CHEMISTRY IN NEW ZEALAND

JOURNAL OF
THE NEW ZEALAND
INSTITUTE
OF CHEMISTRY

Vol. 33, No. 2, April 1969

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Journal of
The New Zealand
Institute of Chemistry

Vol. 33, No. 2 April 1969

Published bi-monthly by the New Zealand Institute of Chemistry Inc. (P.O. Box 250, Wellington)

Contents

Editor: Miss J. Mattingley, B.Sc., A.N.Z.I.C.
P.O. Box 250, Wellington.

Advertising Manager:
D. Howard, M.Sc., A.N.Z.I.C.
P.O. Box 250, Wellington.

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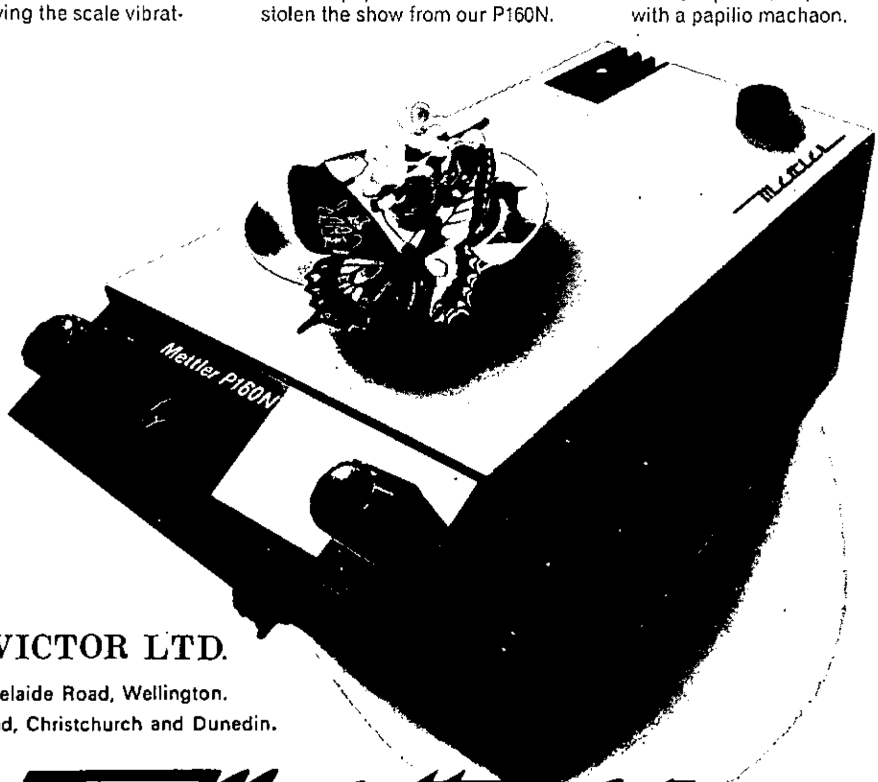

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MEAT PIGMENTS*

Max Carrie, M.Sc., C.Eng., A.M.I.Chem.E., F.R.I.C.
Chief Chemist, Canterbury Frozen Meat Co. Ltd.

Myoglobin and Haemoglobin

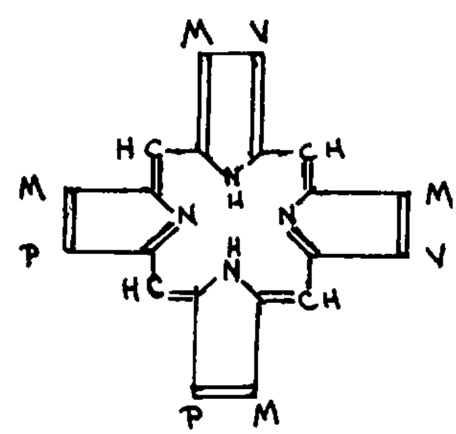
The chemistry of the colour of meat is essentially the chemistry of the derivatives of one substance, myoglobin. Myoglobin and its close relative haemoglobin are both complex proteins containing iron, and the two compounds are vital links in the transfer of oxygen from the lungs to the tissues where it is required for the metabolic processes of the animal. The roles of these two substances are usually stated to be somewhat different in that haemoglobin is concerned with the transport of oxygen in the blood stream, whereas myoglobin is essentially a mechanism for the storage of oxygen in the tissues. This would account for the high concentration of myoglobin in those organs where muscular activity is high, e.g. the heart, and in the skeletal muscles of sea mammals which have to remain submerged for long periods. However, Dr. C. L. Davey of the Waikato Branch has pointed out that the amount of oxygen stored by myoglobin in the tissues of sea mammals was negligible in comparison with the oxygen requirements of the muscles and that the storage theory was quite untenable. He also pointed out that, in general, the larger the animal, the higher the concentration of myoglobin in the tissues. The exact roles of myoglobin and haemoglobin in the transfer of oxygen are not clear.

Both myoglobin and haemoglobin are obviously of very great interest to physiologists to whom much of our knowledge is due. But since myoglobin and haemoglobin to a lesser extent are responsible for the colour of meat, and since colour is an important attribute of any food as far as the consumer is concerned, meat technologists have also played their part in the investigation of the chemistry and biochemistry of these substances.

In chemical behaviour the substances are virtually identical. Although we shall deal almost exclusively with myoglobin, it must be kept in mind that what applies to myoglobin applies equally to haemoglobin. Any differences which do exist are differences in degree rather than of kind.

Structure

Both compounds consist of two portions, a haeme moiety and a globin moiety. The haeme moiety consists of a porphyrin ring containing an iron atom; the haemes of myoglobin and haemoglobin are identical in every detail. The porphyrins in their various forms are widely distributed in both the animal and vegetable kingdoms, but the particular one which occurs in myoglobin and haemoglobin is the one which Hans Fischer named Protoporphyrin IX (fig. 1).



$M = -CH_3$
$V = -CH{=}CH_2$
$P = -CH_2CH_2COOH$

Fig. 1

* Based on the Presidential Address to Branches, 1967.

It reacts with ferrous hydroxide to give the haeme moiety of myoglobin, the iron being in the ferrous state (fig. 2).

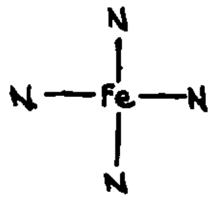


Fig. 2

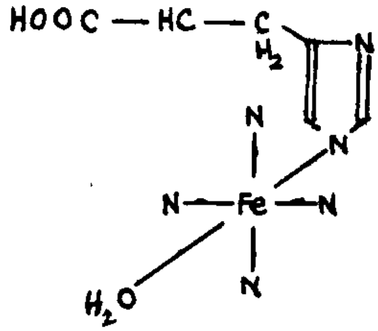


Fig. 3

Of the two remaining co-ordination positions of the iron atom, one is occupied by a molecule of water, and the other by a nitrogen in the imidazole ring of a globin histidine residue (fig. 3).

Classical chemical methods had, over the years, yielded considerable information as to the amino acids present in globin and their order in the molecule. It was known, too, that the molecular weight of myoglobin was about 16,000-17,000 and that it contained one haeme group. Haemoglobin, on the other hand, had a molecular weight of about 64,500 and contained four haeme groups. The similarity between the two substances suggested strongly that haemoglobin consisted of four units each resembling myoglobin. There were also various theories as to the conformation of the protein chain. Then came the work of Kendrew on myoglobin and Perutz on haemoglobin which won them jointly the Nobel Prize for chemistry in 1962. Using X-ray crystallography, they determined the structures of the two proteins and gave us a more detailed picture than we have of any other protein.

Such a major break-through as this should have shed a flood of light on the chemical reactions of these two important compounds. In particular, it would have been hoped that their characteristic reactions with oxygen would have been explained, since an isolated haeme group does not undergo reversible oxygenation. In point of fact, the work of Kendrew and Perutz has not shed even a glimmer of light on the subject. In the years which have followed, progress in this direction has been virtually nil.

The structure of the globin moiety of myoglobin is described in a paper by C. L. Nobbs, *J.N.Z.I.C., 30, (2), 65, 1966,* but since its structure has so far been of little help in understanding the properties of myoglobin there is little point in considering it here any further.

Reactions with Oxygen

The most important property of myoglobin from the point of view of the meat technologist (and the physiologist) is its interaction with oxygen. This can take two pathways, as shown in figure 4.

The reaction on the left-hand side of the diagram is known as oxygenation and replaces the water molecule attached to the iron atom with a molecule of oxygen. At the same time, the bonding of the iron which is ionic in myoglobin, changes to a co-valent bonding. Our understanding of the bonding of the iron in these compounds is due to Pauling and his co-workers who measured their magnetic susceptibility. Myoglobin is paramagnetic while oxymyoglobin is diamagnetic. Other substances which form co-valent bonds with the iron of myoglobin are CO which is more strongly bound than O_2 and NO which is still more strongly bound.

The reaction on the right-hand side of the diagram is true oxidation in which the iron of the myoglobin is oxidised from the ferrous

Myoglobin (Mb)

$+O_2$ ⇅ $-O_2$ R ⇅ O

Oxymyoglobin (MbO_2) — — — — → Metmyoglobin (MMb^+)

Fig. 4

to the ferric state. This compound, metmyoglobin formed by the oxidation of myoglobin, carries a positive charge due to the extra charge on the iron, and the bonds, like those of myoglobin, are ionic. Metmyoglobin will not bind oxygen, but it can form co-valent compounds with OH^- at pH values above 7 and with one or two other ions.

Colour of meat

The changes in the type of bonding are reflected in the colours of these compounds and, of course, in their spectra, and it is these colour changes which are of special interest to the meat technologist. Myoglobin has a purplish colour and is characterised by a diffuse absorption band with a maximum at 555 mμ in the green portion of the spectrum. Metmyoglobin is dull brown and its main absorption peak has shifted back to 505 mμ with a new weaker peak at 627 mμ. All the co-valent compounds, including oxymyoglobin, are bright red and have relatively sharp peaks in the regions of 535-545 and 575-585 mμ, the exact positions of the maxima depending on the compound concerned (fig. 5). This is the colour which the consumer likes to see in his meat, although it obviously has no bearing whatever on its flavour, its nutritive value or its eating qualities in general. The reflectance spectra of the meat itself have been widely used to follow changes in the oxygenation and oxidation of myoglobin, and by measuring the absorption coefficients at selected wavelengths to determine the proportions of myoglobin, oxymyoglobin and metmyoglobin in a meat sample.

When fresh meat is exposed to the atmosphere the interchange illustrated in the diagram is a dynamic cycle and the three pigments, myoglobin, oxymyoglobin and metymyoglobin are constantly being interconverted. Oxygen is constantly associating with and dissociating from the haeme compiex, and at the same time the myoglobin is constantly being oxidised to metmyoglobin which, in turn, is being reduced back to myoglobin. The relative proportions of the three pigments depend on the oxygen partial pressure, the pH, the temperature and the moisture content. Low oxygen pressures, especially in the 1-20 mm Hg range, favour the formation of metmyoglobin. It is not certain whether oxidation to metmyoglobin takes place during association or (as shown by the dotted arrow in fig. 4) during dissociation, but regardless of how it takes place, there is a slow but steady oxidation of myoglobin to the met form at all oxygen pressures. In fresh meat however, as a result of enzymatic oxidation of available sub-

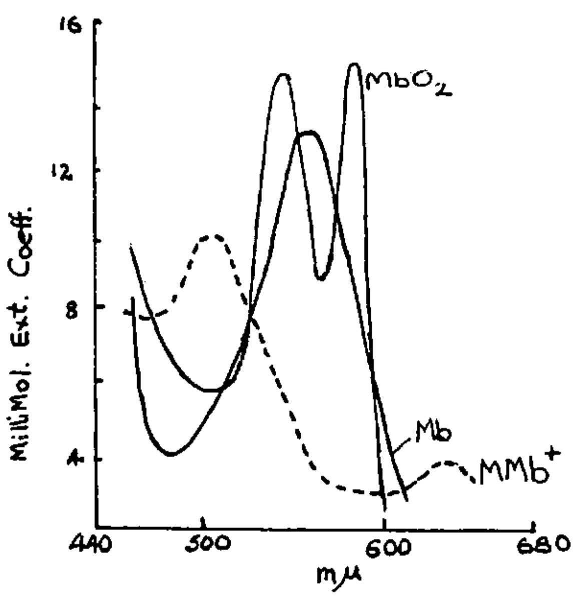


Fig. 5

strates, there is a continual supply of reducing co-enzymes capable of reducing metmyoglobin back to myoglobin and thus of keeping the cycle going.

A sizeable piece of meat, say a steak or a roast of beef, will therefore have the attractive, bright-red, oxymyoglobin colour on the surface where the oxygen supply is ample. The deep layers which are virtually oxygen-free will have the purplish colour of myoglobin maintained by the endogenous reducing substances. Any metmyoglobin present will be found in a layer just below the surface where the oxygen partial pressure is favourable. It is only when the meat becomes stale that the oxidisable substrate becomes exhausted and, owing to the disappearance of reducing substances, metmyoglobin can form in other parts of the meat.

Prepacked Meat

The modern trend towards prepackaging has introduced some problems with regard to colour retention. When the meat is cut into smaller portions the freshly exposed surface will have the purplish colour of myoglobin. It is necessary to "bloom" the meat by exposing it to the air for at least 30 minutes after cutting and before packaging. This is done preferably in a chiller to increase the oxygen uptake, since oxygen is more soluble in meat juices at lower temperatures. Then, since customers prefer to see what they are buying, the packaging film must be transparent—the meat must not only have an attractive colour when it is packaged, it must keep its attractive colour during storage. The nature of the film used is therefore very important. It must have a high oxygen permeability in order to maintain a high proportion of oxymyoglobin at the surface. It has been shown that an oxygen permeability of 5 litres/sq.m/day/atm. is necessary for colour retention. The film must also have a suitable moisture permeability. Too high a permeabiilty will allow surface dehydration, thereby causing undesirable colour changes and an equally undesirable weight loss. On the other hand, too low a moisture permeabiilty allows a film of liquid to form on the surface of the meat. Not only is this unsightly, but it also forms an ideal medium for the growth of bacteria. In addition to having suitable oxygen and moisture permeabilities, the film must, of course, have sufficient mechanical strength. For cellophane the problem has been solved in a rather ingenious manner. The base film is of plain cellulose which is very pervious to water and can be made sufficiently thick to provide the necessary strength. One side of the cellulose is coated with a very thin layer of nitrocellulose whose permeability both to oxygen and to moisture is relatively low. The overall permeability of the film is controlled by the thickness of the nitrocellulose coating. Typical thicknesses are about $1/1000''$ for the film and $1/20$ of $1/1000''$ for the coating. The film is applied to the meat with the coated side outwards. The moisture in the meat soaks through the cellulose so that there is only the coating between it and the atmosphere, and the permeability of the coating is the only factor regulating the transfer of moisture from the meat and of oxygen to it. If the film is accidentally applied the wrong way round so that the oxygen has to pass through the thick dry cellulose film as well as the nitrocellulose coating before it reaches the meat, the bright red colour of the meat surface soon disappears.

The problem of colour retention in finely divided meat such as mince or sausage is even more acute. Here, the exposed surface is very large in comparison with the weight of meat. Oxygen can penetrate much more rapidly right through the bulk of meat, and consequently the oxidisable substrates are very quickly used up. The meat can develop the unattractive, dull brown, metmyoglobin colour in a matter of hours, irrespective of whether it is packaged or open to the atmosphere. This is the type of problem which has prompted the meat technologist to join the physiologist in investigation of the reducing mechanisms in muscle tissue. A great deal has been found out but there is a great deal more to learn. It is fairly certain that an enzyme system is involved since iodo-acetate, for instance, inhibits the reduction, but just which enzyme system and what the mechanism is has still to be discovered. In the meantime, the meat technologist has to do something about the problem and if he can't modify the endogenous reducing systems to suit his purpose, he can only fall back on exogenous ones.

Additives

In this country (as in Australia and the U.K. where its use is permitted) sulphur dioxide in the form of sulphite is a usual addition to mince and sausages. Admittedly its main purpose is to inhibit the growth of spoilage organisms, but because of its reducing action, it aids in colour retention as well and will even restore the colour of meat which has come to the end of its endogenous reductants. In countries where sulphur dioxide is not permitted, ascorbic acid and/or nicotinic acid (or niacin) are commonly used. Ascorbic acid is a reducing agent; nicotinic acid is thought to catalyse the oxygenation of myoglobin to oxymyoglobin. In all cases free access of air is essential if the colour is to be retained.

The use of ascorbic acid can introduce another problem. Many reductants, and ascorbate in particular, can react with the oxygen of oxymyoglobin to form hydrogen peroxide. Hydrogen peroxide in the absence of reductants can cleave the porphyrin ring of myoglobin and produce bile pigments which are polypyrrolic compounds, e.g. biliverdin.

In the presence of reductants the process is slowed down and the green pigment choleglobin is formed. There is some doubt as to the structure of this compound but it would appear that the porphyrin ring is unbroken. If the reducing agent contains a sulphydryl group (e.g. cysteine), another green pigment, sulphmyoglobin, is formed. Again the porphyrin ring is left intact, but there is some doubt as to where the sulphur atom is attached. The exact conditions under which these green pigments are formed are by no means clear and experimental work has given conflicting results. Green discoloration of meat can therefore occur quite unexpectedly and we are still not sure how it can be avoided. Green pigments are more of a problem in cured meats in which they occur more frequently than in fresh meat.

When meat is cooked the globin moiety of the pigment is denatured and the haeme is oxidised to the ferric state, thus giving rise to its greyish-brown colour. One theory as to the nature of the cooked meat pigment postulates that the Fe-histidine bond is broken and that the freed co-ordination position of the iron is then occupied by a carbonyl group of the denatured protein. This is based on spectrophotometric evidence and on the chemical properties of the pigment. The actual colour of cooked meat is, of course, not entirely due to the denatured pigment. At high temperatures such as are encountered during roasting or grilling, oxidised and polymerised fats, sugars and proteins all make their contribution.

Cured Meats

Much more meat is consumed in the cured state than we in New Zealand realise. In the United States and particularly in Continental countries pork is the main meat and a very large proportion of this is converted into ham, bacon and cured meat sausages. The meat-curing industry is a very large one indeed, and a great deal of research into the various aspects of the process has been and is still being done.

The preservation of meat by salting goes back to prehistoric times and it is not beyond the bounds of possibility that on some occasions the solar salt which was used contained as an impurity appreciable amounts of nitrate. Nitrate is the clue to the characteristic colour of cured meat. Just when nitrate in the form of saltpetre was first deliberately added to the curing salt is not known. The ancient literature is not of much help because the classical scholars who translated and copied the old manuscripts were a little shaky in their chemistry and frequently confused "natron" (sodium carbonate) with "nitre". It is not until the late Middle Ages that we find definite reference to the use of nitrate in the curing of meat.

The first step in elucidating the nature of cured meat pigment was taken by Polenske in 1891 when he found nitrite in the meat. It was found that nitrite alone could produce the colour more rapidly and surely than could nitrate. A great deal of work by a number of research workers ultimately showed that the red compound was, in fact, a complex of nitric oxide and myoglobin, now usually referred to as nitrosylmyoglobin.

It soon became clear that the first step in the conventional curing process, as far as colour was concerned, was the reduction of nitrate to nitrite and that this was brought about by bacteria. Since our ancestors were less hygiene-conscious than we are, there was normally no trouble about getting enough bacteria into a curing pickle to do the job. A bucketful of an old pickle or a pig's head or some pigs' feet would always get a new pickle under way if it wouldn't start up on its own. The trouble was usually in the other direction. Too many bacteria and particularly the wrong kinds of bacteria could produce some astonishing results, most of them highly undesirable. But over the years the art of meat curing, relying largely on rule-of-thumb methods, enabled a very large and reasonably successful industry to be developed. Nowadays, there is considerable chemical and bacteriological control of curing brines, especially in Denmark and Holland where cured pork in its various forms is a major item of export. The control methods are largely those used by the old curers—salt concentration, temperature and pH. The methods are considerably refined, of course, and based on scientific tests, but they are still fundamentally the same and the experience, judgment and skill of the curer still count for something.

We need not concern ourselves with the bacteriological reduction of nitrate to nitrite because, as chemists, we would naturally think of by-passing this step and of simply adding nitrite to the pickle. Nitrite is, in fact, widely used as an additive in meat curing; so far as colour is concerned, nitrate and bacteria are unnecessary. This is not necessarily true of flavour and other properties of the cured meat however. The usual procedure is to use a mixture of nitrite and nitrate in the curing brines and to cultivate a suitable bacterial flora. Where the final product is heavily spiced, in sausage for instance, nitrite alone is frequently used.

But after the nitrite stage there are still questions to be answered. How, for instance, is the nitrite reduced to nitric oxide? Then again, nitrite is a strong haeme pigment oxidant, so that the iron will initially be in the ferric state. The cured meat pigment, on the other hand, is a ferrous compound. How is this reduction brought about in the presence of nitrite?

The answers to these questions are by no means certain, although a very large amount of work has been done and is still being done. The endogenous reduction of nitrite is thought to involve the cytochrome c oxidation-reduction system, with addition compounds as intermediates. In the presence of ascorbic acid which is fairly widely used in the curing of meat, the intermediates are thought to be addition compounds of ascorbic acid and its radical.

All the theories tend to be somewhat nebulous, and all that we can be certain of is that nitrite, whether added as such or produced *in situ* by the action of bacteria on nitrate, will react with meat pigments to produce a desirable, cured meat colour, that the reaction is favoured by reducing conditions and low pH values and that the addition of extra reductants such as ascorbic acid is an advantage. The cured meat pigment is usually considered to be nitrosylmyoglobin, but it has recently been suggested that even this may not be strictly true. This may seem a shaky foundation on which to build a very large and very successful industry, but the industry carries on with only a moderate amount of trouble.

When cured meat is heated to temperatures above 150°F, the pigment undergoes a further change. The red colour becomes more pinkish (the colour of cooked ham) and much more stable towards oxidation. The pigment is no longer soluble in water but can be extracted with 80 percent acetone and the extract is free from globin. The acetone-extracted pigment is known as nitrosylhaemochrome and, as is usual in this field, there is some doubt as to its structure. Heating has been shown to break the bond between the iron of the haeme and the imidazole nitrogen, but it is not certain what happens then. It is possible that the denatured globin remains attached to the haeme by, for instance, hydrogen bonds which could then be broken by acetone. In this case, the spare co-ordination position of the haeme could be occupied by acetone, and this is the usual theory. But a more recent theory for which there is quite a lot of evidence is that the excess nitrite in the meat forms another nitrosyl group which occupies the spare co-ordination position, and that nitrosyl-haemochrome is actually a dinitrosyl compound. It has also been suggested that a certain amount of the dinitrosyl compound occurs in raw cured meat, the red colour of which is thus due to a mixture of this compound and nitrosylmyoglobin.

The cured meat colour, both cooked and uncooked, although it is much more stable than oxymyoglobin, is nevertheless affected by light, especially by blue and green lights whose wavelengths correspond to the absorption bands of the pigments. Here, the action appears to be a dissociation of the nitric oxide from the haeme, followed by oxidation of the nitric oxide by oxygen. If oxygen is excluded from the meat by the use of an oxygen-impermeable packaging film, and especially if the meat is vacuum-packed, the second step cannot take place and the colour is stable. The cellophone films used for cured meats are coated with nitrocellulose on both sides. Other impermeable films such as polyethylene are also suitable. Suitable lighting of display cabinets to avoid the undesirable wavelengths is, of course, essential.

Cured meats are also subject to green discolorations, and these may be due to several different causes. The first and simplest is usually referred to as "optical greening". If penetration of the curing pickle has not been complete, the meat which has not been cured will have the dull brown colour of metmyoglobin and this will change to the greyish colour of boiled meat when the product is cooked. The neutral colour of the uncured patches will, of course, appear greenish by contrast with the surrounding cured meat. Bacteria can also cause greening either by producing green pigments themselves or by producing hydrogen sulphide which can react with the meat pigments to form the green sulphmyoglobin type of compound. An excess of nitrite can also produce a green colour under certain conditions, but neither the conditions nor the end products have been satisfactorily determined. Irradiation is another process which can cause greening of meat either by the production of sulphmyoglobin or by the cleavage of the porphyrin ring structure or by both.

The meat pigments have been subjected to a great deal of investigation from various angles and by workers in world class, but the amount of useful information (that is, useful to the meat technologist) which has been gained is disappointingly small. However, the attack continues unabated and perhaps startling results which will revolutionise the meat industry, and particularly the meat-curing industry, are just around the corner.

Correction.—The measurement of Transition Probabilities and Oscillator Strengths, by C. R. Boswell, *Chemistry in New Zealand,* Vol. 33, No. 1, February 1969, page 23, second column, line 4,

A_{mn} should read A_n^m

OBITUARY

Max Theodore Christensen, M.Sc., Ph.D.

Dr. M. T. Christensen, Senior Lecturer in Chemistry at University of Canterbury, died recently.

After schooldays at Christchurch Boys' High School, he went to Canterbury College in 1944. In his third year he won the Haydon Prize for the best student of the year in both chemistry and physics, and was awarded a Sir George Grey Scholarship. He took a First Class Honours Degree in Chemistry, then completed a Ph.D. in physics. While doing his Ph.D. he was appointed to the staff of the Chemistry Department. In 1953, on a Sims Empire Scholarship, he went to Oxford and spent two years working with Dr. H. W. Thompson on infra-red spectroscopy.

He was an outstanding teacher with a profound influence on his students. To him they were all-important and he gave generously of his time to them.

His health had been failing for many years but he took his full part in departmental affairs with cheerfulness and an indomitable will to carry on. He is remembered with affection and respect by all.

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Fees will be $35 and residential costs of $15 for five nights and all meals. We would require notice of requirements for Hostel accommodation as early as possible.

Closing date for enrolments would be Thursday, 1st May, and a prospectus is available from the Secretary, Department of University Extension, Private Bag, Auckland. Please indicate intention of enrolling and make an application for the enrolment form as soon as possible.

L. R. Bedggood,
Organiser of Course.

Announcement . . .

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MASS SPECTROMETRY OF ORGANOMETALLIC COMPLEXES

B. H. Robinson, M.Sc., Ph.D.(Cantuar.)
Chemistry Department, University of Otago

In the last few years a large number of organometallic compounds, many of which are industrially important as synthetic intermediates or as catalysts, have been synthesised. Catalytic uses in particular have increased rapidly in the last decade and are responsible for much of the current interest in this field. Our understanding of these catalytic processes is patchy however, principally because of the inadequacy of our knowledge of the structural and physical properties of such compounds.

Recently it has been realized that organometallic complexes can be profitably studied by mass spectrometry. Neutral complexes are usually volatile, of simple composition and available in extensive series of similar constitution. Besides providing a rapid analysis of reaction products, especially those formed in very small yields, a mass spectrum can give detailed structural information and thermodynamic data from a small sample. Further, with a suitable choice of anion or cation it is often possible to obtain the mass spectra of ionic species.

(A) Analysis

Providing that the parent molecular ion A^+ of a compound A can be observed, mass spectrometric analysis allows a rapid determination of elemental composition and molecular weight from only a nanogram of sample. An accurate mass determination to several decimal places is not required as it is with non-metallic compounds because, in most cases, a consideration of the isotope patterns and the chemistry permits the unequivocal assignment of a given ion.

A pure sample is not necessary as the individual components can be analysed from the one spectrum. For example the novel, unstable metal carbonyl $Os_4O_4(CO)_{12}$ was identified initially, solely from a mass spectrum of crude $Os_3(CO)_{12}$.[1]

'Hidden' atoms or groups such as H and N which have proved difficult to detect in the past are clearly revealed by this technique (Fig. 1).[2]

The current interest in nitrogen fixation and catalytic systems should lead to further applications of this type.

Molecular weights obtained from solution measurements can be misleading and a mass measurement provides a useful check. The complexes $[Mn(CO)_3SR]_n$ were originally formulated as trimers on the basis of osmometric weights in benzene, but only tetrametric ions were found in the mass spectra. Subsequent chemical work agrees with the mass spectral data.[3]

Because of pyrolysis, or fragmentation before the ion reaches the detector, or low abundance, the parent molecular ion may not be present (see Fig. 1), and there is no general method of discovering if this is so. A change in source temperature or electron beam energy may be helpful but more often a complete identification of all fragment ions is necessary.

(B) Structure—Fragmentation Relationships

Fragmentation of the molecular ion by electron impact yields ions, the number and type giving valuable information on the stereochemistry and electronic environment of the metal. In favourable cases further information on breakdown mechanisms may be obtained from the metastable ions.

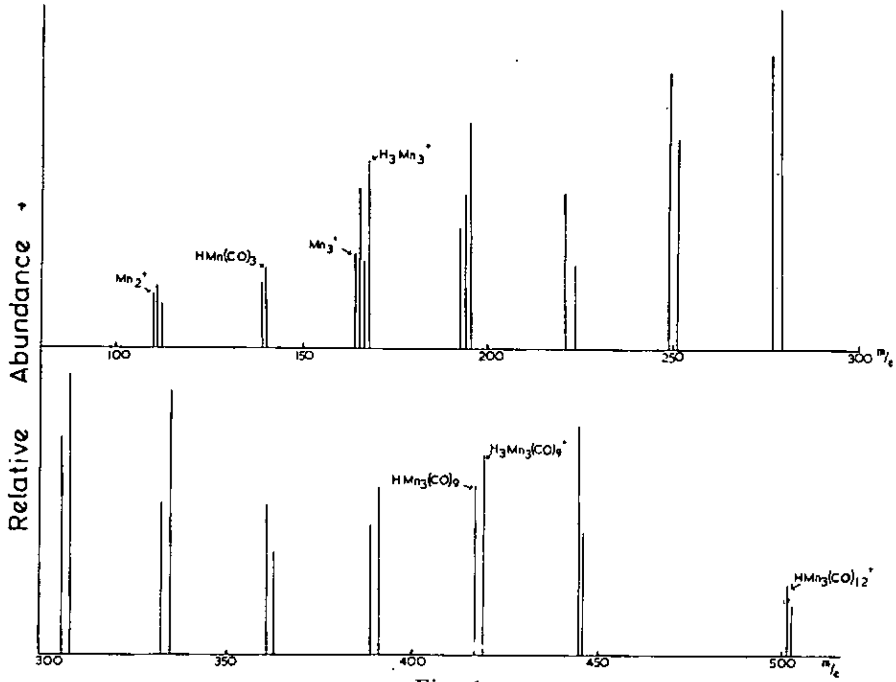

Fig. 1

A feature of the mass spectra of complexes containing π or fluorocarbon ligands is the prominence of ions formed by the transfer of ligand fragments to the metal atom. For example, ions of the type $FMn(CO)_n$ ($n=5\rightarrow0$) are of major abundance in the spectrum of $CF_3Mn(CO)_5$.[4] Transfer of ring substituents in ferrocene-type ions is also common. In general, these rearrangements are favoured when a comparatively stable neutral molecule is eliminated.

Metal Carbonyls and Derivatives

All of the carbonyl-containing complexes that have beeen studied fragment initially by the successive loss of CO (Figs. 1, 2).

$$M_z(CO)^+_n \xrightarrow{e} M_z(CO)^+_{n-1} + CO$$

$$M_z(CO)_{n-1} \xrightarrow{e} M_z(CO)_{n-2} + CO \quad \text{etc.}$$

Analysis of the metastable ions for such breakdowns has confirmed that a simultaneous loss of two CO groups is possible (c.f. Fig. 1). The minimum number of CO groups in a carbonyl complex is therefore readily determined.

Secondary fragmentation of the M_z^+ or $M_z(CO)^+_{n-m}$ ions proceeds either by fission of metal-metal bonds or by loss or decomposition of a ligand, the extent of each process varying with the type of carbonyl complex.

Metal Carbonyls: Metal-metal cleavage is not important with carbonyl clusters[1,5] e.g. $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, and the number of atoms in M_z^+ is the size of the cluster. In contrast, fission often occurs during the loss of CO in binuclear and linear polynuclear carbonyls, and polymeric ions may be in low abundance or even absent (Fig. 2).

The geometry of the metal framework can sometimes be inferred from the fragmentation pattern. Peaks corresponding to the ions $Co_3(CO)_n^+$ (n 0—6) are present in the spectrum of $Co_4(CO)_{12}$, probably formed by the breakdown

$$Co_4(CO)^+_{12} \rightarrow Co_4(CO)^+_n + 12-n(CO) \qquad (n=9-12)$$

$$\downarrow$$

$$Co(CO)^+_{6-m} + Co_3(CO)^+_6 \rightarrow Co_3(CO)^+_m \qquad (m=0-6)$$

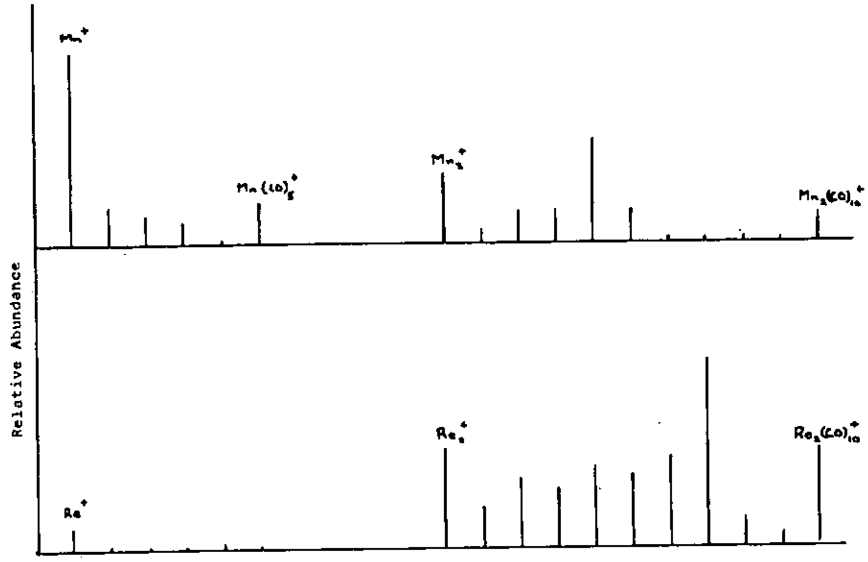

Fig. 2 Spectrum of $Mn_2(CO)_{10}$ & $^{187}Re_2(CO)_{10}$

This suggests that one cobalt is in a different structural environment to the other three, as indeed a single-crystal X-ray structural analysis has confirmed. The appearance of doubly-charged species $Os_3(CO)_n^{2+}$ (n = 0—11) in the spectrum of $Os_4O_4(CO)_{12}$ is consistent with a non-symmetrical cluster. Since the distribution pattern is similar to that in the spectrum of $Os_3(CO)_{12}$ it is reasonable to write this compound as an adduct, $OsO_4.Os_3(CO)_{12}$.[1] The ions probably arise from a disproportionation reaction,

$$OsO_4.Os_3(CO)_{11}^{+} \rightarrow Os_3(CO)_{11}^{2+} + OsO_4^{-}$$

Cleavage of bridging CO bonds usually occurs in preference to cleavage of terminal CO bonds. Ion species, in which the number of carbonyl groups per metal is in excess of that for a symmetrical distribution of CO, indicate the existence of bridging groups, as CO transfer has not been observed. Thus the ion $Fe(CO)_5^+$ occurs in high abundance in the spectra of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$.

Finally, although ions of the type $[M(CO)_nC]^+$ are fairly common, no ions such as $[M(CO)_nO]^+$ have ever been found, consistent with metal-carbon bonding.

Carbonyl Halides: Both halogen and CO are lost from mononuclear carbonyl halides. In dimeric halides there is a strong retention of the M_2X_2 nucleus and CO is removed before cleavage of the bridging unit (c.f. bridging carbonyls). This criterion may be used to differentiate between complexes with terminal or bridging halogen groups.

Carbonyl Hydrides: Apparently the consecutive losses of CO or H atoms are competitive processes in carbonyl hydrides (Fig. 1). Hydrogen-containing metal ions, $M_zH_n^+$, are usually present, confirming that the hydrogen is bonded to the metal.

Carbonyl Nitrosyls: Carbon monoxide is lost before NO. This may be related to the greater stability of the M-NO bond in complexes where the 18-electron rule is not obeyed (as in ion species). In addition, a loss of CO is a 2-electron transfer whilst removal of NO is a 3-electron transfer.

Phosphorus, Arsenic and bridging Sulphur Carbonyl Complexes: There seems to be no general breakdown pattern of $[M_zL_y]^+$ ions for tertiary phosphorus and arsine complexes. In some cases ligand fragmentation occurs, while in others total loss of ligand is the process which predominates to such an extent that it is difficult to obtain anything but the ligand mass spectrum. Phosphorus-bridged ions are more stable and it is possible to differentiate between linear and cyclic-bridged species. Monomeric ions, $[M(CO)_nP_2R_4]^+$ or $[M(CO)_nPR_2]^+$, occur in reasonable abundance in spectra of linear-bridged complexes only.

The metal-sulphur ring structure is apparently one of the most stable units since all dissociation processes in sulphur carbonyl complexes preserve the M_2S_2 nucleus. Carbonyl-free ions tend to lose the $CH_3\cdot$ radical or an olefin with breaking of the C-S bond, even when R is a fluorocarbon group.

π-Complexes

π-Cyclopentadienyl compounds degrade initially by the loss of acetylene,

$$(C_5H_5)_nM^+ \xrightarrow{-C_2H_2} (C_3H_3)M(C_5H_5)^+_{n-1}$$

$$\xrightarrow{-C_2H_2} (C_3H_3)_2M(C_5H_5)^+_{n-2} \quad \text{etc.}$$

Cyclopropenyl ions are also formed preferentially in complexes such as $C_3H_5M(CO)_nC_5H_5$, where C_3H_5 is a σ-bonded allyl group. Carbon monoxide and C_2H_2 losses are competing processes in $C_5H_5M(CO)_n$ compounds. Cyclopentadienyl metal carbonyl derivatives of first-row transition metals also characteristically exhibit $(C_5H_5)_2M^+$ ions in their spectra.

Many other π-complexes have been investigated and found to undergo widely differing degradations. Acetylene, olefin, methylene, hydrogen or metal extrusions are common and, in general, the fragmentation patterns closely resemble those of the free ligands.

(C) Bond Stability and Thermodynamic Data

Winters and Kiser[6] have pointed out that the relative abundances of positive ions produced under electron impact vary with the electron beam energy. The abundance of an ion is a function of the rates of decomposition along several reaction paths rather than upon the energy of the ion alone. Hence caution should be exercised when relating the stability, with respect to dissociation, of an ion to its abundance in the mass spectrum.

Another difficulty is that mass spectra give information on the stability of ionic species in excited states and one can only extrapolate back to bond energies in the ground state, sometimes with results conflicting with the chemical properties of the compound.

Despite these approximations most trends in bond stability within a series of similar compounds are in accord with theoretical and other experimental data. Certainly, as predicted, metal-metal cleavage in ions of polynuclear compounds does decrease as the atomic number of the metal in a Group increases. Other trends have been noted in Section (B).

Consider the fragmentation of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (Fig. 2).

$$M_2(CO)_{10}^+ \xrightarrow{-nCO} M_2(CO)_{10-n}^+ \quad \text{(i)}$$

$$\downarrow$$

$$M(CO)_5^+ \xrightarrow{-nCO} M(CO)_{5-n}^+ \quad \text{(ii)}$$

The total abundance of species (i) compared with the total abundance of species (ii) should increase as the metal-metal bond strength increases. The experimental values are 59:41%(Mn) and 96:4%(Re). Doubly-charged ions, $Re_2(CO)_{10-n}^{2+}$ are also present in the rhenium spectrum indicative of a strong Re-Re bond since it has survived two ionization processes.

These correlations can be placed on a quantitative basis. The minimum energy required to remove an electron from the radical species $\cdot M(CO)_5$ and the ion $M_2(CO)_{10}^+$ is respectively the ionization potential (I.P.) of $\cdot M(CO)_5$ and appearance potential (A.P.) of $M(CO)_5^+$.

$$\cdot M(CO)_5 + e \rightarrow \cdot M(CO)_5^+ + 2e \qquad (1)$$

$$M_2(CO)_{10} + e \rightarrow M(CO)_5^+ + \cdot M(CO)_5 + 2e \qquad (2)$$

Assuming that the ions produced in (1) and (2) are energetically the same, then the difference is the dissociation

$$M_2(CO)_{10} \rightarrow 2 \cdot M(CO)_5$$

Therefore, dissociation energy

$$(M_2(CO)_{10}) = A.P(M(CO)_5)^+ - IP(\cdot M(CO)_5)$$

Svec and Junk[7] found the dissociation energies to be

Mn-Mn	Re-Re	Mn-Re
18.9 ± 1.4	43.7	52.6 kcal

in accord with the qualitative correlations. The value for D(Mn-Mn) may be compared with the 34 kcal obtained from calorimetric measurements. Note also the enhanced stability of the heteronuclear Mn-Re bond.

A number of other molecular ionization potentials, appearance potentials of positive and negative ions, heats of formation and dissociation energies have been reported (see ref. 8) providing useful reference data for the theoretical and synthetic chemist.

Finally, in the mass spectrum of the tetrahedral cluster $CH_3CCo_3(CO)_9$ (Fig. 3) and its derivatives, secondary fragmentation of the $CH_3CCo_3^+$ ion is by loss of cobalt with retention of the apical carbon atom (Fig. 4).

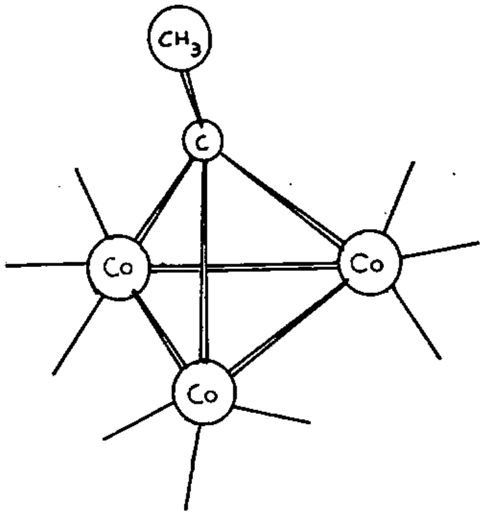

Fig. 3 Structure of $CH_3CCo_3(CO)_9$

Cobalt-cobalt interaction would seem to be weak and the apical carbon atom is necessary for cluster stability. It is likely that Co-Co cleavage increases with decreasing electronegativity of the substituent on the carbon atom (see Fig. 5).[9]

Cobalt-cobalt bond fission is also influenced by the ligands on each cobalt atom. Complexes of Lewis bases, such as $CH_3CCo_3(CO)_8Ph_3P$, show no tendency to lose cobalt whilst facile fission does occur in π complexes like $CH_3CCo_3(CO)_6$ (mesitylene). Indeed it would appear that the mass spectra and a measurement of D(Co-Co) will provide a sensitive method for estimating the relative σ and π contribution to a Co-Ligand bond.

$$CH_3CCo_3(CO)_9^+ \rightarrow CH_3CCo_3(CO)_{9-n}^+$$
$$\downarrow$$
$$CH_3CCo_3^+ \rightarrow CH_3CCo_2^+ \rightarrow CH_3CCo^+$$

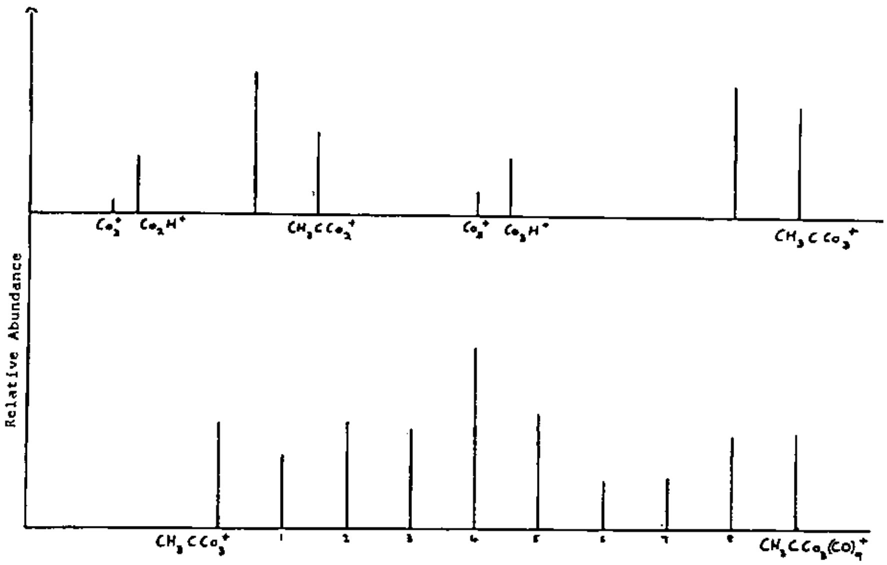

Fig. 4 Spectrum of $CH_3CCo_3(CO)_9$

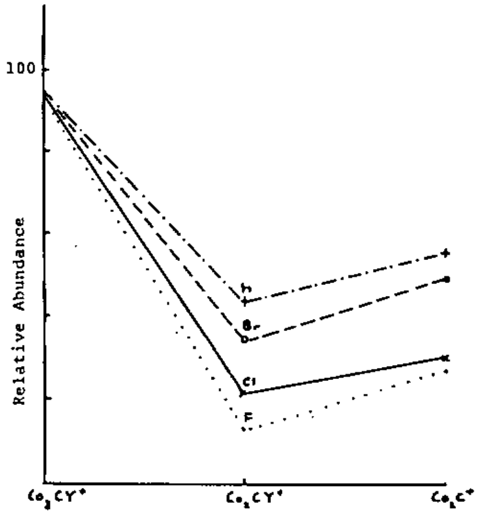

Fig. 5

* * *

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THE MICROBIOLOGICAL QUALITY OF WATER

A. P. Mulcock

Microbiology Department, Lincoln College, Canterbury

THE industrial chemist often finds himself involved in microbiology, particularly when examining potable or process water. This field is one in which most chemists have little background, and misconceptions and misinterpretations can easily arise. The following article by a microbiologist who is a member of the Canterbury branch, explains some fundamentals of the microbiological examination of waters.

There has been a very substantial increase in the use of water in this country recently, due partly to the increase in population and partly to the rapid development of agriculture and industry. This has brought many problems connected both with the supply of good quality water and with the disposal of effluents. These problems are likely to become more widespread and more difficult to solve as the population increases and more industries spring up.

The possibility that water could act as a transmitting agent for disease-producing organisms was suspected many years before bacteriology became established as a science. In 1854 the link between disease and water was first firmly established when an epidemic of cholera was shown to have had its origin in polluted water. In his book "The Cholera Years; the United States in 1832, 1849 and 1866", Rosenberg[1] quotes a contemporary author as saying "a standing joke maintained that city water was far better than any other since it served as a purgative as well as for washing and cooking". Since that time many studies have been made on the types of micro-organism present in water, their importance to public health, and methods of identifying and destroying them.

The present generation has become so accustomed to having a plentiful supply of safe, potable water by simply turning on a tap that the value and importance of this amenity are perhaps not fully realised. With increasing population and industrialisation it will soon become evident that supplies of water suitable for household and industrial use are exhaustable and that, because water is essential not only for day to day living but also for industrial processing, it will have to be paid for, whatever its cost.

Water microbiology is concerned with micro-organisms present in natural waters—rivers, lakes, ponds and oceans, their existence in these environments, their ability to bring about the breakdown of organic matter, and their influence on the balance between plants and animals which are present in these environments. A most important aspect of this work is the breakdown of materials put into water by man in the form of sewage and industrial wastes. The methods of waste disposal currently used serve only to intensify the problems associated with the provision of water suitable for drinking and public recreation.

From the middle of the last century when it became known that water was a potential carrier of micro-organisms which could endanger the health and life of human beings, much effort has been put into finding tests which would reveal the presence of pathogenic organisms in water supplies. The human pathogens most frequently transmitted by water are those which cause infections of the gut, e.g. typhoid and para-typhoid fevers, dysentery and cholera. The organisms which cause these diseases are usually present in faeces and urine of people who have the disease, or who have at one time or another been infected. If domestic or industrial water supplies become contaminated with them further outbreaks of the disease may occur.

The direct search for the presence of specific pathogenic bacteria in water is unlikely to yield satisfactory results for a number of reasons. Firstly, if a water supply receives a single contaminating dose of micro-organisms, e.g., excreta from a carrier of typhoid fever, it will probably be some days or even weeks before a case of the disease appears, and probably still further time will elapse before the disease is recognised by the medical authorities. Secondly, many pathogenic organisms die fairly rapidly in water and it is unlikely that their presence could be demonstrated. Thirdly, because they are usually present as a very small proportion of the total microbial population, the technical difficulties of isolating small numbers of pathogens in the presence of normal aquatic bacteria and soil micro-organisms are very great. Because of this, attention was directed towards the demonstration of bacterial species which were of known faecal origin, but not necessarily pathogenic—in particular the coliform group, the faecal streptococci and *Clostridium welchii*. These often are present in the human intestine in very great numbers, even exceeding those of pathogenic intestinal micro-organisms. Furthermore, they die more slowly in water than the pathogens.

The science of water sanitation and water bacteriology began obscurely. In 1880 von Fritch described *Klebsiella pneumoniae* and *K. rhinoscleromatis* as organisms characteristic of faecal contamination by humans,[2] and thus started the work on bacteria as indicators of microbiological quality of water. Next, Escherich[2] in 1885 published a description of *Bacillus coli*, also an indicator of faecal pollution. At that time it was considered that human faeces were a dangerous polluting agency, whilst those of other warm-blooded animals were not a hazard to man. Subsequent investigations have given rise to very extensive writings on the coliform group, especially on the frequently controversial systems of their identification, classification and the interpretation of their significance in water supplies, so that now they are one of the best documented groups of micro-organisms. Most work has been directed towards finding methods which will differentiate between the so-called faecal coliform organisms and those known as non-faecal types. By definition faecal coliforms are confined to and multiply only in the gut of man and warm-blooded animals; the non-faecal coliform organisms are found living and multiplying in the soil, on grasses and other natural environments. Whether or not it is possible to distinguish simply between these two groups is a matter for debate, but one fact has certainly been shown very clearly—that no one test is able to make this distinction at present. It is now generally conceded that the only possible way to differentiate between the different types of coliform organisms is to use a series of tests to reveal the biochemical and physiological peculiarities of the strain under test.

If a positive faecal coliform test is obtained in a water supply the results must be interpreted with considerable reserve, particularly if they are to be used for enforcing standards governing the use of the water for specific purposes. Because the multiplication and death of a living population of micro-organisms are involved in bacteriological testing, there are a great number of factors affecting these results which would not affect the results of purely chemical tests, such as those for the presence of arsenic, copper or lead.

Since coliform organisms can be detected in very small numbers, as few as one organism in 100 ml water, the presence of this organism affords a very delicate and specific test for contamination. Sometimes comprehensive and complex tests are made to ascertain numbers of faecal coliform organisms. However, it is far more important to examine numerous samples of water using simple tests than to take occasional samples and examine them in every detail. Further, it must be remembered that a positive coliform test is not in itself an indication of pathogenic micro-organisms. *Escherichia coli* is not a pathogen except under special circumstances, e.g. in certain types of diarrhoea in infants and small animals, and although its presence has been considered to be a good indicator of faecal pollution, its absence does not indicate that water is free from pathogenic species. For instance, species of *Salmonella* are highly pathogenic and may be present in water supplies without *E. coli,* as may other pathogenic bacterial species and viruses.

Another frequent source of error occurs when interpreting results from different types of water; for instance, filtered water which has little or no suspended material may give a very different result from water taken from a river in a state of turbulence with a considerable amount of fine suspended matter on to which the organisms may rapidly become absorbed—yet both waters may have the same organisms present. Again, there appears to be considerable conflict of opinion between authorities concerning the ability of coliform organisms from man and animals to survive in sea water.

Bacteria in non-domestic water supplies may prove a very considerable problem; manufacturers of pharmaceutical products, for example, require a water with a much higher standard than that required for domestic purposes. Not only must the water be completely free from all micro-organisms, but their metabolic products such as pyrogens must also be absent. Some water supplies may be quite suitable for drinking yet still have large numbers of micro-organisms in them. Harmless psychrophilic bacteria which are frequently found in potable water can cause problems to manufacturing industries, e.g. a species of *Pseudomonas* in a municipal water supply was responsible for the spoilage of cottage cheese.[3] Another example is the organism *Sphaerotilus natans,* which grows in great tassels attached to solid objects in dirty running water, destroys the recreational value of natural waters and causes a great deal of trouble in water treatment plants.

Bacterial growth may occur even in apparently pure water. Chambers and Clarke[4] refer to the work of Rhines who found that there was a very considerable increase in the numbers of micro-organisms in distilled water from an all-glass system. Rhines heated water from a distilled water line in a building, and after adding H_2SO_4 and $KMNO_4$ distilled it into a final retort venting 50 percent of the output. The water from the retort was distilled through a packed column, the bottom and top layers being respectively Berl saddles (porcelain) and quartz pebbles. Fifty percent of the output of the column was condensed and returned to the retort. The remaining 50 percent was recovered by the Vycor condenser that followed the packed column. After this "pure" water had been stored at room temperature in a glass-stoppered pyrex bottle for four days there were 700 micro-organisms per ml, but after nine days the count had risen to 40,000 per ml. The numbers remained close to this figure for 45 days, after which they began to diminish.

The microbiology of water supplies is basically a study of the biology of the microbial populations' ability to adapt to changing conditions. Thus it is important to know in what way the micro-organisms from the gut of man and animals react to an environment, firstly of sewage, secondly in bodies of water when the sewage has discharged either into lakes or rivers, and finally in the saline environment of the sea. The intensive research on the coliform group of organisms in the laboratory during a period of more than 80 years has shown that they exhibit a marked adaptability and physiological potential, but it is evident that further work into their physiology in relation to survival and activity away from the intestinal tract, especially in fresh and salt water and in soil, is long overdue.

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THE REGISTRY

The following were elected on 7/11/68:

Fellows

BETTY, Stewart Morris, B.Sc., Dip.Ind.Chem., Empire Rubber Mills Ltd., Christchurch (General maanger).

HARTSHORN, Michael Philip, B.Sc.(Hons.) (Lond.), A.R.C.S., D.Phil.(Oxon.), Chemistry Department, University of Canterbury (Reader).

MANN, Bartholomew Robin, M.Sc., Ph.D.(N.Z.), G. L. Bowron & Co. Ltd., Christchurch (Director and Factory Manager).

Associates

BAKER, Kenneth Matthew, M.Sc., Ph.D.(Auck.), University Chemical Laboratory, Cambridge, England (Post Doctoral Fellow).

BANNATYNE, William Reid, B.Sc., Ph.D. (Glasgow), Food Technology Dept., Massey University (Senior Lecturer).

BARRA, Esmonde Michael, B.Sc., Alliance Textiles (N.Z.) Ltd., Timaru (Industrial Chemist).

CLARK, Dallas Graham Sidey, M.Sc.(Otago), Biochemistry Dept., Medical School, Dunedin (Assistant Lecturer).

DANSTED, Erik, B.Sc.(Hons.), Ph.D.(Cantua.), Chemistry Dept., University of Canterbury (Post-Doctoral Research Fellow).

GODFREY, Mrs. Elizabeth, M.Sc.(Auck.), Chemistry Dept., Auckland University (Temporary Junior Lecturer).

GRAY, Ian Keith, M.Agr.Sc.(Massey), N.Z. Dairy Research Institute, Palmerston North (Biochemist).

GREIG, Michael Stuart McRae, B.Sc.(Hons.) (Otago), N.Z. Forest Products Ltd., Tokoroa (Chemist).

GRIGOR, Murray Robert, B.Sc.(Hons.)(Cantua.), Endocrinology Research Dept., Medical School, Dunedin (Research Officer).

LANGDON, Alan George, M.Sc., Ph.D.(Well.), Chemistry Dept., University of North Carolina, U.S.A. (Research Fellow).

LARKING, Peter William, B.Sc.(Hons.)(Otago), Wallaceville Dairy Laboratory, Department of Agriculture, Upper Hutt (Dairy Chemist).

MANNING, Terence David Ross, M.Sc., Ph.D. (Auck.), Chemistry Division, D.S.I.R., Gracefield (Scientist).

MOUNCEY, Robert Ian, B.Sc., Formica (N.Z.) Ltd., Auckland (Development Chemist).

RANDS, David Barrett, M.Sc.(Auck.), Chemistry Dept., Auckland University (Junior Lecturer).

RICHARDSON, Ralph Alan, M.Sc.(Auck.), Chemistry Dept., Auckland University (Junior Lecturer).

ROEPER, Jacob, N.Z. Dairy Research Institute, Palmerston North (Research Officer).

SHOOTER, David, M.Sc.(Auck.), Chemistry Dept., Auckland University (Ph.D. Student).

SUMNER, Rodney Howard, M.Sc.(Auck.), Chemistry Dept., University of Alberta, Canada (Graduate Teaching Assistant).

TAYLOR, Michael William, B.Sc.(Hons.) (Cantua.), N.Z. Dairy Research Institute, Palmerston North (Chemist).

WITHERS, Rhys Bernard, B.E.Chem.(Hons.) (Cantua.), W. Gregg & Co. Ltd., Dunedin (Chemical Engineer).

Resignation

The resignation of Dr. J. M. THORP was accepted.

Cancellation

The membership of Miss R. E. C. MUNRO was cancelled for non-payment of subscriptions.

* * *

R.I.C. PUBLICATIONS

Orders for R.I.C. Reviews Volume 2 (two issues) may be sent to the Registrar before April 30th, accompanied by a remittance for $3.25.

The Registrar again has stocks of all R.I.C. Monographs for Teachers except No. 5, "Principles of Chemical Equilibrium", which is now out of print.

He also has a limited number of the following:

Chemistry, Medicine and Nutrition	$1.80
Laboratory Handbook of Toxic Agents	$2.00
Russian for Chemists—P. L. Wyvill	$2.00
Teacher Training of Chemistry Graduates—An Enquiry	$0.40

BRANCH NOTES

AUCKLAND

University

Three graduates of the University were recently awarded the degree of D.Sc.—Dr. G. N. Jones, for contributions to the field of analytical and radiochemistry; Dr. W. I. Taylor, for contributions to organic chemistry; Associate-Professor T. N. Waters, for contributions to the field of structural chemistry.

Professor L. H. Briggs has returned from refresher leave as Visiting Professor of Medicinal Chemistry at the School of Pharmacy, University of North Carolina and at the Chemistry and Life Sciences Laboratory of the Research Triangle Institute, Durham, N.C. While in the U.S.A. Professor Briggs was elected to Honorary Membership of the American Pharmaceutical Society and was appointed a Robert A. Welch Foundation Lecturer to lecture in Texan Universities.

Dr. G. A. Wright recently returned from leave spent at the Technical University of Lyngby, Denmark, where he held a Rask-Ørsted Research Fellowship.

Enrolments in chemistry have again shown substantial increases—at Stage I to about 850 and Stage II to about 180. They are about the same as in recent years at Stage III and Honours levels.

Technical Institute

Increases in the numbers of students taking chemistry have occurred at most levels.

Fertiliser Manufacturers' Research Association

The new research laboratory of F.M.R.A. at Otara was officially opened on 3rd March by Mr. R. A. Warburton. This extension reflects the growth of this association whose research expenditure this year will exceed $100,000 (60 percent provided by the industry). Recent additions to the staff at Otara are Mr. T. P. Dobbie, B.E.(Cant.) and Dr. M. S. White, M.Sc.(Auck.), Ph.D.(Tas.). Dr. White undertook research at Tasmania and at the University of Pennsylvania before taking up his present post.

Fruit Research Division

Dr. R. L. Bielski was awarded the New Zealand Association of Scientists' Research Medal at a meeting of the Auckland Branch, New Zealand Institute of Chemistry, in November 1968. Dr. Bielski, who received the award for his work on phosphate nutrition of plants, belongs to a small group of workers in the Plant Nutrition Section who have already won the Research Medal twice.

WAIKATO

The University of Waikato has been granted $4 million to establish a School of Science which will open for teaching in 1970. Construction of the first building in the School has begun and it is expected that the first staff appointments will be made shortly.

Mr. F. S. Pickering, Chemist in Charge of the Chemical Servicing at Ruakura Animal Research Station has resigned to join the staff of C.S.I.R.O., Division of Animal Physiology and Pastoral Research Laboratory, Armidale, N.S.W.

Dr. P. Nottingham has returned to the Meat Industries Research Institute after working in 1968 in the Department of Bacteriology, University of California, Davis, studying anaerobic bacteria.

Dr. H. E. Annett and his wife are shortly to visit England for a six months holiday.

WELLINGTON

Chemistry Division

Dr. G. J. Leary and Mr. H. M. Stone have recently arrived back from England. Dr. Leary spent 18 months working at the Royal Institution, under Nobel Laureate Professor Porter, on photochemical reactions relating to photosynthesis. Mr. Stone spent 15 months at the Home Office Forensic Laboratories at Aldermaston.

Mr. D. F. Mertz has accepted a two-year contract with the United Nations to participate in the establishment of a Food Processing Unit in Taiwan.

Dr. J. F. Young leaves at the end of April to take up a two-year appointment with the Portland Cement Association's Research and Development Division at Stokie, Illinois, U.S.A. He will be continuing research in the basic chemistry of cement hydration.

Dr. M. P. Heenan, a graduate in biochemistry from V.U.W., has joined the Pesticides Section to investigate the metabolism of pesticides.

Mr. N. J. Eggers has joined the Food and Drugs Section and will be dealing with wines and fruit juices. Mr. Eggers is also a graduate of V.U.W.

Mr. W. C. Tennant left late in March to spend a year as a Teaching Fellow at the University of N.S.W., Sydney, where he will be working with Professor Golding.

Physics and Engineering Laboratory

Mr. G. J. Schafer was presented with the Corrosion Medal at the Annual Conference of the Australasian Corrosion Association in November last year.

Victoria University

Dr. N. J. R. Field has taken up a Temporary Lectureship in Chemistry. Dr. Field, who studied for B.A. and D.Phil. at Oxford, has research interests in electrochemistry and photochemistry.

Dr. V. C. Reinsborough has arrived from the University of Tasmania to assume the post of Research Fellow in the newly established Joint Mineral Sciences Research Laboratory. Dr. Reinsborough's research interests concern mainly the physical chemistry of molten organic salts.

Junior Branch

The Junior Branch is being organized this year by Miss S. Cocks, of Wellington Girls' College, with the assistance of Mr. C. L. H. Stonyer as Branch Committee representative.

Successful Opening Meeting

The Panel Discussion on Drugs which opened the Wellington Branch's 1969 programme was outstandingly popular and successful. This joint meeting with the Institute's Junior Branch was attended by an estimated 400 people who filled a lecture theatre at V.U.W. to hear three aspects of drug abuse from local speakers directly concerned with the problem. Mr. C. R. Henwood, a toxicologist at Chemistry Division, outlined the effects of drugs and considered the dangers of their unsupervised use. Mr. R. J. Walton, Chief Superintendent of the Criminal Investigation Bureau, discussed drug abuse from a police point of view and emphasized the importance of preventing an increase in drug trafficking in this country. The usefulness and limitations of drugs in psychiatry, with reference particularly to careless prescribing, were described by Dr. D. G. McLachlan, Director of the Department of Psychiatry at Wellington Hospital. The panel then answered a wide range of questions from the audience. It was particularly encouraging to hear personal points of view as well as technical information from qualified speakers.

CANTERBURY

The February meeting of the branch took the form of a lecture-visit to the Medical Unit, The Princess Margaret Hospital, Christchurch. The meeting was preceded by a buffet tea and about 80 members, wives, and students enjoyed a most interesting series of talks from staff members which were linked by a commentary by Dr. A. C. Arcus, Senior Biochemist in the unit.

Dr. R. V. Peryman, who has been working at the Leather and Shoe Research Institute, Gracefield, on secondment, has returned to the Wool Research Organisation, Lincoln.

Mr. L. R. Brown has transferred from Kempthorne Prosser's Hornby works to become Works Manager at their Wanganui plant.

Mr. P. W. Craighead has transferred from Fletcher Plywood, Christchurch, to their Plyco Division at Taupo.

Dr. M. B. Jameson after a year with Volunteer Service Abroad in Borneo has returned to New Zealand and is now with the N.Z. Refining Co., Wellington.

Mr. J. D. Murdoch, formerly Head of Science, has been appointed Deputy Principal at Cashmere High School, Christchurch.

Mr. T. C. Ralfe who recently returned from two years with the Education Department in Sarawak, has been appointed to the Curriculum Unit, Department of Education, Wellington.

Dr. W. S .Metcalf and Mrs. M. G. Metcalf have returned to the University of Canterbury and the Medical Unit, The Princess Margaret Hospital respectively, after a year's study leave in Boston, U.S.A.

Professor L. F. Philips has returned to the University of Canterbury after spending 15 months in U.S.A. on a Harkness Fellowship.

Dr. B. R. Penfold, Reader in Chemistry, Canterbury University, has been appointed to a personal Chair in the Chemistry Department. He is at present on sabbatical leave at the University of British Columbia, Vancouver.

DUNEDIN

Mr. R. G. Cunninghame has resigned from the staff of the Chemistry Department and is en route to London to complete the requirements for his Ph.D. with Professor Nyholm at University College.

Dr. I. D. Watson has returned from sabbatical leave spent at Imperial College of Science and Technology, London, where he worked for a year with Professor J. S. Rowlinson in the Department of Chemical Engineering and Technology.

During his return from study leave at the University of Oregon, Professor M. H. Panckhurst visited universities and research establishments in Japan and Australia.

Professor H. Parton has recently been appointed Acting Vice-Chancellor in the University.

Dr. R. A. Matheson has taken up an appointment as Senior Lecturer in Physical Chemistry at Otago University.

The local committee has been set up to implement detailed arrangements for the Institute Conference in August. It is hoped to make this a fully-residential conference and so the new Centennial Hall hostel will be made available for delegates who wish to live on the campus. Pre-conference symposia in the fields of Organic Chemistry, Biochemistry, Geochemistry and Analytical Chemistry are to be held on the Monday. The first newsletter about the conference should be circulated during the next few weeks.

BOOK REVIEWS

Modern Methods of Chemical Analysis, by R. L. Pecsok and L. D. Shields (John Wiley and Sons, 1968). 480 pages. Price $Aust.9.95.

In this book the authors have attempted to describe Analytical Chemistry, as it is currently practised, to non-specialising students. Within the general categories of separation techniques, instrumental methods and equilibria they have been largely successful. It is particularly pleasing to note that they have attempted to explain in some detail the physical and chemical principles on which techniques are based. Another pleasing feature of the book is the inclusion of examples and problems in most chapters. However it is felt that the chapters on chromatography would be considerably improved by the inclusion of specific examples.

The major limitation of this book is that no attempt has been made to provide a comprehensive cover of modern methods of analysis as one might suspect from the title. The book is primarily concerned with techniques which are normally associated with organic chemistry and biochemistry. Consequently, topics such as atomic absorption spectrophotometry and complexometric titrations are not mentioned, and polarography and related topics are mentioned only briefly. For this reason the book appears inadequate for a general course in analytical chemistry. There are other features which are not entirely satisfactory, e.g. it seems that the chapters on the effects of molecular structure on acidity and kinetics are hardly related to Analytical Chemistry even if one does accept the all-embracing definition proposed by the authors. However, my overall impression is that this is a good book, suitable for those interested in organic and biochemistry, but not for those interested in general or inorganic aspects of analytical chemistry. J. AGGETT.

The Chemistry of Sulphides. Edited by Arthur V. Tobolosky, Interscience Publishers, 1968. 271 pages. Price $NZ12.95.

This book contains some of the papers given at the Princeton Conference on the Chemistry of Sulphides held June 29th-July 1st, 1966, this conference being the third major one sponsored by the Sulphur Institute of Washington and London. The book is divided, as was the conference, into three sections, Fundamental Chemistry of Sulphides, Sulphide containing Polymers, and Sulphides in Biological Systems, but apparently a number of papers in the latter section were not available for inclusion.

The papers vary greatly in length and content. For example, J. B. Hynes and J. W. Greidanus's paper on "Transmission of Electronic Effects in Certain Sulphides" is a general review of the results of recent physical methods, followed by discussion of some of their own results with N.M.R.; W. L. Jolly's paper on "Recent Studies of Sulphur-Nitrogen Compounds" and O. P. Strausy's and H. E. Gunning's papers on "Synthesis of Sulphur Compounds by Singlet and Triplet Sulphur Atom Reactions" are predominantly reviews of recent work in their own laboratories, while T. K. Wiewiorowski's and F. J. Touro's paper "The Sulphur-Hydrogen Sulphur" system is in the format of an original paper suitable for, say, the Journal of Physical Chemistry.

Most people working in the field of sulphur chemistry would find some specific papers to be of great interest and most of the others of general interest as a guide to current research fields. However, this reviewer believes it would be better if papers from such conferences were published in the appropriate standard journals rather than in book form, as the high price of the book ($12.95 in this case) makes it outside the budget of the individual and means that it must be well down the priority list for libraries with limited finances.

J. E. PACKER.

Oxidation and Combustion Reviews Vol. 2. Edited by C. F. H. Tipper, Elsevier Publishing Company, 1967, £7 10s. Sterling.

Contents: Thermal explosion theory, P. Gray and P. R. Lee; Some fundamentals of combustion instability, R. F. Salant and Tan-Yi Toong; The use of adiabatic compression and mass spectrometry in the study of combustion, A. Martinengo and K. H. Homann; Trapped radicals and combustion, A. Thomas.

The first article clearly states the aims of thermal explosion theory, viz.

(i) To ascertain what factors determine whether an explosion will occur or whether a reaction will proceed at a steady rate;

(ii) To determine the temperature distribution in the reaction at the steady state;

(iii) To determine the dependence of temperature on time (and position) prior to the establishment of the steady state;

(iv) To determine the course of events when no steady state is possible.

With these guide lines the author then lucidly reviews the theories, which are of some complexity, which have been put forward.

The second article lies outside the interests of the reviewer but the final two articles are of much greater interest and deal with an area where progress is now to be expected, viz. the nature and composition of radicals to be found in gas phase oxidations.

This series of volumes should provide a useful addition to the literature of gas phase oxidation reactions. T. A. TURNEY.

The Principles of Heterocyclic Chemistry, by A. R. Katritzky and J. M. Lagowski. Methuen, 1967. 183 pp. Price $4.50.

The stated objective of the authors in this volume is to provide a more readable version of their textbook "Heterocyclic Chemistry" (Methuen, 1960). In order to achieve this the amount of factual material has been reduced and a number of the explanatory passages have been simplified, although the essential organization has been retained.

In five of the seven chapters groups of heterocyclic compounds are discussed with regard to synthetic routes, reactivity types, and reactions of the heterocyclic rings and substituents. The reactions are classified according to the type of attacking reagent (nucleophile, electrophile, etc.) and the overall aim is to provide for the undergraduate or graduate student a treatment attempting to rationalize heterocyclic chemistry in terms of current electronic theories.

Chapter 1 contains a concise account of current concepts of the electronic theory of organic chemistry, nomenclature of heterocyclic compounds, instructions on the use of the text, and adequate reference to the literature of heterocyclic chemistry. The final chapter (in 5½ pages) attempts to discuss physical properties of heterocyclic compounds, but although some general trends are listed for melting and boiling points, dipole moments and pK_a values, the space allotted to this section is too small to be of much value. The paragraphs dealing with spectroscopy say little more than that I.R., n.m.r. and mass spectrometry are useful techniques. It seems a pity that this chapter could not have been expanded and put near the beginning of the book so that use could have been made of the physical data in discussion of the reactivities of the various classes of compound.

Although the organization of the remainder of this text is logical and usually manages to cut through the normal mass of detail to reach the essential basis of a reaction or synthesis, there is little improvement in readability over the authors' earlier volume on heterocyclic chemistry. The style is extremely terse, while the policy of referring to structures in the text as numbers and then situating the reaction schemes in a rather haphazard fashion some distance from the related passage of text has only saved space at the expense of clarity.

Although, therefore, the concept of this book is modern and the material is generally well-chosen, I would hesitate to recommend it as an undergraduate text.

M. R. Grimmett.

Vapor Deposition. Edited by C. F. Powell, J. H. Oxley and J. M. Blocher, Jr., J. Wiley & Sons Inc., N.Y. 725 pp. $NZ17.95.

This book is an extensive revision of an earlier monograph entitled, "Vapor Plating". It consists of a brief introduction, followed by three major sections: Fundamentals, Techniques, and Applications, each of which consists of several chapters.

The book appears to have been written for those more concerned with applications than with the basic phenomena involved in vapour deposition. There are available in other works more thorough treatments of the basic physical and chemical processes involved than are found here. Nevertheless, the section of Fundamentals is a valuable part of the book. It relates the basic phenomena to the specific situations existing in vapour deposition and it provides enough background to enable the book to be used as a self-contained source. The usefulness of the section on Fundamentals is reinforced by the attempt that has been made to use consistent notation throughout the book.

The sections on Techniques and Applications are detailed and thorough. That on Applications, covering uses of vapour deposition ranging from decorative coatings through the production of pure metals to encapsulation of nuclear fuels, should be read by anyone interested in the application of basically simple ideas to the solution of complex problems.

Each chapter has an extensive bibliography and the illustrations are clear and instructive.

This book will be a worthwhile acquisition for libraries of technology and will be a valuable reference work for those concerned with the uses and potential uses of an interesting and powerful technique.

A. G. Williamson.

Principles of Organic Synthesis, by R. O. C. Norman. Methven & Co. Ltd., London, 1968, 722 pages. 105/- U.K.

The title of the book is perhaps a little misleading for I had expected it to be concerned with practical aspects of preparative organic chemistry. To the author, Professor of Chemistry at University of York, and Meldola Medalist for 1961, reaction mechanisms are the principles of organic synthesis. But I was not disappointed for I am always interested to see how others describe the making and breaking of bonds in mechanistic terms and here we have the subject presented in a clear and lucid style.

Part I is concerned with a discussion of basic principles and concepts which govern organic reactions and which are so important in a fuller understanding of reaction mechanisms. Topics such as chemical thermodynamics, structural theory, rates of reaction and stereochemistry are treated in such a way as to form an excellent introduction to the more detailed mechanisms which follow. The principal synthetic reactions of organic chemistry, classified according to reaction type, are discussed from a mechanistic point of view in Part II, while the final chapter describes the application of these reactions in the synthesis of ten complex naturally occurring substances such as epiandrosterone and chlorophyll. This book is aimed at the undergraduate student and in this respect it is very successful. It is not a reference work, although reference is made to appropriate review articles which may be consulted by individuals requiring further information. Errors are few but all may not agree with some of the listed mechanisms. Presentation is excellent—the type is good and the formulae are clearly set out.

A. D. Campbell.

Practical Inorganic Chemistry. Preparations, reactions and instrumental methods. G. Pass and H. Sutcliffe. 225 pages. Chapman and Hall Ltd., London, 1968. U.K. £2.

The experimental work described in this text covers most of the principles of inorganic chemistry discussed in an undergraduate course. The authors have attempted to emphasize the relationship between theory and practice. Each chapter or section is preceded by a theoretical discussion (in outline only) which should provide a thread of continuity between lecture room and laboratory.

Much of the experimental work is of a preparative nature. Complementary work, which includes questions, practical exercises and frequently analytical work, follows each preparation. Satisfactory answers to the questions will require some library work which will emphasize the unity between theory and practice. As well as illustrating the theoretical aspects of the subject, many of the techniques used in inorganic chemistry are demonstrated.

Have the authors been successful in their attempts? The answer is yes. This text will provide an excellent basis for a course in practical inorganic chemistry spread over the three years of an undergraduate course. The introductory discussions are good, the general descriptions of the techniques are good, the experimental details seem adequate, the questions in many cases are quite searching and references to the original work are included where appropriate.

A wide range of inorganic chemistry is covered —the typical (*s*- and *p*- block) elements; oxo-acids and oxo-anions; elements of the first transition series; coordination chemistry; clathrate compounds; double salts; stabilization of oxidation states; homogeneous catalysis, and inorganic polymers. Many excellent preparations are included although one or two are rather long. Few undergraduate courses can cope with preparations which need to be left on a steam bath for 12 hours!

The techniques covered are equally wide ranging —high temperature reactions; electrochemical oxidation and reduction; chemistry in non-aqueous solvents; high vacuum techniques; inert atmosphere techniques; spectroscopy (infra red, visible, ultra violet); conductance measurements; gas chromatography; magnetism; potentiometric titrations, and polarimetry. Many of the techniques are used throughout the book to help elucidate the structures of the compounds that have been prepared. Adequate cross references are given.

A few misprints and one or two errors were noted. For instance, in the visible-u.v. absorption spectrum of $V(H_2O)_6^{3+}$ the high energy band due to the $^3A_{2g} \leftarrow ^3T_{1g}$ transition is not observed due to its low intensity and the fact that intense charge transfer bands appear in the same region. In the preparation of ferrocene (p. 58) it is recommended that tetrahydrofuran be purified by refluxing over potassium hydroxide. This method is *not* recommended as serious explosions have occurred. See the warning (supplementary sheet) in "Organic Syntheses" *40*, 94. This warning appeared in 1967.

On the whole the book is a very welcome and worthwhile addition to the small number of practical inorganic chemistry texts.

R. G. Cunninghame.

Electron Spin Resonance in Chemistry, by Peter B. Ayscough. Methuen & Co. Ltd., London (1967). 450 pages. U.K. price 84s.

According to the author's preface this book is written primarily for chemists who might wish to evaluate the potentialities of ESR in their own fields. His approach is essentially non-mathematical with emphasis on the practical and interpretive aspects of the subject.

The theory of the ESR experiment in chapter 1 is almost exclusively along classical lines. The introduction thus loses much of the elegance and simplicity which would have come from a quantum mechanical approach. Further, the discussions in chapters 2 and 3 (on the spin Hamiltonian, theory of the g-tensor, calculation of g-values, hyperfine interactions and so on) necessarily involve quantum mechanical concepts and one finds in fact the various angular momenta operators and perturbation theory produced in formulae "from out of the hat" often without adequate definition. The student wishing to use this book as an introduction to ESR will probably find these chapters rather difficult.

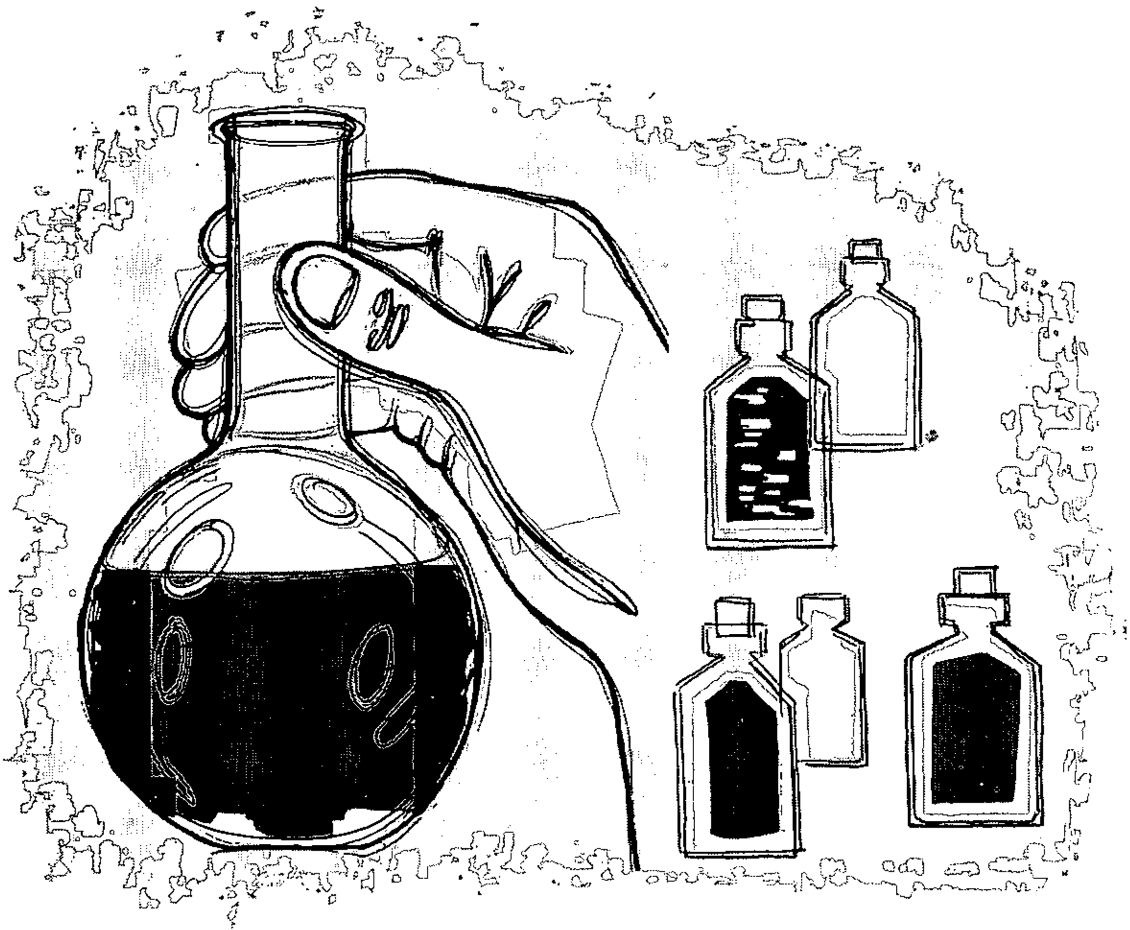
The bulk of the remainder of the book is written with the needs of the practical chemist in mind. Chapter 5 gives a concise and lucid account of instrumentation and various practical aspects of ESR measurements. Chapters 6 to 12 include a comprehensive selection of experimental data with extensive references to the relevant literature up to 1967. This portion of the book reflects to a large extent the author's own interests—radiation damage, radicals and ions in solution and in polycrystalline and amorphous matrices—but there is also an adequate, though standard, coverage of such topics as transition metal ions, radicals in single crystals, F-centres, triplet state molecules and paramagnetic species in biological systems. While it could be argued that the compilations of experimental results in these chapters are somewhat overdone, it is probably their inclusion which gives the book its main value.

The overall impression given by this book is that the author has tried to cover too wide a range of subjects, often in insufficient depth. There are some errors in the text (see for example page 52, paragraph 2 on zero field splittings) though fortunately these are mainly trivial. The book is not recommended as a suitable introduction to the theory of ESR but it should prove a valuable supplement to existing texts with special interest to the experimentalist.

W. C. Tennant.

Reagents for Organic Synthesis. Louis F. Fieser and Mary Fieser. Published by John Wiley and Sons Inc. (1967). 1457 pages. $Aust.27.50.

Of all the highly-regarded publications which have been produced by the Fiesers this may well prove to be the most valuable. This large (and high priced) volume fills a long-vacant niche in the literature of organic chemistry in that it provides, under one cover, a wealth of information on the syntheses, properties and uses of 1120 reagents. These are listed alphabetically with structural formulae, physical constants, preferred methods of purification and preparation, and suppliers. In recommending that it should be standard pro-



cedure to use the exact theoretical quantities of reagents, the authors point out that in only two situations in the book is there any evidence that excess reagent improves the yield or shortens the reaction time. In order that information should be easy to find, the alphabetical order of reagents is supplemented by detailed indices of authors, subjects and reagent types, as well as lists of suppliers and apparatus.

I believe that this book will prove an invaluable aid to all organic chemists, particularly if the authors adhere to their published intention of keeping abreast of new literature with a view to providing paperback supplements from time to time.

M. R. Grimmett.

Comprehensive Biochemistry. Edited by Marcel Florkin and Elmer H. Stotz. Vol. 6. Lipids by Elsevier, Amsterdam, London, New York, Amino Acids and Related Compounds published 1965, 323pp. 95/-.

The aim of the series is to produce an advanced treatise to cover the rapidly expanding knowledge of biochemistry. The chapters of volume 6 include under part A lipids: (1) fatty acids, long chain alcohols and waxes, (2) natural fats and oils and (3) phospholipids and glycolipids. Part B concerns amino acids and related compounds. This is covered in six chapters as follows: (1) general chemistry of amino acids, (2) nitrogenous bases, (3) melanins, (4) peptides, synthetic methods and applications, (5) capsular polypeptides, and (6) synthesis of bacterial glutamyl polypeptides.

For the specialist it would appear undesirable that two such distinct fields are joined together in one volume; furthermore, that in both fields much of the ground covered has already been well described in other text books. A possible justification for this repetition might be a presentation of greater clarity than has hitherto been achieved. However, the reviewer is unable to find evidence of any advance in this direction. Instead, associated with the treatment of well established facts is a tendency to be obscure. We find for example on page 2 "exceptional occurrence of straight-chain saturated fatty acids of quite short chain length in the fats of the milk of ruminants has already been mentioned". The mention of this on page 1 consists of referring to the "unusually short-chain acids found in the milk fat of ruminant mammals". Incidentally, why not call these creatures ruminants. The simple facts are that the milk fats of ruminants contain the n-odd and n-even saturated acids from C_4 to C_{26} inclusive.

In the chapter dealing with neutral fats and oils we find the old story about depot fats and their function as reserves of energy for the organism, yet we know that a fat organism is not necessarily less energetic than a thin one. It may be that extensive depot fat is due to inability to transform this reserve to energy.

This chapter, like several of the other chapters, covers well-trodden ground but with a dash of deep comprehension on the question of evaluation of the current theories on glyceride structure.

The general chemistry of the amino acids shows evidence of enlightenment and comprehension masked by the infusion of general textbook treatment.

The reviewer does not find it profitable to continue with his detailed dissection, having touched upon points that are symptomatic of the book, except to say that he would prefer to read about the chapter on phospholipids and glycolipids from one of the six review articles of the bibliography where at least he could collect the original references about the work described.

In conclusion it may be said that the volume is written by scientists who are in the forefront of their field and that the facts are therefore likely to be of considerable value to the specialist as well as to the student. The issue at stake is whether the volume has succeeded in replacing the earlier text books and the review articles as intended. It is in this direction that the reviewer feels the need for a good hard look. Is it not possible from time to time to recognise text books that are complete up to within say 5 years of the time of the new publication and to direct undivided attention to the latest advances and decide how these affect what was formerly accepted. Apart from that let well alone.

F. B. Shorland.

Progress in Physical Organic Chemistry, Vol. 3. Edited by Saul G. Cohen, Andrew Streitwieser and Robert W. Taft. Interscience Publishers, New York, 1965, 384 pages. Price $NZ14.40.

The 'Editorial Introduction to this series states that the editors "have encouraged authors to review topics in a style that is not only somewhat more speculative in character but which is also more detailed than presentations found in textbooks."

Both these aims are usually fulfilled in the series; the first leads to readable articles, and the concomitant danger of an author neglecting ideas and even facts which do not square with his own interpretations is, as far as I can tell, avoided. This particular volume is now three years old. Published in mid-1965, all five of its reviews include references well into 1964. Badger's review of 'Pyrolysis of Hydrocarbons' is relatively short and very readable, and Streitwieser and Hammons cover 'Acidity of Hydrocarbons' thoroughly. 'Reactions through Charge-Transfer Complexes' by Kosower gives good coverage but is now dated in parts. The other two topics covered are 'Mechanisms of Organic Polarography' and 'Ultrafast Proton-Transfer Reactions.'

A chemist wishing to familiarise himself with one of these fields would find the relevant review a good starting place.

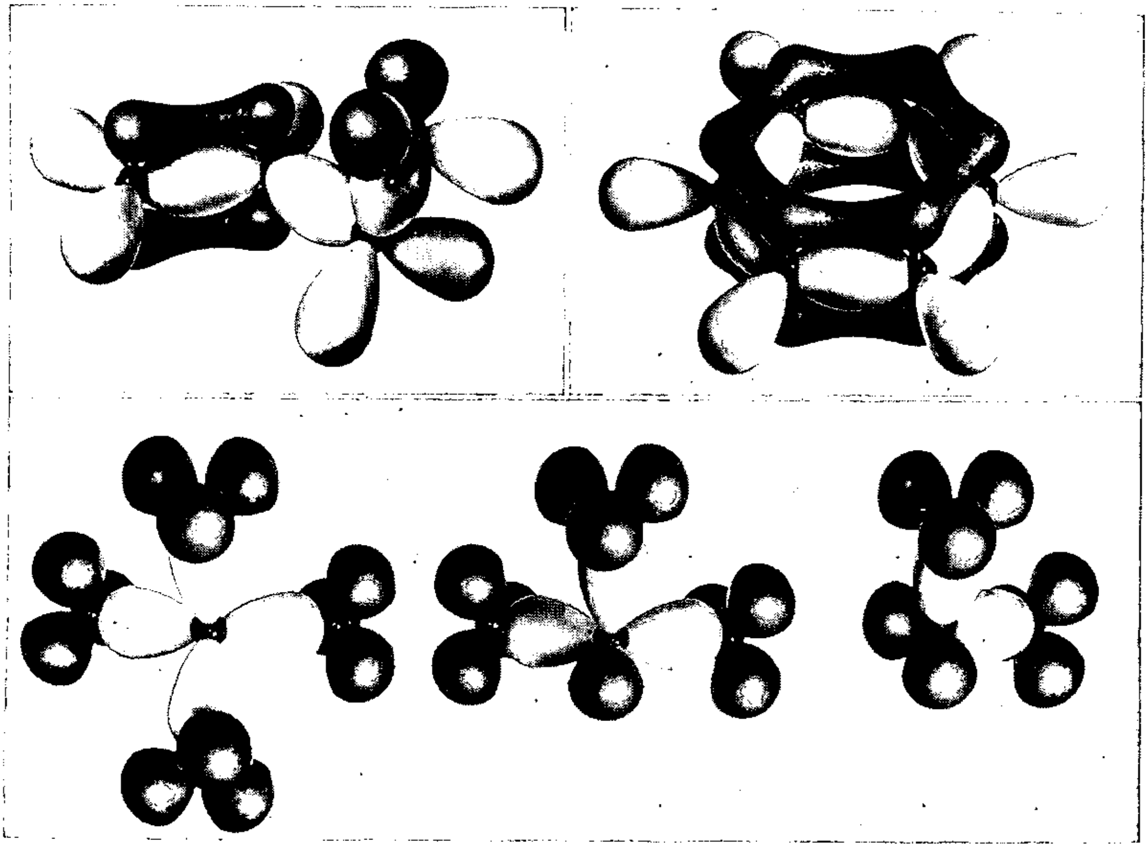
G. J. WRIGHT.

FORTHCOMING INTERNATIONAL MEETINGS

1. Joint Annual Meetings of The Chemical Society (London) and The Royal Institute of Chemistry — Nottingham, U.K., 14-18th April, 1969.
2. 2nd International Pre-Symposium on Carotenoids other than Vitamin A, New Mexico, U.S.A., 6-9th May, 1969.
3. International Symposium on Enamine Chemistry, Salford, U.K., 16-16th July, 1969.
4. Symposium on Surface Area Determination, Bristol, U.K., 16-19th July, 1969.
5. International Conference on Ion Exchange in the Process Industries, London, U.K., 16-18th July, 1969.
6. International Symposium on Conformational Analysis, Brussels, Belgium, 8-12th September 1969.
7. International Committee on Electrical Thermodynamics and Kinetics, 20th meeting, Strasbourg, France, 14-20th September, 1969. This will be a restricted meeting with a single topic, "Transport phenomena in electrochemical systems".

   This will cover four main aspects:

   1. Theoretical and experimental fundamental bases.
   2. Mass and charge transport in solution, in particular in the diffusion layer.
   3. Mass transport in the pores of porous electrodes.
   4. Mass transport towards and through membranes (in particular in biological electrochemical systems).
8. 7th International Symposium on the Chemistry of Natural Products, Riga, U.S.S.R., 22-27th June, 1970.



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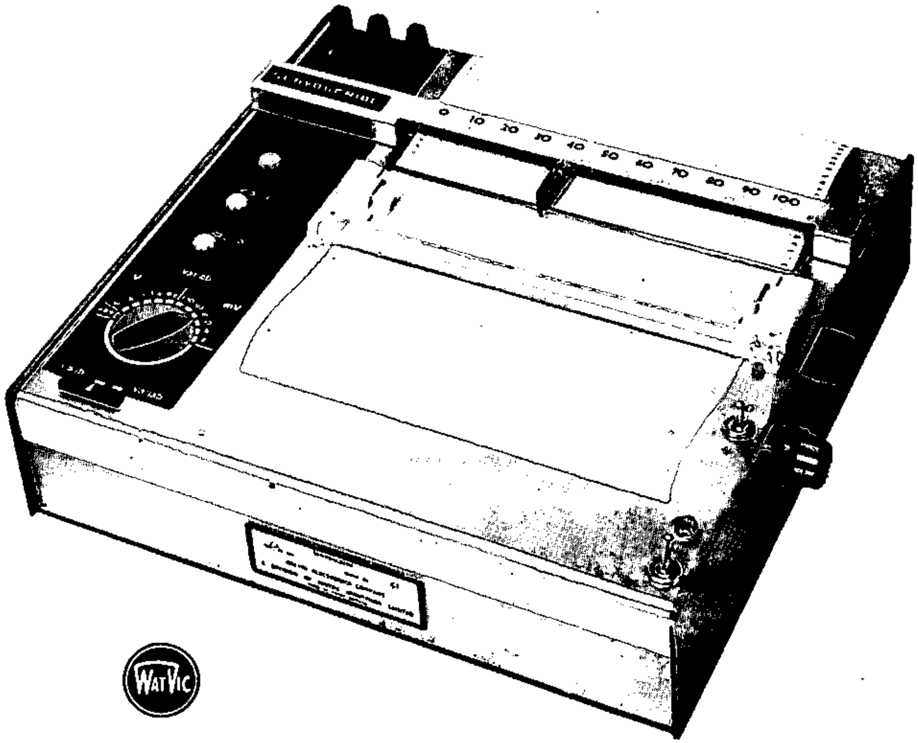

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