

JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

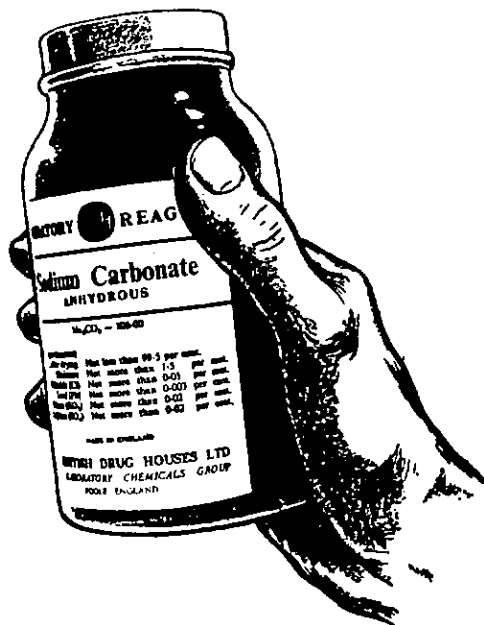
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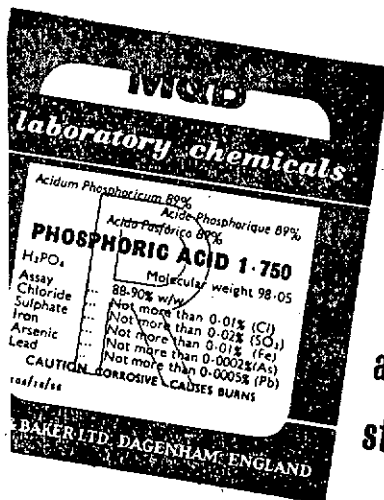
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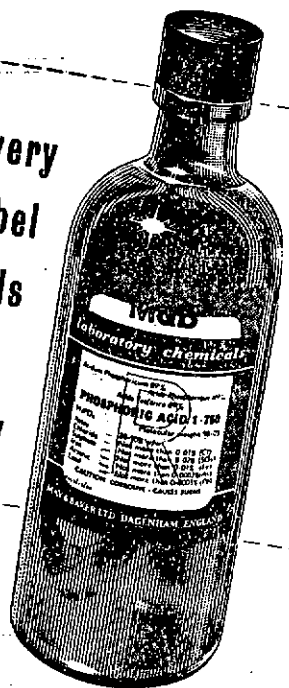
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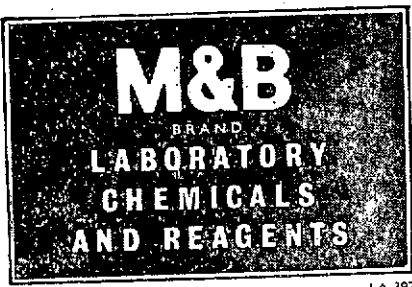
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EDITORIAL

From the point of view of the future of the Institute, the "Report of the Charter Committee" is one of the most important documents which Council has referred to the Branches, and hence to the individual members, for consideration. The question of a Royal Charter was considered by Council nearly ten years ago and a committee was set up to investigate the desirability or otherwise of applying for a Charter or for a registration act. At that time the committee was not in favour of a Charter or registration and recommended as follows:

"That the New Zealand Institute of Chemistry should not make application for a Charter as it considers that the disadvantages outweigh the advantages, and that this should be the policy of the Institute until circumstances change materially.

"That no good or urgent case is made out for registration; that the Institute and its members are reasonably well protected by being an Incorporated Society; and that public recognition of the Institute is providing sufficient safeguard to the public. At the best there are valid arguments for only partial registration and until the need for such is shown to be greater than it is today, no steps should be taken by the Institute to obtain such registration."

The Committee did however add the recommendation that:

"... it is desirable for the Institute at all times to watch the position and suggests that either this Committee or some other be charged with the responsibility of reviewing the position from time to time."

The matter of a Royal Charter (but not of registration) was raised again last year by the Manawatu Branch and as a result the Branch was asked by Council to re-investigate the position. The report of this second Charter Committee, submitted to Council at the August meeting and published in full in this Journal, is unanimously in favour of the machinery being set in motion for an application for a Royal Charter. The Committee feels that the objections raised by the 1948 committee are no longer valid.

Briefly, these objections were based on the small size of the Institute, the inflexibility imposed on constitution and by-laws by a Charter, the high costs involved, and the existence in New Zealand of a section of a chartered body covering the profession. However the Institute has grown considerably since 1948 and its size is now no longer a bar to an application for a Royal Charter. The passage of time also means that the constitution and by-laws are no longer in a formative stage and these could be presented in a form which would not require modification, involving a Supplemental Charter or Privy Council approval, for some considerable time. On the score of cost, it would appear that the estimate of the 1948 committee was excessive and the anticipated cost is well within the means of our Institute. Finally, the New Zealand Section of the Royal Institute of Chemistry now represents only a small fraction of chemists in this country.

In arriving at its decision the present Charter Committee has been guided very largely by the most valuable evidence it could obtain—advice from our nearest neighbour, the Royal Australian Chemical Institute. It does seem certain that Royal Charters have been of considerable value to other groups. Our Institute would derive similar benefits. To quote again from the 1948 Charter Committee report:

"A Charter is granted by Her Majesty the Queen on the advice of the Privy Council, and naturally is only granted to worthwhile bodies performing a function of benefit to the community. Before a Charter can be granted the constitution and by-laws of the body have to be in a form satisfactory to the Privy Council. The main advantage of being granted a Charter is that of prestige. The use of the words "Incorporated by Royal Charter" indicates the official recognition of the standing of the body in the British Empire. Furthermore, where the body grants designations such as Fellow and Associate, these can be safeguarded as far as the body is concerned. On the other hand, the granting of a Charter does not prevent others, not members of the chartered body from practising the profession of the body granted the Charter."

As mentioned in the present report, the granting of a Royal Charter does not necessarily give immediate right to the use of the term "Royal." It would seem that a Charter is granted; subsequently, on further application, the title "Royal" is approved and it is then necessary to obtain a Supplemental Charter including the word "Royal" in the name of the Society. There is some evidence however to suggest that the two applications could be made together and this aspect is being further investigated. In any event, the sooner an application for a Charter is lodged, the sooner will we attain our objective of becoming "The Royal New Zealand Institute of Chemistry".

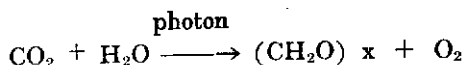
PHOTOSYNTHESIS

By J. W. LYTTLETON.

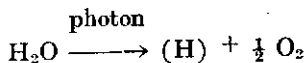
Chief Chemist, Plant Chemistry Laboratory, D.S.I.R., Palmerston North.
(Based on a lecture delivered to the Manawatu Branch, June, 1957)

The reason for my giving an address on photosynthesis, which is a specialised field rather outside my own, is that our studies on the properties of plant leaf cell proteins have at one point yielded information of direct interest to workers in photosynthesis, and this led to my reading up a good deal about the subject. However, I should like to make it clear that throughout most of the lecture, I shall be relaying, at second-hand, information which has been obtained, and theories which have been put forward, by one of the most active groups working on this subject, the group led by M. Calvin at the University of California, Berkeley. All of the diagrams presented here are taken from reports published by this group.

To begin with, the essential point about photosynthesis, which is the key to its tremendous importance in the world of living things, is that it transforms water and carbon dioxide, the normal biological end-products, back to carbohydrates. The energy of sunlight is captured, in the chemical energy of these compounds, in a form where it can be used by plants and animals in normal metabolism, with the production once more of carbon dioxide and water. The study of photosynthesis, then, resolves itself into a study of how the plant utilizes the light energy to carry out this general reaction, which may be written:

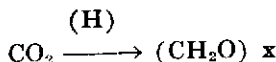


It has been known for some time that this reaction may be divided into two main parts, the first of which is:



In this, the light reaction, the energy of a quantum of light splits a molecule of water, liberating free oxygen and providing an equivalent of reducing power.

The second main reaction is:



In this, the dark reaction, the reducing power produced above is used to bring about fixation of carbon dioxide with the production of carbohydrate. It is this dark reaction that I will talk about first, as its chemical nature is perhaps better understood than that of the light reaction.

In studying this transformation of carbon dioxide to carbohydrate, Calvin and his group used a suspension of green algae as their photosynthetic system. The suspension was illuminated and supplied with a stream of carbon dioxide, so that photosynthesis together with resultant carbon fixation was proceeding at a steady state. The radio-active isotope of carbon C^{14} , was then introduced into the system as $C^{14}O_2$, and the organisms allowed to incorporate this into the chain of photosynthetic reactions for a given time, after which the reaction was stopped by dropping the algae suspension into hot ethanol. This killed the organisms, and simultaneously extracted the products of the reaction. These products were concentrated and separated by two-dimensional paper chromatography. The compounds containing C^{14} could readily be identified by making a radioautograph of the chromatogram, and the first question to be answered by this technique was that of locating the immediate product of carbon dioxide fixation. This first compound to be produced was identified by carrying out the above type of experiment with decreasing times of exposure of the algae to radiocarbon. It was found that whereas if fixation had proceeded for as long as 60 seconds, a multiplicity of compounds were found to contain C^{14} , if the period were cut down to 10 seconds, practically all the C^{14} activity in the chromatogram of the products was confined to the spot corresponding to 3-phosphoglyceric acid (PGA). This, then, seemed to be the first compound formed when carbon dioxide was fixed by the photosynthetic process.

The next question, that of identifying the product which followed PGA, proved much more difficult to answer. Many compounds labelled with C^{14} seemed to appear simultaneously when the period of exposure to radiocarbon was lengthened. These compounds included 3, 5, 6, and 7-membered sugars. It was only by studying the distribution of C^{14} in the various positions in these sugars, and trying to relate it to the distribution in the first product, PGA, that a clue was gained into how the PGA might be transformed into these different compounds. Figure 1 indicates how the problem was dealt with at this stage. This shows by asterisks the relative rate of appearance of C^{14} in the various positions in PGA, ribulose diphosphate, sedoheptulose monophosphate, and hexose monophosphate. In deciding the path by which PGA was converted into these sugars, into all of which C^{14} rapidly finds its way, the only obvious connection is that between PGA and hexose. The carbon skeleton indicates that the hexose could be produced from direct coupling of two triose molecules derived from PGA in such a way that the position 1 atom of the triose fills positions 3 and 4 in the hexose. Figure 2 shows what is

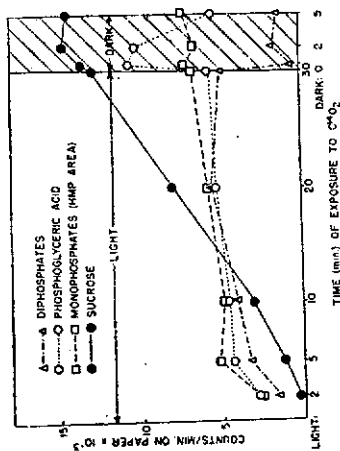
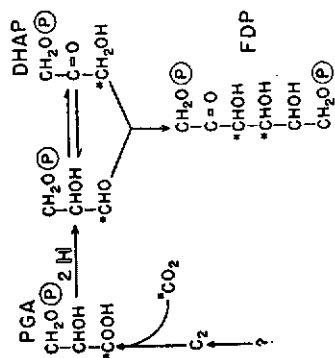
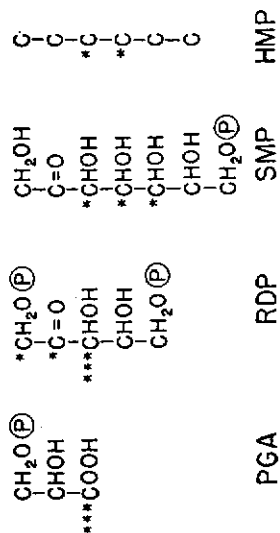
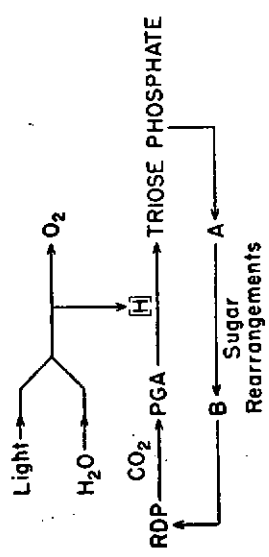


Fig. 1: Top Left. Fig. 2: Top Right. Fig. 3: Lower Left. Fig. 4: Lower Right.



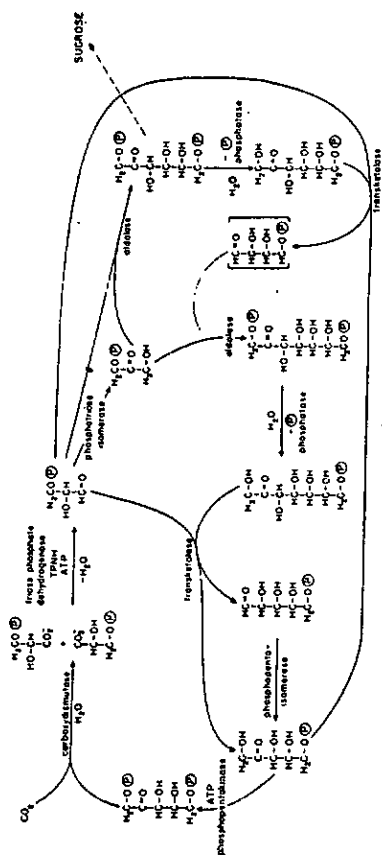


Fig. 5: Top Left.

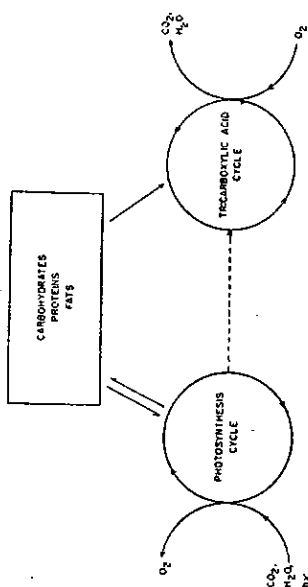


Fig. 6: Lower Left.

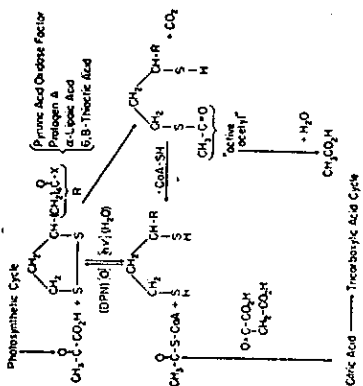
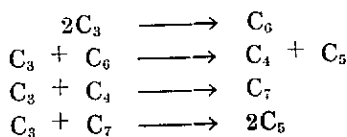


Fig. 7: Lower Right.

postulated here; the PGA is reduced to phospho-glyceraldehyde by reducing power derived from the light reaction, and couples with its isomeric form (dihydroxyacetone phosphate) to form fructose diphosphate, with C^{14} activity in the locations actually found.

This type of argument satisfactorily explained the production of hexose molecules from PGA, but the paths of formation of the C_5 and C_7 sugars were not at all easy to see. By carefully studying the order in which C^{14} atoms appeared in the molecules, it was finally concluded that the reactions were as follows:—



The main trend of these reactions is from triose to pentose, with tetroses, hexoses and heptoses as intermediates. Not all of the hexose produced is transformed to pentose, however; a certain proportion goes to produce storage carbohydrate, with sucrose as the first product. It is by this reaction that the plant draws upon the photosynthetic process as an energy source.

Enzymes for carrying out all these postulated rearrangements had been recognized, and the scheme, which we will examine in more detail later, provided a consistent explanation of the rate of appearance of C^{14} in the various locations where it was actually found.

Some knowledge, then, had been gained of the path of carbon after photosynthetic fixation, but the immediate acceptor of the carbon dioxide molecule with the resultant production of PGA was not yet known. A different type of experiment was used to learn which molecule it might be which directly combined with carbon dioxide, and this is illustrated in figure 3. The levels of various classes of compounds in the algae extracts were measured while the algae were continuously exposed to light in the presence of carbon dioxide, and were therefore carrying out normal photosynthesis. Figure 3 shows that during this stage the diphosphates (of which the most important is ribulose diphosphate), the PGA, and the hexose monophosphates reached a rather steady level, while sucrose, a storage product, rose continuously. As soon as the light was cut off, the PGA rose and diphosphates fell rapidly. The rise of PGA could be explained by the fact that the withdrawal of the reducing power produced by the light would prevent reduction of PGA to triose, with its further transformations, but the fall in diphosphates indicated that probably they were being used up to supply the sudden rise in PGA. The path of carbon which was suggested by this experiment is shown in figure

4. Here ribulose diphosphate is postulated as the acceptor of carbon dioxide, forming PGA as a result. In light the PGA is reduced to triose, which undergoes the conversions we have discussed above, with the ultimate production of pentose phosphate; this is phosphorylated to the diphosphate, and on combining with carbon dioxide, produces more PGA. This cyclic scheme predicted that if the carbon dioxide were cut off, the ribulose diphosphate should rise and PGA fall; and this prediction was confirmed, indicating that the cycle could be blocked between these compounds if the carbon dioxide was withdrawn from the system.

The whole scheme of the dark cycle reaction, as postulated by Calvin and co-workers, is presented in figure 5. This rather elaborate diagram summarises all I have been saying so far; it shows the immediate production of PGA following the carboxylation of ribulose diphosphate, the subsequent reduction of PGA to triose, the inter-conversion of this triose to hexose, heptose, and finally pentose, and the continuation of the cycle with the uptake of a further molecule of carbon dioxide.

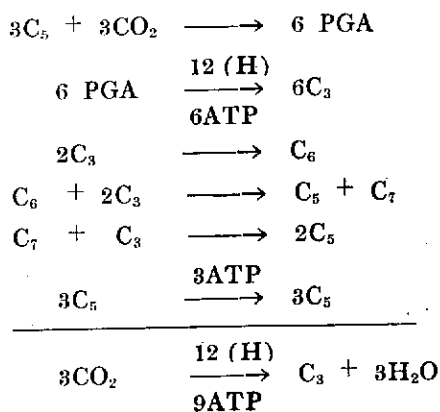
Of all the enzymes concerned in these transformations, the last to be recognized was that which catalyses the combination between ribulose diphosphate and carbon dioxide, with the production of PGA. It was first shown to occur in spinach leaf extracts, and was also shown to follow chloroplasts in the fractionation of leaf components; but only if the chloroplasts were prepared very carefully. Later it was prepared in a purified form by extensive fractionation of spinach leaf extract, and the enzyme activity was found to reside in a protein fraction which was apparently homogeneous when examined in the ultra-centrifuge. It was at this point that our interest in leaf cell proteins began to overlap with the field of photosynthesis, for this purified enzyme had physical properties closely similar to those of a well recognized major component of leaf extracts, the so-called Fraction I.

To summarise briefly the state of knowledge of the soluble protein of leaf cells, it had been recognized by Californian workers under James Bonner and S. G. Wildman, that a wide range of higher plant leaves contained two main soluble protein constituents; 40% Fraction I, relatively homogeneous, molecular weight about 500,000, and 60% Fraction II, a rather polydisperse group of proteins of much lower molecular weight. We had found that pasture plants conformed to this pattern, and had developed methods for purifying Fraction I. We had also observed that this Fraction I occurred only in those parts of the plant in which photosynthesis is carried out, and was absent from tissues such as roots. The question arose then whether Fraction I was in fact identical

with the carboxylation enzyme for ribulose diphosphate in photosynthesis. In favour of their identity were the similar physical properties, and the fact that Fraction I occurred only in photosynthetic tissue; against it were the facts that Fraction I was supposed to be derived from the cytoplasm of the cell rather than the chloroplasts, and as purified by the Californian workers was completely devoid of enzymic activity.

During my visit to the Californian Institute of Technology, we were fortunate enough to be able to resolve these difficulties. We found that spinach chloroplasts, if very carefully prepared, contained large amounts of Fraction I, and were able to show that at least 70%, and probably more, of the total Fraction I of the leaf is associated with the chloroplasts. Starting from chloroplast extracts we were able rapidly to prepare a 95% pure Fraction I, and found that it had the expected enzyme activity; that is, when incubated with ribulose diphosphate and carbon dioxide, it produced PGA. This was highly satisfactory in that a role for Fraction I had been found, whereas before its function in the cell was unknown. The detailed mechanism of the enzymic production of PGA from ribulose diphosphate and carbon dioxide remains to be elucidated, however, as well as the puzzling question as to why there should be so much of this one enzyme in the leaf, while the other enzymes in the photosynthetic cycle are present in trace amounts only.

To return now to the general picture put forward for the cycle of operations in the dark photosynthetic reaction (Figure 5), I should like to consider the energy necessary to run this cycle. At two points substantial amounts of energy need to be fed into the system—first at the reduction of PGA to triose, and again at the phosphorylation of ribulose monophosphate to the diphosphate. We may add up the energy requirements for the cycle as follows:—



Thus for each molecule of CO_2 transformed to triose, we need 4(H) and 3ATP. For those who are not familiar with biochemistry, I should explain that ATP is adenosine triphosphate, a very common metabolite which can transfer energy contained in its "high energy" phosphate group to suitable acceptors.

In normal photosynthesis, all this energy is provided by the light, but as ATP is a common product of normal metabolism in the cell, under some conditions the ATP requirement for the photosynthetic cycle could conceivably be drawn from the energy derived from respiration, thus reducing the amount of energy derived from light to make the photosynthetic cycle operate.

As a test of the energy requirements predicted by the scheme of chemical changes in the photosynthetic cycle as put forward above, experiments have been carried out to find out just how much energy is absorbed from light in the conversion of one molecule of carbon dioxide to carbohydrate. For this purpose it is necessary to make some assumptions about the conversion of light energy to chemical energy, and the most reasonable seems to be to assume that each quantum of light absorbed gives rise to one electron, which in turn gives rise to one equivalent of reducing power at the level of TPNH (triphosphopyridine nucleotide, a coenzyme in biological oxidation-reduction reactions). This implies that to provide the four equivalents of reducing power for each molecule of carbon dioxide (see above) four quanta of light are needed. To provide the ATP, however, it is assumed that more reducing power, as TPNH or DPNH, is produced, and when oxidised it leads by oxidative phosphorylation to the production of ATP. For every two molecules DPNH oxidised, approximately three molecules ATP can be formed, so a further two quanta, making six in all, could be expected to provide all the energy to convert one molecule of carbon dioxide to carbohydrate.

Measurements of the quantum absorption per molecule of carbon dioxide fixed led to a value of about 6.8 quanta per molecule, provided the light intensity was high. If the light intensity fell off to a low value, the quantum requirement dropped, extrapolating to four quanta per molecule at zero light intensity. These results were considered to substantiate the proposed scheme, in that the requirement of 6.8 was in satisfactory agreement with the predicted figure of 6, allowing for some inefficiency, and the fall off to 4 at low light intensity corresponded to the increasing use of metabolic ATP for the cycle, with light providing only the reducing power. At high light, the rate of utilization of ATP is too high to allow that produced in other locations in the cell to diffuse to the site of photosynthesis. It must be made on the spot, and the quantum requirement increases to provide for this.

Up till now I have been talking about the dark reaction of photosynthesis, which is concerned with carbon dioxide fixation. The light reaction, in which water is split into its components, has been mentioned only in so far as it provides energy to drive the carbon cycle of the dark reaction, this energy being provided in the form of reducing power (TPNH) and active phosphate (ATP). From now, I shall concern myself with some speculations, again largely arising from Calvin's laboratory, on the mechanism whereby the chloroplast is able to transform the energy of a quantum of light to form TPNH and ATP.

To begin with, I shall indulge in what may seem to be rather a digression. It has been observed that when plants are supplied with carbon dioxide containing C^{14} , and when the plants are photosynthesising normally in the light, the C^{14} finds its way rather slowly into the two compounds glutamic and isocitric acids. This is not surprising, as these compounds are closely related to the tricarboxylic acid cycle, which belongs to the normal respiratory pathway of cells which are deriving energy from the breakdown of storage products such as carbohydrates. The C^{14} presumably has to find its way through the photosynthetic cycle to storage carbohydrate before it can be used in respiration (Figure 6).

In the dark, however, the C^{14} finds its way much more rapidly into glutamic and isocitric acids, as if some short circuit were established which bypassed the normal route, and enabled some component of the photosynthetic cycle to pass rather directly to the tricarboxylic cycle.

The nature of this short circuit has been suggested to be as shown in Figure 7. This shows the path whereby PGA, the immediate product of carbon dioxide fixation, after conversion by dephosphorylation, enolisation, and loss of water to form pyruvic acid, is coupled with the pyruvic oxidase factor which contains thioctic acid, the key substance in this argument, as prosthetic group. The pyruvic acid is thus converted to an active acetyl group, which, after coupling with coenzyme A and regenerating reduced thioctic acid, can enter directly into the tricarboxylic acid cycle. The point about this reaction is that it will take place only if the thioctic acid is present in an oxidised form; and in plant cells the action of light is to hold it reduced, thus stopping the reaction. Light, then, cuts off the direct pathway of C^{14} into glutamic and isocitric acids, and darkness opens it again; and the controlling point is the thioctic enzyme.

The fact that thioctic acid is found to be held reduced by light suggested the possibility that it might itself be the first acceptor from the chlorophyll of an electron activated by light. This is speculation, but there are some pieces of evidence in its favour.

It is known that the excitation energy of chlorophyll is about 40 kcal/mol., which corresponds to the absorption of a quantum of light of wavelength 6800Å. To utilise this energy efficiently, it must be transferred to a molecule which has a reasonably stable state of high energy about 40 kcal above the ground state, and the splitting of the five-membered ring of thioctic acid to give the free diradical gives about the required energy change.

Again, it has been known for a long time that illuminated chloroplast fragments will break down water to liberate oxygen (the Hill reaction), provided that a suitable substance is present which can be reduced at the same time. Quinone can fill this role, but it is found that thioctic acid is very much more effective on a molar basis than most other materials. Thus it is at least a likely candidate for the position of the molecule first reduced by photo-activated chlorophyll.

The way in which the electron is handed on to the acceptor, whether thioctic acid or anything else, has recently been the subject of interesting speculation. A difficulty of explaining how photosynthesis could be so efficient was that it seemed necessary for the acceptor of energy from the chlorophyll to be present in very high concentration in order that each excited molecule of chlorophyll could hand on its energy to an adjacent acceptor before it decayed to the ground state, emitting fluorescence. No chemical compound, certainly not thioctic acid, seemed to be present in concentration high enough. A rather interesting suggestion has been made which might resolve this difficulty.

Electron microscope studies have shown that chlorophyll in chloroplasts is arranged in definite laminar layers in the grana; and the preservation of some, at least, of this arrangement is necessary for the Hill reaction to take place. It seems that the chlorophyll molecules must be organised in a non-random manner before they can utilise light energy to bring about photolysis of water, and the suggestion referred to above is that the light quantum raises an electron to a conducting level in these laminae of the chlorophyll molecules, so that it can migrate freely away from its point of origin. Further, if the chlorophyll layer is bounded by semi-conductors of the right characteristics (and it seems probable that lipid material found so extensively in chloroplasts could fulfil this requirement), then it would be possible for the electron to migrate right away from the chlorophyll on one side, and the "hole" (or absence of electron) to migrate away on the other. The action of light would thus bring about a separation of charges, and this would be a very much more stable energy source than an excited electron in a chlorophyll molecule. The acceptor of electrons, thioctic acid or anything else, could at reasonable concentrations act as intermediate between the chlorophyll and the

reducing enzymes needed to drive the photosynthetic cycle. Similarly, by a mechanism which has not yet been explained, the positive charge on the opposite side of the chlorophyll lamina is postulated as giving rise to the photolysis of water. In effect the chloroplast contains a vast number of solar batteries which are harnessed to bring about chemical work. Nature has thus antedated the Bell Telephone Laboratories in their invention of the transistor-semi-conductor light battery by a considerable margin.

In conclusion, I should like to make it clear that many of the ideas put forward above are not firmly established. A great deal remains to be done, but I hope I have shown that the photosynthesis reactions, besides being extremely important, are extremely complex and fascinating.

CHEMISTRY OF MILK FLAVORS

BY W. L. DUNKLEY,

Department of Dairy Industry, University of California, Davis.

(Based on a paper presented at joint Conference of New Zealand Institute of Chemistry and Royal Institute of Chemistry, Auckland University College, August 22nd, 1956.)

Milk is recognised as a very nutritious food,—in fact, nature's most nearly perfect food. High milk consumption can be very helpful in maintaining sound national health. But people will not drink milk just because it is good for them,—they must like it. High quality milk, properly served, is a refreshing, appealing beverage. Unfortunately milk is very susceptible to numerous flavour defects. Dairy technologists are constantly on the alert to protect milk's delicate flavour at every step from the cow to the consumer.

Methodology in Flavour Chemistry.

Flavour of a food or beverage is a composite sensation which we recognise mainly through the combined response of the senses of taste and smell. We perceive taste through nerves and taste buds located on the tongue. Physiologists consider that there are only four basic tastes—sweet, sour, bitter, and salty. Odours are detected by olfactory nerves in the nasal passages. To have an odour a substance must be volatile and fat soluble. The term "flavour" applies to the combination of taste and smell as perceived by these two sensory organs. However, our appraisal of flavour may also be influenced by other senses, such as touch which can convey the sensation of richness.

A chemist who studies the response of any of our senses other than taste and smell can usually adopt an instrumental method to assist him. To measure or record visual sensation, we can resort to photometers, radiometers, spectrophotometers, cameras and similar equipment. Sound can be recorded and can be analysed by a device such as the cathode ray oscilloscope. Characteristics detected by feel can be measured with instruments such as profilometers, consistometers and temperature-measuring devices.

Only limited success, however, has been achieved in the study of flavours by instrumental methods. Certain chemical or physical properties have been correlated with individual tastes and odours. Such specialised tests are usually only of limited value, and in any case their reliability must be calibrated against the somewhat variable standard—organoleptic flavour evaluation by selected individuals.

In the absence of suitable instrumental measurements or chemical tests, a flavour chemist or technologist must select some means of defining and measuring, or otherwise specifying, flavour characteristics. Words frequently are inadequate to describe taste and odours. How can I describe the flavour of a Chinese gooseberry to my friends in the States? We don't have Chinese Gooseberries there.

Even if a substance tasted the same to everyone, the problem would be difficult enough; but people are surprisingly variable in their response to certain tastes and odours. For example, phenyl thiourea has a bitter taste to about 70 per cent. of the white race, but is tasteless to the remaining 30 per cent. This difference is a dominant genetic trait. A person who cannot detect the bitterness could never learn to taste phenyl thiourea. Differences in response to other substances have also been reported. It has been suggested that people can be divided into ten different categories, depending on how they describe the taste of selected chemicals.

The numerous factors that influence sensory acuity present a serious difficulty in flavour study. The sensitivity of the organs of taste and smell vary with appetite, fatigue, temperature, and masking by other substances.

To overcome these numerous difficulties in studies of a specific flavour problem, a panel of tasters is usually selected, trained, and used throughout the investigation. Such panels can achieve a high degree of proficiency in identifying and estimating the intensity of an individual flavour if it is not masked by another flavour. However, a panel of trained tasters is not necessarily a reliable guide in predicting acceptability of a food product. For such purposes it is usually necessary to resort to large-scale consumer tests.

It is evident that a chemist is confronted with numerous specialised technique problems when he undertakes a study of either desirable or undesirable flavour characteristics of a food.

Normal Flavour of Milk.

Normal fresh milk has a slightly sweet taste and no odour. The taste is given mainly by lactose and the milk salts. Milk with the best flavour usually contains relatively high lactose and low chloride concentrations.

When people are asked what kind of milk they like, they usually indicate a preference for high-fat milk. But when tested they usually are not able to distinguish between milk with appreciable differences in fat percentage. Solids-not-fat percentage appears to be relatively more important than the fat percentage in determining the richness of milk as judged by taste appeal.

Off-flavours of Milk.

Feed Flavour.—Off-flavours, if present in milk when drawn from a cow are in most cases attributable to feeds eaten by the cow. Flavour-producing substances in feed are carried by the blood from the digestive tract to the udder and appear in the milk. In addition, the strong odour of some substances can be transmitted through the lungs to the blood and finally to the udder, thus appearing in the milk even though the cow does not eat the troublesome feed.

Fortunately, blood provides a two-way street for transportation of flavour substances. If enough time is allowed after the feed is consumed, substances with undesirable odours are returned to the lungs and exhaled with the cow's breath. The strong-tasting substances re-enter the blood, undergo certain metabolic changes, and are excreted, principally in the cow's urine.

The time interval between consumption and milking is an important factor influencing the intensity of feed flavours. Substances transmitted through the lungs may appear in the milk within one minute after the cow is fed, but most of the materials that enter the cow's body by way of the digestive tract are not detectable in milk for at least 20 minutes. The intensity of the defect increases for about two hours, then it decreases. Feeds commonly selected for dairy rations will not cause objectionable flavours if they are fed after milking and withheld from the cow during the four or five hours before milking.

Some of the substances responsible for the off-flavours caused by certain feeds and weeds have been identified. Knowledge of the chemical and physical properties of such compounds helps in understanding and predicting their behaviour in some dairy processes. For example, substances that are very water-soluble but

relatively insoluble in fat are present mainly in the aqueous phase and are largely eliminated with the skim milk and buttermilk during butter manufacture, whereas fat-soluble substances concentrate in the butter. Volatile materials can be removed by steam deodorising treatments, such as provided in the Vacreator, or Cream Treatment Unit.

In general, effective control of feed flavour under commercial dairying conditions depends on selection of feeds that will not cause objectionable off-flavours, elimination of weeds from pastures and feed crops, and withholding troublesome feeds from cows for several hours before milking.

Flavours from Pesticides.—Introduction of modern pesticides has presented a new problem for dairy farmers. Some of the sprayed chemicals are consumed by the cow along with the feed and may enter her milk. One published report described an extreme case. Cows were fed potatoes grown on land treated with benzene hexachloride to control nematodes. For three weeks after the troublesome feed was discontinued, milk from the cows had a flavour suggestive of moth-balls.

Other Flavours Present at Milking Time.—Certain off-flavours other than those associated with feed may be present in milk as drawn from the cows. For example, a salty taste is frequently associated with advanced lactation, or with mastitis. Cowy flavour has been attributed to acetone bodies present in milk when cows have ketosis. However, the flavour defects, other than feed flavour, that are encountered most frequently develop during storage of milk.

Flavour Caused by Bacteria.—Bacteria growing in milk can cause objectionable flavour defects. Raw milk, when carelessly produced and poorly refrigerated, usually develops a sour flavour attributable principally to acids produced from lactose. When milk is pasteurised, and especially if it is refrigerated, the conditions favour growth of proteolytic and psychrophilic organisms rather than acid producers. These organisms produce mainly putrid, bitter, and fruity off-flavours. Recent improvements in sanitary handling of milk and more extensive use of refrigeration are resulting in a decreased incidence of flavour defects of bacterial origin.

Rancid Flavour.—To dairymen the term "rancidity" usually means hydrolytic rancidity, caused by hydrolysis of milk fat by the lipase (fat-splitting enzyme) in milk. Food chemists in other fields usually use "rancidity" to include "oxidative rancidity", which the dairymen call oxidised flavour. This difference in terminology causes confusion for those not familiar with the chemical nature of both defects.

Milk as drawn from the cow always contains lipase or lipases. Under conditions favourable for lipase action, the enzyme causes hydrolysis of milk fat and liberates free fatty acids. The acids of lower molecular weight are responsible for the "goaty" odour and sharp, irritating or bitter taste, which are characteristic of rancid flavour in milk or dairy products. Pasteurisation destroys the lipase so rancidity does not develop in properly pasteurised milk.

Although lipase is always present in milk, it does not always produce rancidity. In most milk it is necessary to "induce" rancidity by an "activation treatment". Three activation treatments are:—

Agitation or foaming—prolonged shaking of warm, raw milk or treatment that cause foaming of warm, raw milk.

Temperature fluctuation—warming pre-cooled raw milk to about 87°F. and cooling it again.

Homogenisation of raw milk, or mixing homogenised milk with raw milk.

These treatments apparently change or disrupt the protective film surrounding normal fat globules in milk, and permit the enzyme to hydrolyse the fat.

In another type of rancidity, known as spontaneous rancidity, it is only necessary to cool milk and store it under refrigeration to favour the development of the off-flavour. This type is encountered most frequently in milk from individual cows in advanced lactation or on dry feeds. If milk that would go rancid spontaneously if stored is mixed with at least four times its volume of normal milk immediately after milking, the mixture will not go rancid. This practical control measure is applied automatically in normal commercial dairy production. The milk from several cows is mixed in cans or tanks. Consequently spontaneous rancidity rarely causes trouble in commercial milk supplies. Induced rancidity is much more troublesome.

Rancid flavour has become more prevalent in parts of the United States in recent years, largely as a result of changes in milk handling practices. Bucket-type milking machines are being replaced by pipeline milkers, which, in some cases, have caused excessive agitation and foaming of warm, raw milk. Some farm tanks have provided conditions where part of the milk may be subjected to temperature fluctuation or to prolonged agitation while warm. Adoption of the farm tank system has been accompanied in some districts by less frequent collection of milk from farms, thus allowing more time for the lipase to act before the milk is pasteurised. Attention is being given to correcting some of these conditions that favour lipase action, and satisfactory progress is being made in prevention of the off-flavour.

Oxidised Flavour.—Oxidised flavour is a relatively common defect of non-homogenised milk, cream, and certain other dairy products. In milk it has been described by such terms as metallic, cappy, cardboardy, papery, oily, and tallowy. The flavour varies appreciably in milk and in other products, as the number of descriptive names indicates.

The defect is generally considered to result from oxidation of unsaturated fatty acids. Differences in the character of the off-flavour are undoubtedly attributable to variations in the nature and amounts of various oxidised compounds present. Carbonyl compounds appear to be primarily responsible for the off-flavour, but there is no general agreement regarding the exact identity of the compounds involved. Some investigators emphasise the role of ketones, others incriminate aldehydes. Recent work conducted at the Dairy Research Section of C.S.I.R.O. in Australia indicates that at least the cardboardy flavour is attributable mostly to 2-octenal, 2-nonenal, 2, 4-heptadienal, and 2, 4-nonadienal.

Although much is known about factors influencing oxidised flavour, there are important gaps. The milk of individual cows varies in susceptibility to the defect, even when the cows are maintained under identical conditions. Certain metals, especially copper, catalyse flavour development. Light generally promotes the defect, but under certain conditions exposure to light may retard or prevent oxidised flavour.

The cow's feed influences susceptibility of her milk, presumably by providing certain antioxidants that appear in milk. Green succulent feeds yield milk that is resistant to oxidised flavour, whereas dry feeds result in highly susceptible milk. However, it is not known what compounds in feed retard development of the off-flavour. Vitamins such as vitamin C, carotene, vitamin A, and tocopherols have been fed and numerous determinations of these vitamins in feed have been made in attempts to establish whether they influence the flavour stability. The lack of consistency in results indicates that though certain of these compounds may be involved, they are not the only ones, and probably not the most important ones. In a recent comparison of several roughages at Cornell University, it was found that cows fed early legume-grass silage gave milk containing the highest concentration of vitamin A, carotene, and tocopherol, but cows fed late-cut silage produced milk with a greater resistance to oxidised flavour. It was concluded that unidentified protective substances from some roughages are secreted in milk and retard development of oxidised flavour.

Although ascorbic acid in feed apparently does not influence oxidised flavour, it may have a marked influence on milk. The prevailing, but not universally accepted, opinion is that ascorbic acid, at the level normally encountered in milk as secreted (ap-

proximately 20 mg. per qt.), or if increased artificially, acts as an antioxidant in delaying oxidised flavour. When the ascorbic acid is only partially oxidised, it appears to accelerate oxidised flavour, but when totally oxidised the development of oxidised flavour is again delayed. Hence, we have two schools of thought on this matter: one advocates control of oxidised flavour by artificial additions of ascorbic acid; the other recommends deliberate destruction of milk's ascorbic acid, either by controlled exposure to light or by a chemical or enzymatic treatment. It is probably because of this variable effect of ascorbic acid on oxidised flavour development that the effects of light and copper are not always consistent. Both catalyse ascorbic acid oxidation, but their influence on oxidised flavour may depend on whether they promote only partial or complete oxidation of the ascorbic acid.

Many antioxidants, when added to milk, are very effective in preventing oxidised flavour. However, the dairy industry has hesitated to adopt this approach for practical control of the defect to avoid the criticism that preservatives are added to dairy foods.

Homogenisation markedly increases resistance of milk to oxidised flavour. This provides a very practical control of the defect in the United States where a large proportion of market milk is homogenised.

Light Flavour.—In addition to catalysing oxidised flavour, light also produces another off-flavour described by various authors by such terms as sunlight, sunshine, activated, solar-activated, burnt, burnt feather, burnt protein, scorched, burnt cabbage, mushroom, and medicinal. As early as 1920, critical investigators differentiated between light and oxidised flavours, yet some publications still cause confusion by referring to the two defects as though they are identical. From 1920 to 1953 considerable evidence accumulated to establish distinct chemical differences between the two defects, one difference in particular being that the light defect is attributable to changes in the protein rather than in lipid material. Recent work at Pennsylvania State University demonstrated that light absorbed by riboflavin in some manner catalysed changes in the amino acid methionine, resulting in the production of beta-methylmercaptopropionaldehyde (methional), the compound responsible for the light flavour. Dicarbonyl compounds, such as dehydroascorbic acid, also promoted development of light flavour in methionine solutions exposed to light. Methionine appears to be the specific source of the defect, because other amino acids and compounds similar to methionine did not give the light flavour on exposure. Both casein and whey proteins, in the presence of riboflavin, yielded the typical off-flavour. This excellent study greatly clarified our understanding of the light defect.

Methods for preventing light flavour are obvious; it is essential to protect milk from exposure to light. Practices generally recommended include the use of covered vehicles, provision of covered milk boxes at the homes, taking milk in promptly after delivery, and use of amber or ruby coloured bottles or paper containers. Direct sunlight is not necessary for production of the light flavour. Prolonged exposure in the shade or even to fluorescent lights can produce off-flavours.

This general discussion outlines some of the progress that has been made in both understanding and controlling the flavour of milk. Encouraging results have been obtained. However, much remains to be done: chemists must continue to elucidate the chemistry of both desirable and undesirable flavour characteristics; dairy technologists must develop and apply new methods to ensure that only palatable milk reaches the consumer.

SOME RECENT ADVANCES IN CLAY MINERALS RESEARCH

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(Based on a lecture delivered before the Wellington Branch, May, 1957.)

In the last twenty years a large amount of work has been devoted to the study of the clay minerals. Fundamental studies of their nature, structure, properties, inter-relationships, and methods of formation have been carried out and are still in progress. Along with increased understanding of the nature and properties of the clay minerals, have come advances in clay technology. New industrial uses of clay minerals are being found each year, and their importance in agriculture and in civil engineering is being increasingly appreciated. It would not be possible within the confines of a short paper to review the recent advances in all these many and varied fields. In this paper, therefore, consideration will be given only to some recent work which has brought new understanding of the structures and inter-relationships of the clay minerals. Readers who are interested in recent comprehensive reviews are referred to the excellent book on Clay Mineralogy by Grim (1953) or to the symposium on Clays and Clay Technology published by the Californian Department of Natural Resources (1955).

The clay minerals may be defined as the hydrous silicates which occur in the clay-size grades of rocks, soils, and sediments. The definition is not exact, but there would be little to be gained

from an exact definition. The word "clay" is itself too vague to allow an exact definition of the minerals which occur in clay. The decision as to what does or what does not constitute a clay mineral rests very often only upon popular opinion. Thus gibbsite and goethite, although very common and sometimes abundant constituents of clays, are seldom included among the clay minerals. The kaolin group, the mica group, the chlorites, and the little known palygorskite or attapulgite group are generally considered to comprise the clay minerals.

The Kaolin Group.

The kaolin group of minerals include kaolinite and its variants, the serpentines, amesite and few other minerals. They all have in common a similar structural configuration in which an open net of silicon-oxygen tetrahedra is condensed with a closely packed net of M-hydroxyl octahedra. In kaolinite and its variants $M = Al^{3+}$, in the serpentines $M = Mg^{2+}$, and in the rare mineral greenalite $M = Fe^{2+}$. Projected upon the *bc* plane the structure is as shown

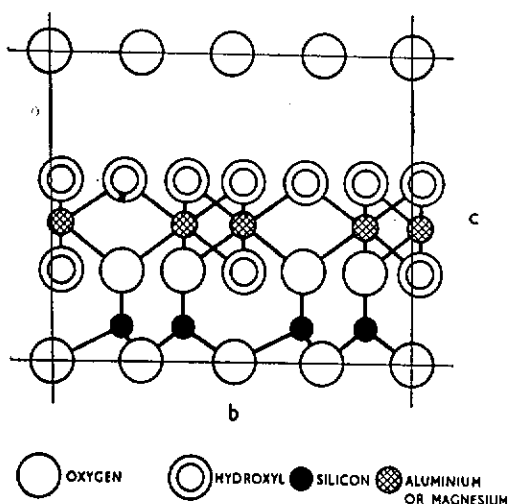


FIGURE 1.—Structure of kaolin group minerals projected on *bc* plane.

in Figure I. Much of the recent structural work concerned with these minerals has been devoted to the clarification of their individual structural arrangements and the types of imperfections they show.

The structure of kaolinite itself has been completely determined by Brindley and Robinson (1946). It is a triclinic mineral containing one kaolinite unit ($Al_4Si_4O_{10}(OH)_8$) per unit cell.

The cell angles are $\alpha = 91.8^\circ$, $\beta = 104.5^\circ$ and $\delta = 90^\circ$. The vertical distance between corresponding sheets is 7.13Å. The cell angles are consistent with a stacking sequence in which the kaolinite units occur immediately above each other along the b axis but are displaced a distance $\frac{1}{2}a_0$ along the a axis. In kaolinite there is virtually no substitution of magnesium for aluminium, and the aluminium ions, which occupy only two-thirds of the available octahedral sites, lie in corresponding positions in successive unit cells.

This well-crystallised, well-ordered kaolinite is not common. Most of the kaolinites found in clay deposits and in soils have their Al ions randomly arranged in the 6 possible octahedral positions. They also have random displacements along the b axis which upset the stacking sequence and destroy the precise triclinic character. Brindley and Robinson (1947) suggested the name "Mellorite" for the poorly-crystalline kaolinite minerals which exhibit randomness in their stacking. It has been generally preferred, however, to refer to them as poorly-ordered or poorly-crystalline kaolinite.

Two minerals of hydrothermal origin, nacrite and dickite, are similar to kaolinite. Nacrite is a rare mineral which has a nearly orthorhombic cell ($\beta = 90^\circ 20'$), and contains six kaolinite units per unit cell. It is formed under elevated temperatures and pressures, its rarity indicating that the conditions for its formation are seldom found in nature. It appears to be perfectly crystalline with no random displacements.

Dickite is more common than nacrite. Its structure has only recently been carefully determined by Newnham and Brindley (1956). It has a monoclinic unit cell containing two kaolinite units. The β angle is $96^\circ 48'$ and the kaolinite units are stacked with a regular displacement of $\frac{1}{2}a_0$ along the a axis and an alternating positive and negative displacement of $\frac{1}{4}b_0$ along the b axis. The mineral has well-ordered crystallinity and displays only to a limited extent the randomness in stacking which is so common in kaolinite.

Although nacrite, dickite, and kaolinite are hydrothermal minerals which show increasing amounts of disorder, presumably as their conditions of formation become less rigorous, there does not appear to be any gradation between them. Apparently there are only slight but nevertheless sharp differences between their conditions of formation.

Kaolinite can also form by weathering and so far no differences have been pointed out between kaolinite so formed and that formed hydrothermally. Halloysite, another kaolin type mineral, can also form both by weathering and by hydrothermal action.

Halloysite exhibits even more disorder than kaolinite, the random displacements extending into the *a* axis as well as the *b* axis. Whether or not the two minerals grade into each other is much debated. There is a difference in morphology between them. Kaolinite, under the electron microscope appears as hexagonal-like plates, but halloysite appears as tubes or cylinders. If the two minerals grade into one another it might be expected that intermediate forms would be found. Such intermediate forms have been seen in electron micrographs of New Zealand clays, both in soil clays containing halloysite and hydrothermal clays containing kaolinite. Hence, at least under New Zealand conditions, this intergradation between kaolinite and halloysite seems clearly established.

Bates *et al* (1950), who first pointed out the tubular morphology of halloysite, considered that the mineral took this shape in order to relieve the strains which occur in all clay minerals because of the misfit between the silicon-oxygen layers and the aluminium-hydroxyl layers. The normal *b* axis repeat distance of the silicon-oxygen layers is about 9.16Å. That of the aluminium-hydroxyl layers is about 8.65Å. Hence strain is introduced when these two are condensed together. In halloysite the strain is relieved by curvature, the layers curving into hollow cylinders with the silicon-oxygen layers on the outsides of the cylinders and the aluminium layers on the insides. It can be easily calculated that, if the two types of layers assume their normal *b* axis repeat distances, the cylinders will have internal radii of approximately 150Å. Most halloysite cylinders do appear to have internal radii around this figure. In the minerals better crystallised than halloysite, the bonding between layers is apparently too strong to allow much curvature. The strain is not relieved to any extent, and hence large crystals do not form. This seems to be the main reason why the clay minerals are clay-size.

Recently a new and powerful instrument has come into use in the study of clay minerals. This is an electron microscope which has facilities for taking electron diffraction pictures of very small portions of the microscopic field. With it, it is possible to obtain diffraction patterns from single crystals of clay minerals. Single crystal pictures of halloysite have proved fairly conclusively that Bates' original idea of plates curved into tubes is correct, but it has not yet provided much information about the intergradation of kaolinite and halloysite.

The serpentine minerals have been included in the kaolin group only recently. They have several analogies to the kaolinite minerals in addition to the general similarities in structural units. Thus antigorite is a platy mineral like kaolinite, while chrysotile is tubular like halloysite. The chrysotile tubes are constructed

similarly to those of halloysite except that the magnesium-hydroxyl layers having the greater b axis repeat distance now are on the outside of the tubes with the silicon-oxygen layers on the inside.

The Mica Group.

The mica group of clay minerals have two silicon-oxygen tetrahedral layers condensed with one aluminium-hydroxyl or magnesium-hydroxyl octahedral layer. On the bc plane, the structure

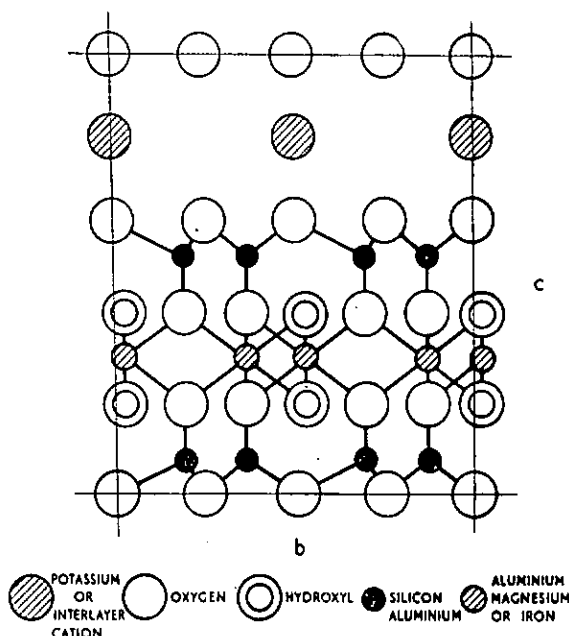


FIGURE 2.—Structure of mica group minerals projected on bc plane.

is as shown in Figure 2. The group includes the true micas such as muscovite and biotite, and also the expanding or swelling minerals, vermiculite and montmorillonite.

The polymorphic stacking arrangements which gave rise to nacrite, dickite, and kaolinite minerals gives rise to about six different varieties of biotite, but muscovite seems to have a unique structure with two mica units in the unit cell.

The inclusion of vermiculite and montmorillonite amongst the micas has been the result of the growing realisation that the differences between them and the true micas are not fundamental structural differences, but merely differences in the type of interlayer cation and the magnitude of the net negative charge upon the layers.

Many workers have contributed to this realisation. The French workers Caillere and Henin (1948, 1949) have shown how easily the non-swelling and swelling minerals can be synthesised from one another. Grim and his associates (1949, 1954) have pointed to the many examples of the formation of non-swelling minerals in marine environments from swelling minerals carried down by the rivers. Barshad (1948, 1950) and Walker (1951) have done much to show that swelling properties are dependent upon the nature of the interlayer cation.

Table I, taken from an article by Brindley (1955), summarises much of the data of Barshad and Walker. The dependence of the spacing and the number of water layers upon the interlayer cation is clear. The ratio n/r (n = valency, r = ionic radius) is a measure of the ionic potential of the cation; that is its charge per unit of distance. The differences in spacings between layers with the same degree of hydration (e.g. Rb-saturated and Cs-saturated minerals) is due to differences in the ionic radii of the cations, the bigger cation causing the bigger spacing.

TABLE 1.—RELATIONSHIPS BETWEEN SATURATING CATION, LATTICE SPACING, AND NUMBER OF WATER LAYERS OF VERMICULITES AND MONTMORILLONITES.

IONS		H	Mg	Ca	Li	Ba	Na	K	NH ₄	Rb	Cs
Radius, A.	0.30	0.65	0.99	0.60	1.35	0.95	1.33	1.48	1.48	1.69
n/r	3.3	3.08	2.02	1.67	1.48	1.05	0.75	0.68	0.68	0.59
DATA FOR VERMICULITES.											
Lattice Spacing	14.3	14.3	15.1	12.6	12.6	12.6	10.4	11.2	11.2	12.0
Number of Water Layers			14.4	15.0	12.2	12.3	14.8	10.6	10.8		
		2	2	2	1	1	1,2	0	0	0	0
DATA FOR MONTMORILLONITES.											
Lattice Spacings	14.5	14.8	15.1	13.4	12.9	11.9	12.0	12.1	12.3	12.9
Number of Water Layers		2	2	2	1	1	1	1	1	1	1

If it is true that micas, vermiculites and montmorillonites are very similar, it is to be expected that minerals would be found in nature which are mixtures of these. These expectations are fully borne out and much literature is accumulating on the occurrence of mixed layer structures or interstratified mixtures as they are alternatively called. Occasionally these mixed layers are regular alternations of swelling and non-swelling layers, but most of them consist of random mixtures in which there is no apparent order in the succession of swelling and non-swelling layers. The recognition of these random mixtures is often difficult, and the identification of their constituent minerals is a task of some magnitude. In general, the methods used depend upon the study of modifications in the X-ray diffraction patterns produced by heating the sample to various temperatures or by filling the interlamellar spaces of the swelling minerals with organic compounds. Recently a mathematical method using Fourier transforms has been applied, in which

the probability that a non-swelling layer will be followed by a swelling or non-swelling layer is calculated from the intensities of the X-ray reflections. The method is difficult and can only, as yet, be applied to simple cases, but it does show much promise. The interested reader is referred to the paper by McAtee (1956) for details.

The Chlorites.

The most recent addition to the clay minerals is the group of minerals known as chlorites. They may be considered as regularly interstratified mixtures of mica layers alternating with layers of brucite ($Mg(OH)_2$) or gibbsite ($Al(OH)_3$). Chlorites have been known for a long time as common products of low-grade metamorphism. They have been identified petrographically and schemes relating optical properties to chemical composition have been drawn up by various people. However, until recently, they have not been recognised amongst the clay minerals.

The main reason for this lack of recognition is that their X-ray diffraction patterns are similar to those of vermiculite and kaolin. The X-ray reflections from the basal planes of these three

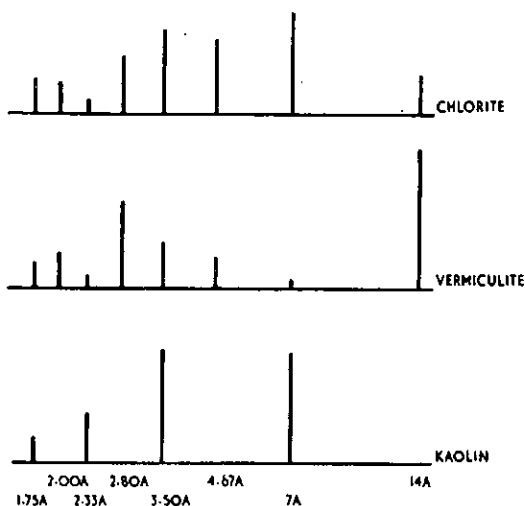


FIGURE 3.—X-ray reflections from basal planes of chlorite, vermiculite and kaolin.

minerals are shown in Figure 3. In a mixture with a moderate or small amount of chlorite the 14A peak could be missed and the mineral identified as kaolin. Even if the amount of chlorite were high, it could still be confused with kaolinite if it contained, as

many chlorites do, appreciable amounts of iron. Under these circumstances the 14A peak may have less than one-tenth of the intensity of the 7A peak. Undoubtedly, many 14A peaks which were properly due to chlorite have been interpreted as being due to vermiculite, and a 14A peak followed by a strong 7A peak has been called a mixture of vermiculite and kaolin.

There are three methods by which chlorites can usually be distinguished from other minerals. Firstly, most chlorites so far investigated are high in magnesium or iron and relatively low in aluminium, whereas kaolins are high in aluminium and low in these other cations. These differences give the chlorites different *a* and *b* dimensions to kaolins and careful work will indicate this. Secondly, the sixth order of chlorites is low regardless of its composition, whereas the corresponding third order of kaolin is fairly strong. This is a useful distinction for routine work. Thirdly, the three minerals, kaolin, vermiculite and chlorite all react differently to heat treatment, and heat treatment has been the most used criterion for distinguishing them.

Around 500°C the lattice of kaolin minerals is destroyed and the series of X-ray reflections from the basal planes disappear. Also, by 500°C, most vermiculites have lost their interlayer water and have collapsed to 10A spacings with corresponding changes in the reflections of the higher orders. Chlorites are usually unaffected by heating to 500°C. At high temperatures (600° - 700°C) the brucite layers between the mica layers of the chlorites are broken down and the intensities of the X-ray reflections are changed, the 7A peak being much reduced and the 14A peak intensified. At temperatures above 700°C the chlorite structure is permanently altered and the 14A peak disappears.

Unfortunately, these distinctions are not quite as clear cut as they may seem. The distinction from kaolin can usually be made with some confidence, but chlorites and vermiculites grade into one another and their properties grade accordingly. Chlorites weather to vermiculites and montmorillonites and these three often occur in interstratified mixtures. Swelling mica structures, deposited by rivers into marine environments, may have small amounts of magnesium hydroxide deposited between the layers and so take on some of the character of chlorites. It seems that the gradations between chlorites and these genetically related swelling minerals may be continuous, and divisions between them must be drawn rather arbitrarily.

One group of workers has preferred to call only those minerals vermiculites which show a 14A peak which collapses to 10A when the mineral is saturated with K^+ or NH_4^+ ions. All other minerals showing 14A peaks would be chlorites. By this criterion most of our New Zealand vermiculites would have to be reclassified as chlorites.

Another group of workers prefers to draw the line at a temperature of $500^\circ C$ saying that those minerals which collapse from 14 to 10A after heating to $500^\circ C$ are vermiculites and those that do not collapse are chlorites. By this criterion the 14A minerals in New Zealand soils would be mostly vermiculites with some chlorites.

A third group, taking a different and perhaps more fundamental line, would use the ratio of intensities of 7A and 14A peaks in the unheated minerals. Those minerals with ratio of I_{7A}/I_{14A} below a certain value would be vermiculites, those above that value would be chlorites. Before the test can be applied, however, the contribution of kaolin to the 7A peak must be allowed for, and

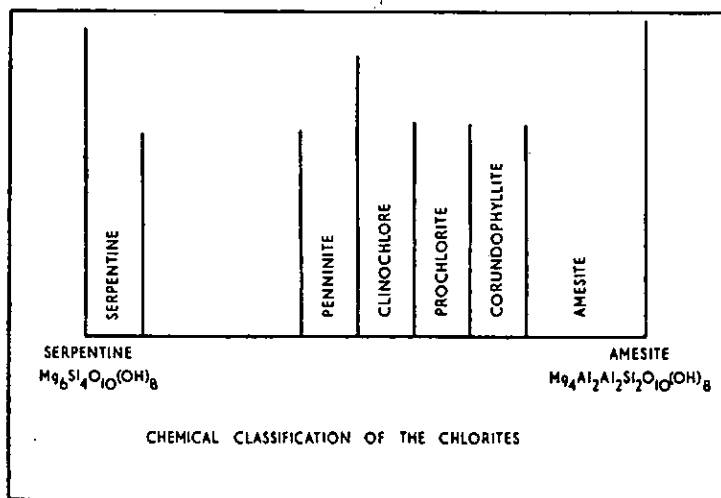


FIGURE 4.—Classification of chlorites (after Tschermak, 1891).

the difficulty of assessing this contribution seems at present so great that the method does not appear practicable.

Hydrothermal Syntheses of the Chlorites.

Because of the great interest in chlorites at the present time, Nelson and Roy (1954) at Pennsylvania State University carried out some hydrothermal syntheses of chlorite minerals. In Figure 4 is shown a modification of an early chemical classification of the

chlorites. The abscissa is increasing Al content, the ordinate increasing Fe^{2+} . Actually neither serpentine nor amesite are chlorites; they belong to the kaolin group, but the original of this classification was made by Tschermak in 1891 and was based on optical properties. Nelson and Roy attempted to synthesise hydrothermally chlorites along the abscissa, i.e. chlorites containing magnesium and aluminium but no iron. They were quite successful and at high temperatures they produced a series of 14Å minerals from penninite to amesite. However, at low temperatures, the same compositions gave rise to apparently single mineral phases which showed only 7Å spacings. Furthermore, they were able to convert these 7Å minerals into the 14Å ones by merely placing them back in their apparatus and raising the temperature. They were not able to convert the 14Å minerals to 7Å ones.

This work, while solving very little, is most interesting. In its light it becomes exceedingly hard to tell what is a chlorite and what is not. Obviously the kaolin minerals and the chlorites are much more closely related than has been heretofore suspected. It has explained one or two previously anomalous results. It shows that Tschermak was not far out when he included serpentine and amesite among the chlorites. It helps explain the controversy that people have had over the classification of the ferrous mineral chamosite which sometimes appears to be a 7Å mineral and at other times a 14Å one. Recently Brindley and Gillery (1954) examined a high-iron chlorite and were able to explain the X-ray patterns only by suggesting that there were kaolinite layers interspersed with the chlorite units. Their suggestion has gained a more ready acceptance because of the work of Nelson and Roy. Very close inspection of some chlorites and vermiculites has recently revealed evidence that some of the silicon ions in the mica units may actually occur outside the oxygen sheet with their apical oxygens, now hydroxyls, pointing towards the interlayer space instead of towards the middle of the mica units. This is the reverse of the shift which must occur when a 7Å mineral is converted into a 14Å one.

Very recently Roy and Brindley (1957) have produced a little piece of evidence to show that the kaolinite minerals themselves may not be entirely free from this behaviour. By dehydrating dickite and heating the product in a hydrothermal bomb they obtained some evidence of a 14Å spacing in the resulting products.

This recent work, indicating the possible existence of structural inter-relationships between the 14A and 7A minerals, serves to illustrate the point that a complete understanding of the nature and properties of the clay minerals is an objective as yet unachieved. With newer instruments and more searching methods of analysis being used, the knowledge and information at present available is being continually reviewed, refined, and advanced. It is anticipated that the next decade will see much clarification of present-day mysteries of the clay minerals, but nevertheless there is little doubt that the clay minerals will provide opportunities for interesting and worth while research for many years to come.

REFERENCES.

- BARSHAD, I. (1948). *Am. Mineral* **33**, 665.
BARSHAD, I. (1950). *Am. Mineral* **35**, 225.
BATES, T. F., HILDEBRAND, F.A. and SWINEFORRD, A. (1950).
Am. Mineral **35**, 463.
BRINDLEY, G. W. (1955). *Calif. Dept. Nat. Resources, Bull*, **169**, 33.
BRINDLEY, G. W. and GILLERY, F. H. (1954). *U.S. Nat. Acad. Sci. Pub.* **327**, 349.
BRINDLEY, G. W. and ROBINSON, K. (1946). *Min. Mag.* **27**, 242.
BRINDLEY, G. W. and ROBINSON, K. (1947). *Trans. Brit. Ceram. Soc.* **46**, 49.
CAILLERE, S., HENIN, S., and MERIAUX, S. (1948). *Compt. rend.* **226**, 680.
CAILLERE, S. and HENIN, S. (1949). *Min. Mag.* **28**, 612.
CALIFORNIAN DEPT. OF NATURAL RESOURCES (1955). *Bulletin* **169**, "Clays and Clay Technology."
GRIM, R. E. (1953). "Clay Mineralogy," McGraw-Hill, N.Y.
GRIM, R. E., DIETZ, R. S., and BRADLEY, W. F. (1949). *Geol. Soc. Amer., Bull.* **60**, 1785.
GRIM, R. E., and JOHNS, W. D. (1954). *U.S. Nat. Acad. Sci. Publ.* **327**, 81.
McATEE, J. L. (1956). *Am. Mineral* **41**, 627.
NELSON, B. W. and ROY, R. (1954). *U.S. Nat. Acad. Sci. Publ.* **327**, 335.
NEUNHAM, K. E., and BRINDLEY, G. W. (1956). *Acta Cryst.* **9**, 759.
ROY, R. and BRINDLEY, G. W. (1957). *Proc. 4th U.S. Conf. Clay Minerals* (in press).
TSCHERMAK, G. (1891). *Sitzungsber Akad. Wiss. Wien, Math-Naturwiss.* **100**, 29.
WALKER, G. F. (1951). "X-ray Identification and Crystal Structures of Clay Minerals," Chap. 7. G. W. BRINDLEY, Ed., Mineralogical Society, London.

ROYAL CHARTER

REPORT OF CHARTER SUB-COMMITTEE.

(This report was prepared by Messrs. C. V. Fife and C. B. Radcliffe on behalf of the Manawatu Branch. The report was subsequently approved by the Branch Committee and forwarded to Council with unanimous support for the recommendations contained in it.)

INTRODUCTION AND TERMS OF REFERENCE:

In the course of recent discussions on ways and means of increasing the prestige of the New Zealand Institute of Chemistry and of raising the standing of chemists in the community, the question was raised in the Manawatu Branch as to whether the time were not opportune to consider afresh the desirability or otherwise of the New Zealand Institute of Chemistry making application for a Royal Charter. It will be recalled that the Charter Committee of 1948 considered that the advantages of such a Charter would be outweighed by the disadvantages and recommended that no application for a Royal Charter should be made at that time. At the request of Council the Manawatu Branch undertook to determine:

(a) Whether the situation had changed sufficiently in the intervening years to nullify the recommendation of the 1948 Charter Committee.

(b) The approximate cost of carrying a petition for a Royal Charter as far as the Prime Minister's Department.

The present sub-committee of the Manawatu Branch Committee set out to report under the above terms of reference.

CONSIDERATION OF THE OBJECTIONS RAISED BY THE 1948 CHARTER COMMITTEE TO MAKING APPLICATION FOR A ROYAL CHARTER.

Four main objections were raised by the 1948 Charter Committee:—

- (1) The New Zealand Institute of Chemistry was considered "in all probability" to be too small a body to induce the Privy Council to make the necessary recommendation.
- (2) The cost of making the application would be high and that at least £1,000 would be required to meet legal and other expenses.
- (3) There was already in existence in New Zealand a section of a Chartered body covering the profession, namely the New Zealand Section of the Royal Institute of Chemistry.
- (4) The necessity for the procurement of a Supplemental Charter to cover any subsequent alterations to the constitution of the New Zealand Institute of Chemistry and the necessity for Privy Council approval of all by-laws would be time-consuming and expensive; it would further bring about a degree of inflexibility not desirable in the case of a body in the formative state such as the New Zealand Institute of Chemistry.

It would seem unlikely that the first objection would at the present time constitute a serious obstacle to the procurement of a Royal Charter. A perusal of the history of the protracted Charter negotiations by the Australian Chemical Institute (Leighton, A. E. (1954). "A History of the Australian Chemical Institute 1914-1932" Proc. Roy. Aust. Chem. Inst. 21 pp. 127-134, 145-154, 167-184) discloses no suggestion that the size of the petitioning body would reduce the chances of success.

Admittedly, at the time (August, 1928), that the Australian Chemical Institute submitted its petition, its membership was 817 as compared with the present New Zealand total of approximately 500. It might be argued however, that, taking into consideration the populations of the two countries, the New Zealand Institute of Chemistry is relatively stronger numerically today than was the Australian Chemical Institute at the time its petition was submitted. Further, in terms of absolute numerical strength the New Zealand Institute of Chemistry more than meets the minimum requirement of over 400 suggested by the 1948 Charter Committee. The fact that no body with a smaller membership than this had been granted a Royal Charter at that time may merely indicate that no such body had yet seen fit to apply.

So far as the second objection is concerned it would seem, on the basis of legal opinion taken in Palmerston North, that the suggested cost of £1,000 for making the necessary application was an overestimate. No indication was given by the 1948 Charter Committee as to the source of its information of this point. In reply to a request for information on the costs of the Australian petition the Registrar of the Royal Australian Institute has provided the following statement. "Due to the lapse of time since the granting of this Institute's Charter, I am not able to indicate the costs involved. A considerable amount of preparatory work was carried out in an honorary capacity in our case, but the legal fees in London were of the order of 100 guineas." It seems hardly likely that costs have risen sufficiently in the meantime to raise this figure to £1,000 or more; as is indicated later in this report the costs in New Zealand are likely to be light.

The suggestion by the 1948 Charter Committee that the existence already in New Zealand of a section of a Chartered body might prejudice the granting of a Royal Charter to the N.Z. Institute of Chemistry calls for some comment. The "List of Members" (1954) published jointly by the New Institute of Chemistry and the N.Z. Section, Royal Institute of Chemistry indicates a total N.Z.I.C. membership of 480 as compared with a R.I.C. membership of 96. The important point is that only 17 of this latter group are not also members of the New Zealand Institute. This sub-committee considers that the N.Z. Section of the Royal Institute must be regarded as playing a very minor role in representing the profession of chemistry in this country and that this will become increasingly the case as time goes on. Nevertheless, to be in the strongest tactical position to obtain official recognition under Charter it would be necessary for the New Zealand Institute of Chemistry to be able to claim to be *sole* representative of the chemical profession in this country.

The final objection cited by the 1948 Charter Committee does not, on the basis of Australian experience, appear to be of very real significance. The initial petition made by the Australian Chemical Institute was made in August, 1928; a further petition for a Supplemental Royal Charter was not required until March, 1952, and appears to have been granted without delay.

COSTS INVOLVED IN CARRYING A PETITION FOR A ROYAL CHARTER TO THE PRIME MINISTER'S DEPARTMENT.

Advice taken in Palmerston North suggests that a sum not exceeding £50 would cover the legal expenses of drawing up a petition. In addition, printing costs would have to be met.

GENERAL.

It seems unlikely that an application for a Royal Charter by the New Zealand Institute of Chemistry would be subject to the delays experienced in the Australian case, provided the correct method of approach was followed. The details of the procedure of application should be readily obtainable from the Prime Minister's Department, but the Institute would be ill-advised to make any move until it had ascertained whether support would be forthcoming from the Royal Institute of Chemistry, since in the absence of such support any application for a Charter would be bound to fail. In the light of Australian experience the measure of support accorded by the Royal Institute would be governed largely by its opinion of the standard of qualifications required for election of our Fellows and Associates. Another matter to which meticulous attention would need to be given in the initial period of "ground-clearing" would be that of bringing the constitution of the Institute to that state of finality which would obviate the need to make further application for the purpose of embodying amendments.

There is one important point to which attention must be drawn, namely, that the granting of the prefix "Royal" may not be possible until some years after the granting of the Charter. The Registrar of the Royal Australian Chemical Institute has informed this Branch in a letter of 30th May, 1957, that the Australian Chemical Institute at the time application was made for the original Charter, was advised of this situation. He considers that similar circumstances would prevail today. The actual procedure which was adopted in Australia to achieve this final objective was that a request was forwarded through the Prime Minister's Department in 1948 and the granting of the prefix "Royal" was made in 1949. It was then necessary for the Institute to make application for a *Supplemental Charter to regularise the use of the prefix*. If, as appears to be the case, this is the procedure which would have to be followed by the New Zealand Institute of Chemistry, there is likely to be a virtual doubling up of costs to achieve the presumably desired ultimate goal of being termed a Royal Institute. Even so, the total expense involved covering both original and supplemental applications is not likely to reach the £1,000 estimate put forward by the 1948 Charter Committee.

The question of a body obtaining permission to preface its name by "Royal" without at the same time becoming a Chartered body has been raised; we have not been able to obtain any reliable information on this point.

CONCLUSION AND RECOMMENDATION.

There is little doubt that the procurement of a Royal Charter would materially assist to further the avowed aim of our Institute to raise the status of the profession of chemistry in this country. In this connection it is of interest to note the opinion expressed by the Registrar of the Royal Australian Chemical Institute in a letter to the Manawatu Branch on 5th November, 1956. He states that: "It is a difficult matter to define the tangible effects accruing to the Institute and the profession by the granting of a Royal Charter, but there is no doubt that the status of the Institute and of the profession have been enhanced, and recognition of the Institute by Governmental authorities has resulted."

In view of the degree of maturity and stability now attained by the New Zealand Institute of Chemistry it is our considered opinion that the time is opportune for the Institute to indicate clearly that it will in due course make application for a Royal Charter. As the first step towards the objective we recommend that Council should immediately take action to ascertain from the Royal Institute of Chemistry under what conditions its support for such an application would be forthcoming.

ACKNOWLEDGEMENT.

We would like to record our indebtedness to the Registrar of the Royal Australian Chemical Institute for making available to us for perusal a copy of the Australian Royal Charter, together with copies of the petitions for the Charter and Supplemental Charter and for his helpful advice generally. We feel that this assistance should receive official recognition at the highest level.

NEWS AND NOTES**MANAWATU BRANCH.**

The recipient of this year's I.C.I. Prize was Dr. F. H. McDowall, Chief Chemist, The Dairy Research Institute, Palmerston North. This award, an annual one for the most significant contribution to some branch of Chemistry in New Zealand as judged by published work over the previous five years, was made to Dr. McDowall for his work on a wide range of problems associated with the dairy industry. Of particular interest to chemists were his papers dealing with fundamental aspects of vapour/liquid equilibrium relationships in the deodorisation of cream. Also included in his publications was his comprehensive book, "The Butter-maker's Manual", which is now the standard text in this field.



Dr. D. R. Dolby has recently returned to The Dairy Research Institute after visiting dairy research centres in Britain, Australia, the Continent and the United States.

WELLINGTON BRANCH.

The Morcom Green Edward's Prize was this year awarded to Mr. T. Marshall, Dominion Physical Laboratory. This award was based mainly on Mr. Marshall's work on geothermal corrosion.

CANTERBURY BRANCH.

Mr. A. Wong has been granted his Ph.D. degree by the University of New Zealand. He graduated M.Sc. from Victoria University College and completed his Doctorate at Canterbury University College. Dr. Wong has now left New Zealand for Hong Kong.

Mr. R. H. Shepherd of I.C.I. Ltd., has been transferred to his firm's head office in Wellington.

Mr. S. R. Gay, Works Manager, Kempthorne Prosser Ltd., Hornby, has been appointed General Manager of Southland Co-operative Phosphate Co., Invercargill, thus ending a long association with the Canterbury Branch.

OTAGO BRANCH.

Dr. G. N. Malcolm has taken up duties as lecturer in Physical Chemistry at Otago University. He has recently returned from Manchester University where he took his Doctorate and had one year on the staff.

OBITUARY

By the death of R. O. Page, D.Sc. (N.Z.), F.N.Z.I.C., F.R.I.C., F.R.S.N.Z., on the 14th July, 1957, the Institute lost one of its very distinguished Fellows and the Canterbury Branch lost, in addition, one who was to many of its members a most stimulating colleague and a valued friend.

Dr. Page was a son of Samuel Page, who for many years, until the end of 1922, was a lecturer in the chemistry department of Canterbury College. After studying under Professor W. P. Evans at Canterbury College and graduating M.Sc. with first class honours in chemistry in 1920, Dr. Page was appointed chemist on the staff of the Woolston Tanneries Ltd. In 1924 he became works manager, which position he held until his retirement a few weeks before his death. In 1924 he visited the United States of America to study tanning processes in that country, and in succeeding years he devoted as much time as possible to work aimed at the elucidation of the processes of vegetable tannage. His contributions in the field of leather chemistry are to be found in twenty-one papers published in *Industrial and Engineering Chemistry*, the *Journal of the American Leather Chemists' Association*, the *Journal of the International Society of Leather Trades Chemists*, and the *Journal of the Society of Leather Trades Chemists*. Dr. Page was quick to apply to the problems of tanning the advances which occurred in protein chemistry during the nineteen-twenties and later. He was rewarded with the degree of D.Sc. by the University of New Zealand for a thesis he submitted in 1932 in which, in addition to his own original contributions, he showed how the recently developed electronic theory of valence could be used to give a better understanding of the processes involved in the tanning of hides. He had the distinction of being the only chemist to be elected to the Fellowship of the Royal Society of New Zealand in recognition of contributions to chemistry made whilst holding an industrial appointment.



The standing of Dr. Page amongst chemists and scientists in this country is shown by the long list of positions of responsibility held by him. He was the second Chairman of the Canterbury Branch of the New Zealand Institute of Chemistry, holding office in 1932 and 1933, President of the New Zealand Section of the Royal Institute of Chemistry in 1941, President of the Canterbury Branch of the Royal Society of New Zealand in 1944 and also President of the New Zealand Institute of Chemistry in the same year. His great interest in New Zealand secondary industries and his informed views on their proper scientific control and relation to primary industry resulted in his appointment in 1937 to the Council of the Department of Scientific and Industrial Research, on which body he served until 1955. At the time of his death he was a member of the

Cawthron Institute Trust Board, the Committee of the Wheat Research Institute and the Leather and Shoe Research Association Committee.

Dr. Page was ever much interested in matters relating to education, especially of the scientist, and he was a keen advocate in Canterbury of "refresher" lecture courses, in which advances in pure chemistry are made available to those whose work lies in applied fields. He was for a time a member of the Board of Governors of the Christchurch Girls' High School. Indeed the last address he gave was one entitled "*A Layman's View of Education.*" It was delivered before the Canterbury Science Teachers' Association towards the end of 1956 and was calculated to cause teachers to think carefully about the purpose and methods of their teaching.

Dr. Page's contributions to society, including as they did cultural and sporting interests, were much wider than this short appreciation of him as a chemist and scientist could possibly indicate. He possessed an active, penetrating and critical mind and considerable physical energy, and New Zealand chemistry and the community at large are poorer for his passing. Dr. Page was a man of deep religious conviction; this showed itself in his courageous attitude to moral problems which he faced without consideration of personal cost. His personal relationships were characterised by sincerity, warmth and deep human understanding and he will be missed by a very large number of personal friends and colleagues.

—J.P.

EQUIPMENT PAGE

(Contributed by G. M. Wallace, Biochemistry Department, Massey Agricultural College, Palmerston North.)

For those who have to analyse milk samples an entirely new approach to the problem of calculating the solids-not-fat content of the milk from the density and fat has been developed. This consists of a nomograph with a cursor engraved in such a way that densities determined within the range 17°-24°C can be used without first having to correct them to 20°C, as has always been the practice in the past. The nomograph scales have been calibrated so that the solids-not-fat content of the milk can be read directly from the nomograph with only one setting of the cursor. It is considered that there will be not only a saving in time but an increase in accuracy with the use of this new calculator. They will be available from the writer.

A design for a modified lactometer jar has recently been published in *Dairy Industries* (1957) 22, 419. In this a side filling tube has been incorporated to ensure that the filling of the jar with milk is done with a minimum of splashing thus reducing quite a potential source of error.

In place of the conventional automatic burettes used for dispensing 1 ml. quantities of amyl alcohol in the Gerber test for fat it has been found very practicable to use a hypodermic syringe with a stop at 1 ml., and fitted with a Becton Dickinson automatic double valve, so that merely by operating the syringe 1 ml. quantities of amyl alcohol are automatically dispensed with accuracy, ease, an absence of leaking, and no frustration from jamming taps. In setting this up it is essential to arrange the input side in such a way that there is always a slight head of liquid available. This is easily arranged by having the tube from the reservoir in the form of a syphon.

LETTER TO THE EDITOR

Sir,—Your article entitled, "*A Scheme for University Development*," makes interesting reading and appears at first sight to have several commendable points. But there are also serious disadvantages in the scheme which I would like to point out.

1. The scheme means further fragmentation of our education system. True education is caught not taught and a student has to be associated with an institution and its teachers for an appreciable time if he is to leave that institution with educated feelings. This is the same criticism that is frequently levelled at our Intermediate Schools which in two years have little opportunity to make a real and lasting contribution to the pupils' personality. This "starry-eyed" criticism is, nevertheless, very real and applies to the proposed Junior College.

2. The first three points listed in the scheme boil down to the suggestion that building additional institutions with their attendant administrative and equipment costs would be cheaper than the present system. I suggest that a modification of the internal organisation of the existing Universities and Secondary Schools would be cheaper and more efficient. If the money for the proposed Junior Colleges were made available to the four main Universities, what big improvements could be made in organising Stage I! Additional Stage I Theatres, Laboratories and staff could be provided within the existing structure and time-tabling difficulties (Point 11) would be reduced. Incidentally would not the Professor prefer to have the staff, courses, students and equipment for which he is to be responsible, in the one institution rather than in several Junior Colleges scattered over the metropolis?

3. With regard to Point 4: highly qualified teachers will still be required in the schools to plan courses and teach to S.C. and U.E. levels. The Junior College would drag these teachers away. The number of hours a teacher spends actually teaching is much greater in Secondary Schools than in Universities so that the scheme would create, not alleviate shortages.

Point 8 suggests a better transition from School to University. 6A teachers are well aware of the nature of University life and spend the year steering their pupils towards this new life. The suggested scheme would merely shift this training and the "shock" of transition a year earlier when the pupils would be considerably less mature.

Point 10: What is the difference between having chaos (caused by poor students in large numbers) at Stage O instead of Stage I?

The other points listed, many of them well worth serious consideration, could be incorporated within the existing system.

In general, I feel that the idea creates more difficulties than it solves. To decapitate Secondary Schools is a very serious suggestion. In country areas where suitable instruction may not be available the situation is met by boarding bursaries.

Certainly the time is due for a reorganisation to cope with the large number of students proceeding to the University; but not along the lines suggested. A really courageous effort could be made to provide University education of a kind best suited to the talent available. Stage I need not offer only a "pass" or "fail." It could sort students into "Honours" or "Degree" or "Diploma" categories, thus making use of all talent available. At present are we not losing many useful technologist and technician types because they fail at Stage I? We cannot afford to lose a single person who might be trained to some useful level of attainment. I fear that the scheme outlined would have the opposite effect.

OWEN L. GILMORE.

BOOK REVIEWS

THE DIRECTORY OF AUSTRALIAN CHEMICALS. Published by Commonwealth Department of Trade, Melbourne, and distributed by Tail Book Company Pty. Ltd., 349 Collins Street, Melbourne. Third Edition, 1956. Price 12/6.

A third edition of the *The Directory of Australian Chemicals* was published recently by the Commonwealth Department of Trade. It lists all chemicals produced in Australia and available for sale. The directory was first published in 1948, and the second edition in 1950. During the last six years the Australian Chemical Industry has continued its high rate of expansion in terms of both physical output and diversity of products. This edition includes nearly 1,000 chemicals and approximately 270 manufacturers. Chemicals are listed alphabetically, with a description, and the name of the manufacturer. To facilitate reference, certain chemicals are arranged in groups under generic headings. Names and addresses of manufacturers are listed separately. An appendix provides a list of the principal minerals and concentrates produced in Australia which are available for purchase and of interest to the chemical industry.

PROPERTIES OF PETROLEUM RESERVOIR FLUIDS, by Emil J. Burcik. Published by John Wiley & Sons, Inc., New York, 1956. 190 pages. Price 7.50 dollars.

This book is compiled from the subject matter of a short University course in petroleum engineering. With the growing interest in oil production in this country it should attract other readers, although it will appeal principally to physical chemists. As well as sections on the hydrocarbons which constitute petroleum and the characteristics of reservoir fluids, the book gives an excellent practical account of the phase behaviour of ideal and non-ideal solutions. It is well and accurately printed, and adequately provided with diagrams and graphs, illustrative examples and problems.

—D.G.H.

THE CHEMISTRY OF ORGANOMETALLIC COMPOUNDS, by Eugene G. Rochow, Dallas T. Hurd and Richard N. Lewis. Published by John Wiley & Sons, Inc., New York, May, 1957. 344 pages. Price 8.50 dollars.

Organometallic compounds, falling somewhere between the two classical divisions of chemistry, have tended to be overlooked in many chemistry courses. The organic chemist has, of course, been interested in compounds like the Grignard reagents but has regarded them only as useful intermediates in the synthesis of a wide range of compounds. Similarly the inorganic chemist has used organic derivatives mainly as tools to expand his knowledge of elements like silicon, tin and lead. The present authors have felt the need for a comprehensive and integral treatment of the subject as a whole, and within the limits of space available have succeeded in presenting a valuable and very readable account of these interesting compounds.

Theoretical, factual and practical aspects of organometallic compounds are covered; the text is well referenced and contains valuable lists of compounds with their properties, etc. Some sixty odd pages are devoted to theoretical considerations, particularly the theory of the carbon-metal bond, and to general preparative methods. Organometallic compounds are then considered in groups according to the periodic classification. Final chapters deal with the use of these compounds in organic synthesis and with special types of organometallic compounds.

The book will be of value to students, research workers and to general readers who are interested in this field.

—W.A.McG.

A GUIDE TO THE LITERATURE OF CHEMISTRY (2nd Edition)
by E. J. Crane, Austin M. Patterson & Eleanor B. Marr. Published
by John Wiley & Sons, Inc., New York, April 1957. 397 pages.
9.50 dollars.

There is no doubt that the great abundance and variety of recorded literature and the accelerating rate at which this literature is growing, makes adequate use of it increasingly difficult. Against this, most chemists will feel that they are sufficiently at home with chemical literature, whether their immediate field or not, at least to know where to look for information and how extensive to make their search. This book extends further however than its title might suggest. In addition to covering the periodicals of chemistry, it deals with Patents, Government Publications, Trade Literature and many other sources of information; it lists reference books in all branches of chemistry; it offers advice on procedures in literature searches; it lists symbols, abbreviations, etc. used in chemical literature; it deals with historical aspects of chemical literature. Information relating to libraries, etc., will be of more value in the United States than in this country.

In passing, it is of interest to note that although publications of general science which include chemical articles are listed, the only New Zealand periodical mentioned is our own Institute of Chemistry Journal.

PROJECT ENGINEERING OF PROCESS PLANTS, by Howard F. Rase and M. H. Barrow. Published by John Wiley & Sons, Inc., New York, 1957. 692 pages. Price 14.25 dollars.

In this teaching text the problems that must be faced by anyone responsible for planning and supervising the erection of a chemical or allied processing plant are logically presented and discussed. The result is a valuable text. It is written by men experienced in project engineering and is planned to acquaint the chemical engineer with the methods, organisation and philosophy of this special combined application of chemistry, engineering and management. It is well illustrated with typical processing and plant equipment and operation charts, and is very extensively referenced.

—G.M.W.

INSTRUMENTAL ANALYSIS, by Paul Delahay. Published by The Macmillan Company, New York, March 1957. 384 pages. Price 7.90 dollars.

This is an extremely useful book. It is written primarily as a class text for undergraduate and graduate students but there are few chemists who will not find much of value conveniently gathered together and presented in a clear and concise manner.

Following a brief introduction on the scope of instrumental analysis, chapters are devoted to, electrode potentials; potentiometry; polarography and voltammetry; amperometric and voltammetric titrations; coulometric methods; conductivity and high-frequency methods; emission spectroscopy; Raman spectroscopy; X-ray methods; mass spectrometry; nuclear radiation methods. Most chapters contain problems dealing with extensions or applications of theory and include a limited but adequate literature survey. Over 50 laboratory experiments are described in detail and suggestions are given for many more. These experiments deal with the verification of essential features of the various methods rather than with their application to analysis of industrial materials, etc.

The text is well and clearly illustrated and is recommended to chemists who wish to extend their knowledge of the newer methods of instrumentation.

The latest parts of GMEIN'S HANDBUCH DER ANORGANISCHEN CHEMIE are (i) Calcium, Part A, Section 2, dealing with the occurrence of the element, as well as its properties and those of its alloys, and (ii) Platinum, Part D, which deals with its interesting complexes with neutral ligands. They are published by Verlag Chemie GmbH, Weinheimbergstr., at DM 147 and 375 respectively.

John Wiley & Sons, New York, have extended their series on HETEROCYCLIC COMPOUNDS by the publication of Vol. 5, dealing with 5-membered heterocycles containing two hetero atoms and their benzo derivatives, and Vol. 6 on the corresponding 6-membered heterocycles. In Vol. 5 the oxazoles have been given extended treatment by J. W. Cornforth on account of the amount of new material available. Both volumes are edited by R. C. Elderfield and sell at 20 and 25 dollars respectively.

—S.G.B.

ORGANIC SYNTHESSES, Vol. 36, Edited by N. J. Leonard. Published by John Wiley & Sons, Inc., New York, 1956. 120 pages. Price 3.75 dollars.

This volume, which closely resembles its predecessors in style of writing and production, describes thirty-five preparations. New or improved procedures for obtaining commonly used intermediates such as diazomethane (from p-tolylsulphonylmethyl-nitrosamide), ethyl diazoacetate, bis-chloromethyl ether, and p-toluenesulphonic anhydride will appeal to many readers, while most will find something of interest and novelty in the synthesis of ferrocene, and the many membered ring compounds such as sebacoin and cyclodecanone.

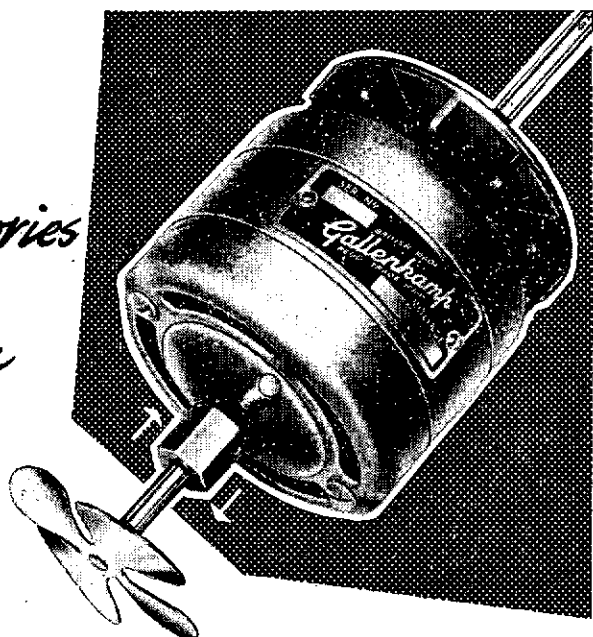
—W.E.H.

INTRODUCTION OF SOLID STATE PHYSICS, by Charles Kittel. Published by John Wiley & Sons, Inc., New York, 1957.

In spite of its title this book is not for the beginner, nor for the casual reader, but it will be welcomed by many physical chemists. One needs only to sample the topics discussed, X-ray diffraction, paramagnetism, free electron theory, semi-conductors, lattice vacancies, etc., to appreciate that most of the field of solid state physics is very much the concern of the modern chemist. For some time there has been a need for a suitable text, unencumbered by unnecessary mathematics, and with only occasional lapses (e.g. a surprisingly formal treatment of crystal symmetry) this book meets this requirement. For those so inclined, much of the mathematics is included in an extensive series of appendices.

—D.H.

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*Accessories
just
push in*



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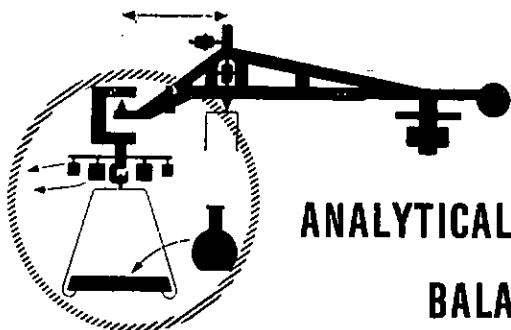
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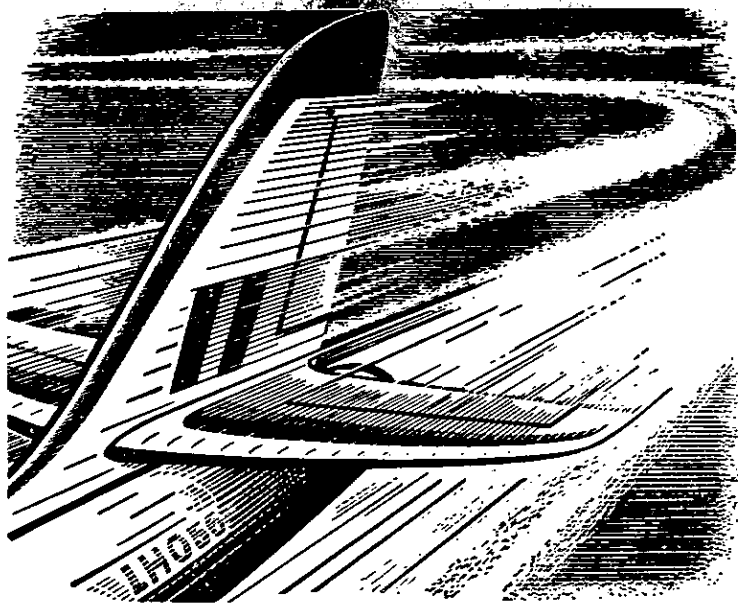
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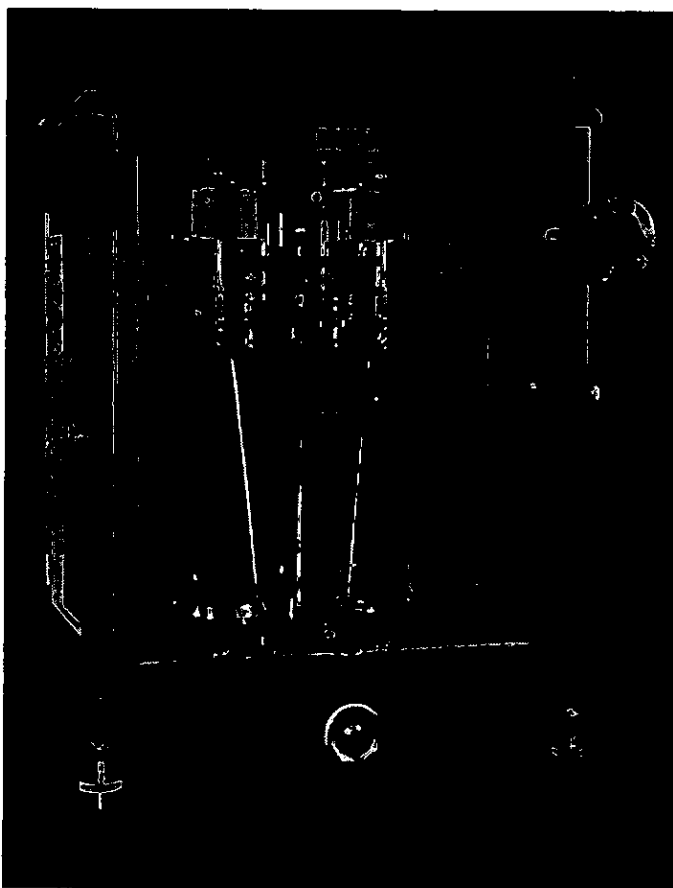
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