who, having been a member of an early *Journal* committee, found some interest in reading proofs and endured a chronic clutter of paper round the house.

Off with the old editor, on with the new. Miss Joan Mattingley is well known to members as Wellington Branch Chairman and Council delegate, positions in which she has revealed constructive and critical ability and a direct approach to matters of organization. Perhaps siting of the editorial headquarters in Wellington may make it easier to bring the *Journal* out more promptly. In wishing her well I hope she will do better than her predecessor and get some brickbats thrown at her editorial comments; for if she provokes our rather lethargic members that far she will merit bouquets as well.

THE INDUSTRIAL CHEMIST IN NEW ZEALAND TODAY

S. G. BROOKER

Abels Ltd., Newmarket, Auckland

Presidential Address to the New Zealand Institute of Chemistry, delivered at the Annual Conference, Hamilton, August, 1964

My two predecessors in the office of President who have been in industry, Dr J. C. Andrews in 1945 and Mr P. R. Parr in 1951, both dealt with aspects of food technology but, having already spoken to the branches on margarine, it would be a banal anticlimax for me to discuss any other food with you. Instead, I would like to turn to some of the problems faced by the industrial chemist with the twofold hope that it may help my brethren in industry in their jobs and my chemist friends in other spheres to gain a greater appreciation of the nature of our work. I have also the student in mind with the perhaps over-optimistic view that it may influence him in the choice of a career. Perhaps what I say may bring university and industry closer together.

It is natural that I should mention first the shortage of graduates entering industry. Professor H. N. Parton in his Presidential address in 1960 raised the question as to whether chemical degree courses were designed for any other purpose than the training of university lecturers. Professor A. E. Alexander has pointed out that in Australia only 13% of those awarded M.Sc. and Ph.D. degrees enter industry; in New Zealand the position is even worse. Yet I feel that unless industry gets life-blood by injection of new graduates, it must be less prosperous, and its lack of prosperity will be reflected in the general prosperity of the country and its ability to support universities and their research activities. While it is to be expected that brilliant students will be our future professors, it is not too much to expect that good students should be urged to consider industrial careers. At present, we are in the ridiculous position where any student has only to do moderately well in the Honours examination to receive a hand-out in the form of a fellowship, bursary, or junior lectureship, which is the first step in an indefinitely prolonged meander through the halls of ivy. If my remarks seem strong, may I say that I have many valued friends in the university who will appreciate that these words are spoken in sorrow rather than in anger.

The attitude taken by many university people in discussing this matter is that there are not enough graduate scientists to go round. This particularly affects industry which comes a poor third in the race for new blood. The remedy that has been suggested in many other countries as well as in New Zealand is to do more to make school children think of chemistry as a career and therefore talks to sixth form pupils and science fairs, in which our Institute has taken a worthy lead, have been instituted. Although I appreciate the effort that has gone into these activities and the spirit behind them, I wonder if they may just produce a larger inflow of undergraduates requiring a larger number of graduates to teach them so that the overrun for industry is little improved. Here it is worth quoting Professor F. L. Clark, my opposite number in South Africa, which has eight universities for three million white people. He considers that there may be too many students with too high a proportion of numbskulls, who cannot hope to graduate, overloading the staff. To get more graduates, says Professor Clark, reduce the number of students. Has this any application in New Zealand?

I said earlier that new graduates could be the life-blood of industry and this statement can be amplified at two points. One point is that the industrial chemist finds it difficult to keep up with new developments in chemistry. To a large extent, this may be his own fault since even if his time for keeping up with the literature is limited, there can be little excuse for not attending Institute meetings where he will learn of new developments both from the lecturers and through contacts made. I feel that this cannot be stressed too highly and I speak from long experience of the help these meetings and contacts made through the Institute have been to me in my professional career.

(An issue that is worth mentioning here in parentheses is that we are beginning to find that chemistry is becoming fragmented in New Zealand just as it is overseas. While we have not gone as far as in U.S.A. where there is a Society for Artificial Internal Organs or in Australia where there are 63 splinter groups of the R.A.C.I., nevertheless we have, for example, dairy chemists going off to the Dairy Science Congress, freezing works chemists to meat and hides conferences and so on. It should be remembered that however valuable these activities may be, only the Institute can maintain professional standards for chemists.) But, even if the industrial chemist does make the effort to keep up with new developments, these often involve totally new concepts, of which he finds it difficult to grasp the full import or to see the applications. How far one can be left behind may be illustrated by my own experience. In 1932 when I did Honours, the electronic theory of valency was required reading, but was not yet mentioned in stage III; recently my sons learnt it in the fourth form. A graduate entering industry today will be halfway through his working career in the climactic year 1984, and only God knows what chemistry will be like in 2004. A suggestion has been made that industrial scientists should be granted sabbatical years to return to university. This suggestion seems to me to have considerable merit though I see difficulties both for universities and industry; nevertheless something might be worked out which could be of mutual benefit. The other solution is that every industrial laboratory should have a new graduate at least every ten years and probably five if its staff are to be kept up-to-date.

New graduates are also required in industry because, generally speaking, results of research are not being converted fast enough or in sufficient quantity into results of economic value. Sir Willis Jackson, F.R.S., of Imperial College, has said, "Moneys available for devotion to research for future purposes either from the central funds of the Government or from the resources of industry are dependent on the effectiveness with which the results of research are translated into goods which can be sold." As long ago as 1933, the Balfour committee set up by the U.K. Government complained about "Information from research simply running to waste . . ." Even in United States, the late President Kennedy, concerned about his country's lagging economy and growing unemployment, pointed out there were no discoveries of science which had been translated into really significant products since the development of television. It must be confessed that with all the chemical research that has gone into M.Sc. and Ph.D. courses in New Zealand, extremely little has ever been translated into commercial practice. I have been tabulating recently the considerable array of compounds which have been isolated from our native flora in research laboratories but to my knowledge only one has been exploited commercially and that with limited success.

Here one could enter a plea for research work at universities having more relation to the needs of the country at large. Mr W. H. Ward, Director of the Physics Division, D.S.I.R., said in 1962 after an overseas tour, "Of all the countries I visited, New Zealand was the only one where the Universities seem to pay no regard at all to the future of the country in which they live". This may be an exaggeration but it is true to say that by and large students graduate with little knowledge of the fascinating problems that face us in our primary and secondary industries. In my own field I will indicate later one or two lines of research which could be suitable for theses and which the universities are better equipped to deal with than industry is. At the University of New South Wales, Professor B. J. Ralph, who was with us last year at our Conference in Palmerston North, has established "Unisearch", a co-operative venture in applied chemistry between the university and commercial interests which promises to establish at least one new industry in Australia as well as giving university staff and students some insight into the practical application of science. There is some indication of the winds of change in New Zealand especially at Massey University where students are being made aware of some of the research problems connected with primary industry and food technology. Perhaps the same may happen in Hamilton where some excellent research connected with our primary industries could be linked with research at the new university.

The brain-drain is worth mentioning in this connection because it particularly affects industry. Incidentally, I have been surprised to find in my reading how old this problem is: great concern was felt in Amsterdam in 1897 when Vant' Hoff took an appointment in Berlin, but over 1,000 years before, in 766, it is recorded that princely stipends were attracting Jewish, Syrian and Persian wise men to Baghdad. As far as D.S.I.R. is concerned, the figures show a satisfactory balance between the number of scientists lost overseas and gained from outside New Zealand. Looking round the universities, it would apear that, if we have lost some good men overseas, we have also gained some, *e.g.*, the Vice-Chancellor of the University of Waikato. Also, if these chemists are prepared to come to New Zealand for miserable emoluments so deplored in some circles, they must be men whose devotion to the science and teaching of chemistry makes them a decided acquisition to their adopted country. But I am convinced the brain-drain is really affecting the supply of graduates going to industry if only because of the better salaries and opportunities in Australia. There are some chemists coming into industry from overseas, but they seem to be few in number.

What are the conditions in industrial chemistry today which should be considered by the young graduate when choosing his career? A general observation is that while universities may be failing in directing graduates to industry, industry in general could do more to make industrial chemistry an attractive career. We may now consider conditions for graduates in industry and, in doing so, see some of the ways in which they could be improved.

I would think that the salary surveys conducted by the Institute have been of greatest value to industry as they set a standard for employers in deciding what is a fair salary to pay graduates. (Incidentally, the Royal Institute sends out 2,500 copies of its salary survey to employers.) Our latest survey in 1962 showed that young graduates in industry were a little behind university in salary and about £300 per year ahead of Government. In general, I would estimate that the security of a government position and the excellent superannuation arrangements are worth about £200 per year, leaving a net balance of £100. However, most firms now have some kind of superannuation varying from small insurance policies to quite generous non-contributory schemes. Also, while there are exceptions, few chemists in industry today need have much worry about the permanency of their employment. The salary survey shows also that as time goes on the margin between industry and government widens and, at age 50 and over, those in industry are on the average the highest paid members of our profession. However, the figures are loaded by the salaries of those in positions of management. Allied to this, there are often other benefits such as being able to buy shares in the concern at an advantageous rate, a car allowance or perhaps even that acme of fringe benefits, a car provided by the firm. Overseas travel with adequate financial support is also becoming more frequent for industrial chemists and most firms give facilities for attending conferences in New Zealand where occasion demands — in fact, it is in their interest to do so.

Future prospects for chemists are wider in industry because advancement can come not only in the laboratory but also in sales and management. Technical sales can be very interesting work and if the salesman is a graduate chemist he commands respect among his potential customers because of the scientist's reputation for honesty. I have had the experience of being accepted and even welcomed where the normal sales staff have been unable to get a foot in the door.

As far as management is concerned, there are some notable examples in New Zealand of chemists who have risen to be captains of industry because of their ability not only as scientists but also as leaders of men. To do this, however, they have to forsake intimate contact with the laboratory and one of the questions to be faced — not only in New Zealand — is adequate compensation of industrial chemists who make good technical contributions in their field while being unable or unwilling to assume positions of management. It has been contended that such workers should potentially receive salaries as high as or approaching those earned by their associates who go into management. While this is certainly a debatable point its present non-acceptance by commercial interests must deter some first class scientists from entering industry. In U.S.A., the most industrialized country in the world, a chemist without forsaking the scientific side can apparently win a seat on the board of directors as Vice-President in charge of research, but in New Zealand I think we rather follow Parkinson's third law which states that "science fits one for nothing except possibly science". Perhaps as time goes on we may follow the American pattern in this respect as we have done in many other ways.

What is the position with regard to accommodation? Sir Howard Florey has related how in order to raise the standard of living in Gambia, an egg-producing scheme was introduced, but it proved an entire failure as the fowls succumbed almost completely to disease. However, all was not lost as the fowlhouses were converted to a teachers' training college where presumably the human students were immune from the ailments which did such havoc with their feathered friends. There are possibly laboratories which one could be pardoned for thinking of as converted fowlhouses. There was certainly the case some years ago where a minor disaster in the laboratory of one of the largest industrial concerns in Auckland was referred to in the press as a "small fire in a shed". However, such days are largely passed and it is realized that laboratories should be specially built and designed for the purpose and, apart from a limitation of area imposed by the management, the chemist can expect a great deal of freedom in planning his own working quarters — in fact, more freedom than his colleagues in other fields who frequently work in large buildings where individual laboratories must of necessity be a compromise design.

As far as apparatus and equipment are concerned, the small size of industry generally in New Zealand limits the range available to the chemist who must accommodate himself to having to be without the array of instruments available now at universities and research establishments. Nor do many industrial chemists have a free hand to spend a budgeted amount simply because business does not work that way with regard to any other of its expenditure and makes no exception for the laboratory. (It is interesting to note in passing that some big American concerns are having doubts about the wisdom of putting research departments on a budget or of ploughing back a fixed proportion of profits into research.) Because of the variety of conditions in industry, only one or two general statements can be made here. Where it can be shown that a piece of equipment will pay for itself in five years by saving time or money in the factory or laboratory, this is a language that management can readily understand; but this naturally does not apply to many items of new apparatus so that the chemist may have really to sell the idea to those that hold the purse strings. It is also true that management should and usually does realize that to employ a chemist without supplying him with adequate equipment is poor economics. Generally, too, it does not save money to have things made in the firm's laboratory or engineering shop when they can be obtained ready-made from a laboratory supply house.

Some firms now have set up quite good libraries; others limit expenditure to a few books and journals which can be perused for salient articles by the staff as they come in. None of us can avoid buying books but I have the feeling that they get out of date so quickly that journals give the better return for money. I would make a plea here for some general reading in chemistry such as *Chemistry and Industry* to be available to all graduates and even some general reading in science. There are one or two journals available now which combine a nice blends of pure and applied research, such as *The New Scientist.*

Another question by the young graduate which must be answered is, for how much of his time will he be using the knowledge and training he has gained at university? An anonymous writer in *Chemistry and Industry* has suggested recently that what is required in industry is not more graduates but better use made of them. A good ratio of technicians to graduates should be maintained and, as trained technicians come forward with the Certificate in Chemistry, it should soon be possible to relieve graduates entirely of routine work so that their talents are best employed in other ways. Here it is interesting to quote recent figures compiled by J. W. Duncan of the Battelle Memorial Institute of Columbus, Ohio, indicating that the ratio of technicians to graduates in U.S.A. is increasing rapidly. In the period 1950–60, the number of graduates increased 46.5%, but technicians increased 101.8%. Junior staff should be encouraged to study for the Certificate in chemistry and incidentally it would be useful to employers if our Institute could give some guidance on the salary to be paid to technicians on gaining the Certificate. As far as non-qualified assistants are concerned, E. S. Hiscocks, Director of the Tropical Products Institute, London, and an authority on laboratory administration, has said, "I prefer girls, preferably young, and if possible, pretty." You may be interested to know his reasons which may not coincide with your own, "I specify youth," he says, "because it goes with dexterity and adaptability; and good looks because, in all probability, some three to six years after recruitment they will marry, and in due course disappear from the laboratory, thus solving the very difficult problem of what to do about assistants who are getting older but not necessarily more able." Under modern conditions, chemists are also being relieved of much paper work. Purchasing officers can help greatly in securing laboratory equipment as well as raw materials for new products and processes — work that in the past largely fell to the chemist's lot. Personnel officers can ease the burden of finding new staff. As the laboratory and its attendant library grows in size, part- or full-time librarians can aid in literature searching, while secretarial assistance should also be available to senior chemists. All these things are becoming standard in industrial laboratories so that the chemist can spend more time at the bench, in the factory or in the library.

What are the prospects of doing research in industry? A good deal will depend on the size of the industry, the nature of the work and the man himself. Obviously the bigger the firm, the more easily it can afford to set aside one or more graduates to do research. The nature of the work influences it because, in some cases, it is an indigenous industry facing problems which are not met with overseas. This applies for instance to pulp and paper making and their by-products. As an example, you will all know something of the work leading to the successful recovery of turpentine by workers at N.Z. Forest Products at Auckland and Kinleith. At Abels Ltd., our work is different from that overseas because we are forced by circumstances to use very large amounts of beef fats as our raw material and are short of vegetable oils so largely used elsewhere. I have dealt briefly with some of these problems in the address on margarine delivered to the branches but a little expansion here could be of value in showing the scope for research in industry in New Zealand. There is only space to mention a few aspects here. Beef fats, when quickly chilled, crystallize in part in unstable forms, which transform into stable forms under conditions which are not fully understood. This change may be accompanied by development of a grainy or friable texture in contrast to the smooth plastic state desired in margarine and shortenings. For this reason, we cannot use the standard methods of margarine manufacture employed overseas and must use methods which are wasteful of labour and refrigeration. Our shortenings based largely on beef fats every now and again but especially in winter develop this grainy texture which renders them much less satisfactory in use so that we must recommend to our customers that they install special storage accommodation, holding the fats at 70° to 75°F. This problem suggests several lines of investigation. On the more practical side, it may be attacked in a rather empirical fashion by changing the physical conditions of manufacture of margarine and shortening and subjecting them to varying regimes of holding at different temperatures for shorter or longer periods. There is also limited scope for subjecting the fats to chemical changes such as hydrogenation and ester interchange before using them in margarine or shortenings.

More fundamental lines of attack can also be tried. It is known that many natural glycerides when quickly chilled solidify in unstable polymorphic forms which melt on heating and resolidify in more stable forms. However, it has yet to be definitely decided whether this phenomenon is the whole cause of our trouble here or whether it is in part at least due to supercooling. We are hoping to investigate this by various physical techniques such as differential thermal analysis. Further, whether it is unstable forms or supercooling, it could be related to the chemical composition of the fat which involves a knowledge of

(a) the fatty acids present and their proportions;
(b) their arrangement in the glyceride molecules; and
(c) the possible occurrence of as yet undetected chemical compounds.

Dr F. B. Shorland and his co-workers have done some good work on (a) but (b) and (c) are largely unexplored. There is obviously room for a great deal of interesting research here.

In addition, we have beef fats and also coconut oil which we produce at Abels as potential raw materials for various useful products, at present undeveloped. At the present time, we are using it to make margarine, shortenings and other products for bakers; emulsifiers, confectionery fats, biscuit fillings, foam retarders, waxes, frying fats, and tropical spreads. What else can we do — particularly in the way of products for export? Only research can tell us.

Some firms do much less research than others because they may be members of research associations to which fundamental and long range problems are referred, or they may be controlled from overseas where all research is done. In the second case, there is always the chance of getting overseas to see the laboratories where this research is done or even working in them for a time.

Finally, what research is done depends largely on the man concerned. He must have the insight to see what problems are worth tackling; the foresight to plan his day so that some time can be found for it where he is not wholly engaged in research; the perseverance to continue despite interruptions and sometimes indifference and misunderstanding by employers; the ability to realize when a line is unrewarding and work on it should cease; and finally the willingness to work often outside the 9 to 5 hours. If, as a by-product, the odd paper can be published or delivered at the Institute Conference, I feel it is an extremely valuable thing which helps the chemist concerned with outside contacts, helps him to feel that he is doing something which is professionally significant and reflects credit on his laboratory and the firm he works for.

This naturally leads into professional recognition, which is certainly helped by getting one's name into print in the scientific literature. However, much of the best work will not be publishable, because of company policy which may prefer secrecy or patents to papers in the scientific journals and because application of scientific principles to an industrial problem does not as a rule make a suitable subject for a paper. Nevertheless, it may involve a flash of genius which is as great as that which earns in a different field a D.Sc. It is therefore a matter for regret that the Institute has recognized few industrial chemists as presidents and, while the Royal Society of London has accepted a number of industrialists for its Fellowship, its counterpart in New Zealand has so far refused to do so. We can only hope that this position may improve in future.

Allied with professional recognition is status or place in the pecking order within the company. Here no general rule can be promulgated but in my opinion no chemist should be expected to take orders from anyone but top management or his superiors in the laboratory. Situations where he is responsible to engineers, sales managers, works foremen and other functionaries should be avoided as being unbecoming for a professionally qualified man. Because of his background, the graduate in industry often thinks differently from his fellow workers: he may and indeed should have a deeper understanding and love of literature, music, art and the drama, he may have advanced ideas on social questions, he may not even play games, he may sprout a beard and his politics may be below pH 7 turning litmus varying shades of red. To these deviations from the norm, some concessions must be made on both sides. The chemist must learn to express his views with restraint but, on the other hand, he has every right to ask that his views be respected and that he be judged on the results of his work for the company and on that basis alone. On this question of status, it should be mentioned that, in a well-run company, the laboratory has the responsibility of deciding what raw materials are accepted and more important what finished goods are fit to go out from the works. This responsibility exercised with restraint and firmness and backed up by the management can be the chemist's best claim to real status within the organization.

It is possible that the young graduate may be repelled from industry by its commercial aspect. It is true that commercialism has its excesses and any chemist could find it a strain on his conscience to work for a firm whose "word-smithing" makes spurious claims of a pseudo-scientific nature for its products. But in general this feeling that there is something degrading about working for a profit-making concern overlooks the fact that most often the main job of the chemist is maintenance and improvement of quality which is surely a service to the community at large that no chemist need be ashamed of. Furthermore, to take an analogy from religion, if all Christians lived in monasteries and convents, Christianity would soon die out for lack of money-earning Christians to support the religious. Similarly, if there were no industry, in which chemists are vital to survival, there would be no funds available to support academic and other centres of research.

I would like to consider now some of the attractions of an industrial career. Some may appeal more than others according to one's nature.

First, there is the stimulus of meeting, working and getting along with people of different backgrounds and interests such as managers, accountants, sales staff, clerks, typists, works foremen, purchasing agents, factory hands, truck drivers, engineers and all the variety of people who work together in modern industry. Where the firm employs three or more chemists, who can stimulate each other in their chosen field, these stimuli from within and without the laboratory complement each other and save the chemist from a narrow and restricting professionalism. You may be surprised that I have included factory workers in my list but I can assure you that to understand the working of their minds and get them to work with you so that the most benefit is derived from your innovations can be quite a challenge. Not only so, the chemist who is willing to go along with the men who actually do the job can often learn things from them that no theory but only long practice can teach.

In some ways the chemist in industry occupies a unique position in that he is in contact with all parts of the organization. He helps the sales manager with technical advice, the engineer in keeping his boilers clean, the accountant in costing the firm's products, and at the same time he is regularly in contact both with management and the workers, who may see very little of each other. In these days when industry tends to become big business and the workers just so many cogs in the works, I like to feel that chemists because of their special training and wide interests can be a humanizing influence in the places where they work.

Secondly, as I have already suggested, there are numerous problems to be faced in any industry which can offer a real challenge to the chemist. Their nature is different from those faced by the university research workers so that comparison is difficult. However, I rather think university research such as the subjects tackled by Honours and Ph.D. students for their theses, *e.g.*, the elucidation of the structure of an organic natural product, is worked out something like a game of chess, with certain well-defined rules. From time to time, it is true, new openings may be discovered leading to new lines of attack but the area is still fairly well defined. To carry the analogy further, while it is nice to win, the game is the thing and a thesis may be good enough for a degree without the real problem being solved or the structure of the natural product completely elucidated.

In industry the rules are not the same. The challenge to solve the problem is more urgent since the chemist is judged by his success in solving problems, not just on excellent chemical work. His solutions must work not only on a laboratory scale but in 5 or 100-ton batches, and they must not only work but produce some material advantage in saving money, improving the product or, particularly in a food factory, rendering the process more hygienic. Having solved the problem, he must sell it to the management particularly where new and costly equipment may be involved. Further to the chess analogy, it is often no game as the whole success of the business may depend on the successful outcome of the chemist's investigations.

While the research worker at the university may and often must confine his interest to one field, the industrial chemist's work has a wider scope — first, in the factory as well as in the laboratory and in the customer's environment. Secondly, he finds an embarrassing wide variety of problems facing him. Every process and every stage of the process offers a challenge for improvement — sometimes minor — sometimes quite radical; he is faced with problems of supplying customers' or potential customers' wants with the equipment and raw materials available to him; he is on the alert to make new products wthin the orbit of the firm's operations and to find markets for them; or, finally, he may have interesting research work to do in his laboratory in working out methods of analysis where none are to be found in the literature, or where the conventional methods are too slow, or of devising accelerated tests giving rapid indication of the shelf life of the products made in the factory. There are problems which can be dealt with by a long range programme of testing. There are others which are urgent so they must be solved in a flurry of what Rutherford described as "perspiration and profanity". Even when a problem is solved, there is the problem of keeping it solved for it may be found that it works well at first, but, when the initial stage is over, and laboratory supervision slackens a little, the natural propensities of workers to avoid work and find short cuts may prevent the process continuing to show its best results.

The chemist may also have a number of problems put to him which are not chemical or even scientific because he has a different outlook — what is described in England as the "stretched mind" which is obtained by a university degree course in any discipline be it arts, science, engineering or law.

Finally, there is the satisfaction to be gained of seeing a new product successfully marketed or a new process brought to fulfilment through work in which you have played a part. This satisfaction is not the less real because it can be measured in terms of pounds, shillings and pence, but it has a greater value in making towards a full, satisfying and interesting life, which, if we have learnt anything at all at the university, we should all be seeking.

DETOXICATION AND MOLECULAR DESIGN

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"Detoxication Mechanisms" is a short convenient chapter heading for the branch of biochemistry that deals with the metabolism of foreign organic compounds. Although the term was adopted in the nineteenth century when it was thought that foreign organic compounds were literally detoxified by the body, it is strictly a misnomer since many compounds have their toxicity or biological effect increased by metabolic reactions. Others are in fact detoxified and others again may have their type of action modified by metabolism or rarely, may not be metabolized at all (1, 2).

Usually, however, the metabolic reactions undergone by foreign organic compounds produce in the end something which is polar and usually more excretable; whether on the way toxic metabolites are produced depends to a great extent on the structure of the original compound.

Most organic compounds can be metabolized and a knowledge of the bio-transformations has been of considerable use to biochemical pharmacologists in understanding some aspects of drug action and in modifying drug structures to produce more suitable drugs. Much of this pharmaceutical-pharmacological work was stimulated by the observation that prontosil rubrum, a systemic antibacterial dye, was effective because it was metabolized to an active drug, sulphanilamide. Other examples of metabolic activations, particularly among organophosphate insecticides, are now known and some earlier examples (*e.g.*, chloral which is reduced to trichlorethanol) are now also understood to be active through their metabolic products.

The biochemical reactions involved in detoxication mechanisms are fairly limited and they have sometimes appeared to be a rather arbitrary group to select for study. In fact detailed study of the enzymology shows that many of these reactions are catalysed by enzymes different from those dealing with the normal run of substrates even though, formally, the reactions of oxidation-reduction or hydrolysis applied to foreign compounds may be the same as those undergone by natural substrates. These reactions may introduce a functional group or unmask a reactive centre which can be attacked by a series of "conjugation" enzymes. These conjugations quite often can deal with large

TABLE 1: Conjugation Reactions of Foreign Organic Compounds

Conjugate formed	*Compounds conjugated*	*Organisms*
β-glucosides	phenols, alcohols, carboxylic acids	plants, many invertebrates
β-glucosiduronates	phenols, alcohols, carboxylic acids, thiols, some amines and amides	all vertebrates
sulphate esters	Phenols, aromatic amines	all animals
phosphate esters	phenols	some invertebrates
N-acetyl derivatives	amines	most animals and plants
methyl derivatives	some phenols, heterocyclic N	most vertebrates
S-substituted glutathiones	epoxides, active halogen compounds, quinones	animals and plants
acylamino acids	aromatic acids	animals and plants

quantities of substrate and usually detoxify in the literal sense a toxic substrate. Some examples of these conjugations are illustrated in Table 1.

Some qualitative species differences are evident in these conjugations (3); the use of glucuronic acid is confined to vertebrates while invertebrates use glucose in equivalent reactions. Glycine is used to detoxify aromatic carboxylic acids in many animals but spiders, ticks and scorpions use arginine (4); plants use aspartate.

Quantitative differences are probably more important, however. The lack of an effective glucuronic acid conjugation in cats, for instance, means that these animals are very sensitive to a variety of drugs that can readily be used in dogs. Dogs, on the other hand, have a very poorly developed acetylation mechanism and do not easily inactivate sulphanilamide. DDT is virtually useless for locust control as these insects have a well-developed dehydrochlorination system that detoxifies the insecticide. Even quite small rates of detoxication of DDT can save the life of an insect since the reaction of DDT with nerve is reversible and slow. Insects with some DDT dehydrochlorinase may be able to recover after an initial knock out as the body concentration of DDT falls. In locusts a slow rate of reduction of the nitro groups of di-nitro-*o*-cresol makes it difficult to build up a lethal concentration of this insecticide in a swarm. Its use in locust control has been discontinued in favour of dieldrin, which is not metabolized.

SOME CONSEQUENCES OF DETOXICATION MECHANISMS

Inactivation of insecticides by insects is usually a bad thing, but, in vertebrates, the termination of the action of a drug or hormone is essential (5). Determination of the rate of metabolism of a drug or measurement of its biological half life is now a routine operation in the development of new drugs. Often, several mechanisms may be able to remove the drug from circulation, depending on the tissue levels to be dealt with. Mechanisms that appear to be insignificant with large doses of foreign compound may be important at physiological dose levels. Thus adrenaline is mostly detoxified by O-methylations at physiological levels, but a large dose of *e.g.* catechol is dealt with by glucuronic acid conjugation (2).

Sometimes it is found that metabolism activates a drug. Acetanilide and phenacetin exert their analgesic action to a great extent because they are metabolized to p-acetamidophenol. The relief of a mild headache is delayed after taking these drugs till enough metabolite accumulates in the blood, a matter of perhaps half an hour. When this was understood, drug manufacturers were quick to provide tablets of p-acetamidophenol which were advertised as providing instant relief. Since this compound is inactivated by glucuronic acid conjugation, commercial formulations often contain phenacetin as well since this liberates its metabolite slowly and prolongs the action.

If the foreign organic compound has the appropriate structure, undesirable metabolites may be formed, possibly carcinogens such as arise from some aromatic amines. Azo dyestuffs, which can give amines by reduction in the body, are usually regarded as unsuitable as food colours for this reason. The actual carcinogen is usually a metabolite of the amine and the incidence of *e.g.*, bladder tumours in different animals can be related to the extent of the production of the carcinogenic metabolite. β-Naphthylamine is highly carcinogenic in dogs but not in rabbits. Dogs convert this compound very largely to 2-amino-1-naphthol which is a carcinogen but rabbits produce mainly 6-hydroxy-2-naphthylamine which is not carcinogenic (1). Another potent carcinogen, 2-acetamidofluorene, is metabolized to a complex mixture of oxidation products in most animals but the active carcinogen is a metabolic product — probably 2-hydroxylamino-fluorene (6).

Thalidomide, the sedative drug which gave rise to malformed infants when taken by pregnant women, may also

Thalidomide

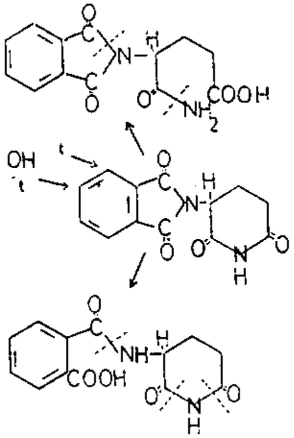

FIG. 1

exert its teratogenic effect through metabolites. Two of these, which are phenolic metabolites formed by hydroxylation at the points indicated by arrows in Fig. 1, are teratogenic in chick embryos. Most of the metabolites in human subjects are hydrolysis products (Fig. 1), the two major ones in human urine being the result of hydrolysis at the phthalimide ring or in the glutarimide ring, but other hydrolysis products are also present. Some of these inhibit glutamic acid enzymes to some extent and it is thought that the sensitive structure in the early embryo is probably an enzyme which incorporates glutamine into a protein. Pregnant rabbits fed on some of these metabolites produce deformed or dead fetuses but can be protected by simultaneous administration of glutamine in the drinking water (7).

Many examples of selective action of pesticides or crop control agents can be attributed to metabolic reactions. Selectivity of phenoxy-aliphatic acids is frequently related to the ease of β-oxidation to a phenoxy-acetic acid in different plants. In the weed "cleavers" (*Galium aparine*) which is not affected by MCPA (Fig. 2), the resistance is associated with ether cleavage to a non-toxic phenol (8). If the molecule is modified to contain an extra -CH_3 the ether-cleaving enzyme is ineffective and the new compound is an effective herbicide.

Malathion is oxidized to a toxic metabolite malaoxon in most animals, and deactivated by hydrolytic reactions (Fig. 3). Small differences in the rates of oxidation and hydrolysis are sufficient to explain the relatively high insect toxicity

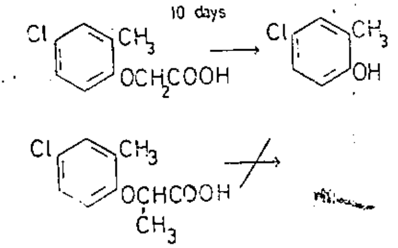

FIG. 2: *Metabolism of* Galium aparine.

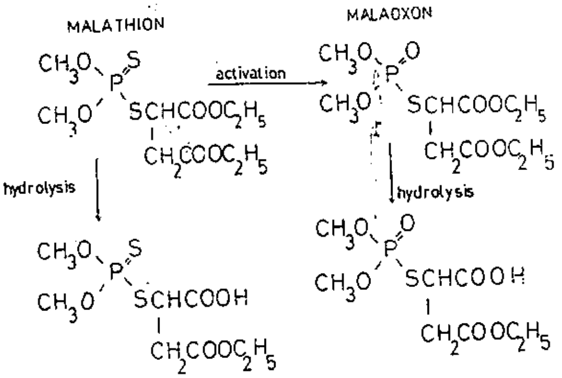

FIG. 3

and low mammalian toxicity (9). Flies oxidize faster and hydrolyse slower than vertebrates. Resistance to malathion, which has developed in insects in a few cases, has been associated with increased ability of the insect to carry out hydrolytic detoxications.

Some of the systemic insecticides depend for their selective action on detoxications. Dimethoate, which can be administered to farm animals to kill their insect parasites, is inactivated in mammals by hydrolysis. Oxidation to toxic metabolites is slow (Fig. 4). Flies, on the other hand, oxidize dimethoate faster than they can hydrolyse it and build up atoxic concentration within themselves (10).

APPLICATIONS OF DETOXICATION MECHANISMS

Knowledge of the things that detoxication mechanisms can do should allow us to use them in some practical problems of pesticide work. In general, there are two approaches possible. It may be possible to design our toxic molecules so

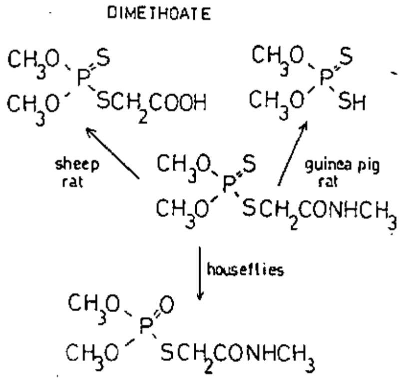

FIG. 4

that they have built-in selectivity for particular organisms. Or ways may be found to inhibit some of the enzymes concerned, or modify their action. Both of these approaches have been used to design molecules for use as crop control agents or as drugs but their deliberate application to pesticide work is as yet only beginning (11).

The search for short-acting barbiturates is an example of the application of metabolic studies to drug design. First it was necessary to find how known barbiturates were metabolized. It was established that the duration of action was related to the rate of oxidation of a substituent group in position 5 of the barbituric acid ring. The effect of variations in the structure of this group on detoxication rates was then determined and the nature of the oxidation enzyme investigated. In the course of this enzymic work a number of factors were found which increased the action of the enzyme, and several inhibitors were discovered which slowed down the enzyme action and acted as extenders of drug-action time (12, 13).

Bifunctional alkylating agents are often used as anti-cancer drugs but they are usually toxic to other body cells as well. Short acting compounds were needed, therefore, which could be introduced into an artery near the tumour and which would not survive long enough to damage the rest of the body tissues. Biological half lives of 5 to 10 seconds were needed for this purpose and glycol esters such as

$$I\ CH_2.CO\ O\ CH{=}CH\ O\ OC.\ CH_2I$$

were studied. Detoxication of these occurred by hydrolysis with serum esterases so the structure of the glycol was modified to give hydrolysis rates appropriate to the desired half life (14).

If it is wished to design insecticides, a major consideration is that they should be selective, *i.e.*, toxic to insects or perhaps a particular insect and not toxic to vertebrates. At present the best molecules to work on are either organophosphate or carbamate insecticides, since molecules of both these groups have generally toxic structures which can be modified without seriously altering the general toxic nature of the compound. Introduction into these molecules of sub-structures which are susceptible to attack by vertebrate enzymes should reduce the toxicity to vertebrates, provided insect enzymes do not also attack these groups. Search is being made in the U.S.A. and elsewhere for these "selectophoric" groups and so far the emphasis has been largely on finding potential sites for esterase reactions. Some of the useful known selective or systemic insecticides, *e.g.*, diazinon, ruelene, and some alkylarylmethyl carbamates, contain alkyl groups which could perhaps act as selectophoric centres. Possible model structures which have been studied are the simple alkyl benzenes like cumene or n-propyl benzene and some of these are in fact oxidized rather more slowly by insects than by vertebrates. The products of oxidation, and the enzymes concerned, are similar to the analogous vertebrate examples.

A second way of using metabolic information is to try to inhibit the enzymes concerned, particularly if the inhibitors act differently on enzymes in insects and vertebrates. Many examples of this approach have been found in connection with drug metabolism. Adrenaline methylation is inhibited by pyrogallol; amine oxidase action, which detoxifies many sympatho-mimetic amines, is blocked by iproniazid; many hydrolytic enzymes are inhibited by organophosphates; the microsomal enzymes which are important in detoxication are affected by a wide range of compounds which include chlorpromazine, chlordane, benzpyrene, phenobarbitone, dimethylaminopyridine, diethylaminoethyl-diphenyl-n-propylacetate, 2,4-dichloro-6-phenylphenoxyethyl diethylamine and 1-isonicotinyl-2-isopropyl hydrazine. Disease, age, cold and sex hormones may also affect the action of the microsomal enzymes. The degree of response to these various agents varies from species to species.

Piperonyl butoxide, which has been used in pyrethrin formulations for many years, has recently been recognized as a microsomal enzyme inhibitor. Its action in synergizing pyrethrins almost certainly depends on inhibition of micro-

TABLE 2: Toxicity to Flies of Carbamates and Synergized Carbamates

	L.D.$_{50}$ in μg/fly of:			
	m-isopropylphenyl-N methyl carbamate		*O*-isopropoxyphenyl-N methyl carbamate	
Susceptible strain	1.4	(0.2)	0.5	(0.14)
Resistant m.i.p.	>100	(1.0)	>100	(0.6)
Resistant m.i.p. + p.b.o.	>100	(1.2)	>100	(0.6)

m.i.p. — selection pressure on S-strain with *m*-isopropylphenyl-N methyl carbamate.
m.i.p. + p.b.o. — selection pressure on R-m.i.p. strain with *m*-isopropylphenyl-N methyl carbamate + piperonyl butoxide.
Figures in parentheses are L.D.$_{50}$ of 1:5 insecticide — p.b.o. mixtures.
Data from Georghiou, (17).

somal oxidation and hydrolysis. Carbamate insecticides are also inactivated by microsomal oxidation and their action is synergized by piperonyl butoxide. More significantly, (Table 2) when resistance to carbamates develops, as it can fairly easily in house flies, piperonyl butoxide can reverse this resistance (15). Moreover, the insects do not appear to become resistant to the synergized insecticide (Table 2). It may be desirable with a compound like a carbamate which is a substrate for microsomal oxidations to use the synergist right from the start. It is not possible to develop resistance in houseflies reared on a synergist-carbamate mixture. The basis of this is probably the way resistance develops. In any statistical operation such as spraying a population of flies there are always some survivors. If these survive because they can detoxify better than their fellows, they will probably pass on their ability to their offspring and a resistant strain may develop. The clever ones will live. A synergized carbamate is more democratic and no fly has an unfair advantage by being a clever detoxifier. The survivors will be just fortunate and a random selection should not give rise to a resistant strain. The practical difficulty with this is, of course, that it is not usually known in advance what detoxications are positive except in well-studied insects like flies of perhaps malarial mosquitoes.

The situation of chlorinated insecticides is different from that of carbamates since each chlorinated insecticide is a uniquely toxic molecule. Little opportunity arises for molecular design but it may still be possible to do something about inhibiting the detoxication enzymes. Many chlorinated compounds are inactivated by reaction with glutathione, and an enzyme catalysing this reaction can be separated fairly easily and studied (16). The insect enzyme is sensitive to inhibition by low concentrations of *e.g.*, pentachlorophenol or bromsulphonphthalein while analogous enzymes in vertebrates are not.

One of the chlorinated insecticides, gammexane, is metabolized to 2,4-di-chlorophenyl-glutathione in insects. It is not yet clear whether the enzyme concerned is the same as that studied with other chlorocompounds, or whether it can be inhibited. The significance of the glutathione transferases in gammexane or DDT metabolism and their possible relation to resistance is something that still has to be settled.

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CALCIUM CARBONATE AND ITS IMPORTANCE AS A RAW MATERIAL IN CHEMICAL INDUSTRY

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The element calcium, Ca, is the fifth most abundant in the earth's crust but it is much too reactive to occur in nature in the elementary state. However, its various mineral forms such as fluorspar (CaF_2), gypsum ($CaSO_4 . 2H_2O$), limestone ($CaCO_3$) and many others, where calcium appears as the doubly positively charged ion, Ca^{++}, are widely distributed. Of these, by far the most common are the various forms of calcium carbonate, $CaCO_3$.

PROPERTIES OF CALCIUM CARBONATE

One of the most important properties of calcium carbonate is its insolubility in water. Only about 0.015 g of the substance will dissolve in a litre of water, a negligible amount. Because of its insolubility, enormous deposits of calcium carbonate have built up, without being washed into the sea as soluble salts such as sodium chloride have been. During the years when the earth's crust was cooling there were large amounts of carbon dioxide and water vapour in the atmosphere. As carbon dioxide dissolves to give rise to the carbonate ion, $CO_3^{''}$, this resulted in the precipitation of insoluble carbonates, including calcium. Other deposits of calcium carbonate have been formed by the accumulation of the shells or skeletons of myriads of minute sea organisms. Many of the limestone formations of the world have been formed by such accumulations.

OCCURRENCE

The calcium carbonate formed by these methods has taken different mineral forms. The most abundant of these, limestone, consists essentially of calcium carbonate, or a mixture of the carbonates of calcium and magnesium. When 10% or more is magnesium carbonate ($MgCO_3$), the rock is termed "magnesian" limestone or "dolomitic" limestone, while if the amount approaches 45%, the rock is composed essentially of the double carbonate of calcium and magnesium ($CaCO_3 . MgCO_3$) and this is the mineral dolomite. The principal impurities in limestone are sand (silica SiO_2), clay and iron oxide (ferric oxide Fe_2O_3). Marble is similar in composition to limestone, and can be used in the same processes, while Iceland spar and aragonite are pure forms of calcium carbonate that occur naturally. Chalk is a natural calcium carbonate consisting of the remains of soft, friable minute marine organisms.

The use of lime, made by burning limestone, according to the equation

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

goes back to antiquity. Mortar, a mixture of lime (CaO), water and sand, was used widely in Biblical times. The cement made by burning limestone, and mixing the lime with volcanic ash, was a basic material of construction when Pompeii was built. Limestone itself was used by the Romans to build hundreds of miles of roads. Today, although two-thirds of the calcium carbonate mined is still used for cement, concrete and roadstone, another, and very important, use has been found for it — as a raw material in chemical industry.

INDUSTRIAL CONSUMPTION

Just how necessary calcium carbonate is to industry is realized by very few people, but an examination of facts will show its importance. Materials as diverse as paper and plastics, cement and insecticides are manufactured with calcium carbonate (usually limestone) as one of the basic materials. In 1945, in the United States alone, 49,800,000 short tons of limestone (1 short ton is 2,000 lb) were used in chemical industry, excluding the cement industry. This amount had risen to about 53 million short tons in 1957. Even this does not give the full picture, for in many processes calcium carbonate, once used, can be recovered and re-used. But the importance of calcium carbonate to industry cannot be measured merely by the tonnage used, or its monetary value, because for many industries it is an essential raw material for which it is impractical to use any substitute.

For many industrial purposes, the limestone is first "calcined" to lime. This is usually done in kilns at a temperature of 700 to 800°C, with producer gas or natural gas used as a fuel. The reaction is that already given ($CaCO_3 \leftrightharpoons CaO + CO_2$), a reversible reaction, but one in which the equilibrium lies well to the right, so that practically all the limestone is converted to lime if the carbon dioxide is removed as it is formed. It the limestone used contains magnesium carbonate the additional reaction

$$MgCO_3 \rightarrow MgO + CO_2$$

is involved, and the resultant lime contains magnesium oxide. For many processes this does not matter, in some it is even preferable, but in others the presence of magnesium in the lime is to be avoided, as for example in the calcium carbide industry. This factor, together with the type of impurity present (silica, iron oxide and so on) determines the use to which various grades of limestone may be put.

The calcination of limestone provides the chief industrial source of carbon dioxide. The lime, as either quicklime or in the hydrated form has many industrial uses also. Some of the uses of lime and limestone are described below.

CEMENT INDUSTRY

Probably the most important of these is the Portland cement industry. This process, combining the sciences of geology, mining and chemistry, used 73,976,000 short tons of limestone in the United States in 1958, far more than any other industry. Portland cement is a closely controlled chemical combination of argillaceous materials (clay containing silica and alumina) and calcareous materials (calcium carbonate) with iron oxide and small amounts of other ingredients to which gypsum is added in the final grinding process to regulate the setting time of the cement. Various raw materials may be used as the source of these ingredients. Natural cements are made from argillaceous limestones, where the natural raw materials are found mixed in the correct proportions, which need only grinding and burning in a kiln to produce a cement. The cement known as Portland cement is usually made from limestone containing calcium carbonate and some alumina (Al_2O_3), silica, and ferric oxide as impurities which are necessary for the formation of the desired silicates in the cement (though magnesium is objectionable in limestone for this use), and clay containing aluminium silicates. But to provide the essential ingredients many other materials are used at different plants — oyster shells (calcium carbonate), blast furnace slag (lime, alumina and magnesia), for example.

These raw materials are first ground and mixed, and fed into horizontal kilns (either dry or mixed with water) where they are heated to about 2700°F. As they pass through the kiln, the raw materials unite to form a new substance, known as clinker, with its own physical and chemical characteristics. The clinker, composed of four principal compounds whose exact formulae are still unknown, is then ground with added gypsum to give the cement.

METALLURGICAL USES

Apart from the cement industry, the greatest amount of limestone consumed by one industry is as a flux in various metallurgical processes. Enormous quantities of limestone are used annually as a fluxing material in blast furnaces, open hearth and electric steel plants, and to a smaller degree in non-ferrous metallurgy. Most iron ores carry with them acidic impurities such as silica and alumina. During the reduction process, the addition of a basic flux such as limestone is necessary to remove these impurities. A slag is formed which is separable from the molten metal.

$$CaCO_3 + SiO_2 \rightarrow CO_2\uparrow + CaSiO_3$$

The carbon dioxide comes off with the hot blast furnace gases, and the calcium silicate forms the slag which is tapped off.

It is evident, therefore, that limestone for this purpose should be relatively free from silica and alumina. If more than small percentages of these substances are present, the stone is less effective, increases slag volume and fuel consumption and slows down production. For blast furnace operation, however, the percentage magnesium carbonate is not critical, as magnesium also forms a silicate.

Alumina (Al_2O_3) is also removed by the flux, with the formation of the aluminate.

$$CaCO_3 + Al_2O_3 \rightarrow Ca(AlO_2)_2 + CO_2\uparrow$$

Lime is also sold in large quantities as a fluxing material.

In 1945, in the United States, 30,524,920 short tons of limestone, or the limestone equivalent of lime were sold for metallurgical purposes, and by 1957 this amount had increased to 39,384,000 short tons. Although the steel industry uses by far the greatest tonnage of flux stone, this total includes flux used for copper, gold, lead and zinc smelters.

USE IN THE ALKALI INDUSTRY

Another large industrial consumer of calcium carbonate is the alkali industry (the manufacture of sodium carbonate, Na_2CO_3) in which seven million tons of limestone were used in 1945 in the United States. Sodium carbonate is one of the most important materials used in industry, and for every ton produced, about 1 to 1¼ tons of high-calcium limestone (dolomitic stone is unsuitable) is consumed.

The basic reactions of the Solvay-ammonia process for the production of sodium carbonate are the blowing of ammonia (NH_3) and carbon dioxide through a concentrated salt ($NaCl$) solution, the use of ammonia ensuring that the carbon dioxide dissolves to form the bicarbonate ion. From the resulting solution containing ammonium (NH_4^+), bicarbonate (HCO_3^-), sodium (Na^+) and chloride (Cl^-) ions, the relatively insoluble sodium bicarbonate $NaHCO_3$ is precipitated, and this is heated to produce sodium carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2\uparrow + H_2O$$

From the solution of ammonium chloride (NH_4Cl) left, ammonia (the most expensive reagent) can be recovered for re-use by treating it with lime (CaO)

$$CaO + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3\uparrow + H_2O$$

For this process, then, the calcium carbonate has two uses. It is burned to give lime and carbon dioxide; the carbon dioxide is passed through the salt solution as indicated, while the lime is used in the recovery of ammonia.

THE CARBIDE PROCESSES

Much calcium carbonate is used in the manufacture of calcium carbide, CaC_2 (1,279,000 tons in 1945 in the United States). On hydrolysis, calcium carbide yields acetylene, according to the equation

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$$

Acetylene has found a wide variety of uses, in welding, and as the basis of a large number of organic compounds. The synthetic rubber called neoprene, and several plastics are derived from vinyl chloride, itself a derivative of acetylene.

Calcium carbide is a product of the electric furnace. It is formed when a charge of lime and coke (mixed in the proportion 3:2) is heated to 2000°C.

$$CaO + 3C \rightarrow CaC_2 + CO\uparrow$$

Very pure calcium carbonate is needed for this product, as if phosphorus is present this results in the contamination of the acetylene with phosphine, PH_3. Magnesium should not be present, as it does not form a carbide, and thus renders the process less efficient.

Also manufactured from calcium carbide is calcium cyanamide, made by heating the carbide in a current of nitrogen. This process is chiefly notable for the fact that the cyanamide was formerly the basis for the manufacture of ammonia, one of the most important industrial chemicals. The Haber process displaced the cyanamide process as the basis for the manufacture of ammonia, and very little calcium cyanamide is now produced.

USES IN PAPER MANUFACTURE

Another of the many industrial uses to which calcium carbonate has been put is in the manufacture of paper. Both lime and limestone are used in the paper industry in the preparation of what is known as the "cooking liquor". Wood consists mainly of lignin and cellulose, the second of which is required for the paper making. By digesting the wood chips with an acid liquor, the lignin is dissolved but the cellulose is left unattacked. The liquor most generally used is a hot calcium bisulphide solution, under pressure.

There are two methods of preparing this liquor, both utilizing calcium carbonate. In the milk of lime method, the bisulphite is prepared by passing sulphur dioxide into milk of lime until no further absorption of the gas occurs. This is necessary to ensure that the bisulphite is formed, rather than calcium sulphite, $CaSO_3$.

$$2SO_2 + Ca(OH)_2 \rightarrow Ca(HSO_3)_2$$

If insufficient sulphur dioxide is added, the sulphite is formed, but on the addition of further sulphur dioxide, is converted to the bisulphite.

Milk of lime is the name given to a solution of calcium hydroxide, $Ca(OH)_2$, in which an excess of the hydroxide (only sparingly soluble) is suspended. It is made from lime, by treating it with water.

For this process, a high magnesium limestone is often preferred, as magnesium bisulphite has greater stability, solubility and reactivity than calcium bisulphite. In the second method (the Jensen tower process in which the liquor is produced by passing a stream of sulphur dioxide up a tower packed with limestone) the presence of magnesium carbonate in the limestone is to be avoided, as it breaks down and clogs the tower, thus hindering gas absorption. The essential reaction in this process is:

$$2SO_2 + CaCO_3 + H_2O \rightarrow Ca(HSO_3)_2 + CO_2$$

This industry used 1,375,000 short tons of limestone (or the limestone equivalent of lime) in the United States in 1945; but this is not really a measure of the true amount of limestone used in the paper industry, as an important re-use of lime has been developed, so that a considerable quantity of limestone is used repeatedly. Calcium carbonate is even more important to the paper industry than the figures indicate.

USE IN GLASS MANUFACTURE

The glass industry is another huge consumer of calcium carbonate. In 1957 in the United States an estimated fourteen hundred million dollars worth of glass products were manufactured, and 1,204,00 tons of limestone were used. Either lime or limestone of high calcium or high magnesium content may be used (though it is essential that the sulphur and phosphorus content be low); high calcium limestone is used in making bottle and window glass, whereas dolomitic limestone is used for special glasses. It is essential, however, that uniform stone be used for each type of glass, so that the product has constant physical and chemical properties.

Common glass is made by melting together sand, sodium carbonate (itself largely produced from calcium carbonate) and limestone, or perhaps lime from first calcining the limestone. In practice, a little charcoal is usually added as well, as it gives a better product. To make the constituents melt together more easily and more fully, a certain amount of broken scrap glass is mixed with them. The product after fusion contains a mixture of sodium silicate and calcium silicate with an excess of silica, and is the common soda glass such as is used for windows and glass tubing.

Different types of glass can be made by using different compounds in the fusion process. For example, a harder type of glass is obtained when potassium carbonate is used instead of sodium carbonate. Cupric oxide or cobalt oxide gives a blue glass. But most types of glass contain calcium silicate, and utilize calcium carbonate as a raw material.

MINOR INDUSTRIAL USES

In 1945 in the United States, the cement industry accounted for over half the calcium carbonate rock used in the chemical and processing industries. The other five industries described — metallurgy, paper, alkali, glass and carbide — used 84.3% of the remainder of calcium carbonate used in industry. A further 8% of this was used in processes which depended upon the magnesium content of the rock, and cannot be considered here. This leaves some 3,800,000 tons of calcium carbonate, sold for use in some aspect of chemical industry, unacounted for. This is devoted to a multitude of minor uses, too numerous to go into in any detail. For instance, there is water purification, where either quicklime or slaked lime, $Ca(OH)_2$, is used for purification and softening of municipal water supplies. Hard water is water which contains calcium Ca^{++} or magnesium Mg^{++} ions, whose presence results in an insoluble scum being formed with soap, and temporarily hard water is that which contains the bicarbonates, usually $Ca(HCO_3)_2$. The addition of the correct quantity of lime removes this, forming insoluble calcium carbonate.

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

The manufacture of insecticides, fungicides and disinfectants is another of these minor uses. Calcium arsenate, lime sulphur and Bordeaux mixture (copper sulphate mixed with lime) are all manufactured using lime from calcium carbonate. High-calcium limestone is an indispensable material in the manufacture of cane and beet sugar, being used to precipitate impurities from the juices or syrup, or to precipitate the sugar from impure solutions. Bleaching powder, a mixture of calcium hypochlorite and basic calcium chloride monohydrate, is manufactured from slaked lime and chlorine. This reaction is always accompanied by side reactions, giving other products. Metallic calcium, principally used as a reducing agent in the production of metals like uranium, thorium and chromium, is manufactured from limestone. Though very little metallic calcium is produced, this is a use which has increased markedly in the last few years, and is likely to increase further in the future.

Various grades of lime are used extensively as neutralizing agents. Notable examples are in the manufacture of soap, glue and in petroleum refining, to neutralize organic acids present in the petroleum.

There are innumerable other uses consuming a few hundred to some thousands of tons of calcium carbonate per year; but enough has been said to show the extreme importance of calcium carbonate as a raw material in chemical industry, in spite of its commonplace occurrence. Who can imagine a world without glass, without paper, without steel, to mention but three of the products of calcium carbonate? It is certain, too, that the uses of both limestone and lime should expand as new processes are developed. They are low cost commodities that are likely to replace other materials whenever substitution is possible. Today calcium carbonate is the most vital of all raw materials, 80% of all rock mined containing it, and it is certain to maintain this position in the future.

THIRTY-FOURTH ANNUAL REPORT for the year ending 31st July, 1964

MEMBERSHIP

Membership of the Institute has, during the past year, changed as follows:

New Fellows, 7; New Associates, 64; Resignations, 3; Struck Off, 2.

Dr R. Gardner, Messrs. T. A. Glendinning, K. M. Griffin and G. A. Lawrence were elected to Honorary Fellowship.

Consolidated membership figures for the last three years are as follows:

	1962	*1963*	*1964*
Auckland	124	134	155
Waikato	33	35	38
Manawatu	58	61	73
Wellington	182	185	197
Canterbury	96	103	105
Otago	72	74	83
Overseas	62	67	70
	627	659	721

SUBCOMMITTEES OF COUNCIL

Standing Committee

The Standing Committee of Council has continued during the present year to be concerned mainly with the handling of applications for Associateship and Fellowship.

Journal

Mr Clare has continued as chairman of the Editorial Committee although he has intimated that he will not be able to continue to edit the *Journal* for much longer because of other commitments. The cost of the *Journal* to the Institute has remained almost constant during the period under review.

Examination Committee

The revision of the Regulation dealing with admission to the Associateship by examination is not yet complete but it is hoped to finalize this matter in the near future. The number of candidates still completing the Laboratory Assistants Certificate is falling, and the expenditure on examinations for the Certificate is now rather high considering the number of candidates. This is, however, only a temporary situation.

The National Certificate in Science (Chemistry) courses are now well established and the first technicians to complete the course were awarded their certificates by the Technicians' Certification Authority during the year. During the year, the New Zealand Institute of Technicians has been formed to look after the interests of such workers and improve their standards.

Membership Committee

Dr W. A. McGillivray, Professor R. D. Batt and Dr J. C. Andrews have dealt with a very large number of applications during the year. While the majority of applications fall into standard categories directly covered by the Rules, there continue to be a considerable number of applications which are difficult to assess, and the experience of the members of this committee is invaluable to Council. Professor S. R. Siemon served on the committee during the absence overseas of Dr McGillivray.

INSTITUTE PRIZES

Prizes for 1963 were awarded as follows:

I.C.I. Prize	Dr R. W. Bailey
Morcom Green Edwards Prize	Dr E Wong
Chemical Essay Prize	T. I. Quickenden

CONFERENCE, 1963

The Annual Conference, held at Massey University of Manawatu, was an outstanding success. The attendance at the Conference was one of the highest ever and it seems to be apparent that members favour a "residential" conference when possible. Professor A. E. Alexander from Sydney was the guest lecturer at Conference and subsequently visited most branches before returning to Australia.

OVERSEAS VISITORS

In addition to the visit of Professor Alexander, the Institute supported a tour of New Zealand by Professor P. V. Danckwerts, Shell Professor of Chemical Engineering at Cambridge, who came to this country following a tour of Australia at the invitation of the R.A.C.I.

RULES

During the year, Council resolved to establish the office of Second Vice-President. The view had been expressed that with the reduced number of meetings of Council held each year the President might have had relatively little experience on the Council before assuming office. It is envisaged that the Second Vice-President will normally become First Vice-President, then President, in succeeding years, although the present system of election to all of these offices will be retained.

ROYAL SOCIETY OF NEW ZEALAND

The Royal Society has admitted the Institute as a member-body. This brings to a conclusion negotiations which have proceeded over a number of years, aimed at bringing the Institute and the Royal Society closer together. Financially the Institute loses nothing since the Royal Society has agreed to accept the Institute's expenditure on the *Journal* and the contributions it makes to bringing scientists to New Zealand as satisfying the requirements of the Society's Rules. The closer association should strengthen both bodies and should do much to eliminate the occasional disagreements which have existed in the past.

NATIONAL RESEARCH ADVISORY COUNCIL

During the year, the National Research Advisory Council was set up by the Government and it is pleasing to note that the Institute is well represented on this body which could play an important part in deciding Government policy on research activities throughout the country.

FINANCIAL

The balance sheet, which was published in the August issue of the *Journal*, shows that the Institute is in a sound financial position. There was an excess of income over expenditure of £308 on the year's operations.

S. G. Brooker, *President*
W. E. Harvey, *General Secretary*

CONFERENCE 1964

The 1964 Conference maintained the high standard which members have come to expect of the annual conference. The good attendance (in the 150 region) was probably due in part to interest in the growing research and educational centres at Hamilton; the provision of a detailed programme at the time of enrolment no doubt also helped. For most members, the major interest at Conference is in the main lectures and these were of a very high standard indeed. Space does not permit detailed comment on all of these lectures but the conference committee is to be congratulated on their choice of guest lecturer — Dr J. S. Shannon of Australia. His lecture on mass spectrometry was to many of us the highlight of the conference and his exposition of the organic chemistry used to give a logical relationship between the fragments detected and the postulated structure of the parent compound was lucid and impressive. The research lectures as usual ranged from good to not so good and from broad to narrow interests. This does raise the main problem facing the organizers of conference programmes and possibly suggests the way that these programmes should develop. Short research papers almost inevitably pose the problem of how to get across in the available time an account of the actual research work, together with enough background information to make the paper meaningful to, on average, at least half of the audience. This problem is not so serious in the main papers where the speaker has sufficient time available. One feels, therefore, that the proportion of longer review papers could well be further increased until if necessary they became the dominant part of Conference. Possibly a main paper followed by invited 10 minute descriptions of related current research from each of four or five workers in the field of the main paper might get the best of both worlds. Presumably, more people attend Conference to hear than to give papers and sooner or later some conference committee should face this challenge of a programme dominated by invited review papers.

As usual, scarcely any of the research papers were from chemists in industry and probably only about 15% of those at Conference were from industry. Whether or not this is a desirable feature, and if not, just what should be done about it is another matter which seems worth considerable thought.

Comparison with last year's Conference does suggest that the residential conference has something which is lacking in the usual type of conference where members are scattered through various hotels. It seems a pity that so far few branches are able to aim at a fully residential conference.

The polished ease of Mr S. G. Brooker's various performances has set a high standard for future presidents while his account of a triplet reaction was among the notable research reports presented to Conference. The social activities provided were also well above standard and the Maori concert party provided an appropriate touch of local colour in a branch whose territory covers many of the major Maori tribes.

Apologetic comments about the small size of the University of Waikato seemed unnecessarily frequent. To one returning to Hamilton after an absence of eight years the phrase, "New Zealand's fastest-growing city" seemed somewhat of an understatement. If this university grows at even half the rate of growth of Hamilton it will be some place by the time the next Conference is held there.

—R.W.B.

BOOK REVIEW

A HISTORY OF CHEMISTRY, Vol. IV, by J. R. Partington. Published by Macmillan & Co. Ltd., London, 1964. 1,007 pages. Price £10 10s. 0d.

This is the third of the four volumes of the *History* to appear (Volume I is still in preparation) and covers roughly from 1800 to the beginning of World War 2. Whereas the earlier volumes possessed the romantic fascination of the archaic this one, dealing with the founders of our present concepts has especial interest because it adds personality to names familiar to all chemists, and perspective to the work of these men. The author is not afraid to add personal reference to some with whom he was acquainted.

The arrangement in the first 560 pages (from Volta to Kekule) is based mainly on individual chemists, partly in chronological order but partly under themes of research which engrossed the chief workers in particular periods. The last 400 pages consider the history of Physical, Inorganic and Organic Chemistry as separate units, and there is a final section on Radioactivity and Atomic Structure. The author has obviously had some difficulty in finding a satisfactory structural organization for this immense work and it is easier to pick out inconsistencies than to suggest a better treatment. If one considers the benzene theories for example, there is a section under the chapter headed "Kekule", another under "Organic Chemistry" (Thiele & Hanies) and a third under "Valency" in the final section. Yet herein perhaps lies part of the charm of this whole work, for in seeking such cross references one is diverted through fascinating byways.

Parts of the *History*, dealing with findings or beliefs of a particular man or period, tend to become a catalogue of snippets of information. While this way assists to apportion and proportion the contributions of various chemists it might have been better to sacrifice some detail and expand the discussion of the most significant contributions and biographical comments. Some of the later biographical notes appear to have been very arbitrarily chosen. Although Rutherford's name dominates the section headed Radioactivity he rates only five lines of footnote (less than Moseley and Mellor) whereas Marie Curie is given over 30 lines, and Soddy is given 10, in the body of the text.

There is one major omission — the whole field of Biochemistry. This word does not occur in the index, and hormones, vitamins and nucleic acids are also not listed. F. G. Hopkins is mentioned as the discoverer of glutathione, but Krebs, Kielin, Warburg and Szent-Gyorgy do not appear. Although the subject is young compared with the three traditional subdivisions of chemistry it is interesting to note how much of the early chemistry in this book was associated with study of physiological processes, and an essay on the subject would have rounded out the 20th century section of the *History*. This may sound like carping criticism when Prof. Partington has given so much. It is in fact a tribute to his catholic abilities that one should expect him to cover this field also.

N.T.C.

THE REGISTRY

Fellows

(*Elected August 24, 1964*)

HARVEY, William Edward, M.Sc., Ph.D.(Cantab.), Chemistry Dept., Victoria University of Wellington (Senior Lecturer).

HOWARD, Bernard Hugh, B.Sc.Hons.(Manc.), Ph.D.(Lond.), F.R.I.C., Lincoln College, Christchurch (Professor of Biochemistry).

LAWS, George Frederick, B.Sc., Ph.D.(Lond.), F.R.I.C., Hydatid Research Unit, Medical Research Council, Dunedin (Research Fellow).

SMITH, John Norman, B.Sc.Hons., Ph.D., D.Sc.(Liverpool), Victoria University of Wellington (Professor of Biochemistry).

WILSON, William Joseph, M.Sc., Research Laboratories, Fraser Companies Ltd., Atholville, New Brunswick, Canada (Supervisor By-products Research).

Associates

(*Elected August 24, 1964*)

BELL, Raymond Douglas, B.Sc.Hons.(N.S.W.), Pinchin Johnson & Co. (N.Z.) Ltd., Wellington (Technical Manager).

COSGROVE, Mark McElroy, B.Sc., Spotswood College, New Plymouth (Science Teacher).

CROKER, John Geoffrey Peter, B.Sc., N.Z. Sugar Co., Auckland (Head Chemist, Chelsea Refinery).

DAVIES, Miss Alma Margaret, M.Sc., New Plymouth Girls' High School (Head of Science Department).

DEVEREUX, Ian, M.Sc., Institute of Nuclear Sciences, Lower Hutt (Scientific Officer).

ENGEL, Graham Bernard, M.Sc., M.P.S., Dept. of Pharmacy, Medical School, Dunedin (Lecturer).

GALE, Mrs Muriel Bertha, A.R.A.C.I., Reckitt & Colman Ltd., Auckland (Chemist).

GUNDERSEN, Brian Donald, M.Sc., Watkins Gardinol Chemicals Ltd., New Plymouth (General Manager).

HALL, Rorison Alexander, B.Sc., N.Z. Co-op. Dairy Coy., Matangi (Chemist).

HENWOOD, Charles Raymond, B.Sc.Hons.(Wales), Mana College, Elsden (Head of Chemistry Dept.).

HUBBARD, Peter John, B.Sc.(Lond.), G. W. Wilton & Co. Ltd., Auckland (Technical Officer).

KENNETT, Arthur Cecil, B.Sc.Hons.(Lond.), A.R.I.C., Chemistry Division, D.S.I.R., Auckland (Principal Scientific Officer).

LATTEY, Janet Mary, B.Sc., Patent Office, Wellington (Chemical Examiner).

McEWAN, Murray James, M.Sc., Chemistry Dept., University of Canterbury (Ph.D. student).

McFARLANE, Bruce Galbraith, B.Sc., Hastings Boys' High School (Head of Science Dept.).

MARRIOTT, Rev. Fr. Sydney Francis, B.Sc.(Cardiff), Rosmini College, Auckland (Senior Chemistry Master).

MERZ, Diederich Frederik, Ing.(Agric. Sci., Wageningen), Chemistry Division, D.S.I.R., Petone (Principal Scientific Officer).

PALMER, Ian Robert, M.Sc., John McGlashan College, Dunedin (Teacher).

PAYNE, Derek Gordon, B.Sc.(Lond.), Polymers (N.Z.) Ltd., Auckland (Chief Chemist).

PEET, Nelson John, B.E.(Chem.), Chemical Engineering Dept., University of Canterbury (Lecturer).

ROBINSON, Brian Harford, M.Sc., Chemistry Dept., University of Canterbury (Ph.D. student).

TAYLOR, Michael Eric Upcott, B.Sc., Ph.D.(Lond.), A.R.I.C., Cawthron Institute, Nelson (Research Fellow).

WATKINSON, John Herbert, B.Sc., Ruakura Agric. Research Centre, Hamilton (Soil Chemist).

WILSON, Alaric Neil, B.A., B.Sc., Dip.Ed., New Plymouth Boys' High School (Head of Science Dept.).

WOODHAMS, David John, M.E.(Chem.), Dairy Research Institute, Palmerston North (Chemical Engineer).

Resignations

G. S. Cox; R. A. da Roza; D. L. Stacey.

LIST OF MEMBERS

Request to Institute Members

This year's revision of the *List of Members* will be based on adidtions and changes notified through the Registrar. *Please inform the Registrar immediately of any alterations in degrees, place of employment or professional status which have occurred since the full revision last year.* As the *List* is used extensively by members and committees inaccurate records can cause delay and annoyance to both the users and you.

EDUCATION IN CHEMISTRY

The Registrar is arranging renewal of subscriptions and enrolment of new subscribers to *Education in Chemistry*, published by the Royal Institute of Chemistry. This quarterly journal was reviewed in the April, 1964, issue (page 70) of the *Journal* and has proved very useful to teachers in New Zealand. If you wish to commence a subscription please complete the attached form and send it with the sum of £2 (or £1 10s. if you are an R.I.C. member) to *The Registrar, N.Z. Institute of Chemistry, P.O. Box 1926, Christchurch.* A renewal notice will be sent to existing subscribers.

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L. O. Desborough
Registrar

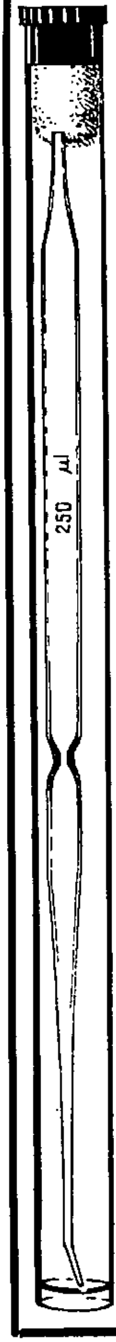
UNIVERSITY OF CANTERBURY

Post-Doctoral Fellowships

Two post-doctoral fellowships will be available in January, 1965, for physical chemists or physicists to carry out research on atomic reactions. The minimum emolument is at present £1,250 per annum, and assistance will be given with moving expenses. Further particulars may be obtained from Dr L. F. Phillips, Department of Chemistry. Applications close with the undersigned on November 30, 1964.

G. G. Turbott
Registrar

Private Bag,
Christchurch.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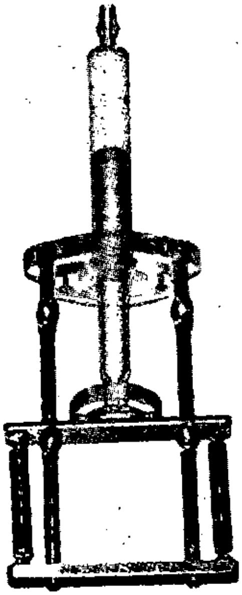

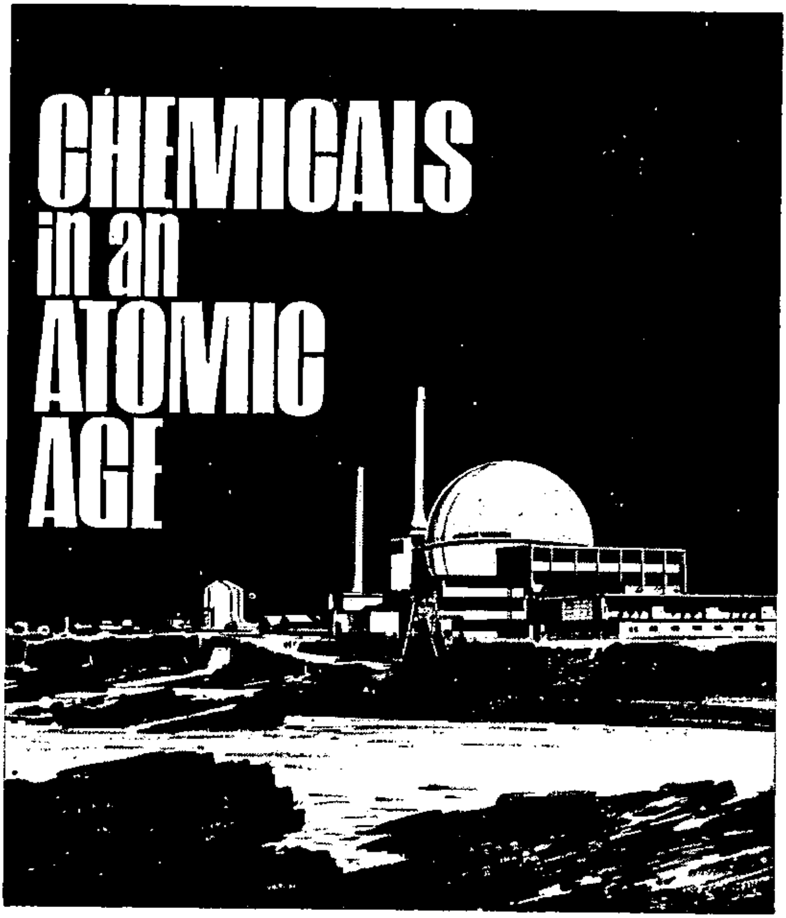
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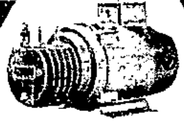

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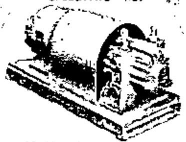

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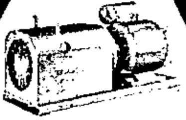

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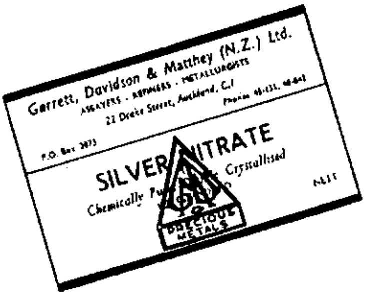
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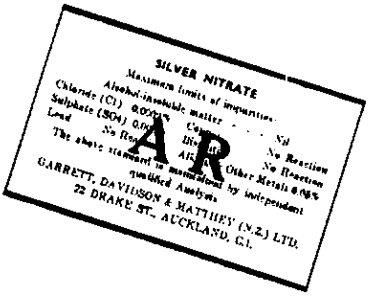
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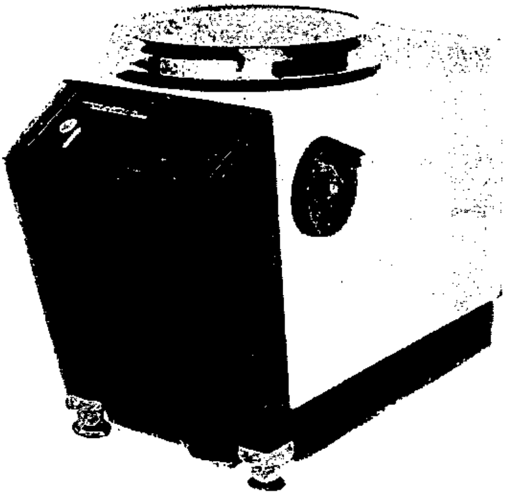

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