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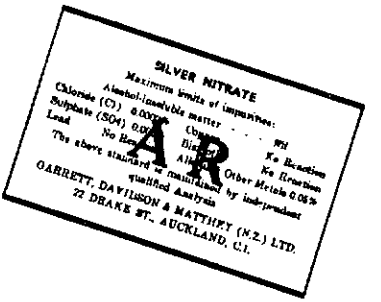

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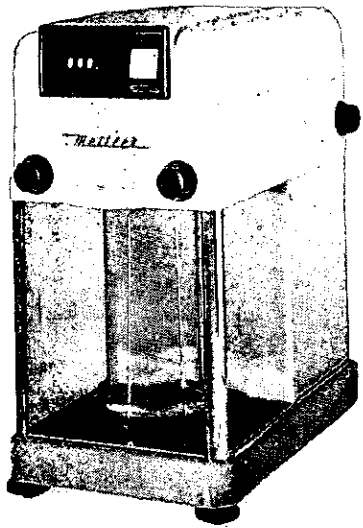

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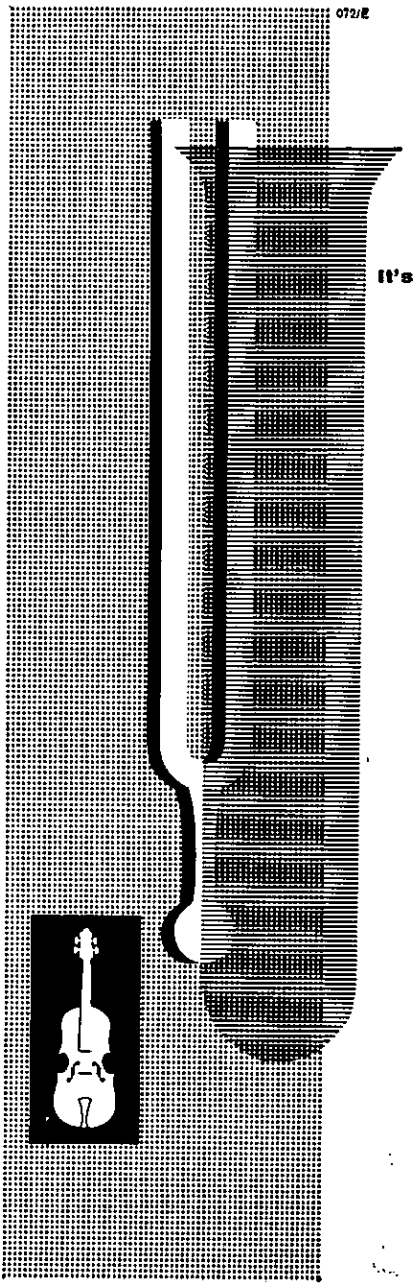

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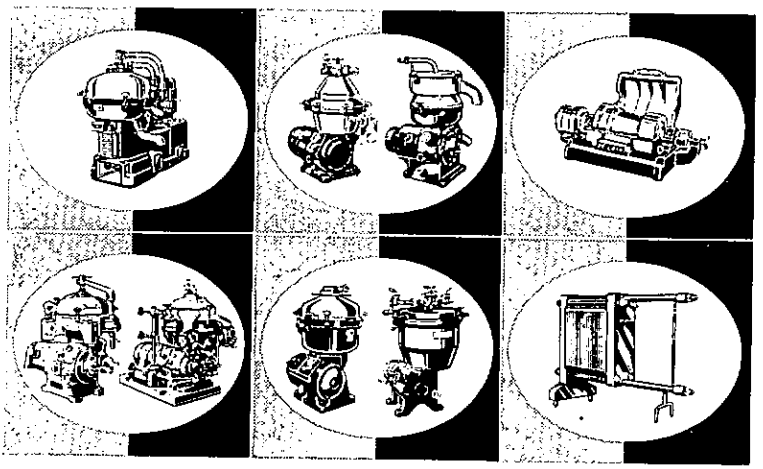

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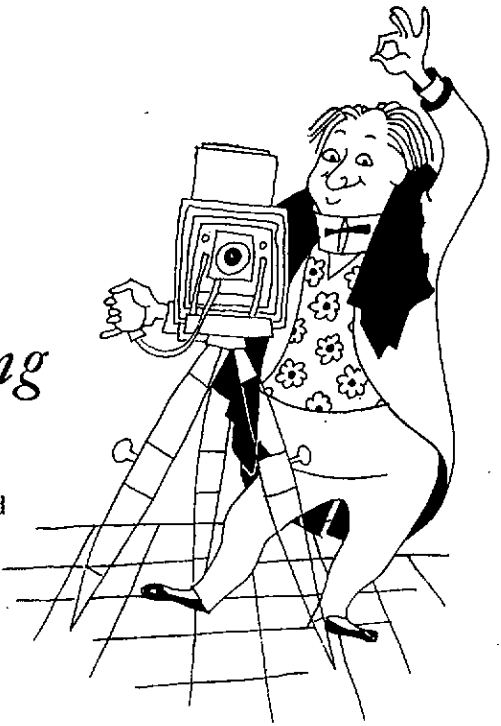

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JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

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CHEMISTRY IN ACTION

The papers published in this issue are adapted from the fourth series of *Chemistry in Action* addresses delivered to sixth-form pupils in Christchurch. They will later be reprinted as a booklet for distribution to schools throughout New Zealand. In this enterprise the Canterbury Branch is fulfilling one function of the Institute by making the principles and procedures of chemistry better known in the community, for many copies of *Chemistry in Action* will be read by parents as well as pupils: but the more important function of these talks is to aid young people to decide for or against a career in chemistry by helping them to understand some of the basic principles of chemical research and the way in which chemistry is applied to practical problems in contemporary living. The members chosen to give these addresses are chemists who think beyond their subject. Behind the facts which they present shines a philosophy, and, to quote from the "Message from the President" in last year's booklet, "something of the fascination which exists in scientific investigation, and which makes it, for some people at least, both a vocation and a way of life".

Reports from Christchurch indicate that these addresses were again delivered to an enthusiastic audience. In 16 schools in and around the city there are over 800 pupils taking chemistry in the sixth form, so that there is close competition for the 300 admission tickets issued to the schools. Tickets were sent also to teachers in a further five new schools which do not yet have a sixth form, and to the special science group at the Teachers' Training College.

Since the addresses were started in 1958, 2,000 copies have been printed each year. In 1958 these were distributed free by the Education Department but subsequently they have been sold to schools in class sets of 40 at £1 per set, the remainder of the cost (about £50) being met by the Institute. The printed page inevitably mutes the personal appeal of a delivered address, particularly one reinforced by illustration and demonstration, but teachers of both chemistry and biology have commented on the usefulness of *Chemistry in Action* in their work.

The advisability of publishing these papers in the *Journal* is another matter. Obviously, the total cost is reduced by doing so but this is not a determinant of *Journal* policy. Are these addresses, aimed at a sixth-form audience, suitable for the more advanced requirements of our members? In our opinion, if Professor Coop's article is too elementary for a biochemist, it is not necessarily at too low a level for a chemical engineer; if Mr Pollard's appears elementary for a chemical engineer it may well be read with interest and profit by a biochemist; and Dr Wilkins's exposition of more basic issues can provide worthwhile reading for chemists in both agriculture and industry. For members 20 years away from graduation a discourse at the comparatively sophisticated level required by the modern schoolboy is not likely to be too general for the specialist out of his field. The favourable comments of a few members on past *Chemistry in Action* papers has influenced the decision to continue publication in the *Journal* but the opinions of a greater number would be welcomed.

Apart from other considerations, publication of the first four series in the *Journal* has ensured that members know the content and style of addresses delivered, in the Institute's name, for the purpose of acquainting today's youth with the manner in which chemistry is being applied in the service of the community.

CHEMICAL SOCIETY INTER-COMMONWEALTH LECTURE TOUR

PROFESSOR C. E. H. BAWN

The Chemical Society has, through its Corday-Morgan Memorial Fund, instituted a scheme to arrange inter-Commonwealth lecture tours for senior chemists. The first of these tours will be undertaken by Professor C. E. H. Bawn, C.B.E., F.R.S., Grant-Brunner Professor of Inorganic and Physical Chemistry at the University of Liverpool. He is a well-known authority in the field of high polymers.

Professor Bawn will be in New Zealand from August 7 to August 23, and Professor S. N. Slater, who is arranging the tour at the request of the Chemical Society, has asked branches to sponsor lectures by Professor Bawn in their centres.

CHEMISTRY, ENERGY AND ANIMALS

I. E. COOP

Professor of Animal Husbandry, Lincoln College.

In this series of papers entitled *Chemistry in Action,* an endeavour is made to give young people interested in chemistry some idea of the breadth and scope of the subject. At the same time, it is hoped in this to make special reference to New Zealand in order to interest young people in chemistry as a career in this country. The particular subject I have chosen is an exceptionally broad one, the conversion of solar radiation into the growth and production of animals. This is, in fact, the primary industry of New Zealand. I will not overstress the part which chemistry has played and is playing in this because that will be obvious. My main concern will be to make a difficult subject appear simple.

The subject material may be classified in many different ways but I want to deal with it in two main sections. These are first to discuss *how* the conversion of solar radiation into animal production takes place and then, secondly, the *efficiency* with which it is effected.

The conversion of solar radiation to animal production proceeds in well-defined stages. The first of these is the absorption of energy from the sun and of carbon dioxide from the atmosphere by green plants to synthesize organic compounds required by the plants for growth—a process known as photosynthesis. The next step is the ingestion and digestion of the plants by animals. The final stage includes the metabolism and chemical transformation of the absorbed nutrients which take place within the animal, so that it also grows.

PHOTOSYNTHESIS

We can represent the overall process of photosynthesis by the formula

$$6\ CO_2 + 6\ H_2O + \text{energy} \longrightarrow C_6H_{12}O_6 + 6\ O_2$$

$C_6H_{12}O_6$ is glucose, one of the sugars, which the plant can fairly easily convert into starch, into cellulose and, together with nitrogen, to protein. The plant thereby possesses the organic compounds required by the cells for growth and multiplication; in short, for plant growth.

There are two main steps in photosynthesis, called the *light reaction* and the *dark reaction*, and light is essential in only the first of these.

Light Reaction: This proceeds as follows:

$$C_3 \text{ phosphoglyceric acid} + H_2O + h\nu \text{ (energy)} \longrightarrow C_3 \text{ phosphoglyceraldehyde} + \tfrac{1}{2} O_2$$

Phosphoglyceric acid (oxidized) and phosphoglyceraldehyde (reduced) are relatively simple organic compounds containing only 3 carbon atoms each plus a phosphate radical. The acid is the oxidized form and the aldehyde the reduced. In future discussion the phospho-group will be dropped. Solar radiation is absorbed by the plant and the energy of the radiation so absorbed is used to reduce the glyceric acid. To effect the reduction the two hydrogen atoms of a water molecule are removed leaving the oxygen of the water to be given off as oxygen gas. The reaction is catalysed by chlorophyll, the green colouring matter of plants. Glyceraldehyde, being in the reduced form, contains more energy than the acid which was in the oxidized form. The solar energy has therefore been converted into chemical energy.

Dark Reaction: The C_3 aldehyde formed in the light reaction can fairly readily be condensed to C_6 units ($2\ C_3H_6O_3 \longrightarrow C_6H_{12}O_6$) or the sugars, and on up to starch and cellulose, the higher plant carbohydrates. But the C_3 acid glyceric acid must be regenerated. This is done in several steps from the C_3 aldehyde to a C_5 sugar. A final step is then made in which this C_5 sugar combines with CO_2 from the air to give an unstable C_6 compound which immediately decomposes into two molecules of the C_3 glyceric acid. This can be represented as follows:

$$5\ C_3 \text{ aldehyde} \longrightarrow 3\ C_5$$
$$C_5 + CO_2 \longrightarrow [C_6] \longrightarrow 2\ C_3 \text{ (acid)}$$

It is in this final step that the atmospheric CO_2 is absorbed and utilized. None of these steps require light. The energy to drive them has already been obtained in the light reaction.

The net effect of both reactions is that CO_2 from the atmosphere, water from the soil and light energy from the sun are all absorbed. The CO_2 is reduced back to organic compounds and oxygen released. The solar energy captured by the plant has been converted into chemical energy in the form of organic compounds such as starch, protein and vegetable oil, plus oxygen, and so plant growth takes place.

The chemical energy can be released and transformed into heat by burning these organic compounds with oxygen back to $CO_2 + H_2O$. If you burn plant material such as grass, straw or wood, this is what happens. Alternatively, the plant material may be eaten by animals and the energy utilized by the animal by transformation into heat, movement and growth of the animal.

METABOLISM IN THE PLANT AND ANIMAL

Now we pass to the transformations which take place within the animal, or to what is usually called *metabolism*. The main organic constituents of plants are:

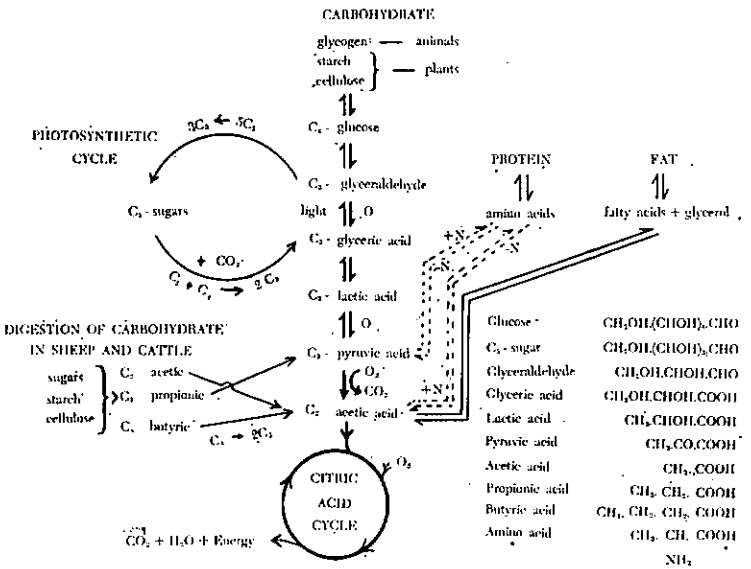
(1) *The higher carbohydrates* such as cellulose and starch which are synthesized by the plant by condensation of hundreds or thousands of the C_6 glucose units.

(2) *Proteins* which are synthesized by the plant by condensation of hundreds of amino acid units. These amino acids are first synthesized by the addition of nitrogen absorbed from the soil to the simple first products of photosynthesis.

(3) *The vegetable oils or fats* which are of minor significance but are synthesized by condensation of C_2 acetic acid molecules.

These plant constituents are mostly insoluble in water and cannot pass through membranes. When the animal eats and digests the plant the digestive juices or *enzymes* produced by the animal break the insoluble constituents up into their units which, being soluble, are absorbed from the gut into the blood stream. The carbohydrates are hydrolysed to glucose, the proteins to amino acids and the fats to fatty acids. Not all the food constituents are completely digested. For example about 25% of the dry matter in green pasture is not digested and this is eliminated as faeces or dung. A vast series of chemical transformations of absorbed constituents are now possible within the animal but there is an underlying system of integration which I have attempted to simplify and summarize in the following diagram.

In this diagram double half-arrows represent equilibria or reactions which may go either way, while ordinary single arrows represent reactions which go in only one direction. Both plants and animals may drive these equilibria which way they like according to the energy needs and energy availability of the organism at the time.



CARBOHYDRATE

The core of this scheme is the synthesis of the higher carbohydrates, starch and cellulose in plants and glycogen (animal starch) in animals, and the degradation of these down the chain to CO_2 and energy. Let us examine this more closely, starting at the top with starch in plants or glycogen in animals. These are progressively hydrolysed and degraded through C_6 glucose, to C_3 glyceraldehyde, to C_3 glyceric acid, to C_3 pyruvic acid, to C_2 acetic acid. The C_2 acetic acid then enters a cycle known as the *citric acid cycle*. There are 8 components of the cycle, eight relatively simple organic compounds containing from 4 to 6 carbon atoms, of which one is citric acid—hence the name citric acid cycle. Into this cycle is poured acetic acid and atmospheric oxygen. The acetic acid is oxidized to CO_2 and water, so out of the cycle come CO_2 and H_2O *plus* the energy derived from the oxidation of the acetic acid.

At each step down this chain there is some loss of energy but the main energy is liberated in the citric acid cycle. This is the mechanism by which animals derive their energy from ingested plant carbohydrate and by which also plants derive their energy of respiration at night when plant cells continue to respire

after photosynthesis has temporarily ceased.

You will see that photosynthesis can be integrated into this mechanism. The photosynthetic cycle produces C_3 glyceric acid from the CO_2 and absorbs solar energy to drive the reaction upwards from glyceric acid to glyceraldehyde. The photosynthetic cycle not only synthesizes these C_3 compounds from CO_2 but pours in enough energy to drive all the equilibria to the higher energy states which in the case of the carbohydrate chain is upwards through glucose to starch and cellulose. In plants the mechanism is driven upwards towards starch by the high input of solar energy during the daytime. At night the reverse trend sets in and the mechanism runs down as starch and glucose are oxidized right through to CO_2 to provide energy for the plant at night.

Now let us look at what happens in animals. The plant carbohydrate is digested by conversion to glucose and is absorbed into the bloodstream as glucose. If the overall intake of food is not high the glucose will be degraded down the chain and oxidized completely to CO_2 to provide the animal with the energy it needs for warmth and movement. If the intake is higher than is required most of the glucose will still proceed down the chain but sufficient energy will be released to spare some to drive a portion of the glucose upwards to glycogen.

PROTEIN

In the plant the high energy input from solar radiation allows the plant to drive equilibria in the direction of synthesis to the higher energy state. Nitrogen in the form of ammonia or $-NH_2$ groups is added on to various organic compounds such as pyruvic and acetic acids to synthesize amino acids. These are linked together to form proteins. In the animal the plant protein eaten is digested in the intestines to amino acids and absorbed as the amino acids into the bloodstream. Here two possible fates await these amino acids. If the intake is low and the requirement of the animal for energy is high the amino acids are oxidized to CO_2 plus energy by removal of the nitrogen and the oxidation of the remainder down the chain from pyruvic and acetic and through the citric acid cycle. But if intake is high and energy requirement not unduly high the amino acids may be recombined to produce protein — animal protein such as flesh, milk or wool. The animal either grows or produces something.

FAT

The last constituent to study is fat. Fat (or vegetable oil) is an ester of the trihydric alcohol glycerol and the higher fatty acids. The plant synthesizes these higher fatty acids from acetic acid by serial condensation and reduction of acetic acid molecules. Acetic acid contains 2 C atoms and the reason why plant and animal fatty acids all contain even numbers of C atoms is thus fairly obvious, C_{16} and C_{18} being most common. The conversion of acetic acid to the higher fatty acids requires a considerable amount of energy. In the plant the source of energy to drive this synthesis is again the solar radiation. Conversely the breakdown of fatty acids to acetic gives much energy. Not much energy is involved in the final step, fatty acid plus glycerol, to give fat.

In the animal ingested plant fat (or vegetable oil) is hydrolysed to fatty acid and glycerol, absorbed and recombined to give now animal fat. Again its fate depends on the overall food intake. If the animal wants energy the fat is oxidized down through acetic acid and the citric acid cycle to yield energy. Alternatively, if this energy is not immediately required the fat is deposited and the animal fattens.

CARBOHYDRATE-PROTEIN-FAT INTERRELATIONSHIPS IN ANIMALS

We are now in a position to look at some of the inter-relationships between carbohydrate, protein and fat metabolism, especially as they apply to animals. The animal can derive energy from all three of these constituents and the pathway from acetic acid onwards is common to all three. The animal can synthesize fat from all three constituents since all can give acetic acid from which fat may be synthesized. Animals can therefore produce fat irrespective of the type of food constituent. We know this from practice because we can fatten them on carbohydrate-rich feeds such as grain, or protein foodstuffs such as linseed meal and meat meal, as well as on fatty diets. Animals must possess a certain amount of glucose and glycogen. This may be obtained directly from ingested glucose, and also, but with less efficiency, from protein *via* those amino acids which yield pyruvic acid. It cannot be obtained from fat because the pyruvic-acetic conversion is irreversible. To synthesize protein (flesh, milk protein or wool), the animal must obtain amino acids. But amino acids contain nitrogen and the only source of such nitrogen is the protein present in the plant.

To summarize, an animal may obtain energy and can synthesize fat from all three food constituents; it can synthesize carbohydrate from food carbohydrate and protein but not from fat; and it can synthesize protein from food protein only. Since so much of animal production consists of animal protein—meat, wool and one third of milk—it is clear that protein has a special significance. The basic requirements of the animal therefore resolve themselves into energy and protein.

Two factors determine the use the animal makes of its food. The first and most important is the level of energy intake relative to the energy requirement, and the second is the balance of constituents. An animal requires a certain amount of energy just to maintain the *status quo*: that is, to keep it alive in normal warmth, movement and health. This amount of energy or food is known as the *maintenance requirement*. Only if the animal eats more food than this maintenance requirement is any left over for synthesis of flesh and fat. It should be clear that if the food eaten by the animal is insufficient to meet maintenance, all constituents will be required to provide energy and all will be oxidized to CO_2 through the pathways described. If, on the other hand, the animal eats more than is required for maintenance there will be a surplus of constituents all contributing to the animal's "energy pool". Some of this surplus, between 30% and 50%, will also be oxidized to CO_2 in order to provide sufficient energy to drive the remaining 50 to 70% of surplus constituents back up the synthetic pathways to glycogen, protein and fat. In order to synthesize protein there must be not only enough energy to drive the synthesis but also enough nitrogen (as amino acid) present.

In the case of a young cattle beast or a lamb, the protein and fat synthesized represents growth or meat and fat production. In the dairy cow and lactating ewe the surplus energy and synthesis goes into milk production.

RUMINANT METABOLISM

I want to digress here for a few minutes to add one further complication. The most important animals in New Zealand are sheep and cattle. They differ from man and carnivorous animals by possessing a very large stomach, or *rumen* (hence the name—ruminant) in which the food is fermented by bacteria before being digested in the normal way. The carbohydrates are fermented to C_2 acetic, C_3 propionic and C_4 butyric acids plus CO_2 and the

gas methane (CH_4). The latter two gases are exhaled by belching and the three acids are absorbed. Sheep and cattle, therefore, do not absorb glucose but instead the three acids. Protein and fat are digested more or less in the conventional manner. Now, of these three acids produced, the C_4 butyric can be split into two molecules of C_2 acetic or is interconvertible with acetic and so virtually there are only two acids. We have already seen that acetic can yield energy and fat but cannot go up the carbohydrate pathway. Only the C_3 propionic can be converted to C_3 pyruvic and so on up this pathway. The maintenance of glucose and glycogen (*i.e.*, carbohydrate) status within ruminants is thus very dependent on the amount of propionic produced. This renders ruminants, sheep and cattle, much more prone to metabolic disorders than man and other animals, a fact of considerable practical importance in animal husbandry and veterinary science.

It is obvious that there is no lack of chemistry in these transformations within plants and animals. The scientists who have evolved this scheme are a particular brand of chemists known as biochemists. They are not greatly interested in classical organic chemistry, in coal or petroleum, detergents or aniline dyes but in living matter, dynamic matter, in trying to understand how the plants and animals function, how cells function, how mitochondria and genes function. Here in New Zealand we have been very slow to recognize biochemistry as a branch of chemistry in its own right and holding its own against inorganic, physical and organic chemistry. The only well-established school of biochemistry giving degrees and post-graduate training in biochemistry in New Zealand is at the Otago Medical School. Victoria has recently started but is at a lesser stage of development. Biochemistry is also taught at the two agricultural colleges but not enough to enable the products of this teaching to be called biochemists. We hope to rectify this sad deficiency in the University system, and it is a sad deficiency, because of the significance of biochemistry to agriculture and veterinary science as well as to medicine, but progress is always disappointingly slow.

Having unburdened myself of that, I now pass on to the overall efficiency of these processes. The purpose of all these transformations is to produce milk, butter, cheese and meat for human consumption to meet the energy and protein requirements of the world's human population, and wool to cover the human so that he can the better conserve the energy he does ingest.

THE EFFICIENCY OF ANIMAL PRODUCTION

The amount of solar energy falling on an acre of land in New Zealand is equivalent to about 3×10^9 kilocalories per year. Only about one third of this is of the right wavelength for photosynthesis, or about 10^9 kcal. Our very best pastures can produce about 14,000 lb of dry matter per acre per year, although at Lincoln we would barely average half of this amount and most farms produce much less still. If we consider 14,000 lb per acre as a potential production this is equivalent to 25×10^6 kcal, or 2.5% of the available incident energy. Some crops such as maize can yield higher efficiencies but pasture is not bad. Some of the research workers in plant physiology in the D.S.I.R. at Palmerston North are seeking to increase this efficiency by studying the factors that affect plant growth such as leaf shape, density and height of pasture, temperature, moisture, intensity of light.

When animals eat any foodstuff much is digested but a portion is always either indigestible or escapes digestion. The foods eaten by humans are highly digestible, to the extent of 90% or better. This is because we eat concentrated foodstuffs such as milk, butter, cheese, fat and vegetable oil, in which there are no cell walls to impede digestion, or food in which the cell walls have been disrupted by cooking or other treatment, such as bread, potatoes and meat. Sheep and cattle eating grass have to contend with the cell walls before they have access to the cell contents. As a result digestibility is lower. Good grass has an average digestibility of about 75%, so that 25% of the food eaten is useless. This represents the first major loss in food utilization. Since we are dealing with sheep and cattle the 75% apparently digested includes the gases CO_2 and CH_4 produced in the fermentation in the rumen. These gases cannot be used by the animal. Furthermore, the acetic and other acids derived from plant carbohydrate and absorbed are at a lower energy state than glucose. This is because the bacteria have taken the difference in energy.. The sum total of these losses represents about another 15%. As a result of all these losses only about 60% of the energy in the grass actually enters the bloodstream and becomes available to the animal.

Experiments have shown that in dairy cows a little under half of this 60% is required for maintenance, leaving 30 to 40% for milk production. In each of the biochemical transformations involved in converting acetic acid to fat (butterfat), amino acids

to casein or milk protein, and C_3 acids to lactose or milk sugar, heat is given out, and some constituents must be oxidized to provide energy to drive these syntheses. These losses as heat represent losses in efficiency, and the overall efficiency is about 60 to 70%. As 60 to 70% of the 30 to 40% energy available amounts to about 20 to 25%, we find that only 20 to 25% of the original energy of the grass is produced in the form of milk. This estimate is not to be taken as accurate but to use a common expression it is "near enough".

Similar calculations suggest that the production of edible beef and lamb on such pasture would be even less efficient, well below 10%. The efficiency drops progressively as the quality of the pasture falls until on the high tussock-lands the efficiency of wool production or store sheep production is probably less than 1%.

Under stall feeding conditions, in which the animals are hand fed, such as practised in Europe and America, it is possible to achieve something approaching the theoretical efficiencies quoted. But from our 14,000lb dry matter per acre pasture the theoretical yield of milk should be 1,600gal. or 900lb butterfat. With lamb or beef we should be able to get nearly 1,000lb of meat per acre at 8% efficiency. No one has attained these production figures. Maximum figures so far attained are of the order of 400 to 500lb butterfat or 300lb meat, or only half of what it should be. Where is the missing production?

Two factors could contribute to the disappearance. Faulty management by the farmer and poor grazing by the animals might lead to not all the grass grown being consumed, some being lost as dead leaf or trampled into the ground. This undoubtedly accounts for some loss, but a 50% loss in this manner is inconceivable. The second possibility is that the grazing animal makes less efficient use of its food than one which is fed in pens or stalls. This latter possibility is being intensively studied at the Ruakura Animal Research Station with dairy cows and at Lincoln College with sheep. To conclude, I wish to describe what we are doing in order to show how chemistry is involved in such research, an application of chemistry which at first sight one would perhaps not expect from the nature of the problem.

One can quite easily measure the production of cows or sheep. To take the example of sheep, one can measure the liveweight gain or loss, the weight of wool grown and in the case of the ewe the weight of milk produced. With sheep fed in pens it is easy to record the feed eaten and so calculate the efficiency of con-

version of feed energy to animal production. The problem with the free grazing animal is to measure how much grass it eats. I think you will agree that that is definitely not easy.

The technique now being used is as follows. If the amount of dung passed per day by a sheep is 200 g dry matter, and if the grass is 75% digestible then the weight of grass eaten must be 800 g dry matter. It requires two measurements—the mean daily output of dung and the digestibility of the grass. The output of dung is measured by dosing the animal twice daily with 1 g chromic oxide and subsequently analysing samples of dung taken at the same time for chromic oxide. The chromic oxide is completely insoluble, is recovered 100% and is known as a marker. An example will illustrate this. If one doses 2 g chromic oxide per day and finds on analysis that a sample of dung contains on average 1% of chromic oxide, that is, 1 g in every 100 g, then the 2 g dosed must be in 200 g dung and so the mean daily output of dung is 200 g dry matter. This calculation assumes that all the chromic oxide dosed appears in the dung and this has been shown by experiment. It assumes also that the chromic oxide is evenly distributed through the dung. A sampling technique has been evolved which provides for this. The digestibility of the grass eaten can be estimated by measuring the percentage of nitrogen in the samples of dung. It has been shown in trials measuring the percentage digestibility of grass that the higher the digestibility the higher the percentage of nitrogen in the dung of the animals eating the grass. From a large number of such trials equations have been established to enable the digestibility of the grass eaten by a sheep to be predicted with reasonable accuracy from the nitrogen content of the dung.

In this way one can estimate the amount of grass eaten by dosing the animals daily with chromic oxide and analysing the dung for chromium and nitrogen. In one study two years ago, 40 sheep were dosed and faecal sampled twice daily every day for three months and 240 samples of dung were analysed for dry matter, ash, chromium and nitrogen, enough to keep a chemist quiet for a while. Down to earth chemistry, if you like—very routine, and in fact done by a technician, not by a graduate, but from experience I would rather be the chemist than the agriculturalist detailed to do the dosing and dung sampling except when the weather is warm and sunny.

A result of this work is that both at Ruakura and at Lincoln it has been possible to show that grazing animals require con-

siderably more energy than pen-fed ones. The difference for maintenance is of the order of 50 to 60% and this must go a long way towards explaining why production which seems theoretically possible cannot be obtained. The interest now is in what causes this increased need for energy—the cold at night, the wind or rain, the distances walked, the time spent grazing, the movements involved in plucking the grass.

It would appear that the grazing animal is thereby less efficient than the non-grazing or stall-fed animal and that this is an energy cost which we in New Zealand, Australia, the Argentine and the great grazing countries must bear as a consequence of running animals in large numbers on grazing, with the minimum of human energy expenditure.

You will be impressed with the low efficiencies which have been mentioned—2.5% for conversion of solar energy to plant energy, followed by theoretical efficiencies for conversion of plant energy to animal production varying from 20 to 25% for milk down to 1% for wool, followed in turn by a 50% conversion from theoretical to the practical realization with grazing animals. No wonder that in the highly populated areas of the world an attempt is made to bypass conversion through the animal, by growing crops such as rice, maize, sugar-cane, potatoes and wheat for direct human consumption. Here in New Zealand and elsewhere scientists are actively engaged in trying to improve these efficiencies. At all stages of this research work chemistry and biochemistry occupy a dominant role.

Is it too much to say that on the success of their work will depend the ultimate maintenance and safeguarding of the animal industry of this country?

CHEMISTRY AND THE HIGHROAD

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It seems usual for textbooks to ascribe most early discoveries to the Chinese. Roads are an exception, for they were most assuredly invented by the Romans, and they made possible the might of Rome. Throughout the length and breadth of the empire the legions marched on the splendid Roman roads. When Rome fell the roads became neglected, and worse, people lost the art of making them at all. Even in Queen Anne's reign, goods which were shipped with care to the American Colonies had to be transported through England by packhorse. As late as 1789 the highways of Herefordshire were impassable for six months of the year. Each spring they had to be re-levelled by ploughs, each drawn by eight or more horses.

Conditions did not really improve until 1815 when one of the brilliant group of civil engineers who were so active in Britain at this time, a man named McAdam, revived and revised the Roman methods of road construction. His name is still remembered daily in *tarmac,* a word descended from tarmacadam, descended from McAdam.

The roads of the Romans and McAdam were made of stony mixtures on firm well-drained foundations, but their makers lacked a material to bind the surface together and keep water and frost from slowly tearing their work to pieces, and the surface would never have stood up to modern traffic. The production and utilization of successful binders is the result of a great deal of work by chemists and engineers—work which is in a state of continuous investigation and revision.

A highroad is expected to do a number of things.

First, it must sustain the maximum loads passing over it. The *point load* is the same as that of the tyre pressures of the vehicles rolling above. In New Zealand, tyre pressures are limited by law to not more than 75lb/sq in. although the local Transport Board buses have a special dispensation to operate at a pressure of 90lb/sq. in. Even that is not as bad as stiletto heels.

Secondly, the road must not disintegrate or unravel under the continued passing of traffic.

Thirdly, it must present a smooth but skid-resistant surface for the tyres to roll on.

Throughout many Christchurch streets there is a thin top cover and below it a considerable depth of blue silt originally laid down by the Waimakariri river. Once wet this material turns to a paste, quite incapable of acting as a road surface or bearing a heavy point load.

Not all areas where roads are laid are necessarily as bad as this, but road construction always involves excavating any soft material, shaping up the base and ensuring it is drained. The excavation is then re-filled with strong material called *base course*. This is usually uncrushed material with stones up to 2.5 in. diameter. On top of this base course is laid a thinner layer of crushed stone called *top course*, which completes the load bearing surface of the road. The depth of these strong layers varies with the amount of traffic the road is designed to carry, and the materials of these layers are more subtle than they look, particularly those used as top courses.

Normally top courses are mixtures of stony particles ranging from about 1.5 in. in diameter down to a few thousandths of an inch. Some 50% or more of the larger material is obtained by crushing big stones, and the proportions are adjusted so that the small particles fill up the spaces between the larger ones until no voids are left. This produces a dense material with a fair self-binding ability. By grading and rolling it works up into a beautifully smooth surface ready for sealing.

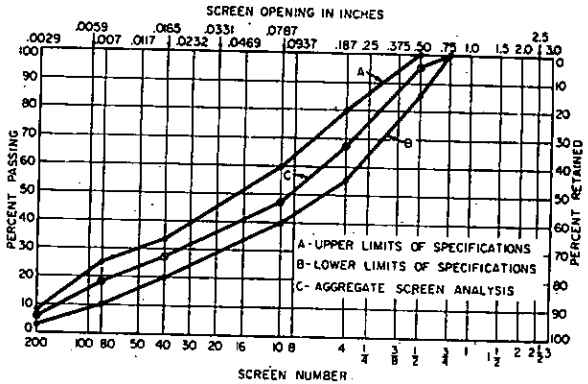
In Canterbury these products are made by crushing the naturally occurring gravels either on the plains or in river beds. The raw products are adjusted by screening out unwanted portions and adding desired fractions.

McAdam wrote the first specifications for this sort of material when he stipulated that no stone should be used which would not pass into his foreman's mouth. Since that time foremen have become less tolerant and modern specifications are based on sieve analyses.

A set of sieves is a most useful industrial tool, and produces a variety of valuable information. Let us consider a typical sieve analysis of a sample of top course that is going to be part of State Highway 1. The sample was brought into the laboratory and divided down until a small representative portion was available for drying and sieving. This was passed through a series of sieves, yielding discrete fractions of different sizes. These were weighed and the results plotted on a special form of graph in which the vertical axis is the percentage of the total which passes through

any given sieve size, while the horizontal axis is the sieve opening in inches. This axis is in a logarithmic scale which effectively compresses the enormous size range concerned. The specification limits are plotted as two outer lines and the actual sample plot should lie between these lines if the material is satisfactory.

This type of plot is standard throughout the roading industry and an experienced person can tell at a glance the characteristics of the material if shown the grading graph.



SPECIFICATION LIMITS	PERCENT	SIEVE ANALYSIS OF SAMPLE	
PASSING $\frac{3}{4}$" SIEVE,	100	PASSING $\frac{3}{4}$" SIEVE,	100 %
PASSING $\frac{1}{2}$" SIEVE,	85-100	PASSING $\frac{1}{2}$" SIEVE,	95.3
PASSING #4 SIEVE,	55-80	PASSING #4 SIEVE,	67.2
PASSING #10 SIEVE,	40-60	PASSING #10 SIEVE,	47.8
PASSING #40 SIEVE,	20-34	PASSING #40 SIEVE,	27.5
PASSING #80 SIEVE,	10-25	PASSING #80 SIEVE,	18.3
PASSING #200 SIEVE,	3-6	PASSING #200 SIEVE,	6.1

Aggregate chart.

In addition to well-graded metal courses, roads have other special features built in, amongst them *camber* to shed the water, and *super elevation,* which is the banking that permits you to take a curve at 60 m.p.h. and still remain on the road to assure the traffic officer at the other end that you were not doing anything like that speed.

All in all roads are very expensive assets; in fact, a good one costs about £19,000 per mile, and it is essential that they be protected. In New Zealand the usual method of protection is by surface dressings of *binder.* Binders are the less savoury residues from the gas and petroleum industries. I always think the operators of these two industries should daily give thanks to the road makers for paying to take away what would otherwise be serious embarrassments.

Coal tar, which is the gas industry's dusky problem child, is the liquid which first condenses from the gas stream as it leaves the retorts. The yield is in the order of ten gallons per ton of coal carbonized. The nature of the tar varies somewhat with both the coal and the carbonization plant used. The crude material is a running liquid which requires processing before it is of much use as a binder. Processing involves heating the crude material to 250°C or more to drive off most of the oils present. In large distilleries it is usual to drive off so much oil that the residue is a brittle pitch. Selected fractions of oil are then blended back to form a tar of the required consistency and setting rate.

The petroleum industry also has a black viscid residue left after the distillation of crude petroleum, but the origin is a little less drastic than the destructive distillation of coal. The end product is correctly called *residual asphaltic bitumen* and is available in a variety of grades. As regards composition it can broadly be described as a colloidal system with high molecular weight compounds called *asphaltenes* as the colloidal particles, and oily lower molecular weight compounds called *maltenes* in which the asphaltenes are dispersed. For the rest, the textbook *The Chemical Constituents of Petroleum* states that "though it is known that the molecules are generally built up of aromatic rings, naphthene rings and/or paraffin chains, uncertainty still prevails as to the structure of these components and how they are interconnected, nor do we know how the elements oxygen, sulphur or nitrogen are arranged in the molecules. We can have no basic knowledge of the matter until the chemistry of asphaltic bitumen has been thoroughly probed, but research in the field presents immense difficulties owing to the complicated nature of asphaltic bitumen." I might add that the state of knowledge concerning the actual composition of coal tar is little better.

No doubt if tar and bitumen were not available, some other material could be used as a binder. However, these two materials are cheap, and have good working properties, so all the research on road binding materials has been concentrated on them. Admittedly, during the depression a little work was done on the effect of wool as an additive—rather a desperate measure. More recently the rubber producers have waxed enthusiastic about the virtues of rubber as an additive to bitumen, usually in the order of 2%. Rubber is an expensive material, and it is rather early to pass judgment on its true value.

When used as a seal coat, a tar or bitumen binder is expected to do a number of things:

First, it has to be spread as a thin layer over the surface of the formed aggregate. This involves wetting the surface. Tar does this rather better than bitumen.

Secondly, the layer must be watertight. Tar again is rather better than bitumen.

Thirdly, the layer must not deteriorate under the action of heat, sunlight and rain. Bitumen is superior in this respect.

Neither tar nor bitumen is capable of withstanding the pressure or abrasion of traffic, so it is necessary for them to be protected by a layer of stone, technically termed *chip*, or a mixture of stone and sand. At this stage the whole matter of seal coats becomes complicated, because in addition to being a sealer the coat is expected to act as a glue, sticking to both road and stone.

To be of much use for these varied purposes the seal coat or binder must be almost solid at road temperatures. Even this is a tall order since road surface temperatures vary from freezing in winter to over 120°F under the summer sun. Both bitumen and tar increase their fluidity very rapidly as their temperature rises, so whilst they must not be so hard as to crack in the winter, they must not be so soft as to run in the summer. Traffic can jar chips out of too hard a binder, and roll chips out of too soft a binder. Morever, a very fluid binder lightly applied can easily disappear into a porous road surface, leaving a desert of loose black stones.

For these reasons the most important binder property to control is viscosity. Viscosity is a measure of the resistance a fluid offers to shearing forces. By way of an analogy you can visualize a fluid such as tar being composed of a series of layers like playing cards. By shearing is meant the sliding of one layer over another, and viscosity is the resistance to sliding. In a viscous fluid a force applied at the top will produce less and less movement down to the bottom layer. In a fluid of low viscosity like water, there is so little resistance from one layer to the next that the whole depth moves together.

The usual method of determining the viscosity of binders is to measure the time a given volume takes to pass through a capillary tube or an orifice.

The Engler Viscometer, used for moderately viscous fluids, operates by flow through a short capillary tube which is attached

to a container for the liquid being tested. The assembly is placed inside a jacket to maintain a constant temperature and three hook gauges inside the container permit instrument levelling and correct setting of the fluid level.

The time taken for 200 ml of water to flow out at 20°C is taken as 1, and this is divided into the time taken by the fluid under test. Thus, if water took 50 seconds and bitumen emulsion 150 seconds the emulsion would have a viscosity of 150/50 = 3° Engler.

This may sound arbitrary, but if you ponder it you will note that an easily obtained flow of known viscosity is used as the calibrating medium. This makes the instrument independent of any errors in making the capillary tube. By re-checking periodically the instrument can be corrected for the wear that inevitably takes place through repeated cleaning of the jet.

When the liquid to be checked is too treacly it becomes necessary to use larger holes if the outflow time is to be kept within reasonable bounds. A suitable instrument is the Standard Tar Viscometer. The liquid is placed in a brass cylinder with an orifice at the bottom. This is closed with a device like a swizzle stick, which also serves duty as a level indicator. The accuracy depends upon careful machining of all parts, and the orifice is held to a standard profile with a diameter of 10 mm $\mp$ 0.025 mm.

After filling, the cup is placed in a constant temperature bath and brought to the test temperature, which for road tar is 30°C. Thermometers in the bath and cup show when equilibrium is reached. The inside thermometer is removed and the sample is ready for checking. The measuring cylinder is oiled to stop tar sticking to the sides. The time taken for 50ml to flow out is measured and the results are quoted in seconds S.T.V. at the stated test temperature. One can turn the idea inside out and vary the test temperature so as to always produce a flow of 50ml in 50 seconds. The appropriate temperature is called the *equiviscous temperature* of the material, a concept which is gaining increasing popularity as it covers a very wide range in viscosity whilst working the viscometer at mid-range.

When the binder concerned is nearly solid one gives up trying to squeeze it through holes and prods it with needles instead. This is done with a Penetrometer. The sample is placed in a cup and brought to 25°C in a water bath. It is removed and a weighted needle allowed to fall into the sample. The needle is made to precise standards and loaded to a total weight of 100 g.

It is allowed to fall for 5 seconds by means of a release button. The depth of penetration below the surface of the sample is measured by micrometer and noted in tenths of a millimetre. The result is called the penetration. Most of the bitumen used in New Zealand has a penetration between 18 and 20mm and in consequence is always referred to as 180-200 bitumen.

I mentioned that the viscosity of binders shifts rapidly with temperature. Rather conveniently, a plot of the log of temperature against the log of viscosity is a straight line over the temperature range that normally interests the chemist. This makes it easy to predict viscosity at temperatures other than the test one, so that it is possible to prepare a chart which gives all the inter-relations between binders and the devices commonly used as viscometers—Engler, Saybolt Furol, Redwood, Standard Tar, and Cannon-Fenske.

The various types of road surface to be sealed, open stone, dense clay and stone, old seal coat, big chip, and small chip, each require binders of varying viscosity to match their needs. In addition, sealing in mid-summer needs a binder of higher initial viscosity than would be used in spring and autumn. The viscosity is varied from job to job by using a stock binder of high viscosity and blending in suitable solvents, usually called *fluxes*.

For tar, high or low boiling range tar oils have to be used as petroleum solvents flocculate or curdle out some of the high molecular weight compounds present in tar. Bitumen may be fluxed with tar oil or petroleum solvents—fuel oil and kerosine are the commonest, although mineral turpentine and petrol are used in special brews. These petroleum solvents are all distillates from crude oil, each with a progressively lower boiling range. Note the term *boiling range*. Unlike pure chemicals, these industrial materials are mixtures of compounds, mainly paraffinic, each with its own boiling point. As a result the mixture commences to boil at one temperature and as the more volatile components evaporate the boiling point rises progressively. For example, *lighting grade kerosine* has an initial boiling point of 155°C, 50% has distilled at 230°C, and the final boiling point is 280°C, so the boiling range is 155–280°C.

Judicious use of combinations of solvents as fluxes gives great control over binder properties. The *amount* of flux determines the initial viscosity, the *type* of flux controls the final viscosity after the binder has aged on the road surface. Bitumen binders in this country are usually made from 180/200 penetration stock

with up to 10% of fuel oil or kerosine added. In special cases, there may be as much as 25% of fluxing agent.

When applied to the road the binder layer is under one-tenth of an inch thick, so it must be sprayed as a thin fluid if accurate coverage is to be achieved. The usual method is to heat the binder until its viscosity is low enough to spray through jets. It is usual to combine tanker, heater, and spraying machine. Such a combination sprays at constant pressure and controls the rate of application by varying the speed of the sprayer as it travels forward. It is a precision combination capable of controlling the rate of application within one hundredth of a gallon per square yard. The heart of the system is the spray bar, which hardly looks a precision object, but all too frequently industrial devices are called on to achieve precision under rugged working conditions.

Once the surface is sprayed, tip trucks back over it tipping chip as they go, so that they lay a clean road surface for themselves. The chip used is granular and tends to lock in a mosaic when laid. Ideally it is 60% embedded in binder. The difficulty lies in getting it to stick or "take". Almost as soon as it hits the road the thin hot binder reaches road temperature and becomes viscous again. The chip is usually cold and damp. Under these conditions adhesion between binder and chip is difficult for binder will not wet stone in preference to water. If the binder is too viscous even a dry chip will deform the surface without adhering.

A great deal of work has been done on the mechanism of adhesion between binder and chip, but in spite of it we are still regrettably ignorant of the physical and chemical properties of the boundary between wet dusty chip and the binder surface. It is not easy to study. Because of the high viscosity, surface tension measurements are difficult and contact angle measurements extraordinarily difficult, so it is hard to make much progress in understanding how binder wets and spreads over chip. Moreover work has clearly shown that chip under road conditions in no way resembles the sort of nicely squared off blocks of stone that would be so precise to use for laboratory measurements.

Water wets chips in preference to bitumen, and in the early stages of adhesion will actually push bitumen off the chip, causing a failure in adhesion. Rain soon after a road is sealed can lead to traffic rolling the chip from the surface—a fault known as *stripping*. This happened in a spectacular fashion on the South Road, Christchurch, at the end of November, 1960.

Provided the binder is not too hard, the chip may be pushed back once the surface dries out. To help this a binder can be temporarily oversoftened with a relatively volatile solvent so that it will remain soft long enough to permit adhesion even after a shower of rain. This is why control of the rate of hardening of binder is important.

Anti-stripping agents are now available to reduce the problem. The most successful have been organic amines of high molecular weight. A typical formula is

$$R\text{-}NH\text{-}C_3H_6NH_2$$

where R is derived from stearin. Even the manufacturers admit that as yet there is no complete understanding as to why an anti-stripping agent prevents stripping. It is believed that the NH_2 group adheres to the chip so firmly that water is displaced. The R group is soluble in binder so the amine acts as a bonding agent between binder and chip.

The study of such agents is hampered by the fact that at present there are no fully satisfactory laboratory methods for determining whether or not a modified binder will adhere to chip in the presence of water. Some workers have been unkind enough to suggest that the tar oil which is often used to dissolve some of these agents is just as effective without the agent added. There is a lot more laboratory work to be done on this problem, combined with proper correlation of road performances after use of the anti-stripping agents.

There is a radically different way of making a high-viscosity binder fluid enough to spray. Materials which are not soluble in water and which require expensive or hazardous solvents are often best handled as watery emulsions. Examples are latex paints, some cooking essences, and white spraying oils. Bitumen may also be used this way. In these oil-in-water type emulsions, the material, termed the *disperse phase*, is spread through the water, called the *continuous phase*, as very small particles, one thousandth of a millimetre or less in diameter.

If one shakes oil and water together, the oil breaks into droplets which soon coalesce again. If, however, a little *emulsifying-agent* is added the oil dispersion becomes stable. Numerous materials act as emulsifying agents, in particular the sodium and potassium soaps of the liquid fatty acids. There are numerous theories as to how they work, one of the most satisfactory being the oriented wedge concept. According to this concept, the most satisfactory emulsifying agents are those whose

molecules consist of long chains of carbon atoms with a strong polar group at one end. *Oleic acid*—$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$—in the form of potassium oleate is typical and is often used as a standard for comparing emulsifying agents.

These molecules have oil-soluble tails and water-soluble heads. If the oil-soluble tails can pack more closely than the polar heads the oil interface will be bent round, forming stable droplets of oil in a watery medium.

In the bitumen industry the most common emulsifying agent is a waste product from the paper pulp industry called *tall oil* which is an impure mixture of rosin acids. The tall oil is made into a soap by heating with either sodium or potassium hydroxide. In emulsion manufacture only a little emulsifying agent is required, usually about 0.75% of the final weight of product.

Whilst the emulsifier can stabilize oil droplets once they have been formed, it is still necessary to provide some means of generating the droplets initially. For bitumen the simplest way is to melt it and pour it into a dilute solution of the emulsifier whilst stirring vigorously. This process does not lend itself to the manufacture of large quantities of high bitumen content emulsion, so it is usual practice to employ a grinding device known as a colloid mill. In this mill two metal surfaces a few thousandths of an inch apart are swept past each other. The water and emulsifier wet the metal surfaces and are dragged round with them. The molten bitumen is introduced between the two and is torn into droplets by the violently shearing liquid. Colloid mills are very commonly used industrial devices for preparing emulsions. They absorb a lot of energy, which is not surprising when you consider that in being emulsified one gram of bitumen acquires an area in the order of 40 sq.ft.

A mill with a 10 in. diameter rotor can produce 1,200 gallons per hour, absorbing 12 h.p. in the process. Usually, a variable speed pump assembly enables the proportion of bitumen to water to be varied. Normally the emulsion contains 55% bitumen by weight. After manufacture the material is subjected to laboratory checks for bitumen content, viscosity, and stability.

Viscosity is giving a lot of trouble in New Zealand emulsion plants at present. Until 1959 bitumen was imported in drums from a number of sources, in particular Trinidad. The emulsion made from this material gave a viscosity acceptable to all users. In late 1959 the importation of bulk bitumen began, the source being Venezuela. This made an emulsion satisfactory in every

respect except viscosity, which was lower than the accepted standard. The cause is not known, nor has anyone found a cheap method of overcoming the trouble.

In manufacturing most emulsions, one aims at a high stability —it would be most embarrassing to have thousands of gallons of emulsion type paint out on shop shelves then discover that the methyl methacrylate resin was curdling out. Bitumen emulsions are different. Although they must be stable enough to store in tanks or drums, they must also be labile enough to separate into bitumen and water a few minutes after use. This can be ensured by varying the strength and type of emulsifying agent, but there is a fair degree of secretiveness about the subject and there is virtually nothing in the textbooks about formulation details. It is an interesting field where odd things happen. Emulsions from some bitumens increase in viscosity on storage, others do not. Emulsions made from sodium soaps are less stable than those from otherwise identical potassium soaps. Some bitumen will not emulsify at all.

The finished product is a thickish brown liquid fully dispersable in water. If it is poured over chips it eventually breaks, leaving the chip coated with bitumen, which soon binds them together. Some 22,000 gallons of this material were recently used on State Highway 1 near Cheviot, to bind a small chip into the spaces between the large chip previously used, the result being a much smoother surface, and one that is considerably quieter to travel over.

This type of emulsion is called *anionic* because the emulsifying agents used cause the bitumen particles to be negatively charged, and the watery phase is a very dilute potassium or sodium soap, alkaline in reaction. Such emulsions break because the watery film spreads over the stone surface leaving the bitumen particles stranded. Only when the water has evaporated does true adhesion take place. If the chip is wet the breaking process will be slow; if there is rain before completion the unbroken emulsion can be washed away.

Recently a new series of emulsifiers have come into use, based on quaternary ammonium salts. A typical one is *alkyltrimethyl ammonium chloride* in which the alkyl chain is derived from soya bean oil. It meets the usual requirements of an emulsifying agent for it has a long chain tail and a polar head fat enough to curl any bitumen droplet. It differs from conventional emulsifiers in that it carries a positive charge, and the watery medium

is kept slightly acid. The emulsion can be prepared in the usual way, provided acid resistant materials are used. Because the bitumen particles are positively charged the emulsion is called *cationic*.

Stone surfaces for one reason or another tend to be slightly negatively charged in the presence of the acid emulsion. As a result the positively charged bitumen particles immediately adhere to the stone surface and the emulsion breaks. The reversion to bitumen and water is not delayed by wet chip, nor is there any risk of wash-out by rain for the bitumen adheres strongly to the stone as soon as applied. Breaking time can be delayed by some additives, and work is going on to produce better ones.

Cationic emulsions have drawbacks. They are expensive, they require acid resistant production plant, and they are completely incompatible with anionic emulsions. This makes one very loath to attempt to use the same plant for manufacturing both types, for industrial plant is not as easy to clean as beakers and flasks. Nevertheless, cationic emulsions look most promising materials, and we shall hear a lot more about them before long.

I trust I have managed to show how an apparently simple process like road-making calls on a variety of scientific techniques and industrial chemicals to ensure that each highway and byway made or maintained is the best our knowledge can produce. I hope, too, you have noticed the gaps in that knowledge. Most industries are like that and there is an urgent need in them for technical people, both to ensure that existing knowledge is used to the full, and to attempt to fill up the gaps. I assure you that the more you seek and the more you learn, the greater the number of gaps you will discover.

CHEMISTRY AND CRYSTALS

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There is hardly need to comment on the fascination of crystals and their beauty of form. Under appropriate conditions minerals can produce very large crystals, bounded always by plane faces intersecting at characteristic angles. The occurrence of substances in crystalline form is more common than some of you may realize. Constituents of rocks—of even the uninteresting greywacke of Canterbury—are crystalline, and so are clays, metals, and the proteins of living cells.

The external form of a crystal is a consequence of the regularity of the internal arrangement of the atoms. This in turn is largely determined by the nature of the inter-atomic forces and so is a matter of particular interest to the chemist. The crystalline state is to be contrasted with the glassy or amorphous state (see Fig. 1). In the latter there is a disorderly array of atoms. Quartz is a crystalline form of silica with a definite regularly repeating arrangement of silicon and oxygen atoms. In the glassy form of silica there is disorder arising because the oxygen will tolerate variations in the angle between the two bonds it forms with silicon.

Our knowledge of crystal structure stems from an experiment on X-ray scattering made in 1912 at the suggestion of von Laue. An X-ray beam was allowed to fall on a crystal behind which there was a photographic plate. Development of the plate gave a regular pattern of spots, showing that the X-ray beam had been scattered in a characteristic way. Within a year the Braggs, father and son, showed that this scattering of the X-ray beam occurs only at certain critical angles (θ) related to the wave-

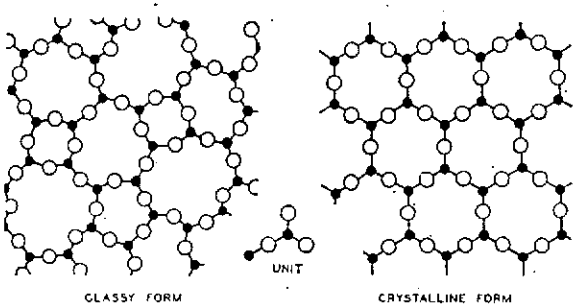

Fig. 1: A diagrammatic representation of the glassy and crystalline states.

length (λ) of the X-rays and to the distances (d) between parallel reflecting planes of atoms by the equation $2d\sin\theta = n\lambda$, with n an integer. From these beginnings X-ray crystallographers have developed methods for determining atomic arrangement in even the most complicated crystal structures. Because X-rays are really scattered by atomic electrons the results enable the drawing of "maps" showing the electron distribution within a crystal. Thus for the hydrocarbon benzene, C_6H_6, the electron density contours are in the form of a series of hexagonal patterns showing the atomic positions within the individual molecules (Fig. 2).

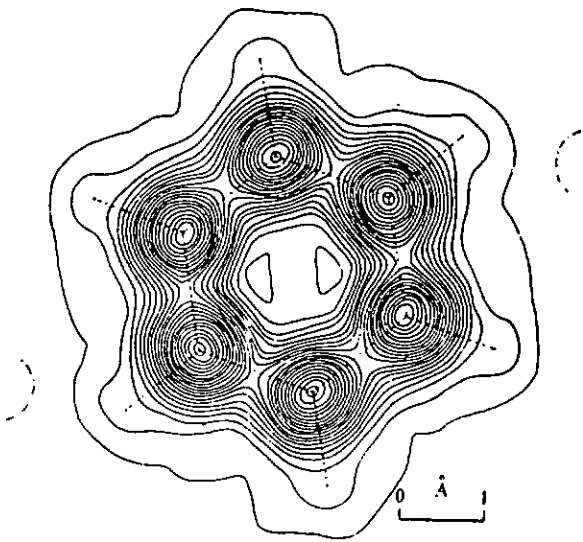

Fig. 2: Electron density contours for the benzene molecule.

Structure determinations are made using single crystals. If on the other hand a powdery mass of very small crystals is used, the X-ray photograph consists of a series of concentric rings. This is because the crystallites are randomly oriented around the whole solid angle and the reflection spots from different crystals merge into one another to form continuous lines (Fig. 3). A crystalline compound usually gives a distinctive powder pattern and so these photographs are often taken for identification purposes, particularly because very small quantities suffice. Isomorphous compounds have very similar patterns, but this can sometimes be used to advantage. In the early examination of the chemistry of plutonium when only very small amounts of the element were available, it was necessary to establish oxidation levels resulting

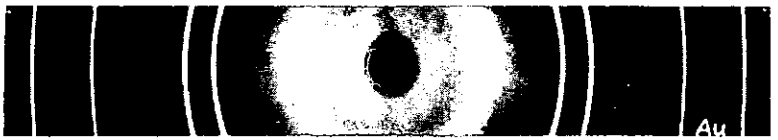

Fig. 3: An X-ray "powder" photograph of gold foil.

from particular treatments. One oxide gave a powder photograph so similar to that of lead dioxide as to indicate isomorphism. This could only occur if the oxides were of the same composition type and so the oxidation level of the plutonium was four.

SOME CRYSTAL STRUCTURES

In the familiar sodium chloride lattice there is a spherically symmetrical field of force associated with each ion. The ions pack together as closely as possible and their relative sizes are such that there is room for just six chloride ions around each sodium ion. In diamond on the other hand, the four covalent bonds of the carbon atoms are developed towards the corners of a regular tetrahedron and this determines the crystal structure (Fig. 4). The hardness of diamond is a direct consequence of the three dimensional network of strong bonds extending throughout the entire crystal. In graphite the four valency electrons of each carbon are used for forming coplanar bonds with only three neighbours. These bonds are shorter and even stronger than the bonds in diamond. Because the strong valency forces are fully used within the planes of carbon atoms the forces between the layers are feeble. It is this layer structure which is responsible for the well-developed cleavage of graphite. Its lubricating properties and greasy feel arise from the ease with which the layers of atoms slide over one another. Boron nitride, BN, is a compound which normally produces a graphite type structure with the boron and nitrogen atoms alternating, but under high pressure it will give a higher density diamond-like crystal. Between them boron and nitrogen have eight valency electrons and the atoms co-operate

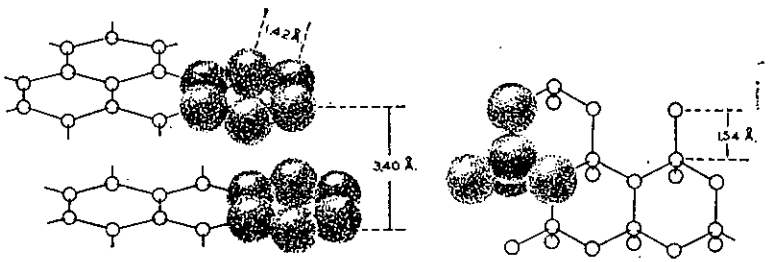

Fig. 4: The graphite and diamond structures.

to use them in the same ways as do carbon atoms.

Most of the other non-metals have fairly simple crystal structures determined by the number and relative directions of the covalent bonds which they must form in order to increase their valency shells to eight electrons. Thus phosphorus forms bonds with three neighbours, sulphur with two, and iodine with one. Iodine provides an example of a *molecular lattice* containing individual molecules (Fig. 6) between which the forces are of the weak "residual" or van der Waals type, as between the graphite layers. Such crystals are characteristically soft and melt at fairly low temperatures.

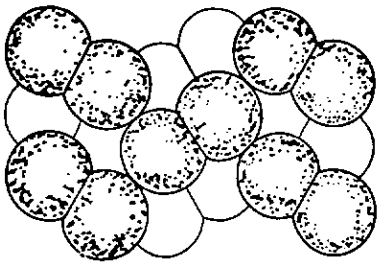

Fig. 5: The arrangement of iodine molecules within the crystal. The layer structure is responsible for the flaky nature of iodine crystals.

Metals too are crystalline. Figure 3 shows an X-ray powder photograph of gold foil which consists of very small crystals. (A piece of meteoric iron with its characteristic etch lines running parallel over the whole polished surface is really one single crystal.) The force field around a metal atom is spherically symmetrical, or nearly so, and so the atoms pack together as closely as possible. In doing so they pool their valency electrons which form a mobile swarm extending around all the atoms, and responsible for the electrical conductivity. When metal crystals are distorted the closely packed layers of atoms slip over one another, but the electron swarm still binds the layers together after the shearing movement.

Besides the ionic, covalent, and metallic bonds and the van der Waals forces, the hydrogen bond can sometimes exert an important influence on crystal structure. Ice provides an example for in the crystal each oxygen is linked to four hydrogens (Fig. 6). Two of them can be thought of as held by covalent bonds and the other two by hydrogen bonds (each an electrostatic interaction between the fractional positive charge on the small hydrogen atom and an otherwise unshared electron pair on the oxygen). The

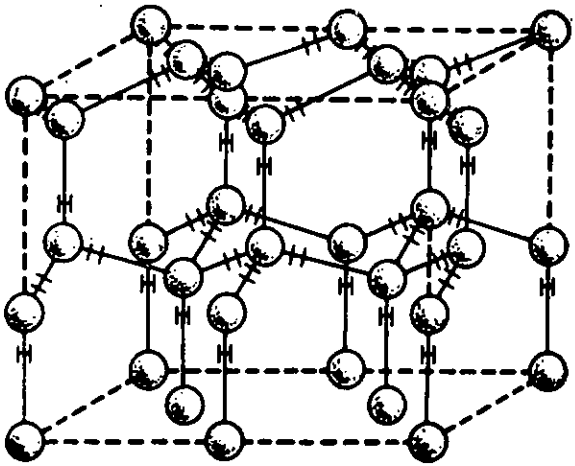

Fig. 6: The crystal structure of ice.

open structure of the ice crystal which causes its density to be lower than that of water is apparent from the diagram.

Simple inorganic crystals were the first to be subjected to X-ray analysis and serve to illustrate the main types of crystal structures, but a very important field of current X-ray crystallography concerns the structures of the complex constituents of living matter. The X-ray approach can yield information on the overall structure of the molecule—information of a complementary kind to that obtainable by purely chemical procedures. The very large protein molecules have been shown to contain rod-like structures. The rods consist of a spiral chain of atoms which are braced by hydrogen bonds between successive turns. Groups of atoms stick out from the coil in a rather ragged way; but to approaching reactants dissolved in the surrounding fluid these groups would offer specific attractions which determine the kind and the course of biochemical reactions taking place in the organism. The relevance of this to any understanding of the processes of normal metabolism and of abnormal diseased conditions will be evident.

Let us now consider some effects and properties on which crystal structure has a bearing.

SELECTIVE NATURE OF CRYSTALLIZATION

It is because crystallization is a selective process that it is so useful for purification. A growing crystal will usually accept only it own structural units since most impurities will be of the wrong size, shape or charge. One exception is the formation of solid

solutions through isomorphous replacement of ions by others of similar characteristics. Cr^{3+} will replace Al^{3+} in an alum. A barium sulphate precipitate will carry down radium from solution for the same reason and this is exploited in the extraction of radium from uranium minerals.

There are also known a few examples of compounds which will deliberately entrap foreign molecules in order to fill what would otherwise be cavities in the crystal lattice. Quinol crystals deposited from aqueous solution under argon or krypton contain entrapped atoms of the inert gases. These atoms contribute a little to the stability of the crystal lattice by augmenting the van der Waals forces.

SURFACE PROPERTIES OF CRYSTALS

Within a crystal the interatomic forces are in balance, but at the surface of the crystal there is a lack of balance. One consequence of this is that the crystl surface can *adsorb* molecules of certain types at least. Adsorption is fundamental to heterogeneous catalysis. It increases the concentration of reactant molecules on the surface and at the same time causes some polarization which renders the molecules more prone to reaction.

Certain crystals such as those of the zeolite class of silicates have rather open structures, being traversed by honeycomb-like channels of molecular dimensions. Because the internal surface area is large these crystals show strong adsorptive properties towards gases and can exchange cations already in the channels with cations from a surrounding solution. Water softening silicates are of this type. They contain sodium ions within the channels but exchange them for dissolved magnesium and calcium ions, and in so doing remove the cause of water hardness.

CRYSTALS OF VARIABLE COMPOSITION

The composition of a quinol-argon crystal (mentioned above) will vary according to the proportion of cavities actually occupied by argon. Oxides of manganese provide another example. Mn_2O_3 and Mn_3O_4 have the same kind of crystal structure with most of the volume taken up by the closely packed oxide ions. Manganese ions fill some of the cavities. When Mn_2O_3 is heated oxygen is lost from the crystal surface and the manganese ions redistribute themselves so as to maintain a statistically uniform composition. The Mn_2O_3 changes progressively into Mn_3O_4 and at no stage does a new crystal structure appear.

Though I have dealt so far primarily with reference to structural chemistry I have hinted at the technical importance

of crystalline compounds. The chemist in industry may be concerned with the manufacture and handling of huge quantities of products, or with precise control of delicate processes. He may be called upon to develop new products. The chances are that at some stage he will be concerned in some way with crystals. Here are examples:

(1) Ammonium sulphate is manufactured in very large quantities and so far as possible is handled in bulk. The crystals from pure aqueous solution have 90° angles between some faces and do not flow freely. Crystallization from a solution containing a little alum leads to development of new crystal faces which bevel off these angles. These ammonium sulphate crystals of different habit no longer lock together, but pour freely. A habit modifier influences the shape of a crystal through being preferentially adsorbed on certain faces and so altering the relative rates at which the faces grow.

(2) In the manufacture of photographic emulsion, which is a dispersion of silver bromide crystals in gelatin, the crystals must be of the correct size and the chemist is called upon to control the conditions which determine crystal size. Crystal size is critical because during the development of the exposed film the action of the reducing agent exends over the entire area of each crystal which has been sensitized by the photochemical decomposition. The size of a crystal therefore determines the amount of blackening caused by a treatment which is otherwise standardized.

(3) This third example is of a different kind. Crystals of the very stable rock-forming silicates contain alternating silicon and

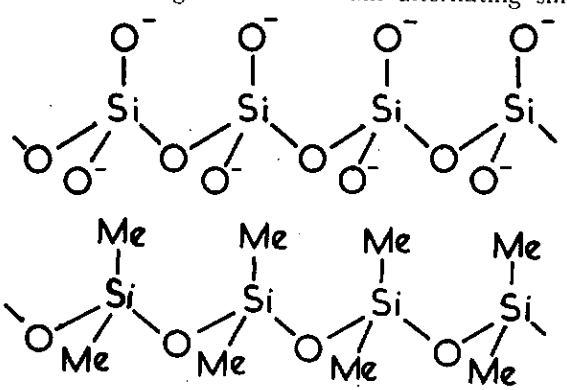

Fig. 7: The chain structures of the metasilicate anion, SiO_3^{2-}, and dimethylsilicone polymer, $(Me_2SiO)_n$.

oxygen atoms (Fig. 7). Knowledge of such stable structures prompted development of the industrial production of neutral synthetic compounds having these same stable skeletal. structures, but in which the silicon valencies not used within the chain are linked to organic groups. They are the compounds known as silicones.

I hope then that you see that this branch of chemistry dealing with the solid state has relevance both to the understanding of chemical theory and to severely practical applications of the subject. But more than this, I hope you are also becoming aware that chemistry impinges on a number of other fields of knowledge. We have just seen examples bearing on mineralogy, metallurgy, and medical science; another lecturer in this series will be particularly concerned with the relevance of chemistry to agricultural science and food production.

Chemistry is continually developing, as are its applications to other fields. The chemist is called upon to contribute both to the development and the application of his subject. As young students of the subject you fall heirs to the fund of information that has gradually been accumulated as a result of the labours of men of science over the years. Those of you with the ability and the desire will have the chance to use and to add to this knowledge. Let me quote Albert Einstein:

> "Bear in mind that the wonderful things you learn in your schools are the work of many generations produced by infinite labour in every country of the world. All this is put into your hands as your inheritance in order that you may receive it, honour it, add to it, and one day pass it on to your children."

It is in the very nature of things that most of us who practise science must be content with very humble contributions to knowledge, but I am reminded that world authorities in two of the fields to which I have referred are in fact graduates in chemistry from the University of Canterbury. Both men are now Fellows of the Royal Society. One, Professor R. M. Barrer, is distinguished for his contributions to knowledge of adsorption by zeolite type crystals. The other is Professor J. W. Mitchell, who has made fundamental contributions to our knowledge of the physics and chemistry of photography. Such men have sprung from our midst in the past: there is every reason to think that men of similar calibre will continue to appear from time to time from amongst New Zealand science graduates.

NEW ZEALAND INSTITUTE OF CHEMISTRY CONFERENCE 1961

The 1961 Conference of the N.Z.I.C. will be held in the Chemistry Department of the University of Auckland. The Conference will commence with an informal gathering on Tuesday evening, August 29, and close on Friday afternoon, September 1.

PROGRAMME

There has been a good response to the request for papers and the following topics have been selected for symposia:

Analytical Chemistry	Isotope Chemistry
Biochemistry	Soil Chemistry
Chemistry of Fats	Spectroscopy

In addition there will be sections on General Chemistry and Organic Chemistry.

CONFERENCE FEE

The Conference Fee is *thirty shillings* payable by those who attend all or part of the Conference. A student concession has been arranged and for *bona fide* undergraduate students the Conference fee is reduced to *fifteen shillings*.

POST-CONFERENCE EXCURSION

A one-day post-Conference excursion has been arranged for Saturday, September 2. Details of the tour are as follows:

Leave Auckland 6.30 a.m.—breakfast at Hamilton—tour N.Z. Forest Products, Kinleith—lunch at Wairakei—tour powerhouse and steam field—dinner at Hamilton—return to Auckland connecting with the south-bound Limited Express at Frankton.

Estimated cost is about £4 0s 0d.

ACCOMMODATION

A limited amount of accommodation is available at O'Rorke Hall which is the University hostel situated in Symonds Street about five minutes walk from the University. The hostel charge will be 17s. 6d. per day. Members staying at O'Rorke will be required to supply their own sheets, pillow-slips and towels.

LOCAL EXCURSIONS

Three local excursions have been arranged for Thursday morning, August 31:

(1) Auckland Metropolitan Drainage Board's Sewerage Plant at Mangere and Korma Mills.

(2) Carbonic Ice Company and Chelsea Sugar Refinery.

(3) Amalgamated Brick & Pipe Company (Crown Lynn Potteries) and Astley's Tanneries.

EXHIBITION

Arrangements are being made for an exhibition to be held during the Conference. Various firms have been approached and it is hoped to have scientific books and apparatus on display.

THE REGISTRY

Fellows

(Elected May 12, 1961)

HUNT, Ian Sinclair, M.Sc., F.R.I.C., N.Z. Wallboards Ltd., Auckland (Chief Chemist).

WHITTON, William Ivo, M.Sc., Ph.D., F.R.A.C.I., I.C.I. (N.Z.) Ltd., Production Manager.

Associates

(Elected February 24, 1961)

BREEN, John Newman, Stratford Dairy Company, Stratford.

RUSSELL, Gordon Richard, Ruakura Animal Research Station, Hamilton.

(Elected May 12, 1961)

BOUSTRIDGE, William, B.Sc., B.A.L.M. Paints, Auckland (Chemist).

BROOKS, Robert Richard, B.Sc.(Hons.), Ph.D. (Capetown), Biochemistry Dept., Massey College (Lecturer).

GLOVER, Richard Brian, B.Sc.(Hons.), Ph.D.(Bristol), Dominion Laboratory, Wellington (Scientific Officer).

GRIMMETT, Murray Ross, M.Sc., Biochemistry Department, Massey College (Assistant Lecturer).

HOUSE, Donald Alexander, M.Sc., Chem. Dept., Victoria University of Wellington (Junior Lecturer).

KING, Donald Wilford, B.E. (Chem.), B.Sc., Dairy Research Institute (Chemical Engineer).

LATIMER, Graeme Bruce, B.E.(Chem.), B.Sc., Dairy Research Institute (Chemical Engineer).

MOUSTAFA, Esam, M.Sc., Ph.D.(Cantab.), Plant Chemistry Division (Senior Scientific Officer).

PACKER, John Edward, M.Sc., Ph.D.(Lond.), Institute of Nuclear Science, (Defence Science Corps).

PAGE, Beryl Edith Winifred, B.Sc. Hons.(Sthhampton.), Medical Unit, Wellington Hospital (Biochemist).

SARGENT, John Driessen, M.Sc., Massey College (Head Microbiology Department).

SIMPSON, William Stanley, M.Sc., Ph.D.(Leeds), Dominion Laboratory, Wellington (Defence Science Corps).

SOMERVILLE, William Campbell, B.Sc.(Hons.), Ph.D.(Edin.), Chemistry Department, Otago University (Teaching Fellow).

STEWART, Rex George, M.Sc., A.R.I.C., Wool Industries Research Institute, Dunedin (Research Officer).

SWEETMAN, Brian Jack, M.Sc., Chemistry Department, Otago University (Research Fellow).

THOMPSON, Megan (Mrs.), M.Sc., Chemistry Department, Auckland University (Temporary Junior Lecturer).

WHITE, Graham Richard, M.Sc., Chemistry Department, Auckland University (Junior Lecturer).

WILLIAMSON, Arthur Gordon, M.Sc., Ph.D.(Reading), Chemistry Department, Otago University (Lecturer).

WOOFF, Alan Herbert, M.Sc., Dip.Ind.Chem., Boys' High School, Christchurch (Science Master).

BRANCH NEWS AND NOTES

AUCKLAND BRANCH

Professor Llewellyn, Associate Professor Odell, Miss Bishop, Dr Swedlund and Mr White attended the A.N.Z.U.S. Conference in Brisbane in May.

Mr Y. L. Hoe has resigned from Amalgamated Brick and Pipe Ltd., to join Arthur Lowe Ltd.

Mr I. S. Hunt, formerly Chief Research Chemist, Hickson's Timber Impregnation Co. (N.Z.) Ltd., is now Chief Chemist for N.Z. Wallboards Ltd. The branch congratulates Mr Hunt on his election as a Fellow of the Royal Institute of Chemistry.

In a reorganization following the amalgamation of N.Z. Farmers' Fertilizer Co. and the Challenge Phosphate Co., Mr W. E. Russell has been appointed Works Superintendent and Mr J. W. Kennedy has been appointed Works Manager, Te Papapa Works. Mr D. W. Jackson has been transferred to the Challenge Works as Chief Chemist and Acid Plant Superintendent.

WAIKATO BRANCH

At the April meeting the Chairman referred to the announcement of the engagement of Mr F. D. Dorofaeff, who has been Branch Secretary for several years, to Miss Julie Perrow, a local member of the Branch.

WELLINGTON BRANCH

Dr and Mrs W. E. Harvey have returned from Harvard. Mrs Harvey is again with the Dominion Laboratory and Dr Harvey with the Chemistry Department of Victoria University. Dr Harvey gave the Institute an interesting lecture on "The Biological Synthesis of Cholesterol".

Mr W. E. Hindmarsh of Tasman Vaccine Laboratory Ltd., Upper Hutt, has transferred to Mair and Co. (Importers) Ltd., Box 1152, Auckland.

Miss Alison Cooke is working on radio-chemistry with the Government Chemist, near the Law Courts, the Strand, London.

Mr N. A. Marris, we regret to announce, has been obliged to retire early from the position of Officer-in-Charge of the Information Bureau, D.S.I.R., Wellington. An affection of his throat limits his ability to speak but otherwise he is in good health and proposes to continue leading an active life. Mr Marris was educated at Nelson College and Canterbury University where he took his M.Sc. degree with Honours in Chemistry. He joined the Dominion Laboratory in 1928 and later became an analyst and gas examiner. He completed his B.Com. degree and moved to Head Office in 1940 where in 1943 he became a senior executive officer. In 1944 he went to Washington to establish the N.Z. Scientific Liaison Office there and after three years returned to D.S.I.R. Wellington. In 1948 he was appointed Officer-in-Charge of the Information Bureau and served in that capacity till 1961. The very nature of his work and his many contacts overseas brought Mr Marris in touch with a large number of scientific people and his personal attributes won him a wide circle of friends.

Mr G. M. Ryburn has transferred from Tasman Vaccine Laboratory Ltd., Upper Hutt, to Lever Brothers Ltd., Petone.

CANTERBURY BRANCH

In his Chairman's Address to the Canterbury Branch, entitled "Educating the Chemist", Mr E. R. Hounsell advocated the inclusion of a humanity in the sixth-form syllabus for pupils taking science courses and an upper sixth-form examination for non-scholarship candidates. Mr Hounsell is Liaison Officer, University of Canterbury.

The Branch Prize for the best student in Stage II Chemistry was presented at the March meeting to Mr J. M. Coxan.

Mr R. H. Hopgood of Fletcher Industries Ltd. is on twelve months' transfer to the Fletcher Manufacturing Co., Waterloo, N.S.W.

Dr F. J. Llewellyn who has been Vice-Chancellor and Rector of the University of Canterbury for the last five years, has transferred to Wellington to take up his appointment as Chairman of the Universities Grants Committee.

The 1961 Chemistry in Action lectures held in Christchurch during April were perhaps the most successful yet held. Interest was well maintained over the three weeks and there was a keen demand for tickets.

OVERSEAS MEMBERS

Mr W. J. Blackie has resigned from the British Colonial Service, in which he was Director of Agriculture, Food and Fisheries, Hong Kong, and is now FAO Team Leader in East Pakistan.

OTAGO BRANCH

Mr A. N. Scrymgeour, formerly of Tasman Vaccine Laboratory Ltd., Upper Hutt, is now Works Manager of Irvine & Stevenson Ltd., Dunedin.

A soil testing service has been established by the Soil Bureau at Taieri Air Station under the direction of Mr J. L. Grigg, who was previously associated with the Winchmore Irrigation Scheme at Ashburton.

Mr C. L. Carter, formerly Reader in Chemistry at the University of Otago, is analyst for the Nevis Oil Shale Company, Ltd.

At the March meeting the Otago Branch awarded to Mr N. S. C. Sullivan the N.Z.I.C. Prize for the best first-year science student of 1960 in Chemistry. The Inglis Memorial Prize was presented by Dr Parton to Mr I. L. Weatherall (best third-year Chemistry student).

Dr A. M. Kennedy addressed the meeting on the topic of "Ion Exchange" and an interesting blend of chemistry and engineering was appreciated by all present.

Dr A. T. Wilson of Victoria University of Wellington was guest lecturer for the April meeting. Members found his lecture on "Radiochemical Research" most interesting and thought-provoking. The desirability of hearing scientists from other centres was once again evident.

AUSTRALIAN BUILDING RESEARCH CONGRESS

The March, 1961, number of the *Proceedings of the Royal Australian Chemical Institute* announces that the Australian Building Research Congress will be held at Monash University, Clayton, Victoria, on August 16 and 17. The field of discussion will cover moisture in materials, modern developments, cracking in buildings and curtain walls. Members interested in this Congress can obtain full details from Mr R. W. Muncey, Acting Chief, Division of Building Research, C.S.I.R.O., Highett, S.21, Victoria.

CANTERBURY JUNIOR CHEMICAL SOCIETY

The Canterbury Junior Chemical Society, a society for upper sixth form students of chemistry, started the 1961 season with a stimulating lecture on chemistry in agriculture by Professor T. W. Walker, Professor of Soil Science, Canterbury Agricultural College, Lincoln. This lecture was followed by a Saturday morning field trip to Lincoln. About 100 of the Society's 150 financial members attended two hours of lectures and demonstrations provided by the Soil Science Department. On the next Saturday 38 members of the Society representing 12 schools sat an examination to determine the four winners of the Lever Bros. Award. This Award, offered to the Society by Lever Bros. last year, consists of a two-day trip to Wellington for four members of the Society and an accompanying teacher, one day being spent at Lever Bros. and one at D.S.I.R. establishments. This generous offer has created a great deal of interest and will be a real stimulus to the young Society.

PROFESSOR N. A. SOERENSEN

Professor N. A. Soerensen, from the Organic Chemical Laboratories, Technical University of Norway, at Trondheim, who has been working at Fisherman's Bend, Sydney, since the IUPAC Symposium last year, paid a short visit to New Zealand early in May. Professor Soerensen has been studying the chemistry of the Australian Compositae as part of a project to trace the origin of flora in different parts of the world. He was accompanied by Mrs Soerensen who is also a chemist and who has been working with him on this project.

Professor Soerensen gave a lecture in Auckland on poly-acetylenic compounds isolated from the Compositae and at Ruakura Animal Research Station discussed chemical aspects of photosensitisation in animals, a subject in which he is interested because he has been associated with studies on a plant suspected of causing a disease of this type in parts of Norway. Professor and Mrs Soerensen made a closer acquaintance with New Zealand flora during a trip to Rotorua with members of the Waikato Branch.

TWENTY-THIRD INTERNATIONAL CONGRESS OF INDUSTRIAL CHEMISTRY

The annual International Congress of Industrial Chemistry will be held in Bordeaux from October 1 to 8, preceded by a three-day meeting on Chemical Engineering (September 28 to 30) at Toulouse at which all the papers of the Chemical Engineering Section of the Congress will be presented. The 23 sections into which the Congress is divided include the main chemical products and processes in use in industry.

The address for further enquiries concerning the Congress is:

Societe de Chimie Industrielle

28 rue Saint-Dominique

Paris (7e).

VICTORIA UNIVERSITY OF WELLINGTON

APPOINTMENT OF TWO LECTURERS IN CHEMISTRY

Applications are invited for appointment to the above posts. Salary scale £1,250 to £1,700 per annum; initial salary according to qualifications and experience of appointee. Conditions of Appointment obtainable from the Registrar of any University in New Zealand. Applications close with the Registrar, Victoria University of Wellington, P.O. Box 196, Wellington, on the 30th June, 1961.

L. O. DESBOROUGH,
Registrar.

ASSISTANT CHEMICAL ENGINEER COMMERCIAL DIVISION : WAIPA SAWMILL N.Z. FOREST SERVICE

Vacancy No. 1493, Assistant Chemical Engineer, Commercial Division, Waipa Sawmill, New Zealand Forest Service, salary up to £1,210 a year according to qualifications and experience.

Qualification in chemical engineering is desired or a degree in chemistry. Experience in the application of chemical engineering principles or industrial chemistry to the treatment of natural products would be an advantage.

Duties: To assist in the supervision and extension of chemical engineering aspects of the utilisation of wood.

After a period of training in Head Office the appointee will be stationed at the Waipa Sawmill, Rotorua. Some travelling will be required.

Applications close on 15th July, 1961, with the Secretary, Public Service Commission, Box 8004, Wellington. Use Form P.S.C. 17A obtainable at Post Office, enclose copies only of testimonials and "vacancy No.".

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★ Saves time Duration of test: 6 hours for full range 5μ to 7μ.
★ Saves labour Recording equipment: releases operator for other work.
★ Easy operation.
★ Simple maintenance.
★ Balance sensitive yet robust: readings by an integral optical system.

British Patent No. 712,434 and U.S. Patent Application No. 320,996.

NOTE—This apparatus is under consideration by the BSI for possible adoption as British Standard.

For particle size determination within the range 5μ to 7μ. If, however, the largest size is not greater than, say, 20μ, the lower limit can be extended to about 2μ provided the temperature is controlled within fairly narrow limits and agglomeration or flocculation does not take place.

A wide variety of materials which have been examined includes alumina, carborundum, china-clay, cement, felspar, flint, flour, limestone, pyrites and plastics and dusts collected by electrostatic precipitators and cyclones from boiler, blast furnace, and flash roaster plants.

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