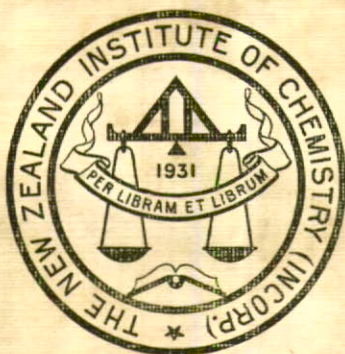


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**EDITORIAL**

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The President's Address for 1943 brings to the notice of those of us who are not specifically interested in soil chemistry, the important centenary of the Rothamsted Experimental Station. It should also cause us to give more than a moment's thought to the achievements of New Zealand's Rothamsted, the Institute which two of our most distinguished members, Sir Thomas Easterfield and Sir Theodore Rigg, have in succession, guided along fruitful paths of enquiry. We have been reading again the former's 1933 Cawthron Lecture, in which the achievements of the first sixteen years were reviewed. Another decade has passed, the work so well begun has been continued and extended, and through the close liaison existing with the Department of Scientific and Industrial Research, the influence of the Institute's fine research team is felt far beyond the Nelson district. In the address published in this issue, the present Director deals largely with work carried out by the Plant Chemistry laboratory and the Department of Agriculture. The soil and plant chemists are seen to be going beyond the necessary first steps in the development of their science, and studying the actual paths pursued by the valuable minerals which long experience in many lands has shown to be essential for plant growth at the level needed to feed our modern communities. The mining, chemical treatment, transport and distribution on the land of these vital minerals occupies the time and effort of vast numbers of workers. The economic value of studies which may determine accurately what application of, for instance, phosphate fertilisers is really necessary to maintain high production, is obvious. We may expect to see great progress in these fields from the combined work of the various research organisations which are concerned with different aspects of these problems. We may expect also a successful response from the fertiliser chemists to the demands on their products which the results of research work will make. The duty to maintain maximum production at the present time is plain enough. It will not be less in the immediate post-war years, when all help must be given to the disorganised countries which have suffered the direct impact of war. Add to those the

duty of handing on to posterity, a land whose soil has not been mined of its plant foods, and the work of the soil scientists is seen in its full importance, and the promise of their future achievements appears as one of our major assets in the years of rebuilding which lie ahead.

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### **PRESIDENTIAL ADDRESS.**

“Some recent advances in Soil, Fertiliser and Plant Chemistry in New Zealand.”

Delivered by the President, Sir Theodore Rigg to the Canterbury Branch on August 20th, 1943.

The wide scope of the work of the chemist in New Zealand is little realised by the general public. He is responsible for the control of chemical reactions in the cement, fertilisers, leather, pottery, gas and many other industries. Whether it be in the testing of foods, drugs or manufactured articles of all descriptions, the work of the chemist is vital to the maintenance of satisfactory standards on which eventually the well being and prosperity of the people depend. In no branch of chemistry have more valuable contributions to agriculture and scientific knowledge been made by New Zealand chemists than in that of soil and plant chemistry.

In directing attention to soil deficiencies of lime and phosphate over many areas in New Zealand, chemists made a valuable contribution to the successful development of agriculture. Following on the valuable work of B. C. Aston in connection with bush-sickness and that of Australian workers on allied stock ailments, New Zealand chemists not only showed that bush-sickness in the North and South Islands of New Zealand and lamb ailment in Southland were overcome by the use of cobalt salts, but established the first convincing proof either in New Zealand or elsewhere that an actual deficiency of cobalt did occur in the soils, in the pasture and in animal organs. In this and in the development of a technique for the use of cobalt, either in licks or in cobaltized fertilisers, New Zealand chemists made an outstanding contribution to science in connection with the treatment of stock and pasture affected with cobalt deficiency.

The identification of arsenic in the thermal waters of certain areas in the Rotorua district solved an abstruse stock problem which for many years had caused concern to farmers.

The chemist has been likewise prominent in the exploration of boron deficiency in different crops in several parts of New Zealand. The work which has been done on the boron status of New Zealand soils on the rate of leaching and the use of

boron compounds in the control of "Internal Cork" of apple, "Brown-spot" of apricots and on "Brown-heart" of root crops has been of great benefit to New Zealand agriculture and to our knowledge of plant nutrition.

More recently the identification of magnesium deficiency of apples in Nelson, contemporaneously with similar work by Dr. Wallace in England, constitutes the first recorded case of magnesium deficiency of apples occurring under field conditions in any country of the world.

The elaboration by New Zealand chemists of chemical methods for the estimation of cobalt, boron, and magnesium and of micro-chemical tests for plant constituents, have been fundamental to the successful conduct of investigations on many soil and plant problems. It is particularly gratifying that methods developed by chemists have not only proved successful in New Zealand but have been adopted by chemists in other countries.

In view of the Centenary of Rothamsted Experimental Station it is perhaps appropriate to confine my address to those aspects of chemical research which have a direct bearing on soil and plant relationships. In doing so I do not under-estimate the very valuable work which has been done in New Zealand in the solution of problems connected with industrial chemistry and other branches of agricultural chemistry relating to the dairy, wheat, and meat industry, etc.

Perhaps no aspect of soil and plant chemistry is of greater importance to our pastoral industries than that referring to the effect of fertilisers on pasture production and composition.

I would remind you that Sir John Lawes, the founder of Rothamsted Station held the first patent for the manufacture of superphosphate from rock phosphate. This was the starting point in the great superphosphate industry of the world which today amounts to many million tons per annum. No discovery has conferred on the farmer such outstanding benefit as the treatment of rock phosphate with sulphuric acid to produce a water soluble phosphate which has given very beneficial results over a range of crops in many countries of the world. In New Zealand, superphosphate has been the most important factor in the development of the dairying industry of New Zealand and has resulted in a great increase in carrying capacity throughout the whole country, particularly in the Waikato. In more recent years the value of lime for a wide range of New Zealand soils has been recognised and although the use of lime is not so extensive as it should be, yet increasing emphasis is being placed on the liming of pastures on a wide range of New Zealand soils.

Generally speaking the results from the use of super-

phosphate on pastures have been remarkable and have resulted in the use of two to six cwts. of superphosphate per acre in the more important dairying districts. Recently, however, experiments at Palmerston North and Canterbury have suggested that the quantity of superphosphate applied by the farmers may be unnecessarily high and may be associated with considerable loss of phosphate. Moreover, attention has been drawn by New Zealand chemists to the relatively small quantity of phosphate under our grazing system which is taken out of the land and to the locking-up in soil of a very large proportion of the phosphate which has been applied in pasture treatments. Furthermore it has been suggested by other workers that the use of a reverted phosphate would be much more economic on certain types of soil than the use of equivalent amounts of superphosphate. Again it is suspected that the continued use of superphosphate to the exclusion of potassium and magnesium has already resulted in the unbalanced nutrition of pastures on certain soil types. In my address it is proposed to review some of the more recent work relating to the use of lime and phosphate in the treatment of New Zealand pastures.

**Use of Lime.**—The great importance of lime in the establishment and treatment of pastures, over a wide range of soils has been demonstrated by many experiments carried out by the Department of Agriculture and other New Zealand research organisations. Very marked response to lime treatment has been obtained in North Auckland, Palmerston North, Nelson, Canterbury, West Coast and Southland. Until recently little agreement existed, however, concerning the quantity of lime which should be used in the treatment of different pastures and how frequently liming should be undertaken. While the degree of soil acidity must be taken into consideration in deciding the rate of the initial application of lime, rainfall and texture of the soil greatly influence the rate of loss from the top 4 inches which is so important in the maintenance of a satisfactory rye, white-clover pasture.

The experiments carried out by the Plant Chemistry laboratory and the Department of Agriculture at Marton, have given important information concerning the fate of lime when applied to a silt loam at Marton under a rainfall of 35 to 37 inches per annum.

The experiments have demonstrated that certain minimum applications of carbonate of lime are required in the initial treatment of the pasture before substantial improvement in pasture production can be obtained. On the Marton soil, lime treatment gave a very marked response when superphosphate at the rate of 3 cwt. per acre was used. Smaller initial applications than one ton of ground limestone per acre lagged behind the higher rates of application for two or three years.

Considered over an eight year period, however, there was little difference in the end result in so far as the pasture production was concerned; i.e. two tons of ground limestone, whether used in one initial application or divided into two 1 ton applications or four  $\frac{1}{2}$  ton applications or eight 5 cwt. applications produced approximately the same total of dry matter over an eight year period. There was, however, a marked lag in optimum production with the smaller initial applications for a period of two to four years.

A study of the lime status of the soil under the different limestone treatments gave very interesting information concerning the loss associated with the use of both large and frequent small applications of ground limestone. In the case of the 2 ton initial application of ground limestone, all free carbonate had disappeared from the top two inch layer at the end of five years. Determinations of exchangeable calcium showed a movement of lime into lower layers, the soil depth below ten inches receiving lime after the fifth year. During the last three years of the eight year period, lime was lost from the top 10 inches of soil at an average rate of 350 pounds of calcium carbonate per acre per annum. The investigators point out, however, that the use of superphosphate at the rate of 3-4 cwts. of superphosphate per acre per annum, not only maintained the lime status of the soil at its initial level, but had a beneficial effect in reducing the loss of calcium carbonate from the lime plots. In the absence of superphosphate treatment the analytical data suggest that 500-600 pounds of calcium carbonate would be lost from a silt loam under Marton conditions after bringing the soil to a satisfactory initial lime status.

An interesting point emerging from the chemical data was the difference in loss of lime over the eight year period with the different lime treatments. In the case of the 2 ton lime application, the loss from the 0 to 10-inches depth at the end of the eight year period was estimated at 1356 pounds of calcium carbonate. In the case of the 1 ton application repeated at the end of four years, the loss of calcium carbonate at the end of the eight year period was 880 lbs. of calcium carbonate per acre. In the case of the 5cwt annual application of ground limestone the loss at the end of the eight year period from the 0 to 10 inch layer was 567 lbs. of calcium carbonate per acre.

When both pasture production and the fate of the lime are considered it would seem that initial application of 1 ton of ground limestone per acre followed by further applications of 6 to 8 cwts. ground limestone per acre every 2 years would result on this soil type in optimum yield and maintenance of the top four inches of soil at a desirable lime status. Sir John

Russell states that the loss of lime from Rothamsted soil is approximately 660 lbs. of calcium carbonate per acre per annum, from Aberdeen, Scotland 152 lbs. of calcium carbonate and from soil at Ithaca, New York, 730 pounds of calcium carbonate per annum.

**The use of Phosphate.**—In the Marton experiments a very detailed investigation concerning the effect on pasture production of superphosphate, basic slag, and Gafsa phosphate used at equivalent rates of 66 lbs. phosphoric acid per acre was carried out and the distribution of the phosphate in different layers of the soil during an eight year period was studied.

In so far as pasture production is concerned, the trial showed the superiority of superphosphate plus carbonate of lime over both basic slag and Gafsa phosphate either with or without lime for pasture top-dressing when equivalent amounts of phosphoric acid per acre were applied in the fertilisers. On the Marton soil the addition of lime to the basic slag treatment did not have any significant effect on pasture production whereas a marked increase in production was found from the use of lime with both super and Gafsa treatments. Herbage analyses showed an increase of lime in the herbage of both lime and basic slag treatments and a marked increase of phosphoric acid in the herbage from the super plus lime plots. In the above experiment, if the yield from the super plot (3 cwts per acre) is taken as 100 then lime and super gave 107.2, basic slag alone 100.9 and Gafsa phosphate 95.5.

An interesting feature of the experiments carried out at Marton has been the estimation of phosphate at different depths in the 0 to 10 inch layers of soil over a period of eight years. The results showed that out of a total of 789 pounds of phosphoric acid added by way of top-dressing only 313 lbs. had been retained in the top 0 to 2 inches of the unlimed treatments. Phosphate accumulation was marked in the 2 to 4 inch and 4 to 10 inch depths. The total quantities found in the three layers added up closely to the known amount which had been added by top-dressing. Roughly 42 per cent of the phosphoric acid was retained by the 0 to 2 inch depth, 31 per cent by the 2 to 4 inch depth, and the balance 27 per cent phosphoric acid was found in the 4 to 10 inch depth. The results obtained indicate clearly that there is an actual loss of phosphate on the Marton silt loam from the top 0 to 2 inch layer to lower depths, caused by the leaching action of rain. Judging by the results obtained on this silt loam, it may well be anticipated that on sandy soils of a more open texture, particularly under high rainfall conditions the loss of phosphoric acid from the 0 to 4 inch layers will be even more marked than that revealed in the Marton investigations.

An interesting feature of the analytical data from the Marton experiment was the effect of lime on the retention of phosphoric acid in the 0 to 2 inch layer of soil. In the case of superphosphate with lime an additional 57 lbs. of phosphoric acid per acre was retained during the period of eight years by the 0 to 2 inch layer. A somewhat smaller result was obtained in the case of Gafsa phosphate but in the case of basic slag there was little difference in the retention of phosphate in the 0 to 2 inch layer between the lime and no lime treatment with this fertiliser.

**Fixation of Phosphate.**—Workers at the Cawthron Institute have drawn attention to the high fixing power of certain soils for phosphoric acid. In a comparison of alluvial soil (Waimea Loam) with Moutere Hills soil the fixing power of the Waimea loam was less than one-third of that found for the Moutere Hills soil. The reactive compounds in the soil were iron and alumina, for when these compounds were removed from the soil the fixing power of the soils was very greatly reduced. In the case of the Moutere Hills soil treated with 3 cwts. of superphosphate per acre, 80 per cent of the phosphoric acid might be fixed by the iron and alumina compounds in the top 0 to 2 inches of soil. It is well-known that other New Zealand soils, particularly in North Auckland and parts of the King Country have similar high fixing power for phosphoric acid and on these soils it may be anticipated that the efficiency of soluble phosphatic fertilizers is greatly reduced in comparison with that on soils of a higher lime status. Here then is another important aspect of soil and fertiliser reactivity which must be carefully considered in any appraisal of the value of particular phosphatic manures or of the quantity per acre which should be applied.

**Loss of Exchangeable Potash and Magnesia.**—The continued use of superphosphate cannot but fail to have an important effect on the status of potash and magnesia in the soil, unless applications or fertilisers containing these plant foods are made from time to time. Officers of the Soil Survey Division have examined the exchangeable potash and magnesia contents in Waikato soils both with and without phosphate treatment. They found that definite losses in both potassium and magnesium were associated with the long continued use of superphosphate as a top-dressing. Their data indicated that while a considerable proportion of the potash losses could be accounted for in products sold off the farm, this was not the case with magnesium. There can be little doubt that the large amount of gypsum contained in superphosphate has forced magnesium into the soil solution resulting in considerable loss by the leaching action of rain. In both cases the losses of potash and magnesia over a period of years are comparatively large and

undoubtedly the time must come when attention must be paid to the use of these plant foods in fertiliser programmes. It must be pointed out that potassic manures are likely to accelerate magnesium losses and their use would make it even more necessary to supply magnesium compounds in pasture top-dressing. Liming would assist in the conservation of magnesium in the soil.

**Use of Reverted Phosphate.**—It has long been known that although phosphatic manures, particularly water soluble phosphate, are extremely valuable in the promotion of pasture growth, yet only a small proportion, possibly 10 per cent, is removed from the soil by products sold off the farm. The Marton experiments definitely show that even under moderate rainfall there is a transference of a proportion of the phosphates, applied in top-dressings, to layers below 4 inch depth. Work on the fixation of phosphates clearly indicates that particular soils will lock up a high proportion of the soluble phosphate in a less available form as iron and alumina phosphates. The question arises as to the best method of pasture treatment whereby phosphate is conserved and the highest return from a given application is obtained.

The use of adequate lime in the treatment of pastures should help in conserving the phosphate, reduce the rate of penetration in the soil and render more available iron phosphate already present in the soil. By far the most important method of control, in so far as loss of available phosphate is concerned, would seem to be the use of reverted phosphates which are not soluble in water but which react slowly with water and give a longer life than would be the case with superphosphate on some of our high fixation soils. Such reverted phosphates are likely to have special value on acid soils particularly under high rainfall conditions. The common method of reverting superphosphate is the use of 15 per cent finely ground carbonate of lime together with 85 per cent of high grade, 20 per cent superphosphate. Slaked lime and burnt lime are also used for reversion. In basic phosphates made in this way, the total phosphoric acid is usually 18 to 20 per cent and practically the whole of the phosphoric acid is soluble in 2 per cent citric acid. For many soils under high rainfall conditions, basic phosphates should prove extremely valuable, giving much longer life for a unit weight of phosphate.

Owing to shortage of superphosphate in New Zealand, serpentine for the reversion of superphosphate has been used on an extensive scale in the North Island. The usual practice is to employ one part of ground serpentine containing 30 to 35 per cent of magnesia ( $MgO$ ) to 3 parts of hot moist superphosphate. When the mixture matures a friable product is obtained con-

taining less than 5 per cent of water soluble phosphoric acid soluble in 2 per cent citric acid. Serpentine superphosphate contains 4.85 per cent of citric soluble magnesia (MgO).

A very large number of field experiments with serpentine superphosphate have been carried out by the Department of Agriculture. The experiments indicate that serpentine superphosphate is a valuable phosphatic fertiliser for some of the higher rainfall districts of New Zealand. In North Taranaki, Waihi, and North Auckland, serpentine superphosphate has given better results than superphosphate used at the same rate per acre. The results suggest that in these localities serpentine superphosphate has a special value possibly on account of its longer life under high rainfall conditions but possibly also on account of its valuable magnesium content. In view of the leached nature and porosity of many of the soils in these localities both potassium and magnesium are likely to have been depleted and on this account serpentine superphosphate may have a special value not shared by basic superphosphate.

In regard to other localities in which serpentine superphosphate has been tried against superphosphate, lime and superphosphate, and basic slag, the evidence for the superiority of serpentine superphosphate over lime and super or basic superphosphate is very scanty. The quantity of phosphate used in the tests and the technique of the experiments were not favourable for the establishment of other than very marked differences in the behaviour of the fertilisers.

**Rate of Application.**—Recent work at Palmerston North and Lincoln College suggests that much smaller applications of phosphatic fertilisers are sufficient to maintain high production. Obviously the rate of application desirable in the case of pasture top-dressing is dependent on pasture production, rainfall and soil type. At Nelson, with an average rainfall of 37 inches,  $1\frac{1}{2}$  cwts. of super gave a dry matter production of 6584 lbs. while 3 cwt. applications of superphosphate gave a yield of 7062 lbs. dry matter per acre, the control plot giving 4123 lbs. In the Waikato, 3 to 6 cwts. of superphosphate per acre have been used frequently in the top-dressing of pastures. While top-dressings at the above rates may have been desirable in the early years of treatment to raise the whole level of soil fertility, it may well be that smaller applications of phosphatic manure would now suffice to maintain pasture production at a high level.

Some support for this hypothesis is available from the work of the Grasslands Division at Palmerston North where it has recently been shown that under favourable conditions for pasture growth, the quantities of plant food returned by grazing

stock to the soil are much greater than farmers have realized in the past.

This and many other points connected with pasture fertilisation can only be solved, however, by the actual conduct of field trials in which comparatively small differences in pasture yield can be accurately measured.

While the results of soil and pasture studies discussed in this address are of great importance to the pastoral industries of New Zealand, much additional work is required before they can be fully applied for the benefit of farmers. Further information is needed concerning the loss of lime and phosphate from typical soils in the dairying districts of the Waikato and Western Taranaki. Cognisance must be taken of the losses of potash and magnesium from sandy soils under high rainfall conditions. The value of reverted phosphates including basic superphosphate and serpentine superphosphate must be studied on a wide range of New Zealand soils, using an experimental technique capable of assessing accurately minor differences in pasture production. Similar work is required in determining the quantity of phosphate which should be applied on typical pastures under different rainfall conditions.

Lastly, the time is ripe for the intensification of research on the manufacture of fertilisers in New Zealand. The profitable utilisation of the Clarendon phosphate rock at Milburn, the improvement of both basic superphosphate and serpentine superphosphate and the manufacture of new basic phosphates are matters of great importance to New Zealand agriculture. In all these studies relating to both soil problems and fertilisers manufacture and use, the chemists of New Zealand have a most important part to play.

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### **COUNCIL MEETING AT CHRISTCHURCH.**

Prior to the delivery of the Presidential Address before the Canterbury Branch on August 20th, the meeting of the Council at which Branch delegates attend in person, was held in the Professorial Board Room of Canterbury College, by courtesy of the Rector, Professor A. H. Tocker. Delegates were entertained at morning tea in the staff common room.

The Canterbury Branch entertained members of the Council at a dinner held in Ballantyne's tea room, at which some thirty members were present.

Dr. M. M. Burns presided and welcomed the delegates on behalf of the branch. A very pleasant function was fully enjoyed by all present.

## DENHAM MEMORIAL LECTURE.

On September 24th, Mr. J. Packer, Acting-Professor of Chemistry at Canterbury College, delivered an address on the life and scientific work of the late Dr. H. G. Denham. Among the large audience were the following representatives of scientific and other bodies with which Dr. Denham was connected: Sir Theodore Rigg (New Zealand Institute of Chemistry and Scientific and Industrial Research Council); Mr. A. E. Flower (Council of Canterbury University College); Dr. J. Hight (Pro-Chancellor of the University of New Zealand); Dr. R. O. Page (N.Z. Section of the Institute of Chemistry of Great Britain and Ireland); Dr. F. G. Soper (representing the Professors of Chemistry in the New Zealand University); Professor A. H. Tocker (Rector of Canterbury College), and members of the staffs of Canterbury College, Canterbury Agricultural College, various divisions of the D.S.I.R., and representatives of the Royal Society of New Zealand, the Manufacturers' Association and the Rotary Club.

Apologies were received from Dr. R. Gardner, Dr. W. P. Evans, Dr. E. Marsden, Mr. W. Donovan, Mr. P. White, Dr. D. B. Macleod, Dr. I. L. G. Sutherland, Professor E. R. Hudson, Dr. C. P. McMeekan, Dr. R. S. Allan, Mr. J. Hutton and Mr. T. R. Pollard.

Dr. M. M. Burns presided.

Mr. Packer said that it was particularly fitting that the lecture should be delivered before the Canterbury Branch of the New Zealand Institute of Chemistry, in the room where Dr. Denham had spoken so often, not only to his own chemistry students, but also to members of the Institute. He was one of those who saw clearly the value of such an Institute as ours, claiming as its members all qualified chemists in New Zealand, and he and a few others were mainly responsible for bringing the Institute into being some thirteen years ago.

After describing Dr. Denham's career as a university student and teacher, Mr Packer dealt in detail with his research work. His earliest investigation, under Dr. W. P. Evans at Canterbury College was on the combustion of methane on palladiumised asbestos, and was published in 1905 in the Transactions of the Society of Chemical Industry. On taking up the 1851 Exhibition Research Scholarship at Liverpool under F. G. Donnan, he applied the hydrogen electrode to the measurement of hydrolysis of salt solutions, being with N. Bjerrum of Copenhagen, the first in this field. His best known work on hydrolysis was the study of aniline hydrochloride which closely confirmed Bredig's data by another method. Many salts gave reproducible results, but salts of zinc, magnesium and lead all gave drifting potentials, and apparent hydrogen ion concentrations higher than would be expected.

To explain this, reactions of the type  $Pb^{++} + H = Pb^+ + H^+$  were postulated. Lead suboxide had been reported by Tanatar (1901) from the action of heat on lead oxalate, and by Briselee in the Liverpool laboratory from the reduction of PbO by CO.

Dr. Denham, with A. J. Allmand, applied a circulation method used by T. W. Richards on copper salts. The reaction  $Cu^{++} + Cu = 2Cu^+$  absorbs heat, so that the equilibrium is farther to the left at low temperatures. Cupric ions react with copper at a higher temperature, and flow to a cooler part of the apparatus where the reaction reverses, precipitating copper. Circulation is carried out to obtain a cumulative effect. With this method positive results were obtained for Pb, Cd, Tl and Bi, and negative results for Ni, As, and Sb. The work was not carried further at this stage, but it laid the foundations for Dr. Denham's later interest in sub-salts. Some investigations on auto-complexes in copper and cobalt salts were carried out in Liverpool, and the catalytic oxidation of titanous by hydrogen ions was studied under Bredig at Heidelberg. During a year spent as honorary lecturer at Canterbury College, Dr. Denham attempted to prepare  $CuI_2$  by the action of  $CH_3I$  on  $CuO$ .  $CuI$  and gaseous products were obtained, and no iodine appeared.

In Brisbane he turned to the study of methods of preparing sub-salts and sub-oxides. He improved Tanatar's method for  $Pb_2O$ , heating the oxalate under reduced pressure at  $270^\circ C$  rising slowly to  $335^\circ$ , and obtaining a dark powder of density 8.345 ( $Pb + PbO$  gives 9.975), which gave a heat of solution in acetic acid less by 5.45 Kgm cals per mol than a 1:1 mixture of Pb and PbO.  $PbI$  was also made, and using the conductivity method in the absence of air, its solubility was found to be one-nineth that of  $PbI_2$ . Other lead sub-salts were prepared from the suboxide, and their properties determined. Tanatar had also claimed  $Cd_4O$  by heating the oxalate in  $CO_2$  at  $300^\circ C$ , and  $Cd_2O$  from the basic oxalate. Repetition of this work in vacuo gave products containing the metal. When this was distilled out, a 4% yield was obtained of a green solid which analysed as  $Cd_2O$ . Other methods reported for the preparation of  $Cd_2O$  by reduction of  $CdO$  were examined and shown to be unsatisfactory. A 5% yield was, however, obtained by the method of Morse and Jones, who dissolved Cd in molten  $CdCl_2$ , and obtained a product  $Cd_4Cl_7$ , equivalent to  $3 Cd Cl_2$ .  $Cd Cl$ , from which  $CdOH$  and  $Cd_2O$  were made. Further work on bismuth led to the preparation of  $BiO$  from bismuth oxalate, and the action of methyl iodide gave, among other products, a small yield of bright red crystals,  $BiI_2$ . At this point, Dr. Denham's appointment to Capetown interrupted the work, and it was not till several years after his return to Canterbury

College that he took up the study of cadmium compounds again with a new apparatus. He was unable to obtain homogeneous preparations of CdI, and his increasing absorption into administrative tasks finally caused him to surrender his research work.

Mr. Packer then discussed more recent work in the field of sub compounds. Hollens and Spencer (1934) prepared  $\text{Cd}_4\text{Cl}_7$  by the method of Morse and Jones and showed that its magnetic susceptibility agrees very closely with that calculated for  $7\text{CdCl}_2 + \text{Cd}$ . Metallic Cd could be extracted from the product by mercury. Cd OH and  $\text{Cd}_2\text{O}$  obtained from it were not homogeneous enough for the magnetic method. They did not examine a product from the oxalate method, with distillation of the metal. Hedger and Terrey (1936) also repeated Morse and Jones' preparation, and showed that the  $\text{Cd}_2\text{O}$  obtained gave 32 lines identical with those of CdO by the X-ray spectrograph. (A slide of this was shown). Melting point curves for the system Cd— $\text{CdCl}_2$  show a eutectic at  $7\text{CdCl}_2 + \text{Cd}$ . The lecturer remarked that the physical methods have not been applied to the sub compounds of lead and bismuth, which the work of Dr. Denham and others show to be much more definite than the cadmium compounds.

It is now possible to make an approximate calculation of the stability of some compounds with respect to likely decomposition products. If heat is evolved in the reaction  $2\text{CuCl}(s) = \text{CuCl}_2(s) + \text{Cu}(s)$ , then CuCl is likely to be thermo-dynamically unstable with respect to  $\text{CuCl}_2$  and copper. More strictly, the free energy change of the reaction measures the extent of the reaction, but for solids, the difference can be neglected. It is possible to calculate the heat of such reactions, the necessary data being the lattice energies of the salts, the heat of sublimation of the metal and the first two ionisation potentials of the metal. Such a calculation shows that CuCl is stable, as is well known. Similar calculations were shown, involving reasonable assumptions for the values of the lattice energies of the sub compounds, and they indicate that CdCl,  $\text{Cd}_2\text{O}$  and PbI are unstable.

At Canterbury College, Dr. Denham returned to the hydrolysis of salts, the quinhydrone electrode being used under his direction by N. A. Marris to give stable potentials, while the hydrogen electrode gave drifting values. These phenomena are probably best explained by the work of Kolthoff, who showed that platinum black adsorbs cations in the presence of hydrogen,  $\text{H}^+$  ions passing into solution. No such adsorption occurs in a nitrogen atmosphere. Hence a hydrogen electrode of the usual type cannot be expected to function satisfactorily in unbuffered solutions. Using plated platinum instead of platinum black, Kolthoff was able to make measurements in KCl and  $\text{ZnSO}_4$  solutions, agreeing with colorimetric values.

There is thus no reason to postulate the existence of sub-ions in solution to explain the hydrogen electrode results.

Mr. Packer briefly described Dr. Denham's other work, on heterogeneous catalysis at Heidelberg and on auto-complexes at Liverpool and Brisbane. He said that he laid considerable stress on the research work, not only because he was speaking to members of the Institute of Chemistry but also because during the last fifteen years, Dr. Denham's great services to the University in other directions have tended, perhaps, to obscure the fact that he was foremost a chemist and university man who appreciated to the full the importance of active research work, by the lecturing staff of a science department for its proper functioning. After discussing the administrative activities which had employed part of Dr. Denham's time in recent years, the speaker explained the plans maturing for courses in applied chemistry and chemical engineering. "In view," he said "of the great interest Dr. Denham always showed in Applied Chemistry and his plans for its development at this College, and because of his own great services in the fields of applied science and industrial research, I wish to take this opportunity of supporting very strongly the suggestion that a fitting memorial to him would be a Memorial Laboratory of Applied Chemistry, within or closely connected with this his old department of chemistry."

Moving the vote of thanks, Sir Theodore Rigg said that it was most appropriate that the first Denham Memorial address should be given by one who had been so closely associated with Dr. Denham at Canterbury College, and spoke of the sound training given to students of the department. Dr. H. N. Parton seconded the vote, paying tribute to Mr. Packer's work during the past twenty years.

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### **RESUME OF MINUTES OF COUNCIL MEETING HELD ON NOVEMBER 11th, 1943.**

Present: Sir Theodore Rigg (President), Dr. R. O. Page (Vice President), Mr. W. G. M. Hughson (Auckland Proxy), Dr. E. B. Davies (Wellington Proxy), Mr. S. H. Wilson (Canterbury Proxy), Dr. J. K. Dixon (Otago Proxy) and Mr. J. A. D. Nash (Hon. Secretary-Treasurer). Dr. J. C. Andrews (Auckland) attended by invitation

**Trust Fund.**—There was some discussion on the final draft of the minutes to govern the Trust Fund. Recommendations were made for reference to Branch Committees. The appointment of Trustees was deferred to the next meeting.

**Associates.**—The following were elected Associates of the Institute: Miss M. J. Taylor (Dunedin), Mr. W. T. H. Paulin (Dunedin).

**Fellows.**—The following were elected to the Fellowship: Mr. C. L. Carter (Dunedin), F. T. Seelye (Wellington), S. H. J. Wilson (Wellington).

**Salaries of Chemists.**—A discussion took place as to whether it was appropriate at the present time, to undertake a survey of the salaries paid to chemists in New Zealand. A recommendation that this should be undertaken in the case of laboratory workers was received from the Otago Branch. It was resolved that the matter be referred to the Wellington Branch with the request that they explore the position and report back to the next meeting of Council.

**Laboratory Assistants' Certificate.**—The Auckland Branch raised the question as to whether the Laboratory Assistants' Certificate examination should be looked upon as a suitable goal for Returned Servicemen. It was resolved that in general a returned Serviceman wishing to enter the profession of Chemistry, should be encouraged to matriculate and take a University degree if at all possible.

**Annual Report and Balance Sheet.**—The draft Annual Report and Balance Sheet were approved for circulation to members. It was agreed that in future the Council should draw up an Income and Expenditure Account and Balance Sheet as well as the Statement of Receipts and Payments.

**Election of Officers.**—The following officers were unanimously elected: President, Dr. R. O. Page (Christchurch); Vice President, Dr. J. C. Andrews (Auckland); Secretary-Treasurer Mr. J. A. D. Nash; Auditors, Messrs. Dymock, McShane and Selanders.

In declaring the officers elected Sir Theodore Rigg offered his congratulations on their election and expressed the hope that they would have a successful year in office.

It was decided to appoint Mr. W. G. M. Hughson as Assistant General Secretary-Treasurer and that he should be acting Secretary-Treasurer during the absence of the General Secretary from New Zealand.

**Recognition of Associateship.**—The Secretary was instructed to write to the Public Service Commissioner requesting recognition of the A.N.Z.I.C. as being at least equivalent to a B.Sc. degree.

**Appreciation.**—Dr. J. K. Dixon expressed the appreciation of Council and of the members to the Institute to Sir Theodore Rigg for the excellent manner in which he had carried out his duties of President during the past two years. Sir Theodore in expressing his thanks and pleasure for the expression of appreciation stated that he hoped the incoming President would receive the same measure of support from the members as he himself had.

## EXAMINATION FOR ASSOCIATESHIP, 1943.

### PRACTICAL CHEMISTRY

Monday, June 28th to Wednesday, June 30th.

The candidate must hand in reports to the supervisor at the end of each day, written in full detail, so that the examiner can follow all the important steps by which the results were obtained. Results of A1, A2, A3, are required at the close of the first day, results of C and D at the close of the second day, and the results of the two quantitative exercises B and E at the close of the third day's work.

Monday, June 28th, 8.30 a.m. to 5 p.m.

Identify the salts A1, A2, A3. Commence analysis of solution B which contains K, Ca, Mg. Quantitative estimations of these three elements are required—identification of anions or other metals is not asked for. Submit results of A1, A2, A3.

Tuesday, June 29th, 8.30 a.m. to 5 p.m.

Identify the mixtures C and D, each of two organic substances. Determine colorimetrically the approximate composition of C. Continue the analysis of solution B. Submit results of C and D.

Wednesday, June 30th, 8.30 a.m. to 5 p.m.

Estimate the total and ammoniacal nitrogen in mixture E. Complete analysis of B (express results as grams per litre) and submit final results.

Free access to literature is permissible.

The substances used were as follows:—

- A 1. Calcium tungstate.
- A 2. Potassium met-antimonate.
- A 3. Aluminium phosphate.

Solution B. Grams per litre.

|                  |      |
|------------------|------|
| K <sub>2</sub> O | 4.58 |
| CaO              | 3.66 |
| MgO              | 4.43 |

- C. 10 grams salicylic acid made up to 100 ml., with, isopropyl alcohol.
- D. Phenol and benzyl alcohol.
- E. Ammoniacal nitrogen — 9.49%  
Nitrate nitrogen — 7.66%

The Institute as a whole is not responsible for statements and opinions appearing in this Journal.

Correspondence should be addressed to Dr. H. N. Parton, Canterbury College, Christchurch.

The address of the Hon. Secretary is P.O. Box 250, Wellington.

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