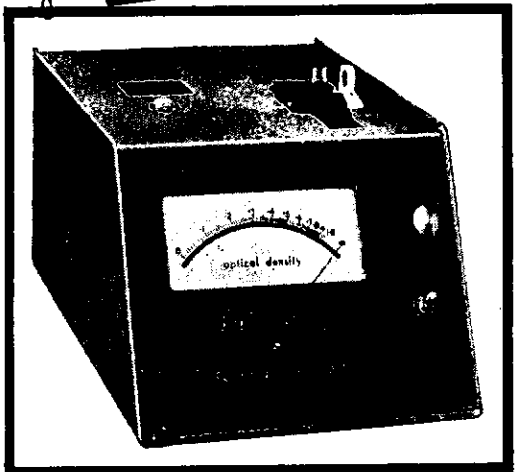
JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

Vol. 30 No. 2
April 1966

Advanced Laboratory Instruments

BY Gallenkamp



Gallenkamp COLORIMETER Mark 3

with transistorised stabiliser circuit

designed in line with the latest thinking for ACCURACY • SPEED CONVENIENCE

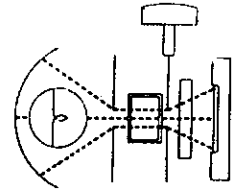
SUITABLE FOR COLORIMETRIC ANALYSES in:

Clinical, pathological and biochemical analysis
Agricultural chemistry
Analytical chemistry
Water analysis
Metallurgy
Food Chemistry

Really stable readings

Rapid response and operation

Robust unitised construction



OTHER FEATURES

Flush meter with antistatic window and 11.5 cm. mirror scale. Two simple controls only. Narrow bandpass filters for maximum sensitivity. High reserve sensitivity. Incorporates drain for spillage. Samples protected by heat absorbing filter. Photocell encapsulated for complete protection.

Price without colour filters or test cells £62/10/-, ex works, London. Also in kit form with 3 colour filters and 3 fused glass test cells, £69/10/-, ex works, London. Flowthrough cell, extra £2/5/-. Ask for Publication 647

Gallenkamp

CHRISTOPHER STREET, LONDON, E.C.2., ENGLAND

Our appointed agents are:
GEO. W. WILTON & CO. LTD.,
Box 9071, Newmarket, Auckland.
Box 367, Wellington.

FROM THE RANGE OF GALLENKAMP INSTRUMENTATION

JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

Vol. 30, No. 2 APRIL, 1966

CONTENTS

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

Edited by JOAN M. MATTINGLEY
P.O. Box 250, Wellington

Advertising Manager
MISS A. DOLLIMORE, P.O. Box 250, Wellington

Registrar, N.Z. Institute of Chemistry (Inc.)
D. J. HOGAN, P.O. Box 1926, Christchurch, N.Z.

Employment Officer
E. S. BORTHWICK, Shell Oil N.Z. Ltd.,
Box 2091, Wellington

Printed by DAVID F. JONES LIMITED, 108 Tory Street, Wellington.

This Table is part of

SALARY SURVEY

Printed in Journal of the New Zealand Institute of Chemistry, Vol. 30, No. 1, February 1966.

TABLE 9

SALARIES

The number of replies, average salaries and salary ranges of groups in Industry, by age groups.

Age Group	Technical Salesman	Chemist	Chief Chemist	Works Manager	General Manager
21-25	1	2	5 1480 (1300–1600)	1	
26-30	5 1690 (1400–2200)	5 1560 (1200–2000)	13 1790 (1500–2500)	1	
31-35	1	5 2100 (1600–2800)	4 1830 (1700–2000)	11 2160 (1500–3400)	3 3300
36-40	1	8 1620 (1400–1800)	25 2070 (1800–2900)	16 2580 (1600–3600)	5 3080 (2400–4000)
41-45		6 1770	6 2070	15 2590	2
46-50		3 1900	9 2050 (1800–2800)	5 2580 (2200–3500)	
> 51	1	2	10 2330 (1750–4500)	4 2760 (2300–3200)	8 3350 (2200–>6000
All Age Groups	9 1840	31 1730	62 2060	53 2470	18 3500

JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

Vol. 30, No. 2 APRIL, 1966

EDITORIAL

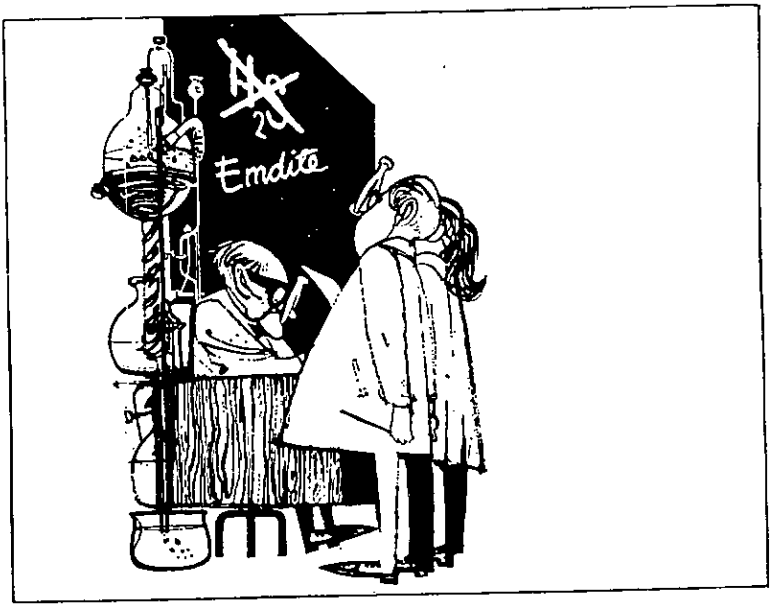
THIRTY YEARS ON

This year the Journal is thirty years old. The first issue, in January 1936, provides interesting material for reflection on the progress of chemistry since then. The very first article was on the estimation of fluorine. It ended with the words, "with the methods now available for the determination of fluorine . . . investigations of its effect in agriculture, and in plant and animal life, should be very fruitful of result". Could the writer have foreseen the controversial results? "Some Applications of the Photo-electric Cell" with its statement that photo-electric "titrations can be made by day or night or by a colour-blind observer" reminds us of how much we take for granted. The difficulties and blind gropings in the biochemical field before the development of electrophoresis and chromatography are illustrated in "The Nature, Properties and Estimation of Iron in Blood".

Industrial chemistry was important. Hydrogen ion concentration in leather manufacture, cellulose pulp from New Zealand flax, corrosion problems, engine performance of petrol and the oxidation of butter-fat all had a place. For the philosophical there was "The Agricultural Scientist Gone Wrong" and "The Frustration of Science". These and others indicate that we are still chewing away on the same old problems, but perhaps the 1966 approach is different.

The first issue contained four advertisements. Two of those advertisers, Wiltons and B.D.H., are still with us. We thank them for their loyal support and interest in the Journal, and would quote from that very first editorial "It is hoped that the advertisements will serve a useful purpose to members and that members will respond by patronising our advertisers, mentioning this Journal wherever possible".

don't keep bad eggs in the laboratory keep 'EMDITE'



EMDITE is the convenient registered name of ethyl-ammonium ethyl-dithiocarbamate (50% aqueous solution) and a complete EMDITE scheme of metal group separation has been worked out in the BDH laboratories.

EMDITE advantages are:
The toxicity, bad egg odour and general inconvenience of H_2S are avoided entirely.

All operations are performed in the open laboratory.

Using, instead of a gas, a solution of defined concentration, the volume and strength of precipitant are easily controlled. No potassium cyanide — copper and cadmium are separated in different groups.

1. Hart, K.K., Hill, A.G. and Savage, B., J. Roy. Inst. Chem., 1964, 418-23 (reprints are available on request).

EMDITE (ethyl-ammonium ethyl-dithiocarbamate 50% w/w solution in water). And in packings of 100 ml, 500 ml.

BDH

The British Drug Houses (N.Z.) Ltd.

CRYSTALLOGRAPHIC BIOCHEMISTRY

by

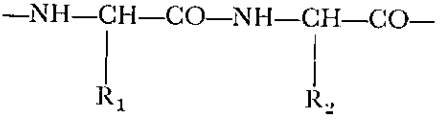
C. L. NOBBS

Chemistry Department, University of Auckland, New Zealand
and
Medical Research Council Laboratory of Molecular Biology, Hills Road, Cambridge, England

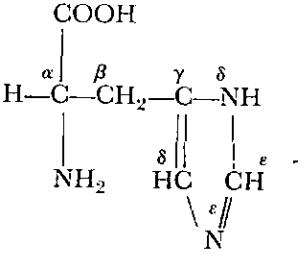
Introduction

A protein molecule is composed of a unique sequence of α-amino-acids linked through peptide bonds (I). Some proteins contain in addition a chemical group which includes a metal cation. Twenty different α-amino-acids occur in proteins, and all of these amino-acids are in the L absolute configuration.

(I)



(II)



The side-chain (R) of an amino-acid residue may contain one of a variety of chemical groups: it may be acidic ($-CH_2-COOH$: aspartic acid), basic ($-(CH_2)_4-NH_2$: lysine), contain an hydroxyl ($-CH(CH_3)-OH$: threonine) or be chemically neutral ($-CH(CH_3)_2$: valine). Other types of side-chain occur, such as in histidine (II). Proteins are extremely complex by classical chemical standards, firstly because one molecule may consist of a chain many hundreds of amino-acids in length, and secondly because in its native state the chain adopts a characteristic and unique three-dimensional conformation. This conformation represents the structure of minimum energy of interaction of the backbone chain and side-chains of the protein amongst themselves and with their environment. The shape of each protein,

its solubility, its cellular behaviour and its enzymatic action (if it has such) are controlled by the nature of the amino-acid side-chains and their distribution about the molecule. That is, the structure of a protein is the mirror of its function.

In a simple way, two main classes of protein molecules can be distinguished. The first class comprises the fibrous proteins such as the collagens, which are the proteins of cartilage and bone, and the keratins, which are contained in hair and horns. These proteins are generally fibrous in nature and structural in function. They are insoluble in many solvents and inert in the processes of cellular metabolism. This class of proteins will not be considered further in this article.

The second class of proteins comprises the globular proteins. These are proteins which either are active in or support cellular metabolism: e.g. hemoglobin in mammalian red blood cells, the proteins of ribosomes and of antibodies, and the important group of specific catalysts of biological reactions—the enzymes. Because of the central role of the globular proteins in the orderly functioning of cells these proteins are a focus of biochemical interest. They are spheroidal in shape, often soluble in simple salt solutions, and most important for the crystallographer who would investigate them, they can often be induced to form crystals.

Protein crystals differ from the crystals of small organic molecules particularly in the high quantity of mother liquor actually within them. On exposure to air these crystals lose solvent, crack, shrink and lose internal order. Because of the extensive regions occupied by liquid quite large chemical groups can diffuse into the crystal without loss of order, and this has provided the key to unlock the door to the complete knowledge of the three-dimensional structure of protein molecules.

Turning the Key

When a protein crystal is placed in a sealed capillary tube containing mother liquor to keep it wet, and is exposed to an X-ray beam, the crystal gives rise to a series of diffracted beams of varying intensity in much the same way as visible light falling on a series of lines ruled on a grating produces a diffraction pattern. Whereas a simple grating may produce several diffracted beams protein crystals produce tens or even hundreds of thousands of beams. Mathematically we can represent each beam by a vector (F) which is fully specified if its amplitude (F) and its phase angle (θ) are known.

The relationship called the Fourier transform links the amplitudes and phases of the diffracted beams with the positions of the atoms in the diffracting crystal. Atoms diffract X-rays in proportion to the number of electrons they contain, so that atoms such as hydrogen diffract X-rays hardly at all; carbon, nitrogen and oxygen atoms diffract moderately well; heavy atoms such as mercury and iodine do so with remarkable power. The crystallographer tries to discover the amplitude and phase of each diffracted beam and to use the Fourier relationship to produce a series of contour maps of the electron density within the crystal, each map in the series being a consecutive slice through the molecules in the crystal. On these maps he tries to pick out and identify the atoms of the protein molecule. The difficulty lies in the fact that although he can measure the intensities of the diffracted beams and deduce their amplitudes, he cannot measure their phases. To get around this "phase problem" a subterfuge is needed.

A chemical group must be found which contains a heavy atom and which, when placed in the mother liquor surrounding the crystal, will diffuse into the crystal as described previously, and attach itself to the protein molecule at specific sites. (Several heavy atom groups have been used successfully, such as $PtCl_4^{2-}$, $UO_2F_5^{2-}$, and para-chloromercurybenzene sulphonate.) By comparing the diffracted beams of these new crystals with those of the native protein, the crystallographer can often discover the locations in the crystal of the heavy atoms, the foci of diffracting power, and hence get a "leg in" on solving the phase problem for the native protein by using the Fourier relationship in reverse. Such a process is very lengthy in practice and is mathematically repetitive, so a high-speed digital computer is required to do the collating, comparing and computing, and without which the solution of the structures of these protein molecules would be quite impossible. By repeating this process with other heavy-atom groups a successively closer approximation to the correct solution of the phase problem is attained.

How clearly can the crystallographer now see the protein structure as a result of his calculations? Generally speaking, the larger the number of diffracted beams he has measured the clearer will be his picture. What shape will the protein have? How will it be folded? Can its behaviour in the cell be predicted or observed directly in the crystal?

The Revelation

Myoglobin from sperm whale was the first protein whose structure was revealed by the X-ray method outlined above.[1] This protein (molecular weight 17,000) consists of a single chain of 153 amino-acids, and associated with this chain one "heme group" (a planar porphyrin ring with an iron atom bound at its centre). In common with other mammalian myoglobins sperm whale myoglobin occurs in muscle cells. Here it receives molecular oxygen from the hemoglobin of red blood cells, stores it (oxymyoglobin) and releases it (deoxymyoglobin) when the muscle is called upon to perform work. The visible absorption spectra of these myoglobins show that the oxygen is bound directly to the iron atom. The iron remains in the ferrous state through the oxygenation reaction. When myoglobin is extracted from the muscle it undergoes oxidation to met- or ferric-myoglobin which does not bind oxygen.

The X-ray analysis, with the help of chemical analysis, identified each amino acid in sequence and was able to place each spatially, relative to one another and to the heme group. The overall shape of the molecule is that of a round-edged prism measuring 45 x 35 x 25 Angstroms. The amino-acids are arranged in eight helical segments of varying lengths: two sharp corners; five non-helical segments; and a non-helical tail of five residues at the carboxyl end of the chain. Figure 1 shows the arrangement of the amino-acid residues along the backbone of the molecule. (The side-chains are omitted for clarity.) The helical segments are lettered A to H starting at the amino-terminal end, and the residues within each helix are numbered from 1 to n in the same sense; interhelical regions are specified AB etc. The important histidine residues E7 and F8 (see below) are drawn on the figure. The helices themselves are all α-helices which are held together by hydrogen bonds between the peptide bond amino group of one amino-acid residue and the peptide bond carbonyl group of the residue four along the chain. All the helices are right-handed and contain only L amino-acids. Almost all the polar side-chains such as lysine, serine and glutamic acid are at the surface of the molecule. Rare exceptions are the histidine residues E7 and F8 which are involved in the physiological functioning of the molecule. On the other hand, the interior is populated by non-polar side-chains such as leucine, valine and phenylalanine, almost all of which have van der Waals contacts with their neighbours.

The heme group lies in a recess in the molecule formed by the C, E and F helices; the polar propionic acid side-chains (P) of the porphyrin nucleus lie at the surface with the remainder of the nucleus thrust deeply into the interior. The fifth co-ordination position of the iron atom is occupied by the ε-nitrogen atom of the imidazole ring of histidine F8. The sixth position is occupied by a water molecule which is in turn hydrogen-bonded to the

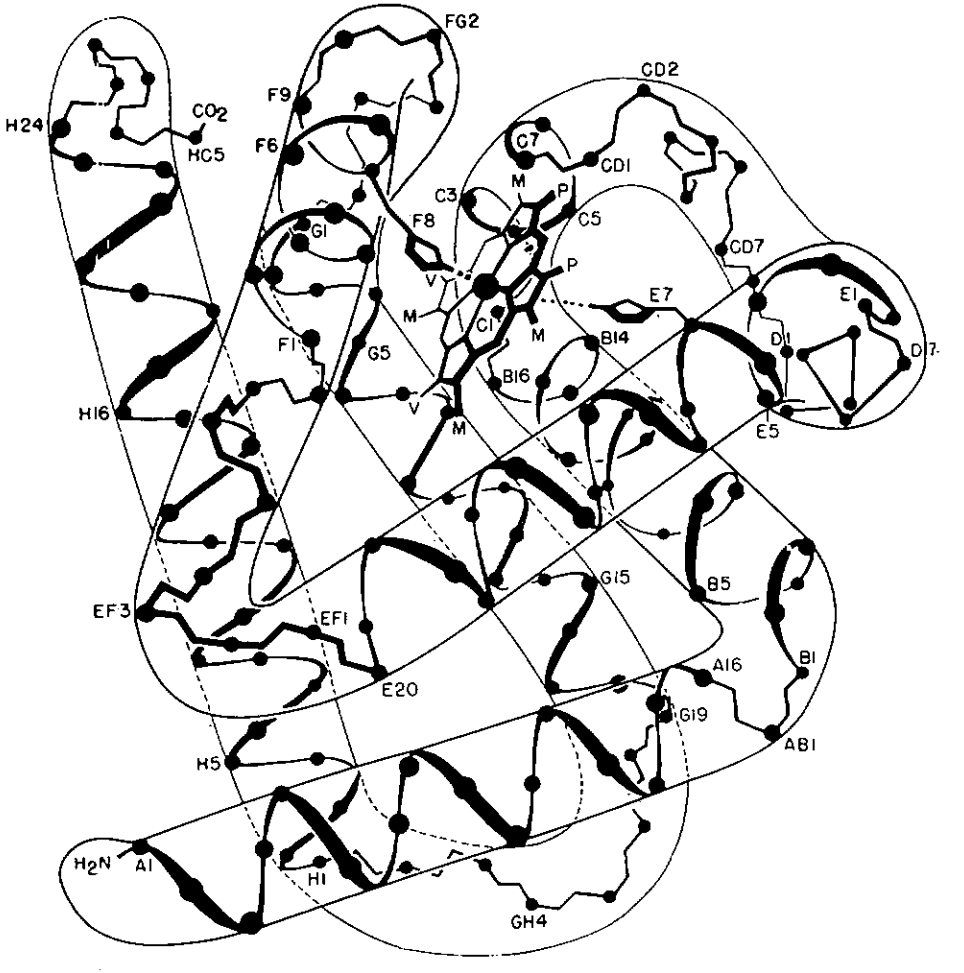


Fig. 1. A diagrammatic representation of the three-dimensional structure of the protein myoglobin. The amino-acid side-chains have been omitted for clarity. For explanation, see text.

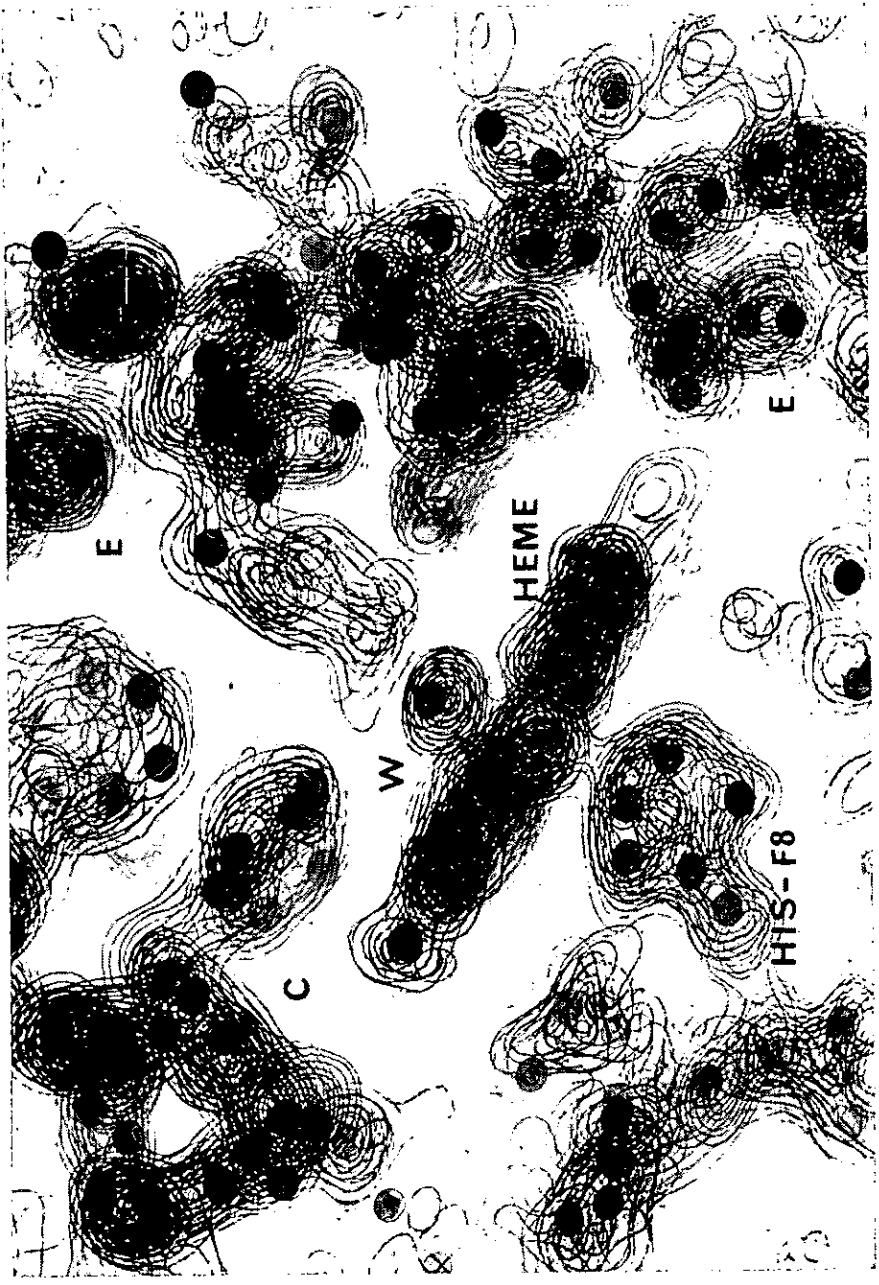


Fig. 2. A stack of contour maps of electron density drawn on sheets of clear perspex: These maps show part of the myoglobin molecule. Details are given in the text.

ε-nitrogen atom of histidine E7. These facts are shown in Figure 2, which is part of the electron density map of metmyoglobin. Part of the heme group with its central iron atom can be seen edge on, while the histidine residues E7 and F8 and the water molecule (W), attached to the iron, are all clearly resolved. The courses of the helices C and E, lying perpendicular and parallel respectively to the plane of the figure, can also be seen. (The block dots represent atom positions.)

Some Consequences

Is it possible to capitalise further on the knowledge of the phases and amplitudes of all the diffracted beams from a protein such as myoglobin? One of the most rewarding ways of doing so is to use the difference Fourier method. As has been seen, it is possible (within limits) to modify the structure of a protein molecule without altering the architecture of the crystal (the crystals are isomorphous). We can react side-chains chemically, diffuse in groups physically, or attempt to obtain isomorphous crystals of a closely related myoglobin from another mammalian species such as porpoise (a formerly equivalent process). In such cases we can compare directly the intensities of the diffracted beams from the native and derivative crystals (while still using the phase obtained for the native crystals), and measure directly by subtraction, the difference between the two structures on an electron density map. This is a relatively simple process.

For example, the azide ion N_3^- is an effective inhibitor of heme proteins. By soaking metmyoglobin crystals in an excess of sodium azide and calculating a difference map it was shown that the azide ion occupied the water molecule site at the heme iron atom, effectively blocking the oxygenation reaction.[2]

Progress has also been made towards an understanding of the physiological reaction of myoglobin. This is a particularly important reaction because of the close relationship which exists between myoglobin and the protein hemoglobin which carries oxygen in the blood. Under special conditions it is possible to prepare crystals of deoxymyoglobin which are isomorphous with metmyoglobin crystals. What does the difference Fourier method reveal this time? Nothing—except that the site occupied by the water molecule in metmyoglobin is now vacant.[3] Physically, this situation seems to offer the lowest possible potential barrier to the oxygenation of the molecule. Crystallographically, this experi-

ment shows that it is possible to detect the removal of one oxygen atom from among 2,500 atoms under favourable circumstances. The manner in which the oxygen molecule is held in oxymyoglobin and the possibility of accompanying changes in the protein structure have not yet been investigated.

Hemoglobin

Hemoglobin is a protein of molecular weight 64,000 and consists of four subunits which are identical in pairs (called the α- and β-pairs). Each of the four subunits contains a heme group and a single polypeptide chain, and is similar to myoglobin in amino-acid sequence, in chemical and in physical properties.

Hemoglobin transports all the molecular oxygen required in the respiratory processes of vertebrate animals. Hemoglobin picks up oxygen in the lungs where the oxygen pressure is high and releases it to the tissues where the oxygen pressure is low. At this point in its cycle, hemoglobin picks up waste carbon dioxide from the tissues and releases it in turn in the lungs. However, the oxygenation curves of myoglobin and hemoglobin as functions of oxygen pressure are remarkably different. The oxygenation reaction of myoglobin shows first order kinetics with respect to both the deoxymyoglobin and the oxygen. Contrarily, the kinetics of hemoglobin are of higher order and indicate that oxygenation at one heme site is not independent of the state of oxygenation at the other three. This phenomenon is known as heme-heme interaction.

The crystallographic investigation of horse oxyhemoglobin has been actively pursued for a number of years, and although insufficient diffracted beams have been collected and analysed to reveal the structure as clearly as has been done for myoglobin, the four subunits can be seen and the directions of each subunit chain followed on electron density maps. These have also shown that the four chains are contiguous and that the centre of each lies at the apex of an approximately regular tetrahedron (very recently, an atomic model of oxyhemoglobin has been proposed[4]). The remarkable nature of heme-heme interaction was displayed when it was found that far from being contiguous, the heme groups of the α-chains were 33 Angstroms apart and those of the β-chains 36 Angstroms apart.

A parallel study of human deoxyhemoglobin showed that although the α-chains occupied the same relative positions in the

two molecules, the β-chains of oxyhemoglobin were 7 Angstroms further apart than in the deoxy-form.[5] It appears that it is this chain movement which facilities the addition and hastens the removal of oxygen to partially oxygenated hemoglobin molecules. Moreover, it is believed that the movement apart of the β-subunits reveals the sites on the molecule at which carbon dioxide attachment can occur, and thus removal of the oxygen from hemoglobin enables its reaction with carbon dioxide to take place. Controlled equilibria of this type involving "feedback inhibition" or "feedback activation" appear to be characteristic of an important class of reactions which enzymes undergo.

Enzymes

In the building up and breaking down of the constituent molecules of living cells, enzymes play a central role. Scarcely is there a biological reaction that is not catalysed by a specific enzyme. The manufacture of amino-acids, the assembly of protein chains (including those of enzymes), the breakdown of nucleic acids and the processes by which energy is stored in the cell are all mediated by enzymes.

For example, the transformation of L-threonine to L-leucine in the bacterium *Escherischia coli* is carried out in five consecutive reactions, each one catalysed by a different enzyme. The first step in this process is the conversion of L-threonine (the substrate) to α-ketobutyrate which occurs at the surface of the enzyme L-threonine deaminase. The reaction is stereospecific. D-threonine does not bind to the enzyme, nor has it been shown that *in vivo* the enzyme will accept any other chemically related compound as substrate. When the supply of isoleucine in the cell exceeds the demand for its use in other metabolic processes the L-threonine deaminase reaction step is specifically inhibited by L-isoleucine itself (feedback inhibition). More surprising is the fact that L-threonine deaminase can be made inactive to the acceptance of inhibitor by gentle heating, while still maintaining an undiminished turnover of substrate molecules. This shows that there are two types of non-overlapping stereospecific sites on the enzyme, one for the substrate (the active site) and one for the inhibitor (the allosteric site). Current theories of enzyme action that the effect of the inhibitor bound to the allosteric site is to induce a rearrangement of subunits of the enzyme, and it is this change which regulates the reaction of the enzyme with its substrate.[6]

Many enzymes are believed to consist of a number of subunits. However, these multi-subunit enzymes are usually much larger and more complex than those consisting of a monomeric unit. Consequently most progress has been made in the study of these latter enzymes. Many enzymes are being investigated crystallographically at the present time. It is hoped to describe the structure of these molecules in the way that was done for myoglobin, and to look for any conformational changes upon reaction, such as were found in hemoglobin. In addition, it is hoped to answer questions concerning the nature of the relationship between enzyme and substrate and between enzyme and inhibitor. .

Already this work has borne fruit with the solution of the structure of the enzyme lysozyme from hen egg-white.[7] This enzyme has the power of dissolving the mucopolysaccharide component of some bacterial cell walls. In *Micrococcus lysodeikticus*, lysozyme breaks the $\beta(1\text{-}4)$ glycosidic bond between alternating units of 2-N-acetylglucosamine and 2-N-acetylmuramic acid. Lysozyme is a small enzyme consisting of a single subunit of 129 amino-acid residues (molecular weight 14,600), and it appears that for this enzyme both the substrate and inhibitors (such as 2-N-acetylglucosamine itself) compete for the same site at the enzyme surface.

The molecule is approximately ellipsoidal in shape. Compared with myoglobin, it is similarly compact, is folded in a much more complex manner and contains very few helical regions. The structure is further complicated by the existence of four disulphide bridges between sulphur-containing amino-acids which occur at various positions along the chain. Isomorphous crystals of 2-N-acetylglucosamine-reacted lysozyme have been prepared, and the difference Fourier method has revealed that this molecule occupies a site in a prominent trench on the enzyme surface which presumably represents the true inhibitor binding site. The contact between enzyme and inhibitor involves three tryptophan residues of the enzyme but the atomic details of the interaction have not yet been fully elucidated.

Conclusion

X-ray crystallography has proved to be a very successful method for discovering the three-dimensional structure of large biological molecules. It is also proving successful in following, at the atomic level, the courses of complex biological reactions

of proteins and enzymes which are often characterised by extreme stereospecificity and by conformational changes in the participating macromolecules. In the long term view of these studies there is the hope of predicting the structure of enzymes from a knowledge of their amino-acid sequences alone, and the hope of revealing general principles of enzyme action.

REFERENCES

[1] Kendrew, J. C., Scientific American (1961), 205, 96.
Kendrew, J. C., Brookhaven Symp. Quant. Biol. (1962), 15, 216.
[2] Stryer, L., Kendrew, J. C., and Watson, H. C., J. Mol. Biol. (1964), 8, 96.
[3] Nobbs, C. L., Kendrew, J. C., and Watson, H. C., Nature (1966), 209, 339.
[4] Perutz, M. F., J. Mol. Biol. (1965), 13, 646.
[5] Perutz, M. F., Scientific American (1964), 211, 64.
Muirhead, H., and Perutz, M. F., Nature (1963), 199, 633.
[6] Monod, J., Changeux, J.-P., and Jacob, F., J. Mol. Biol (1963) 6, 306.
Monod, J., Wyman, J., and Changeux, J.-P., J. Mol Biol. (1965), 12, 88.
[7] Blake, C. C. F., Koenig, D. F., Mair, G. A., North, A. C. T., Phillips, D. C. and Sarma, V. R., Nature (1965), 206, 757.
Johnson, L. N., and Phillips, D. C., Nature (1965), 206, 761.

N.Z.I.C. CONFERENCE 1966

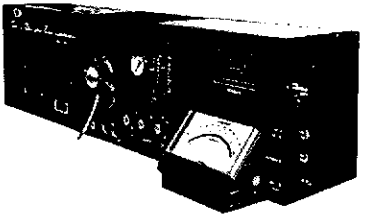
August 16 - 19

Chemistry Department, Victoria University of Wellington.

The main theme of the 1966 Conference will be "Chemistry and Education". A symposium with contributions from Industry, State Services, Department of Education, and Universities is being arranged with the aim of producing some constructive recommendations.

Other papers will be grouped as far as is possible into broad fields to form symposia with the aim of reviewing the subjects as a whole. Emphasis will be placed on the "conferring" aspect, rather than on a purely formal presentation of papers.

accurate, more sensitive chemical analysis by ATOMIC ABSORPTION SPECTROSCOPY



new TECHTRON model AA-100

Atomic Absorption has rapidly emerged as the speedy method of accurately determining traces of individual elements in the presence of high concentrations of other elements.

Now this advanced technique comes within the reach of everyone concerned with maximum analytical accuracy with the introduction of the new **Techtron Model AA-100.** A less complex instrument than the Techtron AA-3, the AA-100 is a compact high-performance model of outstanding versatility.

The AA-100 fills the need for a more simplified unit with minimum controls and adjustments suitable for operation by semi-skilled operators for routine analysis.

Applications: Already widely used in medical research and diagnosis (the Auckland Hospital possess a Techtron Unit), atomic absorption is finding a rapidly increasing number of applications in metallurgy, the agricultural and mining industries, and in the analysis of oils, beverages and effluents.

New Zealand Distributors:

CARREL AND CARREL LTD.

14 McDONALD ST., AUCKLAND S.W.1.

Post the coupon for further details on the application of atomic absorption to your analytical problem.

To CARREL & CARREL LTD., P.O. BOX 2102, AUCKLAND.

Please send me full information on the Techtron Model AA-100.

NAME _____

ADDRESS _____ RT2

SOIL RESOURCES OF TRACE ELEMENTS

by

E. B. DAVIES

Part Two

(2) Induced Deficiencies

Deficiencies may be precipitated through agricultural practices, more particularly when a soil is low in the element concerned.

(a) *Heavy Liming*

Heavy liming, while rendering molybdenum more available may at the same time reduce the availability of other essential trace elements. Reduction of toxic levels of manganese has already been mentioned. The process can go further leading to actual manganese deficiency. Instances in orchards and wheat fields are recorded in New Zealand. Manganese supplied in topdressing in such cases is liable to be rendered unavailable also, and spray treatment of the foliage has been found the best corrective. Boron and cobalt likewise can be reduced in availability, and it is possible that the heavy liming in Southland which was mentioned as rendering molybdenum more available may at the same time have tipped the balance towards deficiencies in these elements. Some limestones contain appreciable amounts of cobalt but the beneficial effect of this is passing.

(b) *Change of Pasture Species*

A point that stands out in cases of W.M.D. and ill thrift in sheep and cattle is that animals on unimproved hill pastures are rarely affected. The lush, clovery, improved pastures lead to trouble. Can the pasture species be concerned? In a very extensive trial at Wairakei, Watkinson and I found indeed that brown top *(Agrostis tenuis)*, a major constituent of third-class pastures, contained several times the level of selenium found in white clover, while ryegrass and cocksfoot contained an intermediate amount. This applied whether or not the soil had been treated with selenium. Peterson and Spedding[24] have confirmed the order of uptake. Of seven species dissected out from a hill pasture at Whatawhata, the desirable white clover *(Trifolium repens)* and ryegrass *(Lolium perene)* (and undesirable ratstail *(Sporobolus capensis)*) contained the lowest levels of selenium, while brown top, yorkshire fog *(Holcus lanatus)*, *Danthonia* and notably sweet vernal *(Anthox-*

anthum odoratum) contained higher levels. Our present knowledge suggests that the species difference could swing the balance towards deficiency or adequacy as far as animal health is concerned.

TABLE V

Se CONTENT OF PASTURE SPECIES AT WHATAWHATA

	ppm
Sweet vernal	0.049
Danthonia	0.033
Yorkshire fog	0.031
Brown top	0.027
Ryegrass	0.020
Ratstail	0.017
White clover	0.013

Levels both of copper and molybdenum in herbage may change with the balance of the species, as affected by season for instance. Which way they change is, however, a moot point. Adams and Elphick[25] showed in an investigation on three South Island soil types that the copper content of white clover was consistently higher than that of ryegrass. Coop *et alia*[26] studying tussock grassland pastures found white clover and the weed cats-ear *(Hypochaeris radicata)* to have double the copper content of brown top. On the other hand both Van der Elst (unpublished data) on a peat, and Davies and Rolt (unpublished data) on a pumice soil (Atiamuri sand) found grasses to contain more copper than clovers. Stage of development could be a complicating factor. The clovers were more responsive in uptake to applied copper on the pumice, while grasses were more responsive on the peat. Molybdenum shows similar anomalies. In discussing them Watkinson (private communication) found that molybdenum level of the herbage, sulphate supply in the soil, and soil pH all had an influence on whether grasses or clovers contained the higher amount of molybdenum. The Mo : Cu ratio, as will be discussed later, is important when molybdenum levels are high.

It has been pointed out to me that the order of selenium contents at Whatawhata (Table V) is roughly that of the order of rate of growth of the species, the slower growing grasses containing more selenium. This brings me to a third method of inducing deficiencies—increasing pasture production and carrying capacity.

(c) *Increased Rate of Growth and Carrying Capacity*

It has been mentioned that Watkinson[17] considers that selenium occurs as iron-bound selenite. There would be a slowly

attained equilibrium between this difficultly soluble selenium and that in solution. Where pasture production is high, equilibrium might not be maintained and the selenium available would become diluted in the greater herbage yield. The variation in selenium content in the herbage species at Whatawhata would give indirect support to the supposition only if the plants were not growing in competition. It was evident from the Wairakei trial that there was a species difference in uptake apart from the rate of growth, for the relative differences between species were maintained even in the presence of excessive selenium. Nevertheless rapid growth may strain the supply of selenium in solution in selenium-low soils.

Cousins and Cairney[27] suggest that the widespread selenium deficiency evidenced on greywacke and schist-drived soils in Otago and Canterbury may be due to the slow weathering in the cool climate, selenium release not being rapid enough to meet stock requirements, when carrying capacity has been raised. They give a dramatic instance of the lambing percentages dropping from over 100 per cent to 27 per cent with increase of carrying capacity from 1,000 ewes to 2,000 ewes on an 1,180 acre property. This effect could equally well have stemmed from a change in pasture species.

Any farm "improvement" scheme—through fertiliser usage, irrigation, introduction of improved species—leading to increased carrying capacity could, it seems, precipitate trouble.

This possibility is not restricted to selenium.

(3) Virtual Deficiencies Through Interactions

Interactions between major and trace elements (the effect of liming has already been mentioned) or even between two trace elements can lead to virtual deficiencies. A particularly interesting one occurs in the case of copper. Deficiencies affecting pasture growth occur in New Zealand on peat soils and highly leached sands, but even healthy pastures, as already mentioned, may not contain enough copper to meet animal needs. Further, a copper molybdenum antagonism is apparent in the animal. Cunningham[28] has distinguished a complicated copper deficiency induced through too high a molybdenum content in the herbage. Notable cases are associated with peat soils on the Hauraki Plains and certain pumice showers at Wairoa. This effect of molybdenum causing a copper depletion occurs only in the presence of a high sulphate content.[29] There is thus a triple interaction of copper,

molybdenum and sulphate. Cases of copper poisoning have been described in Australia when the molybdenum is very low.[1]

A mutual antagonism between manganese and molybdenum has been demonstrated repeatedly overseas, and has been discussed by Walker *et al.*[30] in New Zealand. It is possible that the stated need for heavier dressings of molybdate on some soils is due to a high manganese content which would be much better combatted by liming.

Another type of interaction is illustrated from work on goitrogens present in brassicas and clovers, which affect the ingress of iodine to the thyroid gland. The interaction between supply of iodine and goitrogen would not seem straight forward.[31] Incidentally Butler and Johns[32] have shown wide differences in iodine uptake between species grown on the same soil (7-146 μg iodine/100g), and even between strains of the one species.

Effects such as that of drainage on trace element availability, or of closeness of grazing on cobalt supply could also be considered under the heading of interactions.

(4) Deficiency Through Export of Primary Produce?

A fourth possible cause of deficiencies is often put forward. With the constant removal of primary produce from the land both for export and internal consumption, and apparently no return of micronutrients, will not our soils become exhausted?

I have calculated the order of annual removal of a number of elements in mg/acre in milk, meat, wool and in lucerne hay, for comparison with assessed soil content in the surface three inches. The assessment has aimed at a rather below average figure from the Soil Bureau single factor maps. In the case of zinc I am indebted to Mr. Wells for information. The soil figures are of a different order of magnitude altogether and to make a tabulated comparison possible, results have been expressed as logarithms. The major element potassium has been included for comparison.

TABLE VI

TOTAL MICRONUTRIENTS IN SOIL AND SOME ANNUAL REMOVALS (log mg/acre)

	K	Zn	Cu	Mo	Mn	Co	B	Se
Present in Soil	9.5	7.2	6.4	5.4	8.1	6.1	6.6	5.1
Removals in Milk ..	6.7	4.2	2.6	2.3	2.0	0.3	3.4	1.4
„ „ Meat ..	5.3	3.5	1.5	0.0	0.1	1.1	0.5	
„ „ Wool ..	—	3.3	3.1	0.5	1.4	—	—	
„ „ Lucerne	8.0	5.3	4.7	3.8	5.4	—	5.3	2.2
Additions in fertiliser	7.7	4.9	6.0	4.4	—	4.6	5.6	3.9

(For sources of data see Appendix) ($\frac{1}{4}$oz/acre)

It will be seen that removals in animal products listed are minute compared with the soil reserves, varying from 1/1,000 to 1/100,000,000. One might well ask how it is that deficiencies have arisen. A few points need to be borne in mind.

(1) The soil figure is a low average. Many soils have considerably less total amount of an element than that given, e.g. the cobalt "average" has been assessed at 5 p.p.m. Most bush-sick soils are below 2 p.p.m. and figures as low as 0.3 p.p.m. have been reported.

(2) Only a small fraction of the total is immediately available.

(3) The turnover through an animal, going by that of major elements, may be much greater than the amount secreted in milk or built into body tissues. The bulk of intake could be excreted. The actual need may therefore be greater than the removals.

(4) A crop such as lucerne, if cut and fed off elsewhere, represents the greatest drain on a field, although its mineral content is returned elsewhere on the farm.

(5) With some elements at least, losses through leaching would be far greater than any removal in produce.

The removal of potassium in lucerne in the course of a year represents $\frac{1}{30}$ of the total and may well extend available supplies. Boron at $\frac{1}{20}$, molybdenum $\frac{1}{40}$, copper $\frac{1}{50}$ have all given responses in the field. Zinc $\frac{1}{80}$ and manganese $\frac{1}{500}$ have not. The ratio in the case of selenium is $\frac{1}{800}$ yet deficiency diseases in the animal are wide spread.

In the bottom line I have shown normal fertiliser additions where correction of a deficiency is aimed at—2 cwt potassium chloride, and 3 cwt/acre of copperised, molybdenised, cobaltised or borated superphosphate. Superphosphate manufactured from Nauru or Ocean Island phosphate rock naturally contains some 500 p.p.m. of zinc (the figure given is based on this) and this probably accounts in part for the few reports of zinc responses in New Zealand. T. Fitzpatrick[33] in Western Australia states that once an observed deficiency has ben made good, super contains enough zinc for an adequate supply. He points out too, that the plant level required for optimum growth is higher than the animal's needs.

In the case of zinc the total removed from a fat lamb farm in meat. bone and wool gives a log of 4.1. The amount

represents $\frac{1}{1300}$ of the soil zinc and $\frac{1}{6}$ of that in the normal application of superphosphate.

The possibility of inducing an absolute trace element deficiency through removal of primary produce from the farm would appear negligible.

Toxicity

Both major and trace elements can be poisonous in excess. The trace elements stand out in that the margin between deficiency and toxicity can be dangerously small. Both molybdenum and selenium occur in excessive amounts in the soil in various parts of the world, and resulting high herbage levels have led to poisoning of stock. The symptoms (though not the cause) were well known and described centuries ago, e.g. selenium poisoning of horses is unmistakeable in the writings of Marco Polo (1295). In New Zealand, molybdenosis in stock (Cunningham's complicated copper deficiency) occurs naturally in areas which have been defined by Cunningham[12] through a pasture survey. It could equally well be caused by too liberal or too frequent application of fertiliser molybdate; this is particularly so on peats.

The recommendation for sodium molybdate application is $2\frac{1}{2}$ ozs./acre at not more than about three-year intervals. Heavier rates and at yearly intervals have been applied in some areas, sometimes with some backing from field trials, but more often from the farmer's impression of further response from repeated applications. Such further improvement may well stem from the build-up of nitrogen following the initial application, plus the effect of further superphosphate used as a carrier. Improved results from heavier applications can also arise, as already mentioned, from the combatting of manganese toxicity. Normally we regard the response level for molybdenum as about 0.1 p.p.m. molybdenum in white clover. Yet responses are seemingly obtained when the level is much higher, e.g. 2.5 p.p.m. Where authentic, interactions of the Mn x Mo type are probably implicated. Initial application of light lime applications to look after the manganese, plus molybdenum in moderation, would seem the correct solution. Where annual dressings or heavier rates of molybdenum have been applied with apparent safety, later trouble may be triggered off through a tardy lime treatment.

Detection of Deficiencies

Trace element deficiencies have in general made their presence felt through specific symptoms in livestock, in crops, or in

fruit trees. In the case of herbage the deficiency may express itself through the herbage composition—a failure of legumes and the better quality grasses. Once a specific trouble has been defined, hunting for the cause becomes a matter for research. Once a deficiency is identified, the occurrences of the characteristic symptoms or syndromes themselves give some idea of the areas involved. They may be related to particular soils whose boundaries have been mapped. The usual line of attack in New Zealand has been through a wide coverage of observational trials in the case of pasture, or of dosing trials with measurement of live weight gains in the case of sheep, again with careful attention to soil type. Herbage analyses have been used by McNaught[34] for cobalt and by Cunningham[12] for copper in conducting surveys. Total cobalt in soils was determined by Kidson,[35] and attempts have been made through dilute acid extractions to assess available cobalt and molybdenum. Copper surveys have been carried out by Thornton using the growth of *Aspergillus niger* to measure availability, while Rolt is using a versenate extraction to the same end. He finds total copper useful also, as determined by a perchloric acid extraction. Watkinson has found that total selenium in soils lines up fairly well with weight gains of lambs in selenium dosing trials, and has done some work with selenium fractionations. Such tests have their place.

In actual practice, once farming is well established the trace element status may vary from farm to farm, or even field to field. Are advisory soil or herbage tests possible? Soil tests are empirical and must be checked against results of field trials. Also, tests of any precision are very much more demanding of time, skill, and care than ordinary major element tests. Even with streamlining they may take ten times as long. This often applies to herbage analysis as well. The situation becomes difficult for a routine service. Herbage analyses of single species samples taken at a given stage of growth may be interpreted for plant requirements, once response levels are established. To judge suitability for animal requirements mixed herbage samples representing what the animal actually consumes, are needed. Possibly levels of other elements (copper, molybdenum and sulphate) would influence interpretation.

Is our Present Knowledge being Fully Exploited?

New Zealanders, no doubt owing to the dramatic results achieved through use of cobalt and later molybdenum, are trace element minded. In fact there is perhaps too much of a tendency to regard trace elements as a cure-all. Instances nevertheless are

apparent where present knowledge is not being exploited. A case in point is that of molybdenum. Much molybdenum deficient hill country has yet to be developed, despite the ease of application of molybdenised super from the air. There are, too, instances where there is a marked bias against its use, engendered partly through over-emphasis of the dangers of excess. A frequent remark where molybdenum is not favoured is "Molybdenum produces the feed, but also increases the dags". The change in consistency of droppings is associated with the change from the browntop dominant type of sward to lush clovery pastures, and not to molybdenum excess.

The important trace element deficiencies in New Zealand are boron, molybdenum and to a lesser extent copper, as far as plant growth is concerned, and cobalt, selenium, iodine and copper for the animal. Where failure of crop, death of livestock, or unsaleability of fruit is the result of not supplying an element, it is fairly certain that it will be used. Cobalt, iodine and boron are cases in point. On the other hand borderline deficiencies, ones leading merely to a lower pasture production or lack of thrift in the animal, may be neglected or remain undetected. Liaison between farmer, advisory officer and research worker should lead to their rectification. There are instances where a holding big enough to prove an economic unit is running only one-half ewe to the acre, even though the potential, with use of molybdenum, may be four ewes per acre. Why should the owner bother to bring about the improvement? The pressure for primary production makes it essential to change this attitude, even if subdivision becomes necessary.

The overall picture in New Zealand at present is that some, at any rate, of the trace elements have still a part to play both in the bringing in of new land and in the improvement of existing pastures. Selenium, the newcomer, in the face of a developing deficiency, has great potentialities towards maintaining the fertility and thrift of livestock. The field of the trace element is an exciting and a rewarding one.

REFERENCES

[1] E. J. Underwood. "Trace Elements in Human and Animal Nutrition". New York and London 1962, (2nd edition).
[2] A. J. Mitteldorf and D. O. Landon. Anal. Chem. (1952), 24, 469-472.
[3] W. Skey. Report of Colonial Analyst, 1892, p. 50.
[4] A. J. Anderson. Role of molybdenum in plant nutrition in "Inorganic Nitrogen Metabolism", The John Hopkins Press, Baltimore, 1956, p. 3-49.
[5] Shankat Ahmed and H. J. Evans. Soil Sci. (1960)), 90, 205-210.

[6] C. C. Delwiche, C. M. Johnson and H. M. Reisenauer. Plant Physiol (1961), 36, 73-78.
[7] H. M. Reisenauer. Nature (1960), 186, 375-6.
[8] D. I. Arnon and G. Wessel. Nature (1953), 172, 1039-1040.
[9] N. Wells. N.Z. J. Sci. Tech. (1956), 37B, 482-502.
[10] W. F. Rolt. Trans. Joint Meeting Comm. IV and V, Int. Soc. Soil Sci., 1962, 842-846.
[11] W. J. Hartley and A. B. Grant. Federation Proc. (1961), Vol. 20, 679-688.
[12] I. J. Cunningham, K. S. Hogan and J. N. Breen. N.Z. J. Sci. Tech. (1956), 38A, 225-238.
[13] R. W. Willett in "Outline of the Geology of N.Z.", p. 11. (Booklet to accompany 16 mile to inch geological map).
[14] N. H. Taylor. Austr. Vet. J. (1952), 28, 183-189.
[15] N. Wells. N.Z. J. Sci. Tech. (1957), 38B, 884-902.
[16] N. Wells. J. Soil. Sci. (1960), 11, 409-424.
[17] J. H. Watkinson. Trans. Joint Meeting Comm. IV and V, Int. Soc. Soil Sci., 1962, 149-154.
[18] E. B. Davies. Proc. 14th Conf. of N.Z. Grassland Assn. (1952), 182-191.
[19] J. D. Atkinson. N.Z. J. Sci. Tech. (1935), 16, 316-9.
[20] J. W. Woodcock. N.Z. J. Agric. (1936), 53, 99.
[21] E. B. Davies, G. A. Holmes and P. B. Lynch. N.Z. J. Agric. (1951), 83, 247-250.
[22] J. W. Maclean, G. G. Thompson and B. M. Lawson. N.Z. Vet. J. (1963), 11, 59-60.
[23] W. J. Hartley. N.Z. Vet J. (1953), 1, 137.
[24] P. J. Peterson and D. J. Spedding. N.Z. J. Agric. Res. (1963), 6, 13-23.
[25] A. F. R. Adams and B. L. Elphick. N.Z. J. Sci. Tech. (1956), 38A, 345-358.
[26] I. E. Coop, M. Darling, C. M. Anderson. N.Z. J. Sci. Tech. (1953), 34A, 507-20.
[27] F. R. Cousins and I. M. Cairney. Austr. J. Agric. Res. (1961), 12, 927-943.
[28] I. J. Cunningham. "Copper Metabolism", pp. 246-273. (John Hopkins Press, Baltimore, 1950.)
[29] A. T. Dick. Soil Sci. (1956), 81, 229-236.
[30] T. W. Walker, A. F. R. Adams, and H. D. Orchiston. Plant and Soil VI (1955), 201-220.
[31] Evan Wright. N.Z. J. Agric. Res. (1959), 2, 903-914.
[32] G. W. Butler and A. T. Johns. J. Austr. Inst. Agr. Sci. (1961), 27, 123-133.
[33] E. N. Fitzpatrick. J. Agric. West Austr. (1962), 3 (4th series), 323-7.
[34] K. J. McNaught. N.Z. J. Sci. Tech. (1938), 20A, 14-30.
[35] E. B. Kidson. N.Z. J. Sci. Tech. (1937), 18, 694-707.

APPENDIX

Source of data used in Table VI.

Soil—Low average derived from single factor maps of Soil Bureau. Content taken in acre x 3" at 600,000 lbs. Zn: av. from Wells 55 p.p.m. Se: from Watkinson's data (17).

Milk—Allowed 800 gallons/acre/year and used analytical figures gleaned from Underwood,[1] e.g. p. 166.

Meat—Analytical figures A. J. Mitteldorf and D. O. Landon. Anal. Chem. (1952), 24, 469-472.
Raw composite beef rib muscle. 12th rib: composite of 5 samples.
Average of 7 grades used—choice, good, commercial, utility, canner, cutter, bull.

Yield of meat (beef) 260 lbs. 57% muscle (two-year-old Aberdeen Angus). 148 lbs. muscle.

Wool—Figures ex W. B. Healy, L. C. Bate, and T. G. Ludwig. N.Z. J. Agric. Res. 7, 603-610.
Average analyses of wool from lambs on Hastings soil used. Representative of North Island intensive fat lamb farms.
Allowed 52 lbs. wool of 80% yield.
cf Minerals in Domestic Wools. R. H. Burns et alia, J. Anim. Sci. 23, 5-11.
Analyses from the two sources agree qualitatively except Mn much higher (x 30) in the latter.

Lucerne—4 tons lucerne hay.
Major elements Av. 8 analyses Ruakura Agric. Res. Centre.
Trace elements Av. 2 analyses Ruakura Agric. Res. Centre.

Fertilisers—Zinc in Super 500 p.p.m. (ex Nauru).
3 cwt. super ≡ 76.2 g/acre Zn.
Six times as much as in meat, bone and wool removal.
Molybdenised super: 1 lb. Sod. molybdate/ton.
Copperised super: 56 lbs. copper sulphate/ton.
Borated super: 56 lbs. borax/ton.
Cobaltised super: 3 lbs. $CoSO_4.7H_2O$/ton.

Bone—260 lbs. meat. 15% bone. 400 p.p.m. Zn allowed. i.e. 7072 mg. (log 3.8).

A.N.Z.A.A.S. CONFERENCE

Melbourne, January 1967

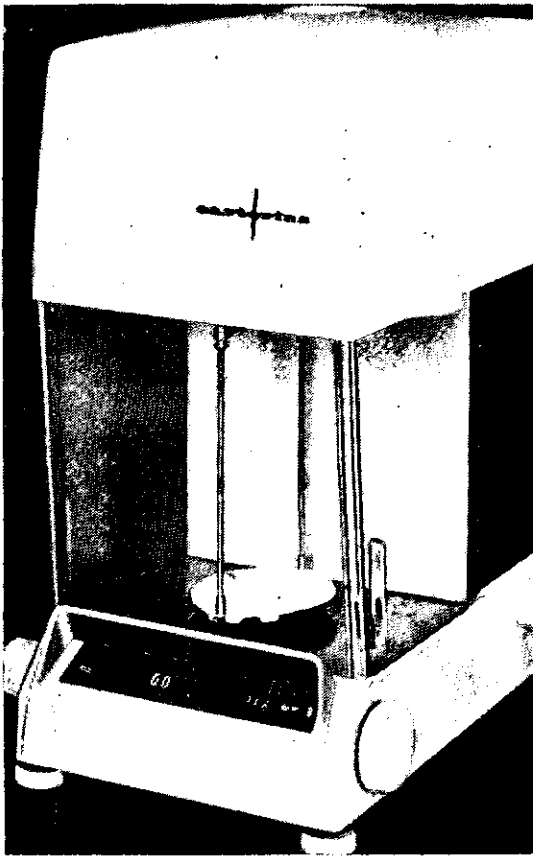
Section H of this Conference will be a *Chemical Engineering Conference* with the theme "The Contribution of Chemical Engineering to the development of Australia and New Zealand".

Papers for this conference, which will comprise a series of symposia on Chemicals and Plastics, Fuels, Minerals, Fertilisers and Agricultural Chemicals, Process Industries, will still be accepted to April 30, 1966.

Enquiries concerning the conference should be addressed to Prof. S. R. Siemon, Department of Chemical Engineering, University of Melbourne, Parkville N.2, Victoria.

sartorius

Single Pan Analytical Balance Series 2400 with Plastic-housing and All-digital Weight Indication



	2401	2402	2403
system	substitution	substitution	substitution
capacity	200 g	200 g	100 g
mechanical weight application	10–190 g	1–199 g	1–99 g
scale range	10 g	1 g	1 g
scale division	100 mg	10 mg	10 mg
reading to (micrometer)	1 mg	0.1 mg	0.1 mg
precision (std. deviation)	0.3 mg	0.05 mg	0.05 mg
accuracy in the scale range	±0.5 mg	±0.05 mg	±0.05 mg
accuracy of the built-in weights	±0.1 mg	±0.1 mg	±0.1 mg
damping	air	air	air

Plus, plus, plus—and everything at a glance!

All-digital weight indication. Easily legible scale image. Colour contrast projection scale. All operating elements on the side of the base. Large weighing compartment, accessible from both sides. Smooth base inside of the weighing compartment, no protruding parts for easier cleaning. Cylindrical built-in-weights, minimum surface, for protection against dust and moisture.

REPRESENTED EXCLUSIVELY IN NEW ZEALAND BY

GEO. W. WILTON & CO. LTD.

P.O. Box 367, WELLINGTON

P.O. Box 9071, Newmarket, AUCKLAND

PURE WATER – H_2O – INSTANTLY

at a turn of the tap

ELGASTAT B113

FEATURES

This simple and self-contained Elgastat provides highly deionised water and Purified Water B.P. Flow starts instantly at a turn of the tap. Flow speed is 20 gallons/90 litres per hour. A conductivity indicator provides a conclusive quality check. No power is required and there is no regeneration or maintenance. Storage of distilled water is altogether unnecessary. The world wide Elgastat Cartridge Refill Service keeps the unit on tap wherever you are—on any part of the globe where purified water is needed. Effluent cost is only a little higher than tap water itself.

OPERATION

Once fixed over the Laboratory sink, purified water may be drawn simply by operation of the control valve. Time taking regeneration is altogether avoided.

QUALITY OF EFFLUENT

	ELGALISED WATER	AQUA DIST.
Quality	2 MΩcm	0.2 MΩcm
Total dissolved solids	2 p.p.m.	10 p.p.m. average

ANALYSIS

Cu, Fe, NH_3	Not detected
Cl, SO_4, CO_2	Not detected
Silica	less than 0.1 p.p.m.
pH	6.6-7.0

Elgalised Water is Purified Water B.P. far exceeding the requirements of B.P. Tests. It contains less than 1/10th of the impurities commonly present in distilled water.

Made in England by

ELGA PRODUCTS LIMITED, LANE END, BUCKINGHAMSHIRE
Phone: LANE END 393 Cables: ELGAMATICS HIGHWYCOMBE

Represented exclusively in New Zealand by

GEO. W. WILTON & CO. LTD.

BOX 367, WELLINGTON **BOX 1980, AUCKLAND**

THE CHEMICAL PRINCIPLES OF THE EXTRACTION OF METALS

by
ALAN F. BROWN
Riccarton High School

This essay won the 1965 Shell Essay Competition, of the Canterbury Junior Chemical Society.

In our modern civilisation, we could not do without metals. Their malleability, ductility, and heat and electrical conductivity are properties which no other elements or compounds can offer. Some 80 of the 103 elements now known to exist are metals or metalloids. (Metalloids, elements such as arsenic or antimony, are borderline cases between metals and non-metals.) These elements tend to lie towards the left and bottom of the periodic table, which means that the metals are, in general, the heavier elements in each family and tend to be electron donors, so forming positive ions.

As long ago as 300-400 B.C. primitive man had worked some native metals like gold and copper, as he would any other kind of "stone", but he soon learned to smelt ores with charcoal in crucibles and furnaces to copper, and soon afterwards to alloys of copper. Here the craft of metallurgy, the winning of metals from their ores, had its beginnings. Over the thousands of years which have passed between then and now, this craft has grown until today major industries are devoted to the metallurgy of different metals. Enough iron ore is converted in the blast furnace to pig iron to produce 10^9 tons of steel each year. Without a knowledge of the principles of chemistry involved in the extraction of metals, man could not have advanced as far as he has in the winning of these important elements from nature.

Minerals and Ores

A few of the metallic elements form water-soluble compounds with the common anions, and are found in appreciable concentrations in the oceans and landlocked seas of the world. The majority, however, form insoluble compounds with the anions present in the earth's crust, and are found as solid deposits. When these deposits are homogeneous, and are composed of reasonably pure substances, they are called minerals. Deposits of minerals worth commercial development are known as ores.

Most minerals are of no commercial importance as sources of the metallic elements, either because of their rarity or because of the difficulty of obtaining the pure element from them. Usually only a few minerals of each element are found as ores. Most ores contain sulphides, oxides, or the metallic elements themselves. Chlorides, sulphates, silicates, and phosphates constitute most of the rest.

Commercial ores, or the minerals they contain, do not always correspond to the pure substances found in the laboratory. Impurities are almost invariably present, and the metallurgy of a particular metal will depend on the total constituency of its ore.

Enrichment of Ores

Only a few ores, such as iron, are pure enough to feed directly into the process for preparing the metal. Most ores require preliminary steps to concentrate the desired mineral and remove impurities which would interfere in later stages of the metallurgical process.

Flotation

This method for removing the mineral from the gangue, or valueless part of the ore, relies on the principle that certain detergents make it possible for water to wet some surfaces without wetting others. The water is beaten into a froth, which presents a much greater surface for wetting the desired material. A detergent is used to cause the water to wet the mineral but not the gangue, and the mineral becomes concentrated in the froth. The froth rises to the top of the flotation bath, is skimmed off, and collapses, letting the mineral settle out. Ores containing less than one per cent of copper become industrially useful after separating copper sulphide from its ore by flotation.

The range of detergents for flotation is so wide that it is possible, for instance, to separate potassium chloride and sodium chloride by choosing the correct combination of detergent and froth.

Selective Solution

Before aluminium oxide ores (bauxite) can be reduced to pure aluminium, the ferric oxide and various silicates, which are major inpurities in the ores, must be removed. Aluminium oxide, because it reacts with acids to form cations, and with strong bases to form anions, is amphoteric. This means that when bauxite is

treated with hot sodium hydroxide solution, the aluminium oxide dissolves to form aluminate ions, leaving the iron oxide and silicate impurities as solids.

$$\underset{\text{solid}}{Al_2O_3} + \underset{\text{solid}}{Fe_2O_3} + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^- + \underset{\text{solid}}{Fe_2O_3}$$

When the solution is filtered and cooled, aluminium hydroxide of very high purity precipitates.

$$Al(OH)_4^- \rightarrow \underset{\text{solid}}{Al(OH)_3} + OH^-$$

The hydroxide is heated to form the oxide and sent to the final stage of the process for producing aluminium metal.

$$\underset{\text{solid}}{2Al(OH)_3} \rightarrow \underset{\text{solid}}{Al_2O_3} + \underset{\text{gas}}{3H_2O}$$

Selective Precipitation

Magnesium chloride, a raw material used for making metallic magnesium, can be obtained by treating magnesium oxide with hydrogen chloride or chlorine. Magnesium oxide is produced by precipitating the magnesium ions in sea water as magnesium hydrochloride, and heating the hydroxide to give the oxide. Although ocean water contains only about 0.1 per cent of magnesium, the magnesium ion is simply and quantitatively precipitated using a calcium hydroxide slurry as the precipitant.

Flotation, selective solution, and selective precipitation are the most important of the enrichment procedures.

Winning of Native Metals

The metals which occur free in nature, that is, uncombined with other elements, are found in the middle of the long periods of the periodic table. Consequently they all have high densities, and may usually be separated from surrounding materials by simple flotation methods requiring no detergent, but merely a rapidly flowing stream of water. The sluice used for recovering gold and silver can be made more effective by covering the bottom with mercury, rather than just having cleats to catch the heavy metals as they settle. The mercury will readily dissolve even the tiniest particles of gold and silver, but not the accompanying rocks. From time to time the mercury is distilled leaving the gold and silver which may be separated by further chemical treatment. This process is essentially a selective solution method.

The Parkes process for removing the silver present in many lead ores further illustrates selective solution. A small quantity

of zinc metal, 1 or 2 per cent, is added to the liquid solution of silver and lead formed when the ore is smelted. Zinc and lead are mutually insoluble, but silver is much more soluble in zinc than lead. The silver concentrates in the zinc which rises to the top of the lead layer. Upon cooling, the zinc layer solidifies first and is broken up and removed from the still molten lead. Solid silver is left when the zinc is distilled.

The prices of silver and gold are now so high that it is economically feasible to utilise ores containing only minute amounts of the metals. Highly dilute ores may be treated with a sodium cyanide solution in the presence of air. The cyanide forms stable complex ions with the gold and silver ions which have been formed by oxidation with the air, allowing air oxidation to proceed until all the silver and gold have been converted into the cyanide complexes. The metals are then precipitated from the solution by reduction with metallic zinc. The equations for silver are:

$$\underset{\text{solid}}{2Ag} + \tfrac{1}{2}O_2 + 4CN^- + H_2O \rightarrow 2Ag(CN)_2^- + 2OH^-$$

$$2Ag(CN)_2^- + \underset{\text{solid}}{Zn} \rightarrow Zn(CN)_4^{--} + \underset{\text{solid}}{2Ag}$$

A physical process often used if the content of free metal in the ore is high, is to heat the ore above the melting point of the metal. The metal usually has a lower melting point than the gangue, and may be run off and cast into ingots. Bismuth is commonly separated from its ores in this way.

Extracting Metals from Their Ores

When metal atoms combine with atoms of another element to form a compound, they lose electrons and are oxidized; that is, they assume positive oxidation numbers. To win the metal from these compounds, a reducing agent must be used which will supply electrons and change the oxidation number of the element from a positive to a zero value. The task confronting metallurgists is to find the cheapest reducing agent and the best conditions for its reaction with the ore. The more electropositive the metal, the more powerful the reducing agent must be.

The reducing agents may be divided into four general classes:

(1) The anion or anions in the mineral may reduce the cation, usually at high temperatures. This method applies particularly to sulphide ores of the least electro-positive metals; when heated in air (roasted) they give the metal plus sulphur dioxide.

(2) The reducing agent may be carbon, in the form of coke, which is the cheapest reducing agent other than the anions of the minerals. The carbon is usually converted to gaseous carbon monoxide, an active reducing agent that can make good contact with the metal and so give a high rate of reaction.

(3) More powerful chemical reducing agents, such as hydrogen, aluminium, or sodium, may be used if their expense can be covered by the cost of the product.

(4) Electrolytic cells may be used to reduce the most electropositive cations such as those of sodium, magnesium, aluminium, and other active metals. Only if the molten compound or its solution in some solvent is ionic can electrolysis be used.

Reduction of the Ore by Roasting

Many minerals, particularly the sulphides, when heated in a limited supply of air, react to give a metal and a gas containing the material formerly present in the anion of the ore. For a sulphide ore the reaction is:

$$\underset{\text{solid}}{MS} + \underset{\text{gas}}{O_2} \rightarrow \underset{\text{liquid or gas}}{M} + \underset{\text{gas}}{SO_2}$$

If the air is not carefully regulated, oxides are formed instead of the metal; however, this regulation is not difficult for the less electropositive metals such as mercury, copper, silver and lead. Mercury formed in this way and condensed is pure enough for immediate sale. The more electropositive metal impurities in lead sulphide ore are oxidized by a slight excess of air and, being insoluble in the molten lead, can be skimmed off. Any silver may be removed by the Parkes process.

Ores of elements more electropositive than copper, mercury, lead, and silver give oxides on roasting. Typical equation is:

$$\underset{\text{solid}}{MS} + \underset{\text{gas}}{\tfrac{3}{2}O_2} \rightarrow \underset{\text{solid}}{MO} + \underset{\text{gas}}{SO_2}$$

These oxides must then be reduced to obtain the metal. The sulphides of molybdenum, cobalt, nickel, zinc, cadmium, tin, arsenic and antimony are commonly roasted to the corresponding oxides in this way.

Reduction with Carbon

All the oxides mentioned above can be reduced to the metal by reduction with carbon in the form of coke. The oxides of iron, manganese, chromium and tungsten are commonly reduced with coke as well.

The roasting reaction in sulphide ores involves a mechanism essentially between gaseous oxygen and the ore; for carbon reduction the mechanism cannot be so simple, since both coke and ore are solid, and are therefore unable to come into close enough contact. Industrial reactions must be rapid in order to produce profitable amounts of product per unit time, but reactions between solids are slow. Usually, the reduction of an oxide with carbon proceeds through a series of reactions, typified in the following equations.

$$\underset{\text{solid}}{C} + \underset{\text{gas}}{O_2} \rightarrow \underset{\text{gas}}{CO_2}$$

$$\underset{\text{solid}}{C} + \underset{\text{gas}}{CO_2} \rightarrow \underset{\text{gas}}{2CO}$$

$$\underset{\text{gas}}{CO} + \underset{\text{ore}}{MO} \rightarrow \underset{\text{gas}}{CO_2} + \underset{\text{liquid}}{M}$$

The carbon dioxide produced can be used again in the second step of the reaction. The equations given here all describe reactions between solids and gases to produce at least one gaseous product. Such reactions are rapid; the gas makes excellent contact with the solid, presenting a good reaction surface, and the gaseous product can readily diffuse away.

In most processes the metal is produced as a liquid which separates from the solids and gases. It can then be tapped off and cast into ingots from time to time. The temperature may even be high enough to allow some of the metal to form as a gaseous product which can then be condensed from the flue gases. Tungsten is a notable exception. This metal, because of its very high melting point, is produced as a powder. The powder is compacted by passing a heavy electric current through it, sintering it together into bulk metal.

Tungsten, molybdenum, cobalt, nickel, zinc, cadmium, arsenic and antimony, produced by the "reduction with carbon" method are pure enough for immediate sale. Occasionally however, it is profitable to separate traces of metals by fractional distillation or electrolytic refining. Cadmium may be distilled from zinc, and arsenic from antimony. Iron, chromium and manganese metals produced by this method contain considerable quantities of dissolved carbon.

Reduction with Hydrogen, Aluminium and Sodium

The least electropositive metals may be reduced from their ores by the anions in the ores. The somewhat more electropositive

elements can be reduced from oxide ores by reduction with carbon. Still more electropositive elements require reducing agents more powerful than carbon. Also, carbon can be undesirable as a reducing agent if it dissolves in the metal and is too difficult to remove; this is the case with chromium and manganese.

Pure chromium and manganese are often made therefore, by reducing their oxides with aluminium in the Goldschmidt, or Thermit, reaction. In this reaction, which is highly exothermic, the ore is reduced to the molten metal and the aluminium is oxidised to aluminium oxide. For chromium the reaction is:

$$\underset{\text{solid}}{Cr_2O_3} + \underset{\text{solid}}{2Al} \rightarrow \underset{\text{liquid}}{2Cr} + \underset{\text{solid}}{Al_2O_3}$$

Columbium and tantulum may also be prepared in this way.

Aluminium is also used as a reducing agent in the Thermit reaction with ferroso-ferric oxide. When this oxide is reduced by aluminium the reaction is so intensely exothermic that molten iron at a temperature of about 3,500°C is produced.

$$\underset{\text{solid}}{3Fe_3O_4} + \underset{\text{solid}}{8Al} \rightarrow \underset{\text{solid}}{4Al_2O_3} + \underset{\text{liquid}}{9Fe} + \text{heat}$$

The iron produced in this reaction is used for welding large steel parts such as railway lines or the propeller shafts of ships.

Although it can reduce all the oxides reduced by carbon, hydrogen is a more expensive reducing agent than coke. It is used sometimes when a more desirable product is formed than would be by carbon reduction, and is also the usual reducer for tungsten oxide. With some elements it forms undesirable hydrides.

Sodium has been used in the past to prepare aluminium and the alkaline earth metals, but these highly electropositive elements are now prepared almost exclusively by electrolysis of molten salts.

Electrolysis of Molten Salts

No reducing agents powerful enough exist to reduce the most electropositive metals. Such metals are separated from their ores in electrolytic cells. Water must be absent from these cells because of the ease with which hydrogen ions in water gain electrons. In most methods the molten ore is electrolysed.

In the liquid salt the cations move towards the electron-rich electrode, the cathode. Here, the ions gain electrons from the electrode and change to the metal. At the same time the anions in the ore move towards the electron-poor electrode, the anode.

Here, they lose electrons and are converted into substances with different electron structures.

The voltage used in an electrolytic cell is very important, for it permits a selective electrodeposition of the metals. There is a definite minimum voltage required by each substance before it can be deposited. If two metal ions are present in the solution the one lower in the activity series (the one that gains electrons most easily) is deposited first.

Electrolytic Refining

Small amounts of impurities are present in many of the metals produced by the processes discussed, and for some metals even traces of impurities can be harmful. For instance, the conductivity of copper is weakened considerably by traces of arsenic and other elements present in the metal. For electrical conductors, therefore, the copper must be very pure. This purity is achieved by electrolytic refining.

The impure metal serves as the anode, from which the metal is oxidised and redeposited on a cathode of high purity. The electrolyte is a solution of a salt of the metal. The voltage to the cell is regulated so that the more electronegative impurities are not oxidised, but form as a sludge below the anode. This "anode sludge" often contains enough of the valuable metals such as gold, silver and platinum to offset the cost of electrolysis. The voltage is also kept low enough to prevent the more electropositive impurities which are oxidised at the anode from being reduced at the cathode. These impurities remain in solution.

Heavy currents are used in electrolytic refining, so that a profitable amount of metal will be produced per unit time. This is in accord with Faraday's first law of electrolysis: "The amount of a substance produced by a cathode or anode reaction in electrolysis is directly proportional to the quantity of electricity passed through the cell."

Reduction of Iron Ore to Pig Iron

Having discussed the different metallurgical processes and the chemical principles involved in them, we shall now go on to look at a few typical or important applications of these processes.

By far the largest metallurgical process using coke as a reducing agent is the conversion of iron ore to pig iron in the blast furnace. As was stated before, enough ore is treated in this way to produce 10^9 tons of steel each year.

The main ores of iron are ferric oxide, Fe_2O_3 (haematite), and ferroso-ferric oxide, Fe_3O_4 (magnetite). These partially hydra-

ted oxides contain varying amounts of impurities, mostly silicates. These silicates, less readily oxidised than the ore, form a viscous, glassy substance at the temperature used for the reduction. Some silicates even stay as solids at blast furnace temperatures. To avoid complications in the removal of these impurities from the furnace, the glassy or solid silicates are reacted with calcium oxide, increasing their fluidity, and allowing them to form a layer of molten "slag" on the surface of the molten iron. The slag is run off from time to time, and is then sometimes dumped as useless, or sometimes used to make slag rock or cement. The calcium oxide for liquifying the silicates is made from calcium carbonate, in the form of limestone, which is added with the coke and iron ore and changes to calcium oxide at blast furnace temperatures. The equations for this reaction, and the reaction of the calcium oxide with the silicate are:

$$\underset{\text{solid}}{CaCO_3} \rightarrow \underset{\text{solid}}{CaO} + \underset{\text{gas}}{CO_2}$$

$$\underset{\text{solid}}{CaO} + \underset{\text{solid}}{SiO_2} \rightarrow \underset{\text{liquid}}{CaSiO_3}$$

The $CaSiO_3$, calcium metasilicate, is just an idealisation of the complex composition of slag.

The important reactions which occur in the blast furnace are the combustion of coke to carbon dioxide, the conversion of the carbon dioxide to carbon monoxide, and the reduction of the iron oxide by the carbon monoxide.

$$\underset{\text{solid}}{C} + \underset{\text{gas}}{O_2} \rightarrow \underset{\text{gas}}{CO_2}$$

$$\underset{\text{solid}}{C} + \underset{\text{gas}}{CO_2} \rightarrow \underset{\text{gas}}{2CO}$$

$$\underset{\text{gas}}{3CO} + \underset{\text{solid}}{Fe_2O_3.xH_2O} \rightarrow \underset{\text{liquid}}{2Fe} + \underset{\text{gas}}{3CO_2} + \underset{\text{gas}}{xH_2O}$$

The blast furnace is designed to conserve thermal energy and to use it as efficiently as possible. The hot air to burn the coke in is introduced just above the slag level at the bottom of the furnace, and the combustion zone, where the highest temperatures are attained, is just above this point. The hot gaseous products are removed at the top of the furnace. The crushed limestone, ore and coke are fed in through the top of the furnace and are preheated as they descend through the rising hot gases, becoming hot enough to permit reduction of most of the ore well above the combustion zone. Excess carbon is always used, so that any last traces of iron may be reduced in the pool of molten iron and slag at the bottom of the furnace.

The blast furnace produces not pure iron, but a product called pig iron. Pig iron contains about 92 to 94 per cent of iron, 3 to 4 per cent of carbon, up to 2 per cent of silicon (from reduction of the silicates) and usually some sulphur and phosphorus. Practically all pig iron is refined to remove undesirable impurities and the iron then used to make alloys called steels. A small amount is also used to make cast iron, a brittle substance with limited uses.

The reductions of other metallic oxides, while not performed on such a tremendous scale, follow the same general principles as those in the reduction of iron ore.

The Metallurgy of Copper

Copper is one of the most important metals produced by roasting the ore in air. Its main ores are sulphide ores; Cu_2S (chalcocite), and $CuFeS_2$ (chalcopyrite).

Low grade ores are first concentrated by flotation. The rich sulphide ore is then roasted in a furnace in a limited supply of air; this process removes some of the sulphur as sulphur dioxide and leaves a mixture of Cu_2S, FeO, SiO_2, and other substances. The roasted ore is then mixed with limestone, which serves as a flux, and is again heated in a furnace. The limestone combines with the iron oxide and silica to form a slag, and the cuprous sulphide melts and can be run off. This impure, molten cuprous sulphide called matte, is then reduced by blowing air through it.

$$\underset{\text{liquid}}{Cu_2} + \underset{\text{gas}}{O_2} \rightarrow \underset{\text{liquid}}{2Cu} + \underset{\text{gas}}{SO_2}$$

The blast of air also forms some copper oxide, which seriously contaminates the metal. Green wood poles are used to stir the contaminated liquid copper, and the vapour from these poles reduces most of the oxide to the metal. The copper obtained in this way has a characteristic appearance and is called blister copper. It contains about one per cent of iron, gold, silver, and other impurities, and is usually refined by electrolysis to form the pure metal.

Although the details of this process differ from those for lead and mercury, whose ores are also roasted in air, the reduction principle is the same.

The Manufacture of Aluminium

Aluminium is a strongly electropositive metal which is reduced from its ores commercially by electrolysis. However, the problem of producing this important metal by electrolysis differs from that of other strongly electropositive metals. The common

ore, Al_2O_3 (bauxite), has a very high melting point, and apart from this, most molten aluminium compounds do not conduct electricity, aluminium forming a macromolecular oxide and molecular halides rather than ionic compounds. The aluminium cannot be deposited from a water solution of one of its compounds, since it is too reactive a metal, and hydrogen is formed instead.

The problem of reducing the aluminium by electrolysis of its molten salts was solved by Charles Hall, a young American, in 1886. The identical process was discovered independently in the same year by a young Frenchman, P. L. T. Héroult. The problem was to find a molten salt bath in which aluminium compounds could be electrolysed, preferably one in which aluminium oxide, the common one, could be dissolved and electrolysed. The salt found by Hall and Héroult was cryolite, Na_3AlF_6. This mineral had the desired property of dissolving aluminium oxide at relatively low temperatures to give a conducting solution from which aluminium could be reduced.

The method used today is essentially the same as the method used 70 years ago; even now the theory and mechanism of the process are only partially understood. The anodes in the modern electrolytic cell are made of carbon. The liquid aluminium formed sinks to the bottom of the molten salt and settles as a layer on the carbon-lined iron cell wall which acts as the cathode.

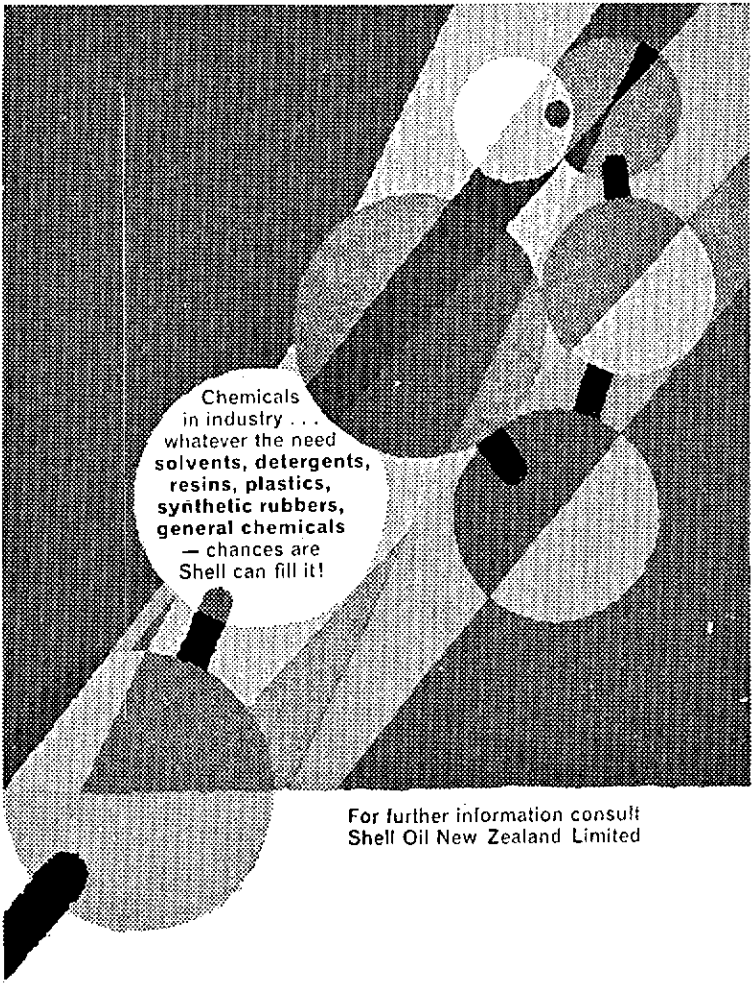
$$\underset{\text{liquid}}{Al^{3+}} + 3e^- \rightarrow \underset{\text{liquid}}{Al}$$

Periodically the aluminium is tapped off. The bath is kept molten, at about 1,200°C., by the heating effect of the electric current. At the anodes carbon dioxide, carbon monoxide and oxygen are produced, the carbon oxides predominating because of their reaction with the electrodes.

$$2O^{2-} + \underset{\text{solid}}{C} \rightarrow \underset{\text{gas}}{CO_2} + 4e^-$$

The electrodes are fed slowly into the cell to replace the parts burnt away.

These three processes, the production of pig iron, of copper, of aluminium, are examples of the way man has utilised chemical principles to perform otherwise impossible metallurgical operations. Metallurgy is now a strongly established craft, but it must always be remembered that a knowledge of the chemical principles involved and their applications is the main factor which has allowed man to advance so far in this field of unquestionable importance.



For further information consult
Shell Oil New Zealand Limited

In New Zealand Industry

Shell Chemicals

SHELL

5B.6

ORIGINALS FOR SLIDES

by
R. M. DOLBY
Dairy Research Institute (N.Z.), Palmerston North

This article was originally printed in the Journal in April, 1955. Because so many slides shown at recent conferences have been unintelligible, many members have asked that it be printed again. Some parts have been re-written to bring them up-to-date. Members who intend to use slides at this coming conference are particularly requested to read this article and to make their slides accordingly.

"Half-way through the lecture the speaker apparently discovers that he needs slides. There is shouting for the lights to be put out, the blinds to be drawn. Down go the blinds and after a frantic hunt the switches are found. Out go lights, including that of the projector. In due course by tolerating one or two lights whose bulbs cannot be reached because of their height, the visual aids come into action. Something resembling the Rosetta stone appears on the screen. After several attempts on the part of the operator, the illumination is adjusted so that the dark shadows disappear and in due course the symbols can be recognised as our normal alphabet and numerals. But can we read them? No, sir! The original was hand printed without guides by an unskilled operator who found that he had more material than the foolscap page would hold so that some compression was needed at the bottom. To add to the hazards a projector was used with a wide angle lens placed well below the screen. The resultant angle made it impossible to have the whole picture in focus at once. The next slide is put in. This time the language is seen to be English but as in a mirror. This is rectified by the operator who produces an image which is upside down. And so it goes on. Our interest has evaporated, we light our cigarettes and pray for light. Do I exaggerate? Unfortunately no. The recital is merely a condensed description of three lectures attended in the recent past—one of them given at one of our universities where the speaker was a famous overseas scientist. The lecturer threw on the screen an assortment of symbols with the comment. 'It is obvious to the meanest intelligence that x shows a marked correlation with y.' The slide was so congested that with the best intelligence, goodwill and eyesight it was impossible to assimilate the material in the time available."

This apt description by Whittlestone[1] pictures a misuse of slides which we have all experienced—even at Institute Conferences. The prevalence of illegible slides shows that many lecturers have a much too optimistic idea of the amount of material that can be included in a slide and imagine that the photographic process can correct the defects of a poorly lettered original. This article is intended to draw attention to the information available on the making of originals for satisfactory slides.

The two principal requirements of slides are:

1. Legibility.
2. Intelligibility.

The letters and figures on the screen must be large enough and sufficiently clear to be readily legible from all parts of the lecture room. The presentation must be such that the meaning is clear to the audience. The amount of numerical data or reading matter should not be more than can be read and assimilated in the short time the slide will be shown. A slide showing a table with many columns and rows of figures will certainly be illegible to most of the audience and the few who can decipher the figures will have difficulty in grasping the significance of the mass of data. If the table is subdivided and shown as two or more slides, each dealing with one section of the data, both legibility and intelligibility will be improved.

Sizes of Slides

The cumbrous $3\frac{1}{4}$ x $3\frac{1}{4}$ inch slides of earlier days and the elephantine projectors needed to show them are now fortunately extinct. The standard size is 2 x 2 inches but a few people favour $2\frac{1}{4}$ x $2\frac{1}{4}$ inch slides. The use of this larger size may cause difficulties as not many projectors are equipped to take both sizes of slides.

Where slides are to be used for only one or two lectures, cardboard ready-mounts are quite satisfactory. For those who make their own slides, the slim one-piece slotted plastic mounts are particularly convenient. Slides which are to be shown repeatedly are probably better mounted in glass.

The discussion below applies to 2 x 2 inch slides which give a frame 35 x 23mm., i.e. a length to width ratio of 3 : 2. The greater dimension may be either vertical or horizontal but in the majority of slides it is horizontal.

Size of Lettering

Saxby *et al.*[2] have concluded that, for optimum legibility in either large or small halls, the height of the letters or numerals should be not less than one-fortieth of the greater dimension of the frame. Taking one letter space (width of letter plus width of space between letters) as $1\frac{1}{4}$ times the height of the letters, the width of the frame is 32 letter spaces (including margins of two spaces each). The maximum number of lines is 12.

Whittlestone[1] recommends approximately the same height of letters but by taking a letter space as equal to the letter height, arrives at 55 letter spaces per line.

Lower case letters, having only about two-thirds the height of corresponding capital letters are less legible. The letter heights given above, though based on capitals, make allowance for use of lower case letters.

Bold letters are more legible than larger, thinner letters. Saxby *et al.*[2] recommended that the thickness of the stem of the letter should be not less than one-sixth of the height of the letter. The thickness of lines on diagrams is also important. If too thin they will be lost in reproduction.

Slides with white lettering on a black background are less legible than slides with black letter on a white background, since white letters tend to blur and run together. The short-cut of projecting a negative instead of a positive is therefore not to be recommended.

Apart from size of lettering, good legibility requires that the letters be sharply defined and show a maximum contrast with the background. It is, therefore, important that lettering and drawing should be done in Indian ink on good quality white paper. The photographic materials used must preserve this contrast.

The application of the above principles to various types of originals for slides will now be considered.

1. Tables

(a) *Hand-lettered material.* No one but an expert should attempt freehand lettering on an original for a slide. Originals of excellent quality can be produced by use of lettering guides (Wrico or Uno). Whittlestone[1] recommends that the original be drawn on paper 18 x 12 inches using letters $\frac{3}{8}$ inch high (Uno U.C.6, U.L.6 or U.F.6) and a pen which gives a line $\frac{1}{16}$ inch wide (Uno No. 4). Lines should be spaced one inch apart between bottoms of letters.

The smallest size letter which should be used on an original is about 0.2 inches high (e.g. Wrico VCN 200) for a frame size of 9 x 6 inches. Spaces between lines should not be less than the height of the letters.

(b) *Typed material.* A typed original gives a slide of somewhat lower quality than one from an original hand lettered as above. In the absence of lettering guides or where time is not available to use them, quite satisfactory slides can, however, be made from typed originals.

With pica type (10 spaces per inch) the table should not exceed 6 x 4¼ inches. The lines should be double spaced. The type must be clean and the typewriter should preferably have a carbon ribbon as a fabric ribbon gives a blurry lettering. If a carbon ribbon is not available equally good results can be obtained by disengaging the ribbon (as in stencil cutting) and typing direct through unused carbon paper on to a white bond paper backed with another sheet of carbon reversed to print on the rear surface.[3]

(c) *Printed matter.* In the reproduction of tables from books or journals the same ratio of letter size to frame should be observed. For a table in which the type corresponds to that used in this article, the maximum size for good legibility would be about 3½ x 2¼ inches.

2. Diagrams

The rules for letter size given for tables apply equally to lettering and numerals on graphs or diagrams. All lines should be bold. Graph lines should be heavier than lines for axes or reference lines. Grid lines on graphs should be kept to a minimum or, better still, eliminated altogether. Whittlestone[1] recommends that on an 18 x 12 inch drawing the principal lines should be 1/16 inch thick and subsidiary lines not less than 1/32 inch thick.

The same principles apply to figures in publications. If the lines are thin or the lettering small in comparison with the size of the drawing, it will not reproduce well. In such a case it would be necessary to re-draw the figure on a larger scale with lines of appropriate thickness. A photographic enlargement of the figure would save a good deal of labour in this operation.

Photographic Technique

Since many books on this subject are available it is unnecessary to discuss it here. For those interested in processing slides the Kodak Data Books on "Copying" and "Slides" will be found particularly useful.

Spotting the Slide

The system accepted as a British Standard and also in current use in the U.S.A. is as follows:

The slide is marked with a single spot on the lower left corner when the slide is viewed as it should appear on the screen. The slide is placed in the projector with the spot in the upper right corner facing the lamphouse.

An older system used two spots which marked the two top corners when the slide was placed in the projector. Confusion can be avoided if the standard single spot system is followed.

REFERENCES

[1] Whittlestone, W. G. Proc. N.Z. Dairy Science Assn. 1953, 1.
[2] Saxby, S. H., Scott, R. H., and Averis, M. W. N.Z.J. Sci. Tech. (1954), 36B, 191.
[3] Kodak Data Book, "Slides".
[4] Kodak Data Book, "Copying".

N.Z. INSTITUTE OF CHEMISTRY CONFERENCES

M. S. CARRIE, Vice-President

Branches have been asked to discuss the future of the Annual Conference, and the attached tables have been compiled to show the trends which have taken place over the past 16 years. These should be a help in any discussion which may take place on the subject.

Notes on Tables

The upper table gives percentages which have been calculated from the figures in the lower table.

Attendances at Conferences have been taken from the lists in the programmes. Actual attendances were probably higher than those shown in the table because of late registrations. Trade exhibitors are included in the lists of some of the more recent conferences, but have been excluded from the numbers shown in the table.

"**University**" includes staff and research students, but does not include staff of Training Colleges.

"**Government**" includes staff of government departments, local bodies, hospital boards, etc., and of Research Associations whose funds are provided partly by D.S.I.R. and partly by industry.

"**Industry**" includes only those employed by private enterprise.

"**Teachers**" includes secondary school teachers, staff of Training Colleges and staff of institutions of higher learning which do not confer degrees.

The remainder, which may be classed as "Miscellaneous" are not listed separately, but their numbers may be obtained by difference. They include consultants, dentists, medical practitioners, housewives, etc. as well as retired members irrespective of their previous occupations and those who do not give their occupations in the List of Members.

The numbers of Teachers attending conferences are not given separately because they are so small. In the same way, the numbers of papers given by Industry at conferences are not shown, but can be obtained by difference.

No extravagant claims for accuracy are made, but the figures should be close enough for practical purposes.

Comments

The Conference has not maintained its popularity with members. Almost half the total membership attended the 1950 Conference as against only 16 per cent in 1965. This is particularly the case with Industry. In 1950, over a third of the Industry members attended as against only 6 per cent in 1965.

University members have increasingly taken over the programme of conferences. This is not necessarily undesirable, even if the conference is intended to appeal to all members. A survey of the titles of University papers, however, suggests that these are largely highly specialised and of interest to a limited audience.

The location of the conference affects the relative parts played by University and Government. The latter is much more prominent, both in attendance and in papers, at Hamilton and Palmerston North which are centres of government research.

If members in general are happy about the present tendency for the University to dominate the conference and for Industry which is the largest single group of the members, to ignore it, things can be allowed to continue as they are. The Annual Meeting is no longer representative of the membership as a whole, but it is difficult to suggest an alternative except a postal ballot on important matters.

If, on the other hand, it is desired to attract more members, and especially Industry members, to the conference, some changes to the programme will have to be made. There are probably many ways in which this could be done, but two of them are:

NEW ZEALAND INSTITUTE OF CHEMISTRY CONFERENCES

Conference		Attendance as % of total attendance			% of papers given by		Attendance as % of membership in each group				Membership as % total membership			
		Univ.	Govt.	Ind.	Univ.	Govt.	Univ.	Govt.	Ind.	Tot.	Univ.	Govt.	Ind.	Teach.
1949	Auckland	15	42	34	—	—	65	62	36	47	14.4	36.9	30.3	8.8
1950	Christchurch	20	48	23	21	79								
1951	Hamilton	15	55	22	28	72								
1952	Wellington	15	51	26	44	50								
1953	Dunedin	26	44	24	47	44								
1959	Dunedin	26	45	23	39	61								
1961	Auckland	27	44	22	49	49								
1962	Christchurch	47	32	18	70	21								
1963	Palm. Nth.	36	40	14	61	37								
1964	Hamilton	34	50	11	60	40								
1965	Dunedin	43	37	13	71	26	30	24	6	16	22.7	24.9	31.9	8.7

Year	Numbers attending				No. of papers given by			Number of members				
	Univ.	Govt.	Ind.	Tot.	Univ.	Govt.	Tot.	Univ.	Govt.	Ind.	Teach.	Tot.
1949	26	73	59	174	—	—	—	57	146	120	35	396
1950	37	90	43	186	5	19	24					
1951	19	69	27	125	7	18	25					
1952	19	65	33	128	15	17	34					
1953	29	49	27	112	15	14	32					
1959	34	59	30	130	12	19	31					
1961	39	64	31	144	18	18	37					
1962	67	45	26	142	23	7	33					
1963	59	66	23	165	23	14	38					
1964	49	71	16	143	25	17	42					
1965	57	49	17	132	30	11	42	187	205	263	72	824

1. Continue the Annual Conference but select papers more critically and reduce the number of highly specialised, academic ones. Ensure, by invitation if necessary, that there are sufficient papers of more general interest to run concurrent sessions with the academic papers.
2. Hold less frequent conferences of a very high standard with invited lecturers, both local and overseas, to deal with specified topics of wide general interest.

As far as Industry members are concerned, it must be remembered that some of the industries (meat, dairy and food technology, for instance) hold their own annual conferences and that members in these industries might find it hard to justify attendance at an Annual N.Z.I.C. Conference, no matter how attractive it was. They would probably be more attracted to less frequent conferences of the type described in the second alternative above.

This should give sufficient background for a thorough discussion by Branch members.

As a postscript, a similar analysis of the attendances at Branch meetings might produce some interesting results.

BRANCH NEWS

Auckland

Dr. G. Nicholls, Chairman of the Auckland Branch, is leaving N.Z. Forest Products to accept an invitation to a position as Research Associate at the Institute of Paper Chemistry at Appleton, Wisconsin. He will be one of three group leaders in the technological section.

Mr. K. Seal, of Amalgamated Brick and Pipe, is the new Branch Chairman.

Professor Hall, Head of the Chemistry Department, University of Auckland, will leave shortly to take up a position in Alberta.

Wellington

Dr. W. E. Harvey, General Secretary of the New Zealand Institute of Chemistry, is at present spending a sabbatical year in North America. Dr. Harvey will be at the University of Rochester, Rochester, New York, until June after which he will be at the University of British Columbia for the remaining six months.

Professor J. F. Duncan presented the chairman's address to the Wellington Branch in the form of a lecture/demonstration on "Solids". The lecture was specifically designed to cater for the members of the junior branch, although the meeting served as the inaugural lecture for 1966 for both the senior and junior members.

Dr. A. G. Freeman of the Department of Chemistry, Victoria University, attended a conference on Crystallography in March at the Australian Atomic Energy Commission's Research Establishment at Lucas Heights.

Professor J. F. Duncan will be visiting India for a short period in June when he will give a course of fifteen lectures on the chemical applications of the Mössbauer effect at a Summer School in Bangalore, South India.

Dr. J. Darby, lecturer in Biochemistry at Victoria University, will be taking up a position in the Department of Biochemistry, Western Reserve University, Cleveland, Ohio, in August 1966.

Canterbury

Mr. T. R. Hitchings, Senior Science Master at Riccarton High School, has taken up his appointment as the first Visiting Teaching Fellow of the Canterbury University, Chemistry Department. During this appointment, which is for the 1966 school year, he will undertake Stage 1 teaching and inorganic research.

Major post-graduate scholarships have been won by Mr. H. P. Gunz and Mr. G. J. Gainsford of the University Chemistry Department. Mr. Gunz will take up a Shell Scholarship in August at the University of Sussex, where he is to work with Professor J. Chatt. Mr. Gainsford, who has been awarded the B. P. Scholarship for 1966, will work on inorganic chemistry and crystallography at the University of Canterbury.

Dr. B. R. Penfold of the University Chemistry Department attended an Australian Crystallography Conference at Lucas Heights, Sydney, on February 24, 25 and 28. The theme of the conference was the application of X-ray crystallography to chemistry, physics and biochemistry. An unusual feature of the conference was the active attendance of a very high proportion of research students.

Mr. K. R. Farnsworth has been appointed as a chemistry teacher at Christ's College.

Mr. D. R. Castaing has been appointed as a chemistry tutor at the Christchurch Technical Institute.

Dr. K. R. Ryan has resigned from a lectureship in chemistry

at Canterbury University. He will leave in May to take up a position with a C.S.I.R.O. upper-atmosphere physics research group near Sydney.

The Junior Chemical Society lecture programme for 1966 is as follows:

March 11—Dr. W. S. Metcalf, "Some Chemical Aspects of Light".

June 10—Mr. W. E. Dasent, "Non-existent Compounds".

September 23—Dr. P. Wiggin, "Physical Chemistry Applied to Cell Physiology".

There wil also be a field trip to Lincoln College and a visit to the new University Chemistry Department (if it is completed soon enough).

The following are the speakers and topics for Chemistry in Action in 1966:

Dr. G. N. Malcolm, "Massive Molecules and Mighty Muscles".

Mr. David Kear, "The Origin of New Zealand Mineral Deposits".

Dr. R. O. Farrelly, "Hormones: Their Chemistry and Their Effects".

Otago

Professor H. N. Parton is spending 1966 on leave at the University of Exeter.

Dr. and Mrs. R. F. Smith (both Associates) have returned from Canada where Dr. Smith did two years post-doctoral study at Queens University, Kingston. Dr. Smith has been appointed as a lecturer at the University of Otago.

Dr. P. K. Grant has returned from a year's leave spent at Cambridge and other U.K. Universities.

Dr. C. G. Pope has returned from a year's study under Professor C. Kemball, F.R.S., at Queens University, Belfast.

Dr. H. Young has left to take up post-doctoral study at the California Institute of Technology, Pasadena.

Dr. M. H. G. Munro has recently taken up a post-doctoral fellowship at the University of Liverpool.

Mr. J. T. Linzey, Chief Chemist at McSkimming Industries has left to take up a position at Crown Lynn Potteries, Auckland.

Mr. D. F. Ingram is now a research chemist at Central Research Laboratories, I.C.I.A.N.Z., Melbourne.

BOOK REVIEWS

Double Layer and Electrode Kinetics, by PAUL DELAHAY, Louisiana State University. Published by Interscience/John Wiley, New York, 1965. 321 pages, price £6/10/6.

Electrode kinetics is the study of the mechanism of reactions at electrified interfaces. This involves knowledge of the state of molecules and ions in the diffuse double layer, adsorption on the electrode surface, electron exchange with the electrode, and the nature of any intermediate species formed. Delahay's monograph brings together material which was previously available only in scattered review articles and symposium volumes. It is undoubtedly the best critical account of the field available at the present time. However, Delahay writes for the research worker or post-graduate student with an adequate knowledge of the subject; his book cannot be used as an introduction by the uninitiated. There is no simple description of the double layer or electrode reactions, and experimental techniques and applications receive no mention at all. Delahay assumes the reader has a good knowledge of mass transfer processes at the electrode. Less than five pages are devoted to this important topic which was the subject of his earlier book, *New Instrumental Methods in Electrochemistry (1954).*

The book begins with a short historical essay on the evolution of ideas and significant milestones in this field. The next five chapters on the theory of the double layer deal with thermodynamics, structural models, specific adsorption, potential-dependent isotherms and related matters. The discussion is mostly concerned with the electrode formed between mercury and aqueous electrolyte solutions, reflecting the scant knowledge of other double layer systems. Then follows an excellent account of the theory of electron transfer kinetics at the electrode, with succeeding chapters devoted to the correlation between the rate of the electrode reaction and the double layer structure, including adsorption effects. Many examples of electrode reaction mechanisms are examined and the theories are compared with the best experimental data. There are a large number of excellent diagrams copied directly from original papers. Topics excluded are semiconductor electrodes, passivation by anodic films and deposition of metals. Tables of experimental kinetic parameters would have been a useful addition. Surprising omissions are work by Conway on the determination of adsorbed intermediates using potential decay curves, and by Matsuda on the kinetics of polarographic reduction of metal complexes.

G.A.W.

Chromatographic Reviews. Progress in Chromatography, Electrophoresis and Related Methods. Volume 6. Edited by MICHAEL LEDERER. Elsevier Publishing Company. 1964. 219 pages, price 70/-.

This volume, covering 1963, contains eight articles, six of which are original reviews. The other two are translations of lectures. The review on commercial equipment for gas chromatography critically appraises a representative selection of equipment available for various purposes at various price ranges. It is a very useful guide for those contemplating the purchase of such equipment. A review of centrifugal chromatography covers the history, theory, design of apparatus, techniques, results, applications and future prospects of the method. Shorter articles on paper chromatography of iodoamino acids and related compounds, chromatography of free nucleotides, and chromatographic methods for pesticide residue analysis are useful. There are also sections on liquid ion exchangers, polymeric co-ordination compounds and the application of paper ionophoresis and electrochromatography to the study of metal complexes in solution.

This volume continues the useful function provided by the previous volumes in this series.

Chromatographic Reviews. Progress in Chromatography, Electrophoresis and Related Methods. Volume 7. Edited by MICHAEL LEDERER. Elsevier Publishing Company. 1965. 202 pages, price 60/-.

Volume 7 covers topics as at the end of 1964. There are six sections. One discusses the principles of gradient elution, and another the application of chromatographic and electrophoretic methods to the study of the Szilard-Chalmers effect. The remaining four are on the paper chromatography of chloroplast pigments and of antibiotics, mapping plant lipids by paper chromatography and thin-layer chromatography of steroids. The many references and critical evaluation of material makes this another very useful member of the series.

J.M.

Monographs for Teachers. Published by the Royal Institute of Chemistry. Nos. 6, 7, 8.

No. 6: *Principles of Titrimetric Analysis,* E. E. AYNSLEY and A. B. LITTLEWOOD.

No. 7: *Principles of Catalysis,* G. C. BOND.

No. 8: *Principles of Atomic Orbitals,* N. N. GREENWOOD.

The first three monographs of this series were reviewed in this Journal in October 1960, and numbers 4 and 5 were received in 1962. Numbers 1 and 2 are again available, and numbers 6, 7 and 8 are now available from the Registrar of the New Zealand Institute of Chemistry.

The monographs have been published with the intention of providing "concise and authoritative accounts of selected, well-defined topics in chemistry, for the guidance of those who teach the subject at G.C.E. advanced level and above". This aim appears to have been fulfilled very well, and the monographs can be recommended wholeheartedly to teachers of chemistry here, as well as to anyone else in need of a compact and up-to-date treatment of one of the eight topics. This "eight-fold way" is not necessarily an easy path to enlightenment, because the authors' treatments of their subjects are invariably accurate and quantitative, rather than woolly and descriptive. Nevertheless the reviewer found that each of the three that are listed above made interesting and stimulating reading, especially number 7.

The material which is covered in these monographs is not meant to be transferred directly to the classroom, but should be of particular value to teachers who feel in need of fresh insight, and who should be given the opportunity to reveal new horizons to the more gifted sixth form students.

The prices of the monographs range from 3/6 to 6/-, and it is clear that both school and university libraries ought to possess the complete set.

L.F.P.

To be precise—PYREX® laboratory ware by Jobling

English PYREX® laboratory glassware offers the highest standards of precision. Consistent quality and durability. And competitive cost. It is produced in a range to meet every known need. (Should new problems arise, expert design and research teams are ready to supply the best possible answers.) If you ever encounter difficulty in obtaining English PYREX® immediately, contact Jobling, the manufacturers. Always be precise — ask for English PYREX® by name.

DISCOVERIES ARE MADE IN

PYREX® (JOBLINGLASS)

JAMES A. JOBLING & CO. LTD., WEAR GLASS WORKS, SUNDERLAND, ENGLAND.

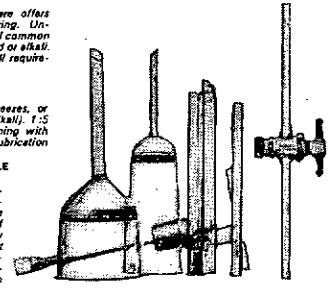
® Registered Trade Mark

JNZ1

SINTERS
PYREX sintered ware offers fast, efficient filtering. Unaffected by nearly all common reagents—either acid or alkali. The range covers all requirements.

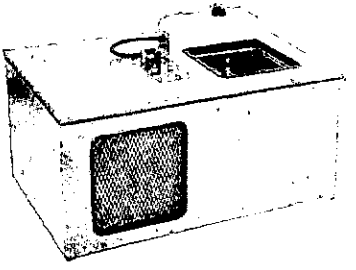
T.S.P.T.F.E. PLUG STOPCOCK
Leak free. Never freezes, or seizes (even with alkali). T.S. taper means of turning with precision — no lubrication needed.

INTERCHANGEABLE JOINTS
Compact, easily replaceable components for routine work (number of joint sizes strictly controlled). Highest quality joints conforming to International and British Standards.

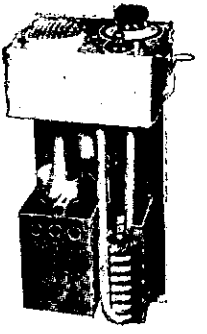


N.Z. Agents: Hart Agencies Ltd., G.P.O. Box 219, 9 Holland Street, Wellington, Ph. 50-844

GRANT
INSTRUMENTS
CAMBRIDGE



LOW TEMPERATURE BATHS
−30 to +60°C.

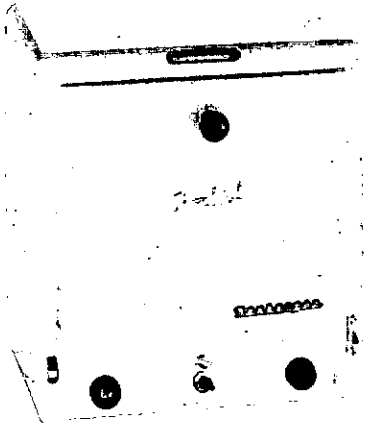


THERMOSTATIC
CONTROL UNIT
10–100°C.

Bacteriological Incubator Incubaril

Based on practical experience — for practical operation — one year guarantee.

The Incubaril is the bacterial culture incubator cabinet for all laboratories, hospitals and medical surgeries.



- Automatic temperature control, steplessly variable adjustment
- Monitoring thermometer
- Furniture for 4 Petri dishes and 30 test tubes, together, or 8 and 57 individually
- Minimum current consumption
- Corrosion-resistant surface finish
- Long working life

SOLE N.Z. AGENT

SCIENTIFIC & LABORATORY EQUIPMENT N.Z. LTD.

P.O. Box 619 AUCKLAND Phone 546–235

Printed by David F. Jones Ltd.