JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

VOL. XVII. **APRIL, 1953** **No. 2**

CONTENTS:

FLUORINE

FROM the famous Blue John mines in Derbyshire comes a mineral called fluorspar. For generations this has been mined in the North of England for use as a flux in metallurgical processes and for making enamels and glass. Today fluorspar has assumed a new importance. It is the chief source of hydrofluoric acid, the compound from which the element fluorine is obtained. Fluorine is chemically so active that it combines with glass and other materials normally used in chemical apparatus. Moissan, the famous French scientist who in 1886 first isolated it, used platinum apparatus which, though attacked, reacted sufficiently slowly to allow him to isolate some free fluorine gas. For over fifty years this elusive element remained a chemical curiosity, but during the war it was needed in large quantities for the manufacture of certain uranium compounds for the atomic energy projects. The result was so to intensify the research on fluorine chemistry (a great deal of it in I.C.I.'s laboratories) that fluorine is now produced on an industrial scale. Certain fluorine compounds are astonishingly resistant to corrosion and decomposition, a property which is of great value commercially.

I.C.I. uses some of these in the manufacture of 'Arcton' refrigerants, which are non-toxic and non-inflammable, and 'Fluon', a new plastic material.

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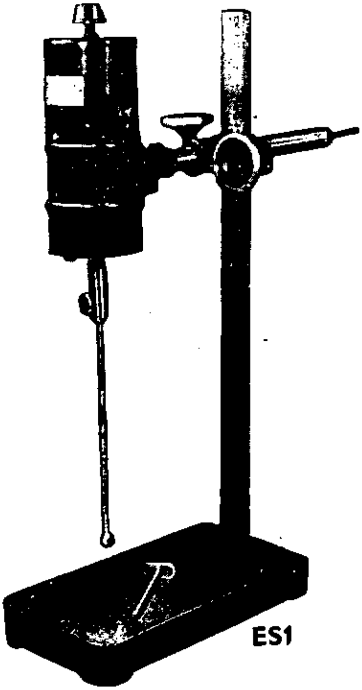
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JOURNAL OF THE
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RESPIRATION IN PLANTS—WITH SPECIAL REFERENCE TO THE FLUE-CURING OF TOBACCO

by H. O. ASKEW
Cawthron Institute, Nelson.

(Mellor Memorial Lecture 1952)

RESPIRATION DEFINED

For our definition of respiration we will use Bonner's, which is as follows: "By respiration is meant the sum total of the biological reactions in which organic material is oxidized to simpler compounds"—which is very general and can cover a multitude of reactions, and suggests that an organism lives by reason of the interplay of many reactions occurring in dynamic equilibrium, reactions concerned with carbohydrates, proteins, acids, fats and other compounds. We are reminded then of Hopkins' dictum, "Life is a dynamic equilibrium in a polyphasic system." So while we shall find it necessary to separate our discussion of respiration into certain divisions we must not think that they are so isolated by the organism.

Respiration is dependent on the presence of oxygen, as distinct from fermentation which is essentially an anaerobic process. Oxidation need not however consist in the direct participation of molecular oxygen: there may be removal of hydrogen, or there may be addition of water followed by removal of hydrogen. The processes of oxidation are carried out by means by enzymes: by oxidases where molecular oxygen is concerned, by dehydrogenases where hydrogen is removed from the compound directly or after addition of a molecule of water. Most of these enzymes consist of two parts, a protein and a non-protein, the former being the apoenzyme and the latter the prosthetic group, which is also known as the co-enzyme in those

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cases where the prosthetic group is easily removable by dialysis. For many of the enzymes too the presence of inorganic ions such as Mg, Mn or Zn is required, and, most important of all, phosphate ions to form esters which act as co-enzymes. These phosphate compounds will be shown to be intimately concerned with the transformations of carbohydrates and organic acids.

THE FLUE-CURING PROCESS

Before going any further let us look for a moment at the process of flue-curing of tobacco and of the main changes which are found to have occurred in certain chemical constituents in passing from the fresh to the cured leaf. In flue-curing of cigarette types of tobacco there are broadly three stages, the first two chemical (or biological if you wish) and the third physical, each being related to the conditions of temperature and relative humidity of the air in the kiln. When the leaf is picked from the parent plant its source of nutriment is removed, and thus any living processes which continue are carried out under starvation conditions, or in other words they must use what chemical compounds are already present in the leaf. Therefore in the first stage of curing, technically called yellowing, or colouring, because of the change in appearance of the leaf from green to yellow, enzyme activity continues owing to the favourable conditions of relatively low temperature (about 30-35° C.) and of high relative humidity (80-100 per cent.). Next, the temperature is raised, finally to about 55-60°C., and the humidity is reduced, with the result that the leaf is too dry for enzymic action to continue. This stage is called fixing, because at the end of it the colour is fixed, not altering appreciably during the remainder of the curing process. The main changes which occur in the leaves during these two stages are breakdown, or at any rate disappearance, of large amounts of starch, and of water-insoluble nitrogenous (protein) material, and the appearance of large amounts of soluble sugars and soluble nitrogenous compounds; there is also a considerable evolution of carbon dioxide and loss of dry matter. Following these two periods of intense chemical activity within the leaf is the drying period for removal of water from the blade and the veins—a physical process ending at a temperature of about 80°C. and a relative humidity of 10-15 per cent. What we are to examine then is the process or processes by which starch, protein, and dry matter are lost, and by which soluble sugars and soluble nitrogenous compounds are developed. The production of carbon dioxide will also interest us. All the reactions are carried out in darkness.

CARBOHYDRATES

Let us begin with the carbohydrates. Analysis of fresh material indicates that in tobacco leaves which are ready to pick, starch is present in amounts up to 35 per cent. of the dry matter, while reducing sugars and sucrose occur to the extent of only one to two per cent. The suggestion therefore is that our inquiries should begin with the starch. In tobacco starch is present as the amylose form. This can be hydrolysed by β-amylase, with addition of water, to give maltose and small amounts of maltose are found in cured tobacco. But we cannot readily go direct from maltose to the hexose sugars and sucrose, although the enzyme maltase occurs in tobacco leaves. There is however, another enzyme, starch phosphorylase, which in the presence of inorganic phosphate, will hydrolyse starch to form α-glucose-1-phosphate and this compound can undergo further change with fructose to form sucrose, or take part in other rearrangements. The important change to glucose-6-phosphate is carried out by phosphoglucomutase. This new sugar ester takes part in a reversible system with hexokinase to form glucose:

$$\text{glucose-6-phosphate} + \text{ADP} \overset{\text{hexokinase}}{\leftrightarrows} \text{glucose} + \text{ATP}$$

We here meet two new compounds ADP and ATP, namely adenosine di- and tri-phosphates, the importance of which we will discuss later. The above equation shows that the phosphate radical from the sugar ester has been added to ADP to form ATP. But glucose-6-phosphate by the further action of phospho-hexo-isomerase becomes fructose-6-phosphate, which may be hydrolysed by a phosphatase to give fructose, so that free fructose is available for reaction with glucose-1-phosphate to form sucrose: for glucose and fructose do not unite directly to produce sucrose. Fructose-6-phosphate by inter-action through the enzyme phospho-hexo-kinase in the presence of ATP produces fructose-1.6-diphosphate (and ADP). This diphosphate by the action of aldolase rearranges to give two molecules of the triosephosphates, dihydroxyacetone phosphate and 3-phosphoglyceraldehyde, which in the presence of the enzyme phosphotrioseisomerase, produce an equilibrium mixture consisting of 96 per cent. of the ketose dihydroxyacetone phosphate and 4 per cent. of the aldose 3-phosphoglyceraldehyde. The latter by oxidation with DPN (diphospho-pyridine nucleotide) forms phosphoglycerate; it is probable however that 1.3 diphosphoglyceraldehyde is formed as an intermediate, being oxidised to the corresponding glycerate, which with ADP reacts in the presence of a phosphokinase to produce 3-phosphoglycerate and ATP. Transphosphorylation to 2-phosphoglycerate follows, and then by the action of enolase 2-phosphopyruvic acid is produced. Enolase is a magnesium-protein compound whose action is strongly inhibited by fluoride ions and interference with hexose breakdown by these ions is usually due to their action on this enzyme. One further step bringing about removal of the phosphate radical leaves us pyruvic acid, an acid widely distributed in plants. The result of all these transformations is that for one mol of hexose two energy-rich phosphate groups (in ATP) have been formed and in addition two mols of DPN have been reduced: the latter can be readily oxidised by atmospheric oxygen. The equation representing the sum of the changes in these hexose reactions is:

$$C_6H_{12}O_6 + O_2 \rightarrow 2C_3H_4O_3 + 2H_2O.$$

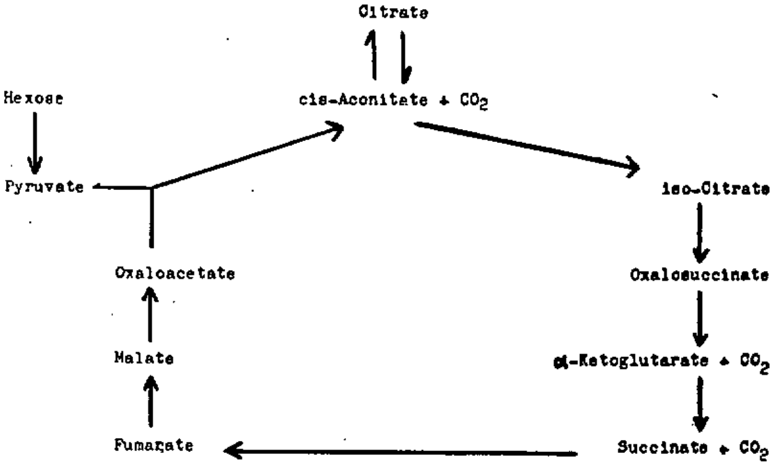
We have noted that most of the reactions have been dependant on the presence of phosphate, either in the inorganic form or as the compounds ADP, ATP and DPN. The phosphorylated sugars are well-known as constituents of plants. Now the addition of phosphate to the sugars absorbs energy, and doubtless some of the energy derived from oxidation of various compounds during the vital processes of the plant is used in this way. Two kinds of phosphate addition are recognised, one requiring about 3000 cals. per mol and the other about 12,000 cals. or even 16,000 cals.: this latter has been termed energy-rich and is the one which takes part mostly in the various additions and removals of phosphate from the intermediates that we have been discussing. We may note that about 80 per cent of the energy of oxidation of the hexose molecule still remains in the pyruvic acid that is formed.

We must be honest and recognise that all the enzymes required in the several processes of the hexose changes have not been found as yet in plant tissue, the above system being based on researches with animals. But certain of the changes have been produced by plant material, and blocking of the oxidation of hexoses can be brought about by the same chemical agents that block the reactions in the animal. Moreover plants do oxidize hexoses so that it is probable that many, if not all, of the required enzyme systems are present in plant material.

In the systems studied above the equations indicate that starch and hexoses have been oxidised to pyruvic acid. However experimental curings of tobacco leaves on both laboratory and commercial scales have very definitely shown that in flue-cured tobacco there is a large build-up of hexoses, particularly glucose, and a smaller development of sucrose. It would appear therefore that the hydrolysis of starch proceeds at a much greater rate than the oxidation of hexoses. Increase in sugar content is progressive throughout the colouring period but is slowed down during fixing. By the time these stages have been completed there may be 25 per cent of hexoses and 2-5 per cent of "sucrose" (the latter including all sugars hydrolysed by dilute acid). It will be remembered that the presence of maltose was mentioned, but we have no data as to the amount in New Zealand tobacco. We believe that there are at least three other sugars present, a trisaccharide (probably) which is not raffinose, a pentose and another of unknown type.

THE PART OF ORGANIC ACIDS

We finished our discussion of the changes of carbohydrates at pyruvic acid. The possible complexity in proceeding further can be realised when it is found that at least fourteen different ways in which pyruvic acid can be oxidised have been reported. We shall however consider a system of reactions in which this acid takes a key position, namely the Krebs, or tricarboxylic acid, cycle, the latter name arising from the important position given in it to citric acid. But in actual fact the exact relation of citric acid to the cycle does not seem to be finalised yet. The reactants in this cycle consist of a number of well-known, and not so well-known, organic acids, all of which, together with the necessary enzymes for their interconversion have been found in plants: thus malic, citric and succinic acids occur in relatively large amounts, while fumaric,



Krebs, or tricarboxylic acid, Cycle

isocitric, aconitic, oxaloacetic and α-ketoglutaric acids are usually found in small quantities only. Again we must be honest and state that not all of these acids or the necessary enzymes for their interconversion have been found in any one plant. Let us now consider the transformations occurring in this cycle.

For a number of years it was believed, owing to the ready transformation of several organic acids into one another in living tissues, that these acids acted as intermediates during respiration. Curiously enough acetic acid was considered to commence the series of reactions, this acid being formed from pyruvic acid, and then to be converted to succinic acid by a condensation reaction. This scheme was not satisfactory owing to there being no known means of bringing about this condensation. It is of great interest however, to find that present ideas include the conception of an "active acetate", possibly acetyl phosphate, as the first product from pyruvic acid. The experimental basis for the cycle is that citric, succinic, malic and fumaric acids are all readily utilised. This is true of animals as well as of plants, and specifically of tobacco. Thus Pucher and Vickery found that all of these acids, together with acetic, and isocitric, are metabolized but acetic was utilised only at a late stage. With tobacco, as with animal tissue, malonic interferes with the oxidation of succinate to fumarate. While β-ketoglutaric acid has not been tested to my knowledge, except in the synthesis of amides in plant materials, it occurs in plants and is probably present in tobacco leaves. This acetate is placed in the cycle between oxalosuccinic and succinic acids. In the present version of the cycle citric acid is placed in a branch position, not in the main system. The first reaction of the cycle is condensation of the pyruvic acid residue with oxaloacetate by loss of a molecule of carbon dioxide and two hydrogen atoms to form *cis*aconitic acid, which by action of the enzyme aconitase takes part in an equilibrium mixture of citric 80 per cent, aconitic 4 per cent and isocitric 16 per cent. Hence no matter which acid is formed first the same final mixture is obtained. Direct reaction between acetate and oxaloacetate may also occur, so that in spite of the placing of citric acid in a side-arm position, there is still the possibility that it should be in the main cyclic system. Iso-citric acid dehydrogenase with TPN oxidizes iso-citric acid to oxalosuccinic acid. Another enzyme aconitase converts aconitic acid as well as citric, specifically in the latter case, to iso-citric acid, as we have seen above. By the action of oxalosuccinic carboxylase with loss of carbon dioxide the oxalosuccinic acid forms β-ketoglutaric acid. This last acid by loss of two H atoms and a molecule of carbon dioxide yields succinic acid, but the precise means by which this is brought about in the plant does not seem to have been examined. Succinic acid by the action of succinic dehydrogenase is oxidised to fumaric acid, which in turn through the operation of fumarase yields malic acid. Fumarase is widely distributed in plants and usually an equilibrium mixture of fumaric and malic acids is formed in its presence. In the final step malic acid is oxidized to oxaloacetate by malic dehydrogenase in the presence of DPN. Thus we have oxaloacetate ready to react with further quantities of pyruvic acid. The net result of this cyclic series is that a molecule of pyruvic acid is oxidised thus:

$$C_3H_4O_3 + \frac{5}{2} O_2 \rightarrow 3CO_2 + 2H_2O.$$

There is one further point to consider: how does the atmospheric oxygen enter the system? It appears to be generally agreed that this is through the action of the cytochrome C system, but we will not discuss this further.

It should be pointed out that this cycle is probably not reversible, and must therefore proceed in one direction, namely progressive oxidation of substrates, because two steps (1) the change of pyruvic acid to active acetate and (2) the oxidative decarboxylation of α-ketoglutaric acid are probably not reversible.

IMPORTANCE OF PHOSPHATE

We have noted that in the oxidation of the hexoses to pyruvic acid various phosphates were required as carriers of energy. The same applies to many of the reactions in the Krebs cycle, in particular to the oxidation of succinate, fumarate and α-ketoglutarate. But it has not proved possible yet to account for all the energy released by the combustion of a mol of glucose: this would be 680,000 calories. Of this quantity only about 290,000 calories can be accounted for as energy-rich bonds in the scheme. This simply means that the precise pathways by which the various transformations are carried out are not known.

Baldwin in his "Dynamic Aspects of Biochemistry," has drawn attention to this, and has the further comment to make: ". . . succinate, malate and the rest . . . would fail to undergo dehydrogenation if inorganic phosphate were rigidly excluded from the medium, but, in the past, it has been an article of biochemical faith that enzymic reactions should only be studied in buffered media, and the buffer of choice has usually been one of the phosphate series. Certainly no one has dreamed of trying to exclude every trace of phosphate from his experiments, but, had this been done in the past, we might well have known more than we do today about the mechanisms of these apparently simple dehydrogenation reactions and, incidentally, about the generation of new energy-rich bonds." May I say that as a chemist coming to deal with living material, the habit of biologists and biochemists of flooding their material with liquid has always seemed to me to be introducing the tissues to completely abnormal conditions. I was interested to find recently on visiting Dr. Mulder, well-known to many of you for his work on the use of fungi for determining trace elements, that he had the same idea and was proceeding to examine biological reactions on tissues supported free in the air and not swamped in liquids. The results of his work will be awaited with great interest.

Let us further consider for a moment the organic acids of tobacco. The two acids found usually in the greatest amounts are malic and citric, the former in cured cigarette leaf and the latter in cigar leaf. Lesser amounts of oxalic acid occur, together with small quantities of succinic and other unknown acids. In flue-cured tobacco malic acid may be present up to 10 per cent and citric and oxalic each at about 1 per cent. A large amount of work has been carried out by Vickery in the U.S.A. on the transformation of malic to citric acid during air-drying. However for flue-cured tobacco the evidence of Garner and others is that this change does not take place. To date we have no information on this point in respect of New Zealand tobacco, but I hope that this omission will soon be overcome. Oxalic acid is strangely unresponsive: not only in tobacco but in other plants also oxalic acid does not seem to take part in the respiration processes—and you will have noticed that there is no place allotted to it in the Krebs cycle. It is possible that it may be formed by a branch reaction at the acetate stage through glycolic and glyoxylic acids. Can it be that by precipitation as calcium oxalate it is removed from any effective part in further reactions?

We have now studied two oxidative reactions represented overall by the equations:

$C_6H_{12}O_6 + O_2 \rightarrow 2C_3H_4O_3 + 2H_2O$ aerobic glycolysis

$2C_3H_4O_3 + 5O_2 \rightarrow 6CO_2 + 4H_2O$ Krebs acid cycle.

these by summation give

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

which is the usual simple, inoffensive-looking, text-book equation for the oxidation of hexose during respiration. Notice that the ratio of carbon dioxide produced to that of oxygen used, the respiratory quotient, is unity. On the other hand the complete oxidation of malic acid would give a quotient of 1.33 ($C_4H_6O_5 + 3O_2 \rightarrow 4CO_2 + 3H_2O$).

One method therefore of explaining the overall reactions during respiration is to determine the respiratory co-efficient. If carbohydrate is the sole oxidised constituent then the ratio will be 1; acids give greater values and proteins lower values. It is commonly found that in early stages this co-efficient is unity or greater, but that it may rapidly fall to lower values. This has been explained as being due to the exhaustion of the carbohydrate supply and recourse by the organism to other constituents to supply energy. This explanation is not by any means satisfactory: different species may behave differently, and again the experimental conditions have not always been such that the participation of other compounds, for example starch or protein, was sought for at a sufficiently early stage. In many experiments where this has been done early participation of protein in the reactions has been detected. We shall therefore now examine the changes in protein content during respiration. The researches of a number of workers show that, except under conditions of high internal supply of sugars, especially sucrose, breakdown of protein commences very soon after removal of the leaves from the parent plant. So suddenly does this occur that hormonal control of the reactions has been suggested. Let it be said too that this type of change occurs in the dark, not in the light: under the latter condition synthesis of protein may continue even after removal of the leaves. That some form of control is exercised is shown by the stated failure of tobacco leaves to cure if the main vein is removed or even split—an experiment that it is hoped to carry out sometime.

PROTEIN BREAKDOWN

Although, in view of the interdependence of different classes of compounds and of the many types of reactions occurring in living matter, no constituent can really be claimed to be more important than another, yet it can be truthfully said that the class of compounds most characteristic of living matter is the proteins. So we shall now examine further some of the reactions in which they take part.

All proteins are made up from about 25 amino acids, the combination of the acids to form the complex material that we call protein being probably through the amino (in an α position generally) and the carboxyl groups. Because of the number of amino-acids it is clear that an almost infinite number of combinations is available so that many proteins of differing properties should be possible: these will vary in the ease of hydrolysis and so on. Therefore on hydrolysis there may be amino-acids released, or there may be more complex substances (peptides) composed of several amino-acid residues in combination. Some ammonia may be set free to combine with amino-acids to form amides. The carbon skeleton from which the ammonia was derived may then enter into other reactions.

A considerable amount of experimental work suggests that these carbon skeletons enter the Krebs acid cycle, and also that the acids of this cycle may react with nitrogen-containing residues.

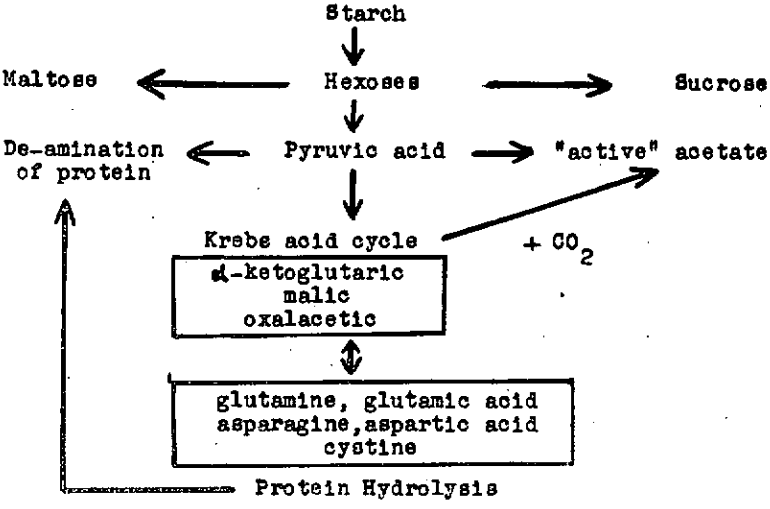
The most active of the amino-acids are glutamic and aspartic. There are mechanisms known by which these can be formed through the Krebs cycle; and if derived from hydrolysed protein they can react readily with acids of the cycle through the reversible action of enzymes called transaminases whereby for example, glutamic can lose its amino-group to, say, pyruvic acid with resultant formation of α-ketoglutaric acid and alanine; glutamic acid can also take part in reactions leading to the formation of aspartic acid. Both aspartic and glutamic acids are very active metabolically and appear to be placed in a very important position in the amino-acid sequence of reactions. And both readily form the corresponding amides, asparagine and glutamine. In practically all experiments with leaves held under starvation conditions one or both of these amides appear as a major conversion product of the nitrogenous catabolism. In one species it may be asparagine, in another glutamine. Tobacco, at any rate the cigar types, shows the interesting behaviour of producing almost wholly asparagine in the dark but both asparagine and glutamine in the light. Seeing that flue-curing is a darkness procedure we shall look for an increase in the asparagine content of the leaf: but the evidence is that there is practically no increase in amide nitrogen until very late in the curing process. As yet we have no data on glutamine and asparagine or on α-amino-N content, for our own experimental curings. For cured leaf other workers have found that α-amino-N represents about one-sixth of the total soluble-N.

As another line of approach to the problem of protein breakdown a possibly important position has been given to cystine by some workers, using it is true mainly gramineous species, because it was found that cystine disappeared in the largest amount from protein in starved leaves. A certain amount of work has been done on this question in Nelson but we have not reached finality in our ideas as to whether cystine may have the same key position in the tobacco leaf. The interest in cystine too is because its reactions can be linked up with Krebs cycle. We have found, with others, that in fresh tobacco leaf about 70 per cent of the total sulphur is in the inorganic form, precipitable directly by barium chloride. There is also other water-soluble sulphur present. In cured leaf, and in leaf in process of being cured protein-S does disappear as such, but a corresponding amount of sulphate-sulphur or other water-soluble sulphur does not appear. So we do not know just what happens.

Enzymes of considerable activity for decomposing proteins are present in tobacco leaves. They are of the protease type, which will act on whole protein, and of the peptidase type which will only decompose the partially broken-down protein material, namely the peptides. Each peptidase reacts specifically with a relatively simple peptide consisting of only a few amino-acid groups. Peptidases too apparently require a metal ion—usually cobalt, magnesium or manganese—to be present if they are to be active. On the other hand proteases appear to depend for their activity on the presence, among other compounds, of a sulphydryl group, such as occurs in cysteine: this amino-acid is easily produced by reduction of cystine.

We have now covered the three great groups of compounds, carbohydrates, acids and proteins, in the leaves. Other reactions occur too because of the change in colour from green to yellow, due to destruction of chlorophyll. It is known too that other complex carbohydrates such as the dextrins take part in the reactions during curing. But in just what manner these may be linked into the main channels of the reaction streams is not clear.

As a summary of what we have been discussing the following brief diagram is offered. Only the most important of the compounds probably taking part in the reactions are set out. The



grouping at the Krebs cycle and the protein hydrolysis positions indicates the compounds which are the most active connecting links between the two systems.

I feel that the connections suggested in the literature between the Krebs cycle and the protein system are not at all satisfactory and that much more information of a very detailed nature is required before this situation is overcome. One cannot say for certain that the Krebs cycle exists in plants: it can only be said that such work as has been done with plants to test it has generally given results not in conflict with it.

EXPERIMENTAL RESULTS WITH TOBACCO

We have now covered in outline some of the changes which occur during respiration. The whole process is thus an integrated one (as we were warned at the outset!) of several series of reactions and types of compounds. What experimental evidence is there for inter-relationships in these changes during flue-curing? Firstly let it be said that leaf of varieties suitable for flue-curing has a low protein and a relatively high starch content when harvested. It is therefore of quite a different type from the cigar varieties with which most of the intensive work in tobacco chemistry has been done.

In a laboratory investigation using single leaves it was found that the hourly rate of respiration was approximately 1.5 mg. of carbon dioxide per g. of fresh material, or 5 mg. per g. of dry matter. Thus about 350 c.c. of carbon dioxide are evolved per hour per pound of fresh material. Other workers have shown too that the reactions can be interfered with if the carbon dioxide content of the air becomes too high. The rates of respiration were proportional to the protein-N content of the leaf—a relationship that has been obtained by other workers using other species of plants. The evolution of carbon dioxide was fairly steady in some cases over periods of up to 60 hours. During this time a large proportion of the protein-N was rendered water soluble, at an average rate per hour of 0.65 per cent of the original amount. This was independent of the original percentage of protein-N, which varied from 1.07 to 1.49 per cent on the dry matter basis. In recent experiments in a commercial-size kiln breakdown of protein, loss of starch, and increase in hexose sugars content could be detected 6 hours after the leaf had been placed in the kiln. In another trial, with progressive breakdown of protein, which occurred at an hourly rate of 0.60 per cent of the original protein content of 0.90 per cent, reducing sugars, mainly glucose, increased in a linear relationship to the amount of protein-N hydrolysed: sucrose increased to a smaller degree. There was also a linear relationship between the absolute percentage of protein-N rendered water-soluble and the reduction in percentage content of starch. Then taking the starch equivalent of the soluble sugars and subtracting that from the over-all loss of starch left a figure which was again linearly related to the amount of protein-N hydrolysed. This figure is a measure of the loss of dry matter through evolution of carbon dioxide in the respiratory processes, and agrees fairly well with the determined loss of dry matter. There is of course, in view of the earlier discussion, an addition of carbon-containing residue from protein to be made to that figure for loss of dry matter as determined analytically.

In the laboratory experiments, four trials indicated that the average carbon content of the disappearing organic solids was 46.0 per cent. In the large scale trial approximately the same figure has been found. Calculation from the data of Vickery in U.S.A. yields approximately the same figure. It would appear, therefore, that, in tobacco at any rate, the compounds completely oxidised in the respiratory processes are of very constant composition, although being present in material of widely varying original starch and protein contents.

We are in New Zealand building up a body of information on the chemical changes occurring during the curing of our cigarette-type tobaccos, but we still have a large amount of work to do before we will be able to understand at all fully just what is happening in the leaf. We require information on: the respiratory quotient throughout the curing process, the classes of sugars present and their amounts, what amino-acids and amides (and their concentrations) are present, the fate of phosphorus and sulphur-containing compounds, and of the fats, oils and structural materials. There is no visible shortage of research projects in tobacco chemistry! And finally, in what way are all these changes related to quality as shown by consumer preference and demand?

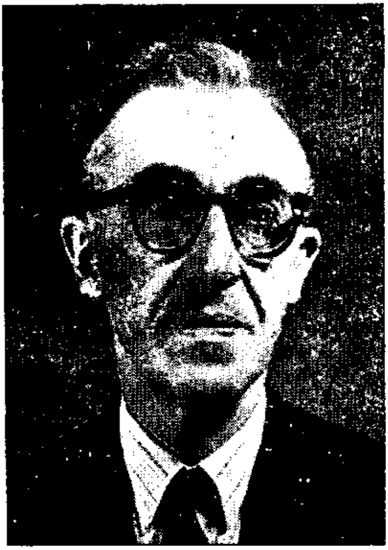
CONFERENCE NEWS

Confirmed dates for Conference are Wednesday 26th August to Friday 28th August, inclusive. On the Tuesday evening there is to be a brief official welcome and the enrolling and on the Friday evening the Conference will be concluded with a social function.

Programme details are still being decided but one feature of the sessions will be a symposium entitled "Contributions of Chemical Science to New Zealand Economy."

Professor Emeleus is expected to be in N.Z. during Conference and it is hoped that he will be free to attend at least part of the time.

OUR NEW VICE-PRESIDENT


DR. H. O. ASKEW

Dr. H. O. Askew was born in Whangarei but early removed to Christchurch where he was educated at Boys' High School and Canterbury University College. During the University course he obtained several College prizes for Chemistry and finally graduated M.A. with first class honours in Chemistry. Having worked during long vacations in the New Zealand Refrigerating Company's laboratory, he entered the employment of that company in 1920 and remained there until August, 1924, when he went to England as a holder of a Dominion Research Scholarship to the Imperial College of Science and Technology. At the Imperial College he studied for the London Ph.D. degree under the late Professor J. C. Philip, F.R.S. This degree was awarded for a thesis dealing with the production of fogs during certain chemical reactions. In addition he was awarded the Diploma of the College. During 1927 Dr. Askew was at the Fuel Research Station at Greenwich. Returning to New Zealand at the end of that year he became Research Chemist with the Refrigerating Company, but left there in the middle of 1928 to become Pasture Research Chemist at the Cawthron Institute. From that date to the present he has been at the Cawthron Institute being later successively Agricultural Chemist, Head of the Chemical Division and Chief of the Biochemical Department. For a number of years Dr. Askew has been intimately associated with laboratory and field work dealing with nutritional disturbances due to deficiencies of trace elements; in addition he has worked on the chemical composition of fruits, hops and tobacco. During most of 1951 Dr. Askew was overseas following the award of a Visiting Lectureship by the Nuffield Foundation. He visited a large number of research stations in Great Britain and on the Continent and also attended the First World Tobacco Congress at Amsterdam.

In addition to being a Fellow of the New Zealand Institute of Chemistry, Dr. Askew is also a Fellow of the Royal Institute of Chemistry and of the Royal Society of New Zealand.

Dr. Askew is married, with three children. He is an omnivorous reader, a keen bowler, and a gardener as necessity requires.

DR. M. L. McGLASHAN

Canterbury Branch Chairman this year is Dr. M. L. McGlashan senior lecturer in physical chemistry at Canterbury College. He was born in 1924, and graduated from Canterbury University College in 1945 with first-class honours in chemistry. He was appointed to the staff of the chemistry department the following year. In 1949 Dr. McGlashan was elected as the first holder of the Sims Empire scholarship. During the tenure of this award he worked with Professor E. A. Guggenheim at Reading University and published a number of papers on applications of statistical mechanics to liquid mixtures and to gases. Dr. McGlashan graduated Ph.D. from Reading in 1951 and was also temporary lecturer in chemistry at that University until his return to New Zealand early last year.

DR. M. L. McGLASHAN

Dr. McGlashan is keenly interested in the wider aspects of university education. He is a Life Member of the Canterbury University College Drama Society. He likes to spend his holidays in the Southern Alps.

DR. A. T. JOHNS

The Manawatu Branch Chairman is Dr. A. T. Johns of Grasslands. Receiving his University training at Canterbury College he graduated M.Sc. with 1st Class Honours in Chemistry in 1940. He worked for a short time during 1939-40 with Dr. C. R. Barnicoat on fat chemistry at the Dairy Research Institute while holding a National Research Scholarship. Dr. Johns went into camp with the Artillery of the 4th Reinforcements, 2nd N.Z.E.F.

in October 1940 and was withdrawn from this unit to take a radio physics course at C.U.C. early in 1941. After a short time at the 10th Heavy Regiment Coast Artillery he went to Australia for nine months on radar liaison duties, spending some time at the Radio Physics Laboratory, Sydney University. On returning from Australia he was instructor in Coast Artillery Radar, School of Artillery, Wellington, attaining the rank of Captain. In 1944-45 he served with the 4th Field Regiment of Artillery in Italy. At the end of hostilities in Europe Dr. Johns was posted to Westgate, England, in the Education and Rehabilitation Service for ex P.O.W.'s from Germany In 1945 he was granted a Rehabilitation Bursary studying at the Sir William Dunn Institute of Biochemistry, Cambridge University. In 1948 he was awarded the degree of Ph.D. in Biochemistry, studying in particular the mechanism of propionic acid formation by bacteria. Since 1949 he has been at the Grasslands Division in the Plant Chemistry Laboratory studying the digestive processes in the ruminant animal. Dr. Johns went as one of the three New Zealand representatives to the 75th Anniversary Conference of the American Chemical Society in New York in 1951. He has been Secretary of the Manawatu Branch during 1951 and 1952.

MR. O. H. KEYS

Chairman of the Otago Branch this year, Mr. O. H. Keys is the Government Analyst for Otago and Southland. This is his second term of office as Branch Chairman having been chairman during 1947. Mr. Keys has taken an active interest in Institute affairs after being admitted as an associate in 1932. He was the first Editor of the Journal; then in 1940 he was secretary of the special committee set up by Council to enquire into quackery and patent medicine abuses and headed the deputation to the Minister of Health from which interview resulted the Medical Advertisements Act 1942, incorporating most of the committee's recommendations. Mr. Keys has been the Otago Branch delegate to Council since 1948; he is chairman of the Institute's Examination Committee and also this year's Conference Committee. Besides this imposing list of offices in the Institute's affairs Mr. Keys holds a variety of offices in other professional organisations.

ITEMS FROM THE MINUTES OF COUNCIL 26-2-1953

Present—Dr. H. O. Askew, Vice-president (in the Chair), Mr. G. S. Lambert (Auckland), Mr. I. G. McIntosh (Waikato proxy), Dr. A. T. Johns (Manawatu), Dr. L. G. Neubauer (Wellington), Dr. M. L. McGlashan, (Canterbury), Mr. L. H. James (Otago proxy), Mr. W. G. Hughson (Hon. General Secretary), Mr. A. P. Oliver (Asst. Secretary) and Mr. H. K. Palmer (Registrar). Prof. Slater, Dr. Dixon and Mr. B. E. Jackson were also present by invitation.

An apology was received from the President, Dr. H. E. Annett, on account of illness.

Conference—The Canterbury Branch felt that the standard of papers at Conferences should be improved, and in order to do this, the full text of papers should be submitted to referees before the Conference. If accepted, the full text would be cyclostyled and circulated to members who would then have an opportunity of studying the papers prior to Conference. Council felt that the running of the Conference should be in the hands of the Branch concerned, which did not preclude them from accepting Canterbury's suggestion if they thought fit.

Laboratory Assistant's Certificate to be awarded to Mr. D. M. Lennox who has fulfilled all the requirements.

New Members Elected—Mr. R. N. Woodward, F.R.I.C., Chief Chemist, N.Z. Farmers' Fertiliser Co. Ltd., Auckland, to be a Fellow.
Mr. S. R. J. Cotton, Auckland City Analyst, Associate.
Mr. G. R. Selfe, Works Manager, Kempthorne Prosser & Co., Westfield, Associate.
Mr. T. H. Wilson, Auckland University College, Associate.
Mr. T. G. Nash, Hickson's Timber Impregnation Co. Ltd., Auckland, Associate.
Mr. L. Osgerby, Kiwi Bacon Co., Palmerston North, re-elected Associate.

Visit of Prof. Emeleus—It was announced that Prof. Emeleus will arrive in Auckland on August 16th, and leave from Wellington on September 1st. It is hoped that he will be at the Conference in Dunedin. It was decided that half the surplus funds from the 1952 Conference be applied to this purpose.

International Union of Chemistry—Branches are to be asked to consider ways and means of raising the subsciption (approximately £120 per year) to the International Union of Pure and Applied Chemistry.

Rules—Further consideration was given to the draft of the rules and several alterations approved. The new draft is now to be circulated to Branches and extra copies will be available to any member who is interested.

Important Notice—The closing date for the Laboratory Assistants' Examination will be *June 30th.*

NEWS AND NOTES

Dr. C. E. K. Mees, F.R.S., Director of Research for the Eastman Kodak Corporation, Rochester, New York, spoke to the Auckland Branch on March 3rd on "The Road to Wealth." Dr. Mees, who went from England to take up his present position in 1912, gave a brief outline of man's technological development, reinforced with his own ideas on economics. Snippetts from his address were as follows:

"Progress since the death of Newton has been greater than in whole period up to his birth. The drains of Queen Elizabeth's (I) London were inferior to those of ancient Rome.

"The road to Wealth is the increase of scientific knowledge and its application to industry and technology.

"The total expenditure on research by the Eastman Kodak Corporation per annum is more than twice the total spent in the whole of New Zealand. (Mr. Holland please note.)

"The value of the whole industrial productivity of India does not equal the amount spent in U.S.A. on replacing old equipment and building new."

Mr. R. B. Miller has returned to the Soil Bureau, Department of Scientific and Industrial Research, after two years carrying out research on soil phosphates at the Royal Agricultural College of Sweden, Uppsala. Dr. W. E. Harvey, who also studied in Sweden (at Stockholm) is now on the staff of the Dominion Laboratory, Wellington.

Dr. Val. Armstrong, who was Scientific Liaison Officer in U.S.A., has been transferred to London to work with Dr. E. Marsden, F.R.S.

After spending two years at Cambridge under Professor Todd and gaining his Ph.D. Dr. J. Murray is now back on the staff of the Chemistry Department at Otago.

Congratulations also go to Dr. A. D. Campbell who took his Ph.D. at Otago University, his thesis being "Some Applications of Acrylonitrile to the Synthesis of Polycyclic Compounds, and some new Polycyclic Systems."

NEW ZEALAND INSTITUTE OF CHEMISTRY

BALANCE SHEET

for the year ended 31st October, 1952.

1951 £			£ s. d.
92	SUBSCRIPTIONS PAID IN ADVANCE		93 12 4
3	JOURNAL SUBSCRIPTIONS PAID IN ADVANCE		- - -
212	SUNDRY CREDITORS		324 19 6
-	PROVISION FOR PRINTING		100 0 0
30	PROVISION FOR ESSAY PRIZE		30 0 0
	ACCUMULATED FUNDS:		
	Balance 31st October, 1951	836 6 5	
	Less Transfer to Trust Fund	75 0 0	
		761 6 5	
	Add Excess of income over Expenditure for the year	157 6 8	
836	Balance 31st October 1952		918 13 1
514	TRUST FUND		602 18 10
£1,687			£2,070 3 9

1951 £			£ s. d.
	TYPEWRITERS—		
	Balance 31st October 1951	41 0 0	
41	*Less* Depreciation for year	4 0 0	37 0 0
	ADDRESSOGRAPH PLATES—		
	Balance 31st October 1951	11 0 0	
11	*Less* Depreciation for year	2 0 0	9 0 0
	SUBSCRIPTIONS OVERDUE—		
	1 for the year ended 31/10/49	1 11 6	
	5 for the year ended 31/10/50	7 1 6	
	20 for the year ended 31/10/51	31 10 0	
	63 for the year ended 31/10/52	119 15 6	
		159 18 6	
79	*Less* Amount Reserved	20 0 0	139 18 6
79	SUNDRY DEBTORS		45 0 0
	NATIONAL SAVINGS A/C. (due 1/7/53)	500 0 0	
520	*Add* Interest Accrued	35 15 0	535 15 0
	CASH BALANCES—		
280	Bank of New Zealand	537 2 2	
146	Post Office Savings Bank	149 12 5	
17	Petty Cash on Hand	13 16 10	
			700 11 5
	TRUST FUND INVESTMENT—		
514	Post Office Savings Bank		602 18 10
£1,687			£2,070 3 9

INCOME AND EXPENDITURE ACCOUNT

EXPENDITURE

1951 £		£ s. d.	£ s. d.
	To Administrative Expenses—		
3	Audit Fee	12 12 0	
6	Branch Expenses Allowances	6 0 0	
7	Depreciation	6 0 0	
26	Honorarium—Secretary	26 5 0	
-	Legal Expenses	3 3 0	
31	Postages and Sundries	25 8 6	
40	Printing and Stationery	43 9 11	
145	Salary—Registrar	200 0 0	
61	Typewriting, Duplicating and Addressing	79 8 8	
62	Travelling Expenses	68 6 8	
17	Expenses — Re A.C.S. Project		470 13 9
„	Institute Journal—		
382	Printing, Blocks etc.	425 4 6	
16	Postages and Sundries	31 16 6	
11	Honorarium—Editor	10 10 0	467 11 0
„	Chemists Employment Committee—		
7	Duplicating and Sundries		1 16 6
„	Examinations Committee—		
8	Duplicating and Sundries		7 1 9
- „	Provision for Printing (Half estimated cost of Rules and List of Members)		100 0 0
- „	Donation, Rutherford Memorial		5 5 0
50 „	Travelling Expenses (Special Allowance)		- - -
38 „	Excess of Income over Expenditure for year transferred to Accumulated Funds		157 6 8
£910			£1,209 14 8

INCOME

1951 £		£ s. d.	£ s. d.
639	*By* Subscriptions		950 5 0
„	Interest—		
4 „	Post Office Savings Bank	3 6 9	
15 „	National Savings Account	15 15 0	19 1 9
„	Institute Journal—		
25	Subscriptions	53 9 11	
153	Advertising	168 0 0	221 9 11
„	Chemists Employment Committee—		
9	Subscriptions		5 10 0
„	Examinations Commitee—		
15	Entry Fees and Sundries		8 2 0
„	Conference Committee—		
	Surplus of Receipts over Payments	7 0 0	
6	*Less* Share R.I.C. (N.Z. Section)	1 14 0	5 6 0
44 „	Travelling Expenses Reserve Reversed		- - -
£910			£1,209 14 8

Mr. W. Fyfe, of Otago, has been awarded a Fullbright Scholarship at Berkeley California, where he intends to study "Reactions in Solids" under Professor Verhoogen.

Dr. P. Nottingham after obtaining his Ph.D. at the University of Aberdeen has been seconded by the Defence Scientific Corps to the Dominion Laboratory to work with the Meat Research team.

Dr. J. C. Hawke, who graduated recently from Cambridge having been there on a N.Z. Defence Science Corps Scholarship, has returned to Wellington where he will be attached to the Fats Research Laboratory. Besides his Ph.D. he won a double blue in athletics and cross-country running, represented Cambridge twice in inter-university contests and has been promoted to the rank of Captain in the Army.

Dr. F. B. Shorland has returned from his extensive trip overseas during which, besides visiting laboratories working on problems related to fats, he delivered 14 lectures to audiences in a number of countries and was able to meet again Professor Hilditch under whom he worked at Liverpool. He also met the Nobel Prize Winners Professor H. Dam of Copenhagen and Drs. Martin and Synge. Dr. Shorland has been asked to contribute a guest editorial to the Journal of the American Oil Chemists Society and a Chapter on lipids in the series "Progress of Fat Chemistry" edited by Lundberg Malkin and Holman.

Dr. William Blum, formerly head of the Electrodeposition Section of the American National Bureau of Standards has addressed audiences of chemists and allied sciences and interested manufacturers on "Recent American Research in Electroplating" in both Auckland and Wellington. Dr. Blum's lectures were very much appreciated by his audience. They covered a wide range of applications and technical details and were of definite value to all those interested in electroplating.

Mr. M. H. Panckhurst, who has held a University Research Fellowship at Canterbury College for the last two years, has recently been elected to a Shell Postgraduate Scholarship. Mr. Panckhurst will join the staff of the chemistry department at Auckland University College until he leaves for overseas towards the end of the year.

Mr. M. T. Christensen, lecturer in chemistry at Canterbury College, has recently been awarded a Sims Empire Scholarship. Mr. Christensen will be leaving for England later in the year, and hopes to carry out research in the field of molecular spectroscopy.

Dr. B. W. Doak, Chief Chemist at the Grasslands Division, Palmerston North, has been appointed Director of the N.Z. Fertiliser Manufacturers' Research Association, a post held by Dr. M. M. Burns prior to his appointment as Principal at Lincoln Agricultural College. Dr. Doak has been with the Plant Chemistry Laboratory since its inception in 1938, and previous to that was Chemist to the Plant Research Station, Palmerston North. Dr. Doak will take up his new appointment in May.

A former student in chemistry at Auckland University College Dr Leo Vining has been awarded a Fellowship at Rutgers University, New Brunswick, New Jersey. Dr. Vining will work under the well-known authority on antibiotics Professor Selman Waksman, who was recently awarded a Nobel Prize. After graduating Ph.D. at Cambridge, Dr. Vining has been working for the past 12 months at Kiel University, Germany.

Mr. W. J. Wilson, for some time attached to the Dominion Laboratory at Wellington, has been appointed to the staff of the Government Analyst at Auckland.

At their annual general meeting the Manawatu Branch listened to a very interesting address by Dr. T. H. Pullar of the Palmerston North Public Hospital on "Clinical and Medico-legal Aspects of Biochemistry."

Mr. A. W. Mackney, chief chemist of New Zealand Forest Products Ltd., is visiting Canada, Scandinavia and Finland with the company's pulp and paper mill superintendent to engage trained employees for the Kinleith pulp and paper mills.

Mr. A H. Horn who has been at the Rukuhia Soil Research Station has transferred to Winchmore Research Station, Ashburton.

DR. L. G. NEUBAUER

DR. L. G. NEUBAUER

Now in charge of the Wood Chemistry and Organic Section of the Dominion Laboratory, Dr. Neubauer is Chairman of the Wellington Branch of the Institute this year. Commencing at the Dominion Laboratory in 1936 he graduated from Victoria College in 1939 with first class Honours and was awarded the Jacob Joseph Scholarship the same year. Dr. Neubauer worked on organic problems mainly, investigating amongst other things resins, ragwort alkaloid, and phormium fibre.

In 1946 Dr. Neubauer was awarded a National Research Scholarship and in 1947 at McGill under Professor C. B. Purves, he commenced studying for his Ph.D. on wood and cellulose chemistry, graduating in 1949. After spending six months in the Technical Service Department of the Southland Paper Mills in Texas he spent four months visiting other paper mills, Government Laboratories and Universities where wood chemistry research was being undertaken.

Returning to the Dominion Laboratory Wellington in 1950 Dr. Neubauer's special interests are the structural components of wood, and their relation to pulping processes and papermaking.

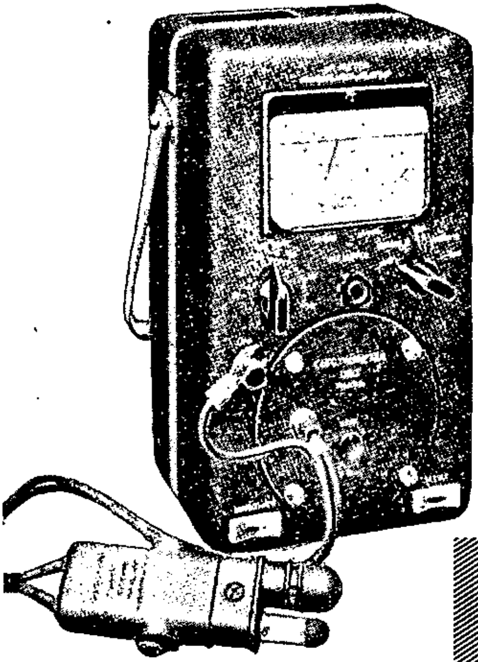
BOOKS RECEIVED

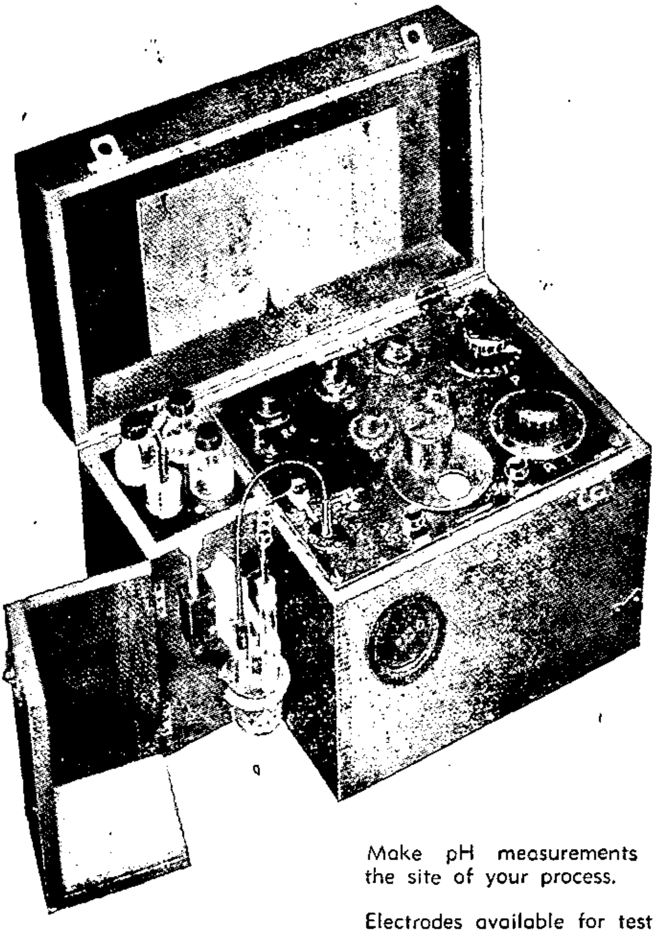
Inorganic Chemistry—An Advanced Text-book. By Therald Moeller, Associate Professor of Chemistry, University of Illinois. 966 pages. New York: John Wiley & Sons, Inc. London: Chapman & Hall Ltd., 1952—$10.00. Without doubt the best Inorganic Chemistry text-book of its scope (Stage III and Honours), which has been published in recent years. The method of presentation is essentially modern and vitally interesting. Its approach is from the structural point of view throughout, the exposition of the subject matter being clear and concise. Numerous tables of physical constants are included, although some could well have replaced by graphica illustration. Over 2000 original authors are listed in the references. The subject index has been well compiled, the type is clear and the binding excellent. A minor criticism is merited by the cheaper quality paper used in a text-book which will undoubtedly be frequently consulted. H.B.

Encyclopedia of Chemical Technology. Vol. 9: Metal surface treatment to Penicillin. Edited by R. E. Kirk and D. F. Othmer 1952. 943 pages. Interscience Publishers, New York and London; Angus & Robertson, Sydney. Subscription price $25.00, single copy, $30.00. With the publication of Vol. 9 the completion of this work is now in view in a commendably short space of time. Perhaps the most valuable article is that on mixing and agitating (34 pages); there is also a good article on methanol (30 pages). Academic questions are not neglected for there are articles on nomenclature and onium compounds and the coverage on nitrogen compounds includes many which as yet have no commercial significance. This Encyclopedia has been elaborately produced, but its very magnificence gives one misgivings. How much more could have been included without any obvious loss by the use of a slightly smaller type face, narrower margins and the elimination of the many blank spaces at the end of the monographs! As it is the work is short on illustrations and many of the articles could be much fuller. The section on micro-analytical methods is so condensed (8 pages) that it is questionable if it serves any useful purpose at all. In the article on paper there is no reference to the sulphuric acid process for producing vegetable parchment. This work has recent such enthusiastic praise in America that it seems churlish to criticise it, but it seems doubtful if many outside the dollar area can afford it. —I.C.

Papierchromatographie. By Friedrich Cramer. 1952, 81 pages. Verlag Chemie, Berlin. DM.19.80 (about 17/6). This is No. 64 of a series of small monographs published by Verlag Chemie and which deserves to be better known. Other volumes recently printed deal with Oxidation of Cellulose; Raman Spectra of Olefins; the Gas Centrifuge; Siliceous Materials; Organic Peroxides; Fluorine; and Phosphorus-containing Insecticides. The present volume, after dealing with the general technique of paper chromatography, gives exhaustive lists of organic and inorganic applications and concludes with a bibliography of 283 references. It is well illustrated and contains several tables of Rf values. —G.S.

Chemie Lexikon by Hermann Römp. 3rd Edition. Vol. 1, A-K 1032 pages. 1952: Franckh'sche Verlagshandlung, Stuttgart. Price for 2 vols. DM. 168 (About £15/10/-). This chemical dictionary contains a great deal of useful information. The articles on the various chemical substances give the usual physical and chemical data, uses, German (and sometimes other) manufacturers and a recent price. Besides these there are articles on the chief German and many foreign chemical concerns. Here I.C.I. gets over half a page, Du Ponts a few lines, and B.D.H. no mention at all. There is also a very full inclusion of German trade names and most of the leading foreign ones. (The reviewer noted the absence of any reference to "Dowtherm" either under that name or under the names of its constituents.) There is also a list of the leading publishers of chemical books and a list of German chemical consultants with their addresses and telephone numbers. There is also much information that we would hardly expect such as a series of formulas for bath salts, and detailed notes on the removal of stains from textiles and clothing. It is perhaps not surprising in a German work that the longest article (12 pages) is on alcohol, but many other subjects have several pages devoted to them with references up to 1952. The illustrations are poor, but the binding is magnificent with two ribbon book marks. It is doubtful whether this work would be worth its rather high price to chemists in New Zealand.





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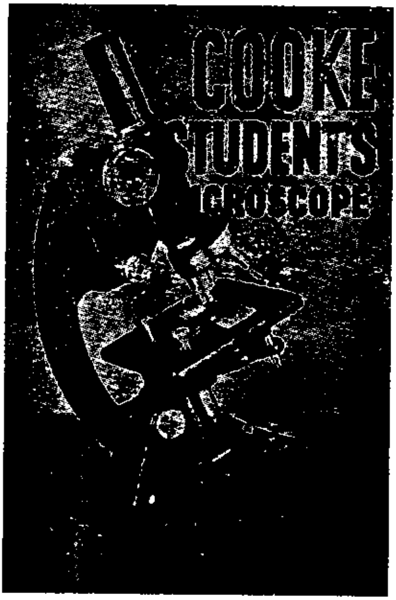
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