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## *The Hon. Robert Boyle*

*was the man who formulated the theory on which all chemical reasoning is based—namely, that an element is the simplest form of matter, and cannot be resolved into other substances. He first stated his theory in a treatise entitled "The Sceptical Chymist", published in 1661. Before that time, scientists had clung to Aristotle's hypothesis, dating back to the fourth century B.C., that the four "elements" were fire, water, earth and air, and that all matter consisted of these in different proportions. Boyle's appreciation of the true nature of an element changed the whole trend of scientific thought.*

*Son of the Earl of Cork, he was born at Lismore Castle, in Ireland, in 1627. At the age of eight, he was sent to school at Eton. Thence he proceeded to Oxford, and spent much of the rest of his life at the university carrying out scientific work which covered a vast field. Among his achievements were the invention of the first efficient air pump, the preparation of methyl alcohol from wood, and the propounding of Boyle's Law, which is still used to describe how the volume of a gas varies with pressure. Before Boyle's time, chemistry was the happy hunting ground of the quack physician and alchemist. His work at Oxford raised it to the status of a dignified branch of natural science. It is not without good reason, therefore, that Robert Boyle is regarded throughout the world as "the father of chemistry"*

*No. 5 in the "Ancestors of an Industry" series inserted by*

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## EDITORIAL

The report of the Consultative Committee on the Scientific Manpower Resources of New Zealand, which has just been published, should be studied by all our members, as a thoughtful and valuable document. Chemists should be especially interested, not only because they were well represented by Messrs. McCombs, Dixon and Andrews, but also because, as the report states, "the subject of greatest numerical importance is chemistry."

To be dangerously brief, the Committee thinks that our scientific manpower resources are more adequate in quantity than in quality, and they make a number of useful suggestions to remedy this defect. One is that there should be a closer relationship between Government and industry on one hand and the Universities on the other, and we like the proposal that scientists from Government and Research Institutes and from Industry be appointed honorary lecturers at the Universities under approved conditions. Another interesting proposal is that our brilliant young men who get first-class honours and overseas scholarships be given short appointments in New Zealand before they go so that they can sample some of our interesting problems to increase their desire to return.

It is to be hoped that this report will be given wide publicity, because it is equally important to the layman as to the scientist in this scientific age. But there is another aspect of some interest. The "Chemical Age" has referred editorially to chemists and public relations in Britain as compared with U.S.A., but we venture to think that in no country are chemists more deplorably served in this direction than in ours. It was not so long ago that a large commercial undertaking had its chemical laboratory destroyed by fire—the press referred to this nerve centre of the concern as a "shed" without qualification. New Zealanders as a whole are not insensitive to science, but, while the whole report is important to the layman, it would be gratifying to us for him to realise that two-fifths of the scientific work of this country is in the hands of our profession.

**SIR NORMAN HAWORTH, Sc.D., F.R.S.**

It was a great pleasure for many of our members to meet Sir Norman Haworth when he visited this country for the Pacific Science Congress. Sir Norman has been a fellow of the Royal Society for many years; he secured the Nobel Prize for chemistry in 1937 for his synthesis of vitamin C in its active form; he was knighted in the New Year Honours, 1947; was President of the Chemical Society, 1944-46, and is still a Vice-President of that body.

Known as the "sugar king" because of his outstanding contributions to the chemistry of this class of organic compounds, Sir Norman announced the cyclic oxide formula in 1926, and on this our present views of the structure of sugars are based. It is less generally known that he made his mark with his researches on the terpenes before turning to the sugars. In this field he was a co-worker with J. L. Simonsen. Sir Norman commenced his career as a student under W. H. Perkin, jun., at Manchester and published his first paper in

association with him in 1906. He retired last year from the Mason Professorship at Birmingham, where he was also head of the Chemistry Department, and is now associated with the Colonial Products Research Council. It was work done in connection with this body that he discussed in his lecture, which we publish in this issue.

Sir Norman has a few contacts with New Zealanders. He was on the staff of Imperial College, London, at the same time as Prof. Robertson, of Victoria College. Prof. F. J. Llewellyn, of Auckland, was associated with him at Birmingham before coming to New Zealand in 1947, and Prof. R. J. McIlroy, until recently of Canterbury College, was one of his pupils.

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## SUGAR AS A SOURCE OF CARBON COMPOUNDS IN INDUSTRY

SIR NORMAN HAWORTH, Ph.D., Sc.D., F.R.S.

Benzol, phenol, plastics, newer fibres, many industrial solvents and detergents, dyestuffs, newer drugs, chemotherapeutic products and photographic chemicals are at present derived from coal and oil. It is well known that accumulations of coal and oil are not inexhaustible and that at our present rate of consumption they will be used up in the not far distant future. We expect that atomic energy will eventually replace coal and oil as a major source of power. Even now we should be considering alternative raw materials for the manufacture of organic compounds. In 1937 attention was directed to the possibility of utilising cane sugar for this purpose. At that time there was an over-production, some 13 million tons of cane sugar of 99% purity being produced in 1938. The price for this in the United Kingdom was £7/10/-, which compared favourably with that of coal and oil. Supplies of cane sugar are renewed year by year and are thereby inexhaustible. The crop is rapidly regenerated. There are large areas of land eminently suited to the cultivation of cane sugar which could not produce other crops of such economic value. Although the recent war has restricted production in sugar-growing areas, this production is rapidly approaching pre-war levels and could be easily expanded to three times the pre-war figure if a market were available. Further, by working with a 30% solution of crude sugar as the raw material, distribution would be simplified and prices further reduced. Cane sugar therefore has all the properties of an excellent raw material.

The question is how can it be utilised? The following will give an idea of the experimental work performed in this direction.

(1) The present most valuable products are alcohol, acetone and butanol. It must be remembered that during the production of alcohol one-third of the carbon is lost as carbon dioxide, whereas in some of the processes to be described there is a more efficient utilisation of the carbon.

(2) Sucrose octo-acetate can be obtained in high yield and is an excellent plasticiser. Sucrose nitrate is manufactured in the form of white crystals and is used as a blasting explosive.

(3) Catalytic hydrogenation of sucrose yields sorbitol (60% yield) and mannitol (30% yield). These can be separated by crystallisation. Manitol nitrate is used as an explosive. Sorbitol is used in the synthesis of vitamin C and as a sweetening agent for diabetics. Sorbitol, on treatment with acid, undergoes dehydration to form a very stable dianhydride which contains two fused furane rings. Methylation of this produces a stable high-boiling liquid which is an excellent solvent. Esterification of the dianhydride with polymerisable acids will produce plastics of the perspex type, and with fatty acids such as linoleic or linolenic acid, will produce drying oils.

The chlorine in sorbitol dichloride, after protection of hydroxyl groups with formaldehyde, can be replaced by amino groups to produce a compound which can be condensed with adipic acid to form a nylon-like product. This reaction has not been completely developed.

(4) A 40% soluton of sucrose heated with calcium oxide at 250° C. gives a 70% yield of pure lactic acid. Lactic asid is a source of a number of compounds, including acrylic acid, which is used in the synthesis of the acrylic resins.

(5) Sucrose autoclaved with hydrochloric acid under the correct conditions gives an 80% yield of levulinic acid. Formic acid is also produced in the reaction. The sodium salt of levulinic acid is a non-corrosive solid and is used as an antifreeze. Levulinic acid on catalytic hydrogenation yields γ–valero lactone. This has a boiling point of 200° C and is a valuable solvent, being miscible with both water and organic solvents. Further reduction of γ–valero lactone yields a glycol which on dehydration yields a methyl butadiene which may be used in the synthetic rubber industry.

Levulinic acid forms condensation products with hydrazine which, by further reactions, can be converted into a number of products which have valuable analgesic properties or, by

coupling with sulphanilamide, can be converted into valuable compounds of the sulphonamide series.

(6) Sucrose heated by itself in 30% solution gives a 40% yield of hydroxy methyl furfural, which is formed from the fructose fraction. This can be reduced to the corresponding glycol, which is a useful industrial solvent, or can be converted to adipic acid, which is used in nylon manufacture.

(7) Certain bacteria (Streptococcus mesenteroides) act upon the glucose fraction in sucrose to form a polymer known as dextran, from which unchanged fructose is readily removed. Dextran is a very clear viscid gum, the viscosity of which can be graded. It can replace many plant gums in industry and is a possible substitute for blood plasma. This property is being investigated at the Lister Institute. It has been found that dextran has little deleterious effect in the blood stream, being hydrolysed eventually to glucose, which is a normal constituent of blood.

With the fructose left in dextran is an excellent syrup, being better than golden syrup for some purposes.

The foregoing by no means exhausts the possible compounds which can be derived from cane sugar. They are merely given as examples of useful compounds which can be derived from raw materials other than petroleum and coal.

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**Mr. B. C. Aston. M.B.E., M.Sc., F.R.S.N.Z., A.N.Z.I.C.**

One of the few scientists to be so honoured, Mr. Aston was mentioned in the last New Year Honours, and we offer our congratulations. Until he retired a few years ago, he held the position of Chief Chemist to the Department of Agriculture, where he did a good deal of work on mineral deficiencies, his most notable achievement probably being the introduction of limonite as a successful large-scale treatment for bush sickness, then believed to be due to iron deficiency. As a keen botanist, many of Mr. Aston's investigations were of a biochemical nature, including (with Sir Thomas Easterfield) the isolation of the poisonous principle of the tutu, investigations of the tinctorial properties of many native plants, and the direction of the work on the mineral content of pastures. He is a past President of the Royal Society of New Zealand, and was Secretary on two occasions. Mr. Aston is unmarried and lives in retirement at Karori, Wellington.

## CONFERENCE, 1949

AUCKLAND, AUGUST 22nd-25th
N.Z.I.C., R.I.C.

Only about half of our members have so far returned the cards sent out, and as hotel accommodation in Auckland is a real problem, the committee would be much assisted in their preliminary bookings if the other 50 per cent would come to light. Be careful to make the appropriate entry about your wife if any; doubts have been raised in our minds by the fact that one single lady has advised that she is bringing a wife!

Registration for the Conference will be on the morning of Monday, 22nd, with the official opening at 11.30 a.m. The following subjects have been selected for symposia:—

Antibiotics.
Utilisation of New Zealand natural resources and Waste Products. (A.M. & V.)
Food Technology.
Structural Methods—X-ray analysis; Electron diffraction; Magnetic susceptibility; Polarography; Infra-red and Ultra-violet Spectroscopy.
Analytical Chemistry.
Surface Chemistry—Flotation of Non-metallic Minerals; Biochemical Applications.
Silicates; Ceramics; Soils.
Chromatography.

Members who are able to contribute papers on any of these topics should advise the Secretary as soon as possible. For the Analytical Chemistry Symposium, short papers are desired, and there will be a place for those not necessary of striking erudition, but conveying useful ideas and tips. In addition there will also be informal discussions for which the subjects of Fuel and Laboratory Organisation have been suggested. Members interested in these, or who can suggest any other suitable subjects, should communicate with the Secretary.

A post-Conference tour of Rotorua, Waitomo Caves and Tongariro National Park will be held if there is sufficient support. Some interesting afternoon excursions and a dinner are being arranged.

G. L. Calnan (Hon. Secretary),
Dominion Laboratory,
Durham Street West,
Auckland, C.1.

# THE CONTRIBUTION BY NEW ZEALAND WORKERS TO THE CHEMISTRY OF PLANTS

## PART I.—INVESTIGATIONS ON PLANTS OF AGRICULTURAL IMPORTANCE

By J. MELVILLE, Plant Chemistry Laboratory, Palmerston North

The dependence of New Zealand's prosperity and high standard of living on her agricultural industry with its very limited range of exportable primary produce has been stressed too often to require further comment. The desirability for diversification of her industry has long been widely recognised, but it would appear that the necessary prerequisites for any major diversification simply do not exist, and there is little reason to believe that the basic pattern of New Zealand's industrial effort will undergo any marked change in the near future. It is therefore natural that, in the huge expansion of scientific services which has taken place in New Zealand during the past twenty years, the major part should have been in those fields with a direct bearing on the efficiency of her primary industries. A large proportion of the country's scientific manpower is directly engaged on problems relating to soil, plant and animal.

In this, the first of the series on the contributions made by New Zealand workers to our knowledge of plant chemistry and plant physiology, an attempt will be made to summarise the investigations of plants of importance to New Zealand agriculture. At the outset it must be emphasised that many hundreds of analyses of pastures and of agriculture crops have been performed by chemists in various research institutions, and that the vast majority have been performed in the course of field trials of one kind or another—fertiliser trials, strain trials, nutrition and husbandry experiments, animal health investigations and many others. In all such cases the field worker has required analytical data (or at least has thought he required them) for a correct interpretation of his field results. It is most unusual that any new principle has been involved or that other than standard methods of analysis have been used, while the emphasis in interpretation has been on the user aspects of the problem rather than on the chemistry of the plant or plants under investigation. This point is considered in somewhat greater detail later, but it is felt that no good purpose can be served by attempting a complete account of the chemical aspects of such trials, and that for agricultural plants only the main conclusions should be given. When this is done the number of papers which deal with the chemical composition and metabolism of agricultural plants and which make a significant contribution to plant biochemical knowledge is relatively small.

### Pasture Plants

The grasslands of New Zealand almost justify the adjective "unique." In no other country in the world does pasture herbage form so important a part of the diet of farm animals—a phenomenon which reaches its peak in the plains and rolling country near the west coast of the North Island, where pasture furnishes practically the whole of the feed consumed by stock. The ability of our grasslands to cater so fully for the feeding of livestock is the main reason why New Zealand farmers are able to produce animal products, and particularly dairy products, more cheaply than their competitors in other parts of the world. It is important to remember also that present production is only a fraction of the potential production of our grasslands, which are certain to play a part of increasing importance in our national economy. It is equally certain that increasing productivity will go hand in hand with increasing knowledge of the chemical composition, metabolism and nutrition of pasture plants.

Agricultural chemists and plant physiologists have, ever since Liebig's day, been largely pre-occupied with the question of whether the nutrient elements absorbed by the plant are adequate to its needs. New Zealand workers have played their part in investigating the nutritional requirements of agricultural plants in general and of pasture plants in particular, and the number of fertiliser trials conducted by the Departments of Agriculture and of Scientific and Industrial Research, by the Agricultural Colleges and by the Cawthron Institute must by now run into thousands. The chemical analyses which have been made on the plant material drawn from a proportion of these trials and from farm pastures throughout New Zealand have enabled some conclusions to be drawn about the efficiency of any particular fertiliser, while they provide a growing body of information on the concentration in the herbage of certain nutritionally important elements under a wide range of root environmental conditions.

Before considering individual elements in detail it is, however, necessary to bring in some aspects of the problem which may at first sight be considered irrelevant in a paper intended for consumption by chemists. The digression is made with the purpose of emphasising the biological complexity of the raw material which the chemist has to handle, a complexity which has far-reaching effects on the interpretation of the mass of available analytical information.

In the first place pastures are never homogeneous with respect to botanical composition, and some idea of the wide variations which occur can be gained from Madden's survey of the grasslands of the North Island. Excluding marsh, swamp, sandhill, etc., Madden divides pastures into ten types ranging from ryegrass-white clover dominant (Type I) to ratstail-Yorkshire fog-Danthonia dominant (Type X). Hardly a single plant of the species in Type X pasture would be present in Type I, while the difference in productive capacity would probably range from about 12,000lb. of dried herbage per acre per annum for the latter to less than 1000lb. for the former.

Samples from both types may be legitimately described as "pasture samples," but it is obvious from this example that analytical results from one pasture cannot be transferred to another without detailed information of botanical composition. Further to the chemist who is interested in plant metabolism and in the way in which the nutrient elements are elaborated and built into the tissue of the plant, pasture samples containing the leaves of even two species are practically useless.

Quite apart from these variations which are related to soil type, climate, topography, etc., marked variations in botanical composition under constant environmental conditions can be brought about by fertilisers. To take the earliest example in which this is clearly illustrated, Doak found a marked decrease in lime content of pasture subjected to fertilisation by ammonium sulphate and then went on to show that the effect could be explained by the encouragement of grasses (with a lime content of about 1%) to the detriment of clovers (lime content about 2% on dry basis.)

The botanical composition of pastures must also be considered in relation to their utilisation, i.e., to the effect of the animals grazing on them. Sheep and cattle show marked preferences for different species in the pasture, and this differential defoliation may result in marked changes in botanical composition; the tramping of pasture plants by animal hooves may encourage one plant, while inhibiting the growth of another; the effect of animal droppings is a factor of great importance in the building of soil fertility, and this in turn has marked results on the composition of the plant association. It is not generally realised that the fertilising capacity of the animal in our higher producing pastures is very much greater than any amount of artificial fertiliser

applied by the farmer. The extent to which these and other factors related to the grazing animal apply in any particular pasture is capable of considerable variation, and stock management, just as much as fertiliser treatment, can produce marked botanical changes.

Purely botanical considerations such as these are essential for the interpretation of analytical results, and a critical review of much of the earlier chemical work is impossible because only the scantiest information on botanical composition is available.

The variability associated with all field trials is another factor which makes the reviewer's task difficult. It is only within the last twenty years that the necessity for replication, randomised layout and statistical interpretation of results has been realised by agricultural workers, and it is impossible in many cases to determine whether effects found by earlier workers are statistically significant or not.

These are relatively recent concepts and their expression in quantitative terms is a matter of the present, the immediate past and of the future. I particularly wish to make it clear that this digression is not made to disparage in any way the work of earlier investigators. Their results, achieved through techniques which would be regarded as incredibly laborious by present-day chemists, laid the foundations for all our present ideas and provided a rational basis for the use of fertilisers. The digression was made to emphasise the necessity for a proper appreciation by the chemist of the biological complexity and variability of his raw material, and to illustrate a few of the difficulties which face the field investigator before he hands over a sample of pasture herbage for chemical analysis. For real progress in the field of pasture chemistry the chemist must think of himself, not as an analyst concerned with the chemical composition of a sample of leaf powder, but as a member of a group of scientific workers who are investigating the infinitely complex biological system of soil, plant and animal.

## MAJOR ELEMENTS

### CALCIUM

Lime has played an important part in raising the productivity of our grasslands, and there are extensive areas which without lime would probably never have been brought into production. Although in many cases lime has been applied in order to bring about changes in the soil to make it more suitable for plant growth, it is only natural that a large number of lime analyses of mixed pasture herbage should have been reported. In this, as in all cases of mineral analyses, the aim is to determine fertiliser requirements by leaf analysis, and it must be admitted that the information available allows only very general conclusions to be drawn. It is felt that no good purpose would be served by quoting results obtained by various investigators on mixed pasture herbage, but the bibliography contains a selection of the more significant contributions by New Zealand workers. Of greater interest to plant physiologists are analyses of pure species dissected from a mixed sward, and the best trial for the purpose known to the author is one initiated by Grasslands Division three years ago and still in progress, on the effect of clovers in mixed swards in the presence and absence of added lime and phosphate. Herbage production has ranged from 1500lb. dry matter per acre per year to 14,000lb., and dissection of the herbage into the main species has been made at each cut, with chemical analysis on three monthly bulkings. Calcium levels in grass (expressed as percentage CaO in the dried sample) range from a minimum of 0.61 to a maximum of 1.17. It is of interest that values over 1% have been obtained only on plots from which clover is excluded and which are botanically more complex than those where clover

forms part of the sward. In the latter case ryegrass is practically the only grass species present, and its lime content varies between 0.61 and 0.98%.

The values for clover are very much higher and range from a minimum of 1.54 to a maximum of 2.45%, and the point may again be made that any management practice which changes the balance between clover and grass in the sward will markedly affect the lime content of the mixed pasture herbage. In this particular trial changes in lime content of each species due to differential liming treatment appears to be of less importance than seasonal variations on any single treatment, i.e., the highest producing plot shows variations with season between 0.66 and 0.99% for ryegrass and between 1.67 and 2.06% for clover. This picture may well be changed on other soil types, and the duplication of this carefully conducted trial at Lincoln and Gore should provide valuable information.

It must be mentioned in closing this section that our knowledge of the role played by calcium in plant metabolism is practically a closed book, and the significance for instance of the higher levels in clovers than in grasses is unknown.

**PHOSPHORUS**

Phosphates enjoy the distinction of being by far the most widely-used fertilisers in New Zealand, and their effect in raising agricultural production have been of almost inestimable value. The general remarks made under "Calcium," however, are equally applicable to phosphate, and the stage has not been reached where analysis of pasture herbage supplies more than a very general answer as to whether a response in production will result from phosphatic fertilisation.

For phosphate levels in individual species dissected from a mixed herbage sample, reference is again made to the Grasslands Division trial. Phosphate levels in ryegrass vary from 0.88 to 1.50% with an average value over all determinations of 1.14%, while corresponding levels in clovers are 0.79 to 1.39% with an average value of just under 1%. Although the species difference is not so great as in calcium levels, it is noteworthy that of the hundred samples under consideration the phosphate concentration in ryegrass is always slightly higher than in clover from the same plot. Seasonal variations are marked and follow a more regular pattern than do the variations in lime content, reaching a peak in the early summer months and declining to a minimum in late autumn.

Differences between plots with and without added phosphate are small but regular for both species. It is hoped that a more marked phosphate response as measured by leaf phosphate levels will be obtained in similar trials on other soil types.

The part played by phosphorus in the metabolism of living cells is much more clearly defined than is that of calcium, and a series of organic phosphorus compounds which are known to be of importance have been isolated. These include the nucleic acids which are of such importance in the composition of cell nuclei, the phosphoproteins such as casein, the phosphorylated sugars which are key substances in the synthesis and degradation of carbohydrates, and phospholipids which are surface active agents of importance in transfer of metabolites through cell membranes. Organic phosphorus compounds which are important in metabolism may be divided roughly into two groups: (1) Those compounds in which the phosphate residue is linked to hydroxyl (as in glucose phosphate) and which hydrolyse with a free energy decrease of 2000-4000 calories per mole. These linkages are known as "energy poor" phosphate bonds. (2) Those compounds in which the phosphate residue is linked to another phosphate residue, to a carboxyl or to a guanidino residue

and which hydrolyse with a free energy decrease of 12,000-15,000 calories per mole. To these the description "energy rich" is given. The conception of "energy-rich" bonds has been extraordinarily fruitful in explaining cellular reactions in which energy must be supplied to the reacting system, and cases have been found where relatively large storage of compounds containing energy rich bonds takes place against future energy requirements by other reactions in the cell metabolic cycle.

Although a number of reactions involving organic compounds of phosphorus have been investigated in plant tissues, there remains an enormous gap which must be bridged before any correlation can be attempted between total phosphate concentration in the leaf and the basic phosphorus requirements of the leaf for its wide variety of reactions. To such fundamental problems the New Zealand worker has contributed nothing.

**NITROGEN**

Plants are by far the most important synthesisers of protein on this planet, and so far as human needs are concerned they are practically the sole source. This sweeping statement should perhaps be amended in one respect in that one family, the **Leguminoseae**, relies on symbiotic bacteria to fix nitrogen from the air within its root tissue. There is, however, no reason to assume that the processes of protein synthesis in this family is markedly different from that in other plants: the difference lies in the way in which the nitrogen is absorbed by the roots. In any case it is hardly surprising that the study of nitrogen metabolism of plants has been vigorously pursued by chemists in many countries of the world.

The high production pastures of New Zealand are extraordinarily efficient protein producers. Up to 3000lb. of protein per acre per year have been recorded on pastures at Palmerston North, which is equivalent to saying that the plants of the sward absorb up to 550lb. of nitrogen per acre through their roots. It is remarkable, in view of this figure and of the low nitrogen supply in the soil, that only the smallest amounts of nitrogenous fertilisers are used for pasture top-dressing. The explanation lies in the clovers, which are an essential component of all high-producing pastures. A collaborative investigation by grass-clover relationship in high production pastures has been in progress for some years, and the following brief summary gives the conclusions which have been reached:—

(1) Grass plots from which clover is rigidly excluded will produce, under mowing and without nitrogen fertilisation, about 1500lb. dried herbage per acre per year with an average nitrogen content of about 2.2%. Nitrogen is the limiting factor, and by the application of artificial nitrogenous fertilisers production can be increased to over 10,000lb. with an average nitrogen content of over 4%.

(2) Grass and clover plots produce under the same conditions about 10,000lb. dry matter, to which grass contributes about 3000lb. with a nitrogen content of 3.5%. Hence not only does more grass grow in association (and incidentally in competition) with clover, but the percentage of nitrogen in the grass component is markedly increased. The relative yields of protein from grass are equivalent to 33lb. and 105lb. N respectively, and the only possible conclusion is that there is considerable underground transport of nitrogen from legume to non-legume. The agents through which this transference occurs and the biochemical processes involved are matters of present concern to both institutions.

(3) Under grazing conditions where dung and urine, almost equivalent in nutrient elements to the pasture consumed by the animals, are returned to the pasture, yields of 13,000-15,000lb. dry matter are obtained, to which grass

contributes 10,000lb. with an average nitrogen content of over 4% The nitrogen content of clover in this treatment, as in the previous one, ranges between 4.4 and 5.8%. Thus the percentage of grasses has changed from 30% where animal residues are not returned to over 70% where they are returned. Nearly all the nitrogen necessary for this enormous grass growth comes originally from the clover in the sward, but the nitrogen, through the intervention of the animal, is used again and again by the grasses in the association.

This summary gives only the barest essentials for a proper understanding of the nitrogen cycle in pasture, but it provides a rational approach to the interpretation to be placed on the numerous total nitrogen values quoted in the literature. It gives no indication, however, of the processes whereby nitrate, ammonia and, in the case of legumes, the primary products of atmospheric nitrogen fixation are converted into protein. This problem is one which has occupied a great deal of our time in Palmerston North during the past ten years, and although our real interest has been physiological, a disproportionately large part of the expanded effort has gone into investigations of methods of analysis. Of the dozens of water soluble nitrogenous compounds which are known or presumed to be present in leaves, only two, viz., nitrate and ammonia, can be accurately estimated on a routine basis. Even with the latter grave doubts exist as to the accuracy of many of the published values because insufficient attention has been paid to the way in which the extract was prepared for analysis.

Glutamine and asparagine, the amides of the dicarboxylic amino-acids glutamic and aspartic, are recognised as key compounds in nitrogen metabolism. Any sudden influx of ammonium into the plant, whether by absorption through the roots or by degradation of protein synthesised by the leaf, has an immediate effect on the amide levels in the leaf. Estimation is by differential hydrolysis of the amide group, and ample evidence has accumulated that under certain environmental conditions such indirect estimations are subject to gross errors of unknown origin. Work is directed at the moment to the development of entirely independent analytical methods, and our aim is to have at command two and perhaps three methods which can be applied to these compounds.

As a result of work carried out in Palmerston North during the past two years, a third amide, urea, has been added to the list as a normal metabolite in plant tissue, but the part played by urea in nitrogen metabolism is still obscure. The work has one particularly interesting phase; we have found that urea is very rapidly absorbed from soil by grass plants, and that within a few hours of application marked increases in leaf urea levels take place. This is in direct contradiction to the usually accepted doctrine that ammonia and nitrate are the only nitrogenous compounds absorbed by plants, and is of particular interest when it is remembered that more than half the nitrogen excreted by stock is in the form of urea. The extent to which urea is directly absorbed by pasture plants from a urine patch is a matter of considerable practical and theoretical importance.

Of the water soluble nitrogen in green leaf tissue, about half is due to the amino nitrogen of amino acids. Amino-nitrogen figures for a variety of tissues are available in world literature, but reliable figures for single amino acids simply do not exist, largely because only within the last ten years have techniques become available for their detection and estimation. This problem is being vigorously pursued at Plant Chemistry Laboratory, and results to date indicate that the amino acid pattern within the leaf protein complex is quite different from that of the soluble amino nitrogen fraction. In the latter glutamic acid, aspartic acid, glutamine and asparagine usually account for more than 70% of the total.

The story of our ignorance can be extended by pointing out that a considerable portion of the soluble nitrogen of plant sap is not characterised even into rough groups, but sufficient has been said to indicate how far we are from an understanding of the chemical composition of green leaves. How much further we are from any understanding of mechanism of this vital synthetic process may safely be left to the reader.

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**EFFECT OF THE GRAZING ANIMAL:**

P. D. Sears and R. P. Newbold: The Effect of Sheep Droppings on Yield; Botanical Composition and Chemical Composition of Pasture. N.Z. Jour. Sci. and Tech. **24**, 36A (1942) and continuation in press.

**NITROGEN STUDIES:**

I. Reifer: Several papers in N.Z. Jour. Sci. and Tech. between 1939 and 1948.

I. Reifer and J. Melville: The Source of Ammonia in Plant Tissue Extracts Part II. The Influence of Urea. J. Biol. Chem. in Press.

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IMPERIAL CHEMICAL INDUSTRIES PRIZE: Attention is drawn to the closing date for this prize—30th of this month. For conditions of award see our December issue, p. 131.

## THE EIGHTEENTH ANNUAL REPORT
## FOR THE YEAR ENDING OCTOBER 31st, 1948

In this Annual Report, Council wishes to submit to members a brief record of the year's activities from November 1st, 1947, to October 31st, 1948.

OFFICERS FOR THE YEAR:

President: Dr. J. K. Dixon.

Vice-President: Professor J. Packer.

Delegates: Auckland—S. G. Brooker. Wellington—J. L. Mandeno. Canterbury—F. H. G. Johnstone. Otago—Dr. S. N. Slater and O. H. Keys.

Hon. General Secretary-Treasurer: W. G. Hughson.

**MEMBERSHIP:** Membership figures over the last three years are shown in the following table:—

| | 1946 | 1947 | 1948 |
|---|---|---|---|
| Auckland | 75 | 71 | 76 |
| Wellington | 113 | 122 | 132 |
| Canterbury | 46 | 51 | 55 |
| Otago | 43 | 47 | 44 |
| Overseas | 25 | 29 | 40 |
| | 302 | 320 | 347 |

**ELECTION OF HONORARY FELLOW:** Emeritus Professor F. P. Worley has been elected an Honorary Fellow of the Institute in recognition of his services as founder of the Auckland Chemical Society and his early interest in the New Zealand Institute of Chemistry. He is also a past President of the Institute and has given valuable service to the profession of Chemistry in general.

**ON LEAVE:** Leave was granted to the following members temporarily overseas:—Messrs. R. V. Perryman, G. B. Beath, S. J. Bennett, P. A. Ongley, W. I. Taylor, J. C. Dacre and W. S. Metcalf.

**RESIGNATIONS, ETC.:** Dr. P. R. McMahon and Messrs. H. S. Gibbs, F. N. Fastier, T. A. Pressley and B. W. Collins have resigned and the names of Messrs. S. C. Denham, W. Moss and J. W. Shiels have been removed from the Register.

**OVERSEAS MEMBERS:** Our membership overseas is increasing and we now have 18 members stationed overseas and 22 members temporarily overseas or on leave.

**APPOINTMENT OF REGISTRAR:** The Registrar has now completed his second year of office and it has been found that the clerical work of the Institute is quite extensive and time-absorbing.

**GENERAL WORK OF THE INSTITUTE:** As in past years, we are indebted to a large number of our members for voluntary work on behalf of the Institute.

**CONFERENCES:** The Annual Conference was held in Dunedin at the University August 24th-27th, 1948. It was splendidly organised and was most successful from every point of view. Conference 1949 is planned for August 22nd-25th in Auckland.

**CHARTER:** A special committee spent a considerable amount of time collecting and examining information relating to charters, and a special report was recently submitted to Council for consideration.

**EMPLOYMENT REGISTER:** Circulars have been sent out regularly, and altogether 124 vacancies in New Zealand and Australia have been notified. Members of the Institute requiring staff could make more use of this register.

**EXAMINATION COMMITTEE:** This is one of our most active Committees, and they are assisted by a number of voluntary examiners and supervisors, who prepare theoretical and practical examinations for Laboratory Assistants to sit each November. This examination is recognised by the Public Service Commission and has been used as a basis for the organisation of examinations for other groups of technical assistants. This year there was twenty applicants sitting forty-three subjects (including four from the optional group). To date three certificates have been awarded.

**JOURNAL:** Journal Headquarters have now been transferred from Christchurch, where Dr. Parton was Editor for eight years, to Auckland, where Mr. S. G. Brooker and his Editorial Committee have now completed a year's activities. Future policy is fraught with possibilities, and one of the main aims in view is the more frequent publication of the official organ of the Institute.

**MEMBERSHIP COMMITTEE:** This important Committee, consisting of three Senior Fellows, has deliberated on the applications made for enrolment as Fellows or Associates. Recommendations have been made for the election of one Honorary Fellow, three Fellows and thirty Associates. Leave of absence has been granted to Professor L. H. Briggs, a member of the Committee, during his absence abroad, and his place is being taken temporarily by Professor J. Packer, President-elect for 1949.

**SALARIES:** The Institute for some years has taken an active interest in the salaries paid to Chemists, and information collected last year covering all branches of Scientific work has been a valuable store of information. This year it was decided to issue another questionnaire to all members, and the results were arranged and reported on in such a way as to give the maximum amount of information. A summarised report appeared in the June Journal and another statement on salaries paid to Industrial Chemists appeared in the December issue.

**STANDARDS INSTITUTE:** Our Institute is represented both on the Council of the Standards Institute and on a profusion of chemical committees or committees on which it is desirable to have a chemist. This work involves the expenditure of a considerable amount of time attending meetings and deliberating on specifications.

**STANDARD METHODS:** The determination of Standard Methods of analysis in various New Zealand Laboratories dealing with similar materials was commenced in 1945. There are now a number of sub-committees dealing with specific sections such as animal tissue, plant materials, soils and fertilisers. A number of methods have been reviewed and the results published in the December Journal, 1947. Further detailed work is being continued on particular problems, viz., minor elements, quick tests, animal feeds and residues. Membership of each Committee is confined to those Institutions actually working in that special field.

**FOOD PARCELS:** We are pleased to be able to say that the Institute has continued to dispatch regular parcels to members of the Royal Institute of Chemistry benevolent group in Great Britain, and the fact that every parcel is so gratefully acknowledged amply repays us for our efforts.

**CONTRACTS FOR SERVICE:** Attention is at present being given to the possibility of preparing a "Contract of Service" in order to define the relations between a Chemist and his employer. This, we feel, will be of particular interest to young chemists.

**UNION REGISTRATION:** The position of chemists in relation to particular Unions has been discussed with various Government officials. It is felt that Chemists are generally advisory to, or part of the management, and should not be members of the Workers' Union.

**U.N.E.S.C.O.:** Mr. Nash, nominated by the New Zealand Institute of Chemistry and the Department of Scientific and Industrial Research, has been appointed to the National Commission for U.N.E.S.C.O. in New Zealand and is maintaining a general interest in activities, particularly the Scientific work. We were fortunate in that Mr. Nash, a past General Secretary of the Institute, attended the Mexico Unesco Conference on behalf of the New Zealand Government.

**PATENT LAW AMENDMENTS:** This matter has been under consideration during the year, and we have studied various aspects of the regulations relating to Chemical substances and processes. A number of our chemists are closely interested in these regulations and we may find it necessary to consider further action.

**A.N.Z.A.A.S.:** The Annual Meeting of the Australian and New Zealand Association for the Advancement of Science is regularly attended by a number of New Zealand Scientists and generally by three representatives of our Institute. Three members will officially represent the Institute at the Tasmanian meeting in January, 1949, and a number of other members will be submitting papers.

**OTHER EMPIRE INSTITUTES:** Mostly by interchange of Journals and Publications we have maintained interest in the Royal Institute of Chemistry of Great Britain and Ireland, and in the Australian and Canadian Institutes. We are indebted to these Institutes for the regular supply of information regarding proceedings and general activities.

**NEW ZEALAND SECTION OF R.I.C.:** A large number of our activities are undertaken as joint efforts of our own Institute and of the local section of the Royal Institute of Chemistry, e.g., the Annual Conference and certain sub-committees dealing with methods of analysis, Employment Register, etc.

**INSTITUTE PRIZES:** The Industrial Chemical Essay will be awarded next in 1950 and will be of the value of £25. A prize of 25 guineas has been offered by Messrs. Imperial Chemical Industries (N.Z.), Ltd., for original published research and the offer has been accepted by the Institute. The prize will be awarded for the first time in 1949 (closing date April 30th), and the regulations governing the prize will be published in the Journal.

**FINANCE:** The Balance Sheet shows another successful year, but very careful consideration of the financial policy is still necessary. The cost of the Journal was helped this year by a refund of £70/19/3 from sales tax which should not have been charged over the last few years. For various reasons Conference expenses this year were light and a surplus of £68/10/- resulted. Printing of the List of Members cost £33/7/-.

## THANKS

Our thanks are due to all officials of the Institute and to many others who have occupied acting-positions or have assisted sub-committees, especially supervisors and examiners for the Laboratory Assistants' Examinations.

Our special thanks are again due to Mr. W. A. Joiner for inscribing all membership and examination certificates.

For and on behalf of the Council:

J. K. DIXON, President.

W. G. HUGHSON, Hon. General Secretary.

## NEW ASSOCIATES

BAKER, Owen John, M.Sc. (1946).—After a period with N.Z. Farmers' Fertiliser Co., Ltd., Mr. Baker is now Assistant Chemist, Coal Survey Section, Dominion Laboratory, Wellington.

BROOKER, Edgar George, M.Sc. (1947).—Assistant Chemist, Fats Research Laboratory, D.S.I.R., Wellington.

CAMDEN-COOKE, Alison Peevor, B.Sc. (1946).—Miss Camden-Cooke spent a year with B.A.L.M., and is now at the Dominion Laboratory, Wellington.

CAVERHILL, Alan Ryton, M.Sc. (1947).—Junior Lecturer in Chemistry at Victoria University College since January, 1947.

CHAPMAN, Lewis Peter James, M.Sc. (1948).—After war service as Meteorological Officer at various R.N.Z.A.F. stations, Mr. Chapman completed his M.Sc. degree in 1946 and joined the Dominion Compressed Yeast Co., Ltd., Auckland.

DOLBY, Richard Malcolm, M.Sc. (1928)., Ph.D. (Lond.).—Dr. Dolby joined the Dairy Research Institute, Palmerston North in 1928. He is now engaged on Research work on the chemistry of butter and cheese making and other dairy subjects.

HURST, Frances Blackie, M.Sc. (1947).—Assistant Chemist at the Soil Bureau, Wellington.

HURST, Frank, M.Sc. (1946).—After a year at the Wheat Research Institute, Mr. Hurst joined the Dominion Laboratory, Christchurch.

MONIGATTI, John David William, M.Sc. (1947).—Mr. Monigatti spent four years at the Soil Bureau, Wellington, and is now Agricultural Chemist at the Ruakura Animal Research Station, Hamilton.

MURRAY, James, M.Sc. (1946).—Mr. Murray has been Assistant Lecturer in Chemistry at Otago University since 1946.

NICHOLLS, Gordon Alfred, M.Sc. (1947).—Studying for his Ph.D. at the Auckland University College.

POLLARD, John Scott, B.Sc. (1945).—After qualifying for the Canterbury University College Diploma in Industrial Chemistry, Mr. Pollard was appointed Assistant Chemical Engineer at the Dominion Laboratory, Wellington.

ROSS, Desmond Joseph, M.Sc. (1946).—Joined the Dominion Laboratory in 1941 and in 1945 was appointed Junior Organic Chemist.

ROTHBAUM, Henry Peter, M.Sc. (1947).—After completing his degree, Mr. Rothbaum joined the staff of the Dominion Laboratory, Wellington, (Physical Chemistry Section).

SEARLE, Ernest Johnstone, M.Sc. (1934).—Science Master at the Auckland Grammar School since 1932.

SEWELL, Owen Keith, M.Sc. (1947).—Assistant Chemist at the Galloway Laboratory, Ruakura Research Station, Hamilton.

SPROTT, Thomas James, M.Sc. (1947).—Has had experience with Mr. L. S. Spackman, A.N.Z.I.C. (Public Analyst), and is now Ph.D. student at Auckland University College.

TING, Ivor, M.A. (1946).—Assistant Chemist at the Fats Research Laboratory, Wellington.

## CATALYTIC HYDROGENATION

W. G. H. EDWARDS

**(A lecture delivered to the Otago branch)**

The reaction of organic compounds with hydrogen in the presence of a catalyst has developed from a chemical curiosity of limited scope to a valuable tool of organic chemistry and a useful industrial process. In 1863 Debus found that when hydrocyanic acid and hydrogen were passed over hot nickel, methylamine was obtained. The implications of this were not fully grasped until in 1897 Sabatier and Senderens began their researches on vapour phase hydrogenation. They found that a great variety of organic substances could be reduced by passing their vapours, mixed with hydrogen, over a nickel catalyst at about 300° C.

This procedure has limitations: it can only be applied to volatile substances, the starting material and product must be reasonably heat-stable, and the hydrogenation cannot easily be controlled (e.g., ketones give traces of hydrocarbon as well as alcohol). An important practical application was in hardening liquid fats, a process fully developed by the beginning of the 1914 war, but the real value of Sabatier's work lies in the stimulus it gave to research in the fields of catalysis and hydrogenation. Immediately following this work came the use of noble metal catalysts for liquid phase hydrogenation, associated with the names of Willstatter, Skita and Paal. This in turn gave rise to the modern technique of hydrogenation developed by Adkins, Adams and others. The method is simple. The substance to be hydrogenated was dissolved in a suitable solvent, a catalyst added and the whole shaken in hydrogen gas. The best solvent was, and still is, acetic acid, which usually provides a faster and more effective reduction than other solvents, though it is only of value for noble metal catalysts. Among the reductions carried out are olefins to paraffins, aromatics to cycloparaffins, aldehydes and ketones to alcohols, nitro-compounds, oximes and nitriles to amines.

Unfortunately, at this stage a number of factors prevented catalytic reduction from competing seriously with chemical methods. The most important of these was the difficulty in preparing catalysts of a reproducible degree of activity. The preparation itself was tedious and sometimes hazardous, owing to the tendency of colloidal platinum and palladium to promote oxidation of organic materials. Perhaps the most successful of the early methods was due to Skita, who introduced the use of gum arabic as a protective colloid for the finely-divided metal catalyst. This was effective in both acid and alkaline media, and a palladium-gum arabic catalyst is still used to-day.

The second serious defect of the method as it then stood lay in the sensitivity of the catalysts. Minute traces—only a few parts per million—of such elements as sulphur or arsenic rendered a catalyst useless.

Finally, some reductions were extremely slow and there was no way of increasing their rate.

The development of catalytic hydrogenation after this point is substantially the progressive removal of these difficulties. The difficulty in preparing these noble metal catalysts, coupled with the development of fat hardening, focussed attention on the use of nickel for liquid-phase hydrogenation. Progress in this field was facilitated by research into pressure reactions, for which Ipatieff was largely responsible. As equipment developed, it became possible to carry out hydrogenations at present of 50 to 200 atmospheres. This much affected the rate and course of hydrogenation, and made feasible the use of nickel catalysts which are usually slow-acting at atmospheric pressure. A finely-divided nickel was produced by heating nickel formate or carbonate in a suitable solvent with hydrogen under pressure; another method was to reduce

kieselguhr impregnated with nickel nitrate in the same way. With the application of new techniques and equipment, progress was rapid, and to-day we have a wide range of catalysts and reaction conditions, with every facility for carrying out reductions rapidly, cleanly and easily.

Between 1925 and 1927 the two most effective present-day catalysts were discovered, namely, platinum oxide (Adam's catalyst) and Raney nickel. In platinum oxide we have the answer to the preparative difficulty of noble metal catalysts. Chloroplatinic acid or ammonium chloroplatinate is fused with sodium nitrate, and the salts extracted with water, leaving the brown oxide. This may be reduced before use with hydrogen, or better, reduced in the presence of the unsaturated compound. It should be mentioned that in the writers' experience Adam's catalyst has never worked in alkaline solution, and indeed under these conditions it did not even reduce to the metal. Sodium benzoate has been reduced using this catalyst, but all excess alkali had to be neutralised first.

Raney nickel is produced by the action of alkali on a 50% Ni-Al alloy. The aluminium is dissolved, leaving a grey nickel powder which is highly reactive. To be most effective, however, it must be used under pressure, although elevated temperature is not always essential. Acetone, for example, can be smoothly reduced by Raney nickel at atmospheric temperature and 30 atmospheres pressure. The aromatic nucleus in benzene requires higher temperature and pressure, but polycyclic hydrocarbons reduce under less vigorous conditions.

Raney nickel has two special uses which make it an invaluable catalyst. The first is its value as an amination catalyst. When aldehydes or ketones are treated with ammonia and reduced with hydrogen in the presence of Raney nickel, amines result. The reaction is probably:

$$RR'CO + NH_3 \longrightarrow RR'C = NH + H_2O$$

$$RR'CH.NH_2 \longrightarrow RR'C = NH + H_2$$

Unfortunately there is a tendency towards formation of secondary amines, which may represent 40-50% of the products, and in practice this is appreciably reduced by using 5—6 times the theoretical amount of ammonia. The yield of primary amine may then be of the order of 90-100%. It has been reported that if a Raney cobalt is made in the same way as Raney nickel, the proportion of secondary amine formed is much less, but experiments carried out in London did not bear out these assertions. The conditions required in the case of cobalt are, moreover, much more drastic than those for nickel—about 100° and 50-100 atmospheres. The reduction of nitrites to amines may be mentioned here.

This may be carried out at 20—60° and 20—30 atmospheres using Raney nickel, but here again it is necessary to have about 5 mols of ammonia present to minimise secondary amine formation. This indicates that the molecules responsible for the formation of the secondary amine is the imine:—

$$RR'CH.CH=NH + RR'CH.CH_2NH_2 \longrightarrow RR'CH.CH=N.CH_2.CHRR' + NH_3$$

The addition of ammonia suppresses this reaction. An interesting example of the amination process is in the hydrogenation of glucose in the presence of excess methylamine in methanol solution. At 60° and 30 atmospheres pressure the product is N-methylglucamine, a solubilising base favoured in certain pharmaceutical preparations. A further example is afforded by the preparation of 1-methyl-4-diethylaminobutylamine, used in the production of such antimalarials as pamaquin and mepacrine and made by amination of the ketone diethylamino-4-pentanone.

The second special application of Raney nickel is its use as a hydrogenation catalyst in the absence of gaseous hydrogen. Within the last two years

investigations by R. Mozingo and co-workers in the U.S.A. have shown that certain groups can be reduced by refluxing the compound with an excess of Raney nickel in alcoholic or aqueous solution. The hydrogen for the reduction is present in an adsorbed layer on the nickel. The proportion varies according to the method of preparation, but in the best samples the composition corresponds approximately to $Ni_2H$. The most useful application of this method is in removing the sulphur, thus—

$$CH_3COSH \xrightarrow{[H]} CH_3CHO \qquad HS.CH_2.COOH \xrightarrow{[H]} CH_3.COOH.$$

There are also reports that Raney nickel will act as a catalyst in the Cannizzarro reaction.

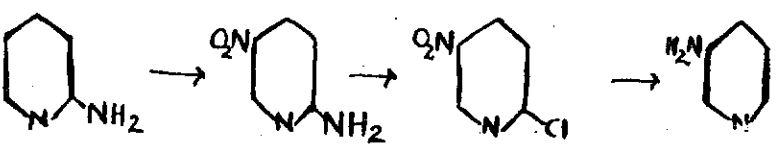
In reducing an unsaturated acid a very good method is to add the Raney Ni-Al alloy to an alkaline alcoholic solution of the acid; thus 3:4:5-trimethoxycinnamic acid is readily reduced by this method, the product being obtained by filtering and acidifying the reaction mixture.

Adam's platinum oxide is of great use for a variety of hydrogenations, particularly for those who are not fortunate enough to have an autoclave, since its activity is not so much influenced by pressure as in the case of Raney nickel. The extent of its action may sometimes be influenced appreciably by suitable choice of solvent. Thus it was found that p-hydroxybenzoic acid in glacial acetic acid solution gave chiefly cyclohexanecarboxylic acid, whereas in neutral aqueous solution a 50% yield of 4-hydroxy-1-cyclohexane carboxylic acid was obtained. Adam's catalyst is not very suitable for amination, though it will reduce imines quite satisfactorily. An interesting property of Adam's catalyst is its activiation by acids, traces of HCl or HBr increasing its activity very considerably.

There are certain palladium catalysts which are of great value in hydrogenation. The first and oldest is palladised charcoal, obtained by shaking in hydrogen a suspension of charcoal in palladous chloride solution. Its use may be illustrated by the preparation of aminomalonic ester, large quantities of which were required in connection with the synthetic penicillin project. It is made by reduction of isonitrosomalonic ester.

It is not, I think, generally known that with careful use palladised charcoal will act as a selective catalyst. In connection with some work on substituted stilbenes, an attempt was made to reduce 2-nitro-4-cyanophenylacetic acid to the corresponding 2-amino compound. Adam's catalyst reduced the nitrile group also, but this could be avoided by the use of palladised charcoal. Subsequently 2-nitro-4-cyanophenol was similarly reduced.

The second catalyst is palladised calcium or strontium carbonate, made by addition of freshly-precipitated alkaline earth carbonate to palladium chloride solution and heating. The chloride hydrolyses and the hydroxide deposits on the surface of the carbonate. It is used as such, being reduced in situ. Its particular value is in dehalogenation. For instance, the only really satisfactory route to 3-aminopyridine is as follows:—



The last stage is a reduction using a $Pd/SrCO_3$ catalyst. This catalyst has been used in the absence of hydrogen by Sir R. Robinson and co-workers, who merely reflux the halogen compound with the catalyst in the presence of hydrazine, which acts as the reducing substance.

The third catalyst is palladised barium sulphate, made in the same way as the last. Its use is in the reduction of acid chlorides to aldehydes in a high-boiling solvent (e.g. xylene). The catalyst must be selectively "poisoned" by "sulphurised quinoline." Recent work has improved on this by using Adam's catalyst with thiourea as "poison."

The last of these palladium catalysts are the truly colloidal preparations. These originated with Paal and Skita, but recently noble metal sols stabilised by polyvinyl alcohol, polyvinyl acetate and methyl methacrylate have become available. Here the palladium hydroxide is precipitated in the presence of the appropriate solution, giving a golden-yellow to brown liquid. This is a valuable catalyst in that it is extremely resistant to poisoning, and may be used in reducing compounds containing the thiol or disulphide link.

Finally, a catalyst which deserves some mention is the so-called copper chromite. This is actually a complex catalyst which contains barium as well as copper and chromium. It has the property of reducing the CO group in esters and amides. It requires about 200 atmospheres and 100-200° for this purpose, and under such conditions readily attacks any other reducible parts of the molecule. Thus p-hydroxyphenyl acetic acid will give cyclohexyl carbinol, although the first step is apparently reduction of the carboxyl group. An outstanding example of its use is in the preparation of the nylon intermediate hexamethylene diamine by reduction of adipic diamide.

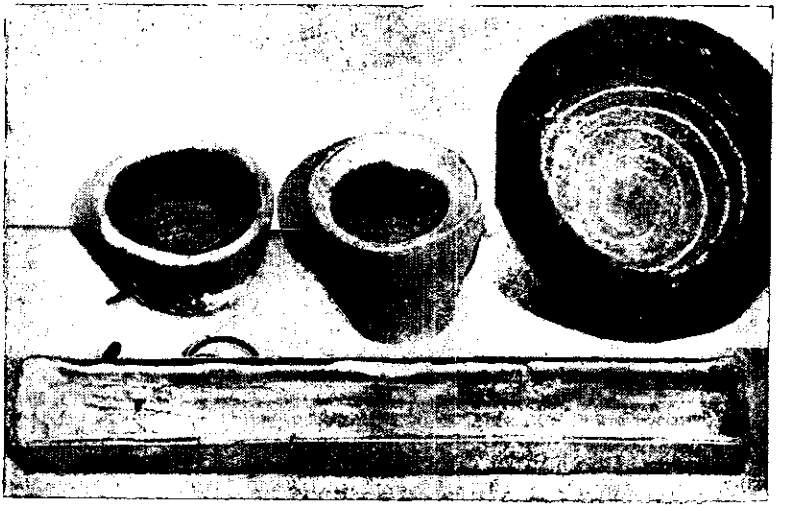
In such a review as this it is inevitable that many useful applications of catalytic hydrogenation should be omitted by reason of space, and it would be desirable to mention the use of Raney iron catalyst for selective reduction of acetylenes to olefines, the value of quantitative hydrogenation as a guide to the elucidation of structure, and the application of many of the catalysts referred to as dehydrogenating agents. However, catalytic hydrogenation as a reliable and versatile tool of the organic chemist and the manufacturer needs no additional emphasis, and it should maintain its position for a long time to come.

## A VERSATILE METHOD OF CONSTRUCTION FOR LABORATORY ELECTRIC HEATERS

M. S. BUTLAND

This article describes the construction of Electric Heaters which have proved very useful over a number of years in this laboratory. Constructed from readily-available materials, they are adaptable to heating any manner of non-conducting vessels and may be controlled conveniently by heavy duty, continuously variable resistances.

For example, to fabricate a heater for 1 litre R.B. flasks, one is turned upside down and wound roughly with 1in. diameter asbestos lagging rope, commencing from the bottom centre of the vessel and following its contour until an inverted hemispherical "bird's nest" is formed, enclosing the lower five-eighths of the vessel. This is then unwound and a strand of ⅜in. diameter asbestos lagging rope is cut to a length equal to that of the 1in. rope, less twice the maximum circumference of the flask. On to the ⅜in. rope is then wound the element, consisting of a length of nichrome ribbon (1/32in. x .036in. is a convenient size for most purposes) which may be stripped from a 600 watt electric toaster or iron element if not otherwise obtainable. This winding may require a little patience, and is best performed by stretching the rope loosely between two supports and winding the ribbon tightly around it so that it will retain its spacing when heated. It is important to space the ribbon out



evenly along the full length of asbestos to ensure even heating and no inter-turn short circuits in the element. The ends of the ribbon are seized in place with a 1½in. x 3/16in. brass nut and bolt, the asbestos rope and ribbon passing between two large washers on the bolt. The flask is then rewound with both the strands, starting them simultaneously. It is necessary to sew them temporarily in position with needle and thread, picking up with each stitch the two immediate strands, together with the two strands of the preceding turn. The element strand finishes two complete turns before the 1in. strand, and the bolt is left projecting through to form the contact on the outside of the heater. While still in place on the flask, the "bird's nest" is plastered over with successive layers of asbestos lagging pulp mixed to a paste with water and reinforced with criss-crossed strands of ⅜in. asbestos rope and the whole smoothed off to a finished thickness of 1½in. It should then be allowed to dry thoroughly, after which the power may be applied gradually until the element comes up to red heat, burning away the sewing thread and leaving the inside of the heater quite clean. The outside is best finished with several coats of heat-resisting aluminium paint.

If desired the heater may be permanently housed in an earthenware flower pot, which gives it protection and support. A heater made for a six-litre reaction vessel containing two 600w elements which can be connected to give imputs of 1200w, 600w or 300w,, has been used for many purposes without further control. A heater to take eight Soxhlet extractors has also been built up inside a copper box lined with sheet asbestos ⅜in. thick, and the usual construction followed. It will be realised that this construction is not actually fireproof, but ether, alcohol, acetone and benzene have been distilled without the windings being hot enough to constitute a fire risk, and any solvent spilt evaporated away harmlessly.

The author wishes to thank the directors of Abels, Limited for permission to publish.

P.O. Box 12, Newmarket, Auckland.

## THE ALKALI REFINING OF OILS CONTAINING VITAMIN A

L. HARTMAN, Fats Research Laboratory, Wellington

**(Summary of a lecture delivered to the Wellington Branch, November, 1948)**

Oils and fats for human consumption are usually subjected to a refining process which consists in treatment with alkalis to remove free fatty acids, bleaching with fullers' earth and deodorising with superheated steam under reduced pressure. In the case of oils containing vitamin A, refining has to be carried out in such a manner as to preserve the vitamin intact, and the usual refining procedure has often been severely criticised in this connection. This applies especially to the alkali treatment, and several authors, including the well-known German authority, Prof. H. P. Kaufmann, have stressed the disadvantages of such treatment. The main evidence against alkali refining, however, is contained in H. N. Brocklesby's book "The Chemistry and Technology of Marine Animal Oils," published by the Fisheries Research Board of Canada, and in a paper published by Brocklesby and Kuchel in 1938 (J. Fish, Res. Bd. Can. 4 (3) 174-183).

Brocklesby and Kuchel conducted a series of experiments on neutralisation of fish liver oils and arrived at the conclusion that caustic alkali solutions removed vitamin A from these oils by absorption, which increased with the dilution of the caustic and with the free fatty acid content of the oils. The losses of potency observed by them were high, amounting in some cases to 70 per cent of the original value.

These results have been naturally a deterrent with regard to the alkali treatment of fish liver oils. The difficulty in finding other means than alkali refining for vitaminic oils lead to a systematic re-investigation of the problem in the Fats Research Laboratory of the Department of Scientific and Industrial Research (N.Z.) and resulted in a complete reversal of Brocklesby's and Kuchel's figures. It was found that under normal refining conditions the neutralisation of fish liver oils results in an increased, and not diminished, potency. This increase is approximately proportional to the free acid content of oils, and if this content is high the increase of potency can be quite substantial. In some oils an increase of 10 to 16 per cent as compared with the original potency was observed. But even when following the peculiar technique of Brocklesby and Kuchel, which consisted in using very dilute caustic solution never occurring in practice and in adding oleic acid to the oils before neutralisation, their results could not be confirmed.

From the work carried out in the Fats Research Laboratory it appears that, contrary to the earlier opinions, alkali refining is still the most economical and simple means of removing free fatty acids from vitaminic oils. This is of importance to industries producing vitamin A concentrates by molecular distillation, because such distillation requires oils of very low acid value and free from impurities, and this can be best achieved by alkali refining.

## LETTERS TO THE EDITOR

The Editor,
Journal of the N.Z. Institute of Chemistry,
P.O. Box 12, Newmarket,
AUCKLAND.

Fats Research Laboratory,
Sydney Street West,
WELLINGTON, N.1.

Sir,—

### Standards for Saponification Equivalents and Iodine Values

The current universal acceptance of a standardised procedure for the determination of saponification equivalents and iodine values is an invaluable step towards the elucidation of values of fats. It does not, however, eliminate inconsistencies arising either through personal error on the part of the manipulator or impurities of the reagents used. For instance, the Wijs reagent used in the determination of iodine values is liable to give inconsistent results for no apparent reason.

As a check, it has been the practice in the Fats Research Laboratory to incorporate in each batch of determinations of saponification equivalents and iodine values a suitably stable oil which has been accurately standardised.

In the case of saponification equivalents, the standard used is methyl palmitate (S.E. 270.0) prepared in the Laboratory and purified by fractional distillation so as to give a saponification equivalent unchanged by subsequent refractionation. In the case of iodine values, the standard is peanut oil (I.V. 93.4), stabilised by the addition of an inert anti-oxidant. The true respective value of each standard is first ascertained by carrying out a large number of determinations and calculating the mean and the standard deviation.

The inclusion of the appropriate standard in every batch of samples thus provides a convenient means of checking the accuracy of the determinations.

It is suggested that the adoption of such a procedure in all laboratories in New Zealand concerned with the estimation of these values would provide a highly satisfactory basis for universal accuracy and for comparison of results. To this end a scheme whereby standards could be exchanged between laboratories for cross-checking would be an ideal arrangement.

Another use for the above standards is in the training of laboratory assistants and chemists. For example, if a worker makes, say, six determinations, it is possible to obtain an estimate of the accuracy of working before starting upon the investigation of unknown materials.

The Fats Research Laboratory would be prepared to supply quantities of methyl palmitate and peanut oil at an appropriate charge to any other laboratories interested, but it is pointed out that these would necessarily be limited. The methyl palmitate at present used has been slowly accumulated over a period during the course of ester-fractionation analyses of butterfat, while availability of peanut oil depends largely on fluctuating local supplies.

If requests for material cannot be met, it is alternatively suggested that laboratories interested in the scheme might independently acquire and standardise suitable oils which could then be exchanged with those of other laboratories for cross-checking. This would serve equally well in establishing standards in each laboratory which would ensure accurate and comparable results for saponification equivalents and iodine values.

Yours faithfully,
F. B. SHORLAND,
Director.

## PERSONAL NOTES

The congratulations of all our members will go to Mr. John Rogers, our genial Conference Secretary of last year, who has been awarded a Nuffield Scholarship, and will leave later this year for a six months' tour of American establishments dealing with mineral ore dressing, in which subject he is research lecturer at the Otago School of Mines. Mr. Rogers is a graduate of Canterbury College, and spent five years in Australia with the Council of Scientific and Industrial Research before taking up his present appointment. He was elected an Associate in 1946.

Mr. Maurice Sutherland, of the University of Queensland Chemistry Department, has been spending the long vacation in New Zealand.

Mr. S. H. Wilson, of the Dominion Laboratory, Wellington, delivered a paper to the Pacific Science Congress on the "Chemical Investigation of the Hot Springs of the New Zealand Thermal Region."

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## BOOKS RECEIVED

**OUTLINES OF PHYSICAL CHEMISTRY.** by Farrington Daniels, University of Wisconsin. Pp. 713. New York: John Wiley and Sons. London: Chapman and Hall. 1948. Five dollars.

This book is the lineal descendant of one of the same name written by Getman in 1913. It is now so changed that nothing of the original author's book remains, and it now definitely Daniels'. This seems to the reviewer to be a very useful text-book; the presentation is clear and modern; the subject is well covered; the printing and binding good. This book will also appeal to the practising chemist as a reasonably-priced general reference book in physical chemistry. There are references to the original literature (mainly American) for those who want to go further, author and subject indexes and logarithms.

**WORKING WITH PLASTICS.** by Arthur Dunham. New York and London: McGraw Hill Book Co., 1948. 3.50 dollars.

This book gives precise directions for making various articles in the workshop from plastics. There is very little chemistry in it, but the book will be of interest to many chemists. Some may find in this work a satisfying hobby.

**PRINCIPLES OF HIGH-POLYMER THEORY AND PRACTICE.** Fibres, Plastics, Rubbers, Coatings, Adhesives. By Alois X. Schmidt and C. A. Marlies, College of the City of New York. Pp. 743. 1948. New York and London: McGraw-Hill Book Co. 7.50 dollars.

It is pointed out in the preface that one-third of all American chemists and chemical engineers are engaged in the fields covered by this book, which is written on general lines for students. It deals with natural and synthetic polymers, their chemistry and methods of working or modifying them (including, e.g., permanent waving of hair). Chapter headings include: Molecular force, Some special behaviours and properties of high polymers, Polymer formation and modification, Structure of high polymers, Solubility and molecular weight relationships, Rheology, Moulding and manipulation, Mechanical properties, Electrical, optical and thermal properties, Fibres and fibrous products, Rubbers, Surface coatings, Adhesives, Phenolic resins. For those who want a good general and comprehensive book on high polymers, this seems to be the one to get.

**ORGANIC REACTIONS.** Vol IV. Edited by Roger Adams. Pp. 428. New York: John Wiley & Sons. London: Chapman & Hall. 1948. Six dollars.

This latest addition to a very useful series covers the following subjects:—The Diels-Alder reaction with maleic anhydride, the Diels-Alder reaction with ethylenic and acetylenic dienophiles, the preparations of amines by reductive alkylation, the acyloins, the synthesis of benzoins, the synthesis of benzoquinones by oxidation, the Rosenmund reduction of acid chlorides to aldehydes and the Wolff-Kishner reduction. The Diels-Alder with quinones and other cyclic ketones will be dealt with in Vol. V. The value of these reviews lies in their exhaustive nature, and any organic chemist would be glad to have them.

## LABORATORY ASSISTANTS' EXAMINATION, 1948

The following candidates were successful in the recent examinations:—

**THEORETICAL CHEMISTRY.**—COOK, Joan P., GEE, Beverley C., LOFTUS, T. M. RUSSELL, Vigette V., STRAWBRIDGE, N. S., WERREN, D. J., WOODS, Alwyn.

**ELEMENTARY CALCULATIONS.**—ASHMAN, N. R., CLINTON, O. E., DICKINSON, J. W., FISHER, Judith E., LOFTUS, T. M., SANDERS, I. D., TREWERN, Lillian C., WERREN, D. J.

**ELEMENTARY PHYSICS.**—RUSSELL, Vigette V.

**PRACTICAL CHEMISTRY.**—CLINTON, O. E., COOK, Joan P., GEE, Beverley C., GEORGE, J. S., LOFTUS, T. M., SANDERS, I. D., TREWERN, Lillian C., UNDERHILL, A. P., WERREN, D. J.

**PHOTOGRAPHY.**—HULL-BROWN, I., UNDERHILL, A. P.

**METAL WORK.**—GEORGE, J. C.

## LABORATORY ASSISTANTS' CERTIFICATE EXAMINATION

### THEORETICAL CHEMISTRY

**November, 1948.** **Answer Seven (7) questions.** **Time: Three (3) hours.**

Give equations where possible.

(1) What do you understand by Hard Water?
What are the main impurities found in Natural Water that cause hardness? And how are they removed? Given the necessary standard solutions, how would you estimate the hardness of a water?
Describe briefly one suitable method of softening a town water supply containing Calcium bicarbonate.

(2) (a) From what groups of chemicals can you obtain oxygen by heating? Give one example of each.
(b) A sample of nitrogen gas is assumed to contain traces of oxygen. How would you test this and remove a trace of oxygen?
(c) Give an example of oxidation of a substance by:—
(i) Addition of oxygen to it.
(ii) Removal of hydrogen from it.
(iii) Changing it to a higher valency state (not addition of oxygen).
In each case show the initial and final product of the oxidised substance; state the substance which brings about this oxidation; discuss the change that takes place in the oxidising agent during the oxidation reaction.

(3) Explain briefly **any** four of the following statements:—
(a) The pH of the blood is 7.4.
(b) Zinc Oxide is amphoteric.
(c) The empirical formula of a certain sugar is C $H_2O$.
(d) Stannic Chloride is a covalent compound.
(e) $\frac{N}{10}$ — $H_2SO_4$ — and give its strength in grams per litre. (H = 1, S = 32, O = 16).

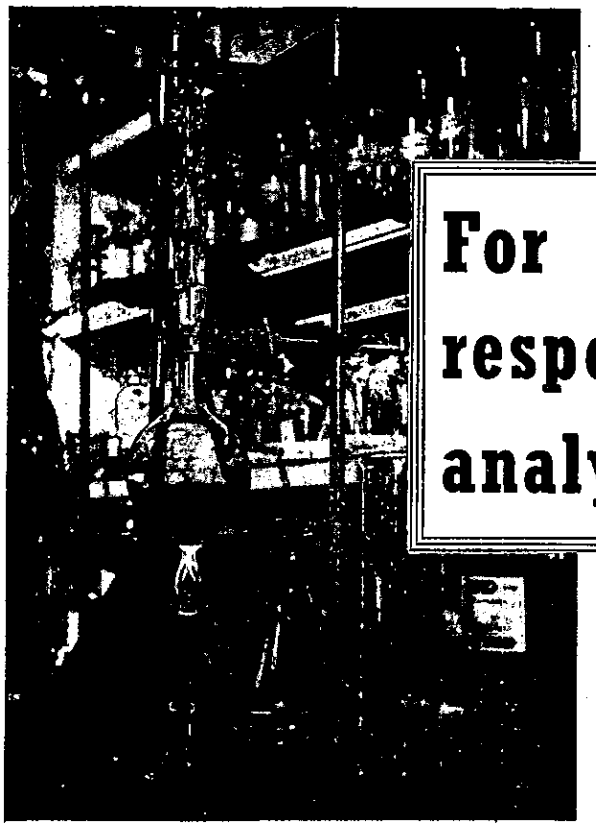
(4) State Gay Lussac's Law and Avogradro's Hypothesis.
An octane fuel C8H18 undergoes perfect combustion in air. What are the products? Give equation.
What would be the minimum volume of air at 15° C. and 750 m.m. pressure and containing one-fifth its volume oxygen to ensure complete combustion of Octane vapour calculated to occupy 100 c.c. at N.T.P.?

(5) Give an outline of the preparation of industrial alcohol. Give a brief account of the reactions which occur during the production of—
(a) Ether. (b) Acetic Acid. (c) Ethyl Acetate from alcohol.

(6) Give the conditions under which the following substances react; visible changes which occur during the reaction; new products formed; and equations where possible:—
(a) Chlorine and potassium iodide.
(b) Sulphur dioxide and potassium permanganate.
(c) Hydrogen and animal or vegetable oil.
(d) Ammonia and copper sulphate.
(e) Phosphorus pentoxide and water.

(7) Describe briefly one electrolytic method for the extraction of either Aluminium OR Sodium from its natural source. Outline briefly a laboratory method to prepare—
(a) Lead sulphate.
(b) Sodium hyposulphite or thiosulphate.
(c) Potassium chlorate.
Give in each case one reaction and use.

(8) Sketch the apparatus, label the materials, etc., that you would use to prepare a solution of hydro-bromic acid. Give equation.
How would you distinguishe between—
(a) Hydrobromic and hydrochloric acid.
(b) Sulphuric and Ortho phosphoric acid.



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## CONTENTS



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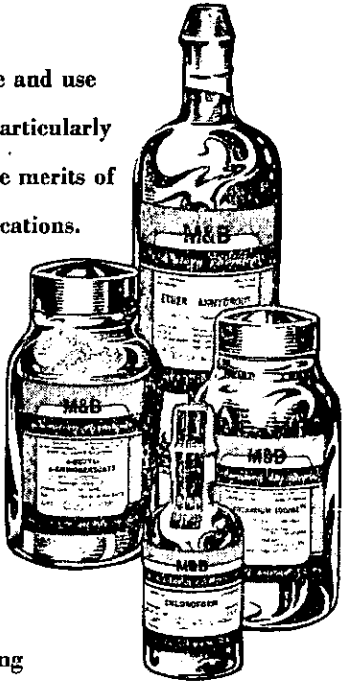


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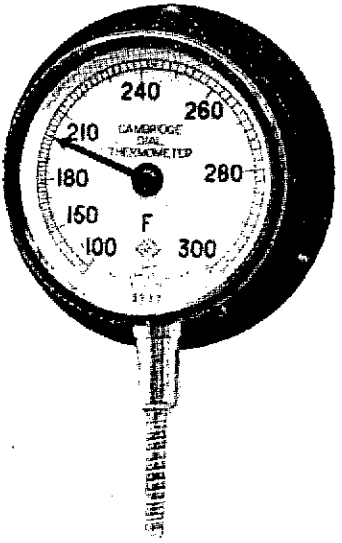


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