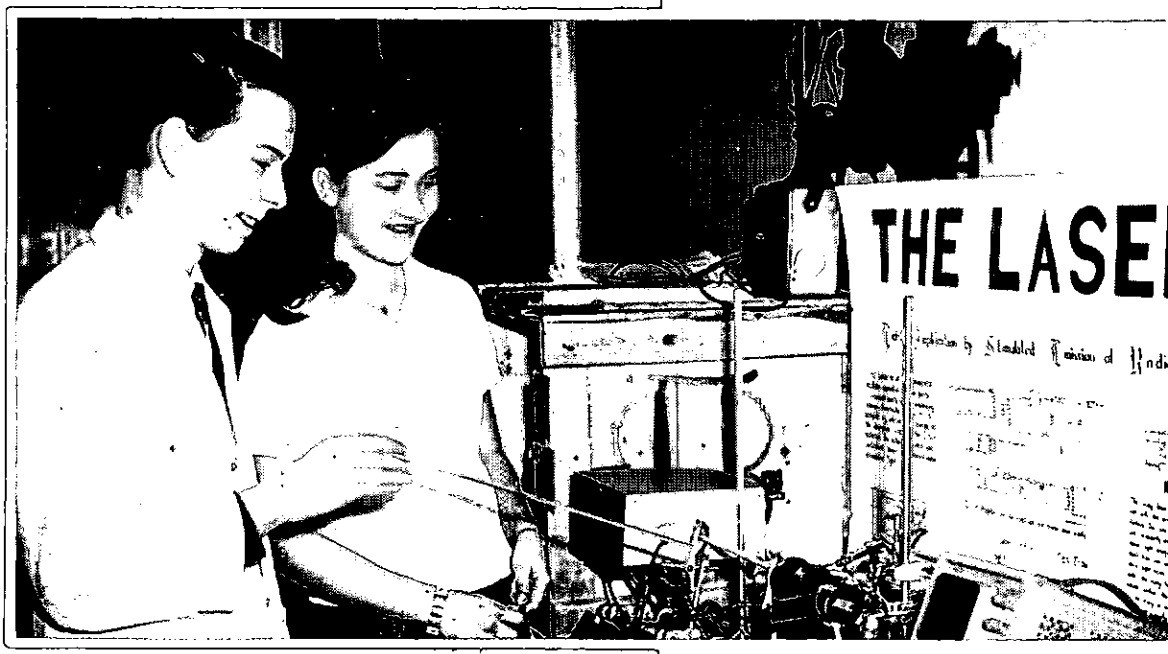
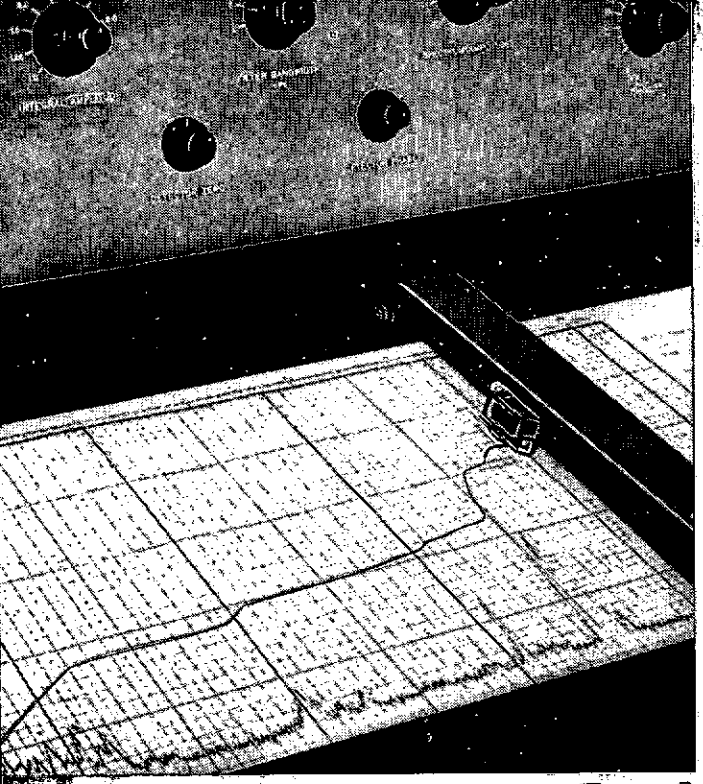
CHEMISTRY IN NEW ZEALAND

JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY



Wellington Science Fair — National Publicity

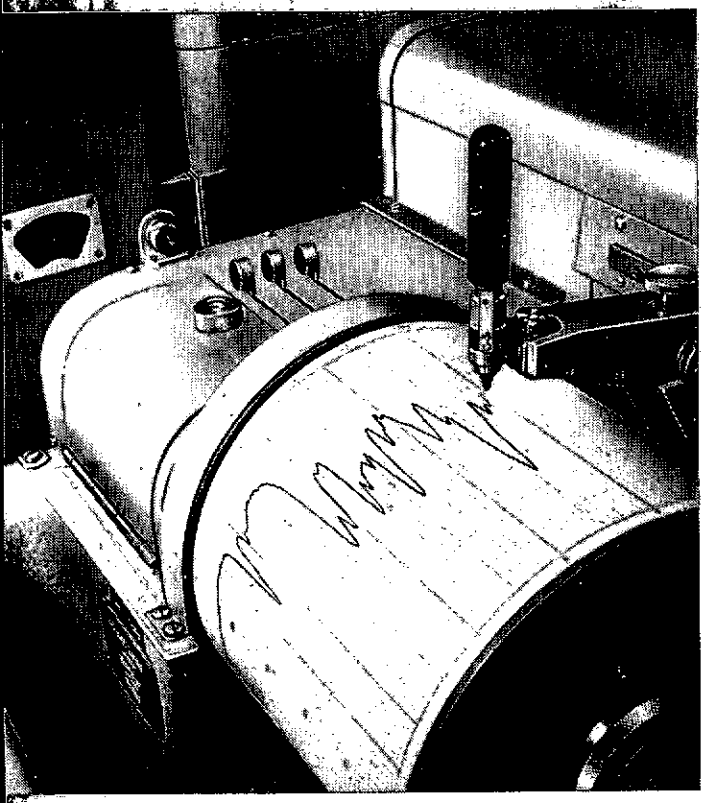
Vol. 31, No. 1 February, 1967



Uvasols®

Uvasol Acetone
Uvasol Ethanol
Uvasol Benzene
Uvasol Chloroform
Uvasol Cyclohexane
Uvasol Diethylether
Uvasol Dichlormethane
Uvasol N,N-Dimethylformamide
Uvasol Dioxane
Uvasol n-Heptane
Uvasol Hexachlorobutadiene
Uvasol n-Hexane
Uvasol Potassium bromide
Uvasol Methanol
Uvasol iso-Octane
Uvasol Paraffin
Uvasol iso-Propanol
Uvasol Pyridine
Uvasol Carbon sulphide
Uvasol Tetrachlorethylene
Uvasol Carbon tetrachloride
Uvasol Tetrahydrofurane
Uvasol Tetramethylsilane
Uvasol 3-(Trimethyl)-propansulfonic acid sodium salt

optically pure solvents for UV, IR and NMR-Spectroscopy



Deuterated compounds

Uvasol Deuterium oxide
Uvasol Deuterochloroform
Deutero-hydrochloric acid
di-Deutero-sulfuric acid
Uvasol Deutero-trifluoroacetic acid
Uvasol Hexadeutero-acetone
Uvasol Hexadeutero-benzene
Uvasol Hexadeutero-dimethyl sulfoxide
Uvasol Pentadeutero-pyridine
Uvasol Tetra-deutero-acetic acid
Uvasol Trideutero-acetonitrile

Please ask for our special pamphlet.

Sole agents in New Zealand:
HENRY H. YORK & CO. Pty. Ltd.,
P. O. B. 6434, Wellington

Supplies of Laboratory Chemicals through:
WATSON VICTOR Ltd., Auckland, Wellington, Christchurch, Dunedin

156/II-ENZ

E. MERCK AG **DARMSTADT**

JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

Vol. 31, No. 1 February, 1967

Contents

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

Editor: Miss J. Mattingley
P.O. Box 250, Wellington.

Advertising Manager: Miss A. Dollimore
P.O. Box 250, Wellington.

Distribution. The Registrar: D. J. Hogan
P.O. Box 1926, Christchurch.

Honorary General Secretary: Dr. E. Harvey
P.O. Box 250, Wellington.

Employment Officer: E. S. Borthwick
P.O. Box 2091, Wellington.

The Journal of the N.Z. Institute of Chemistry has an audit circulation Certificate of New Zealand Advertisers.

Printed by David F. Jones Ltd., 108 Tory Street, Wellington.

Editorial

A professional body must carry out certain activities if it is to be worthy of its name. One of these is the publication of a journal. It is largely the Journal which makes us all members of the national body rather than of just a local branch. The majority of our members, for one reason or another, have little or no contact with a branch. Many live in areas outside the branch centres and cannot attend meetings. For these people the Journal is almost their only contact with the Institute and with other members.

Of course, if Institute news was all that mattered, a cheap, cyclostyled sheet would do. But as a professional body we also have a duty to our members to keep them in touch with the progress of chemistry in general. For those who cannot attend branch meetings the Journal is our only means of doing this.

The stage had been reached with the previous Journal format where the cover would hardly fit around the number of pages, and where the small page size was a distinct disadvantage for getting advertising. The new format is more attractive to advertisers and is similar to the proposed international standard for publications.

In exchange, we receive the publications of chemical institutes of other countries. The policies of those journals is the same as ours. By matching the format of our Journal with theirs the standing of our Institute in the eyes of overseas people should be enhanced.

MATERIALS FOR ELECTROPHORESIS

WHERE can I find a comprehensive list of materials for any aspect of electrophoresis?

A BDH leaflet, 'Materials for Electrophoresis', describes gel media, chemicals for preparing buffer solutions, stains and indicators, solvents and miscellaneous reagents.

HOW are the various methods of zone electrophoresis carried out?

Detailed descriptions illustrated by plates and line drawings are given in a new BDH publication, 'Methods in Zone Electrophoresis', by Dr. J. R. Sargent. This immensely practical book deals with general theory, apparatus, high and low voltage electrophoresis, electrophoresis on various media, immunoelectrophoresis, etc.

Sargent, J. R., 'Methods in Zone Electrophoresis', a BDH publication, 1965, 8vo., 107 pp., 9s 6d, (95c) post free.

The leaflet on 'Materials for Electrophoresis' may be obtained free from The British Drug Houses (N.Z.) Ltd., P.O. Box 151, Auckland.

BDH

For further information consult Shell Oil New Zealand Limited

34.6

In New Zealand industry **Shell Chemicals**

SHELL

OBITUARY

Dr. John Clark Andrews

THE SUDDEN death of Dr. John Clark Andrews at New Plymouth on October 23, 1966, came as a great shock to his many friends and is a considerable loss to New Zealand in the scientific, academic and industrial fields.

Jack Andrews was born at Mercer in 1903, and moved to Auckland at an early age. He was educated at King's School and King's College where he was dux and won a University Junior National Scholarship. He graduated B.Sc. from Auckland University College and completed his M.Sc. with First Class Honours in Chemistry. He won a National Research Scholarship and an 1851 Exhibition Scholarship and was nominated for a Rhodes Scholarship. He obtained a Ph.D. with his work in sugar chemistry.

He went into industry and with Mr. T. Crosbie Walsh, F.R.I.C., established the first control laboratory at R. & W. Hellaby's plant at Otahuhu. He was appointed Works Manager in 1936, resigning in 1941 to take a similar position with the Challenge Phosphate Company, where he did considerable research into the application of artificial fertilisers to farmland and in soil copper deficiencies.

During the war, working under the Food Controller, he made an overall survey of food processing equipment in New Zealand. His investigations into the organisation, transport, canning, freezing and dehydrating of food involved him in several trips overseas. Following studies in the United States, he pioneered "iron rations" for commandos.

After a period spent as Works Manager of Brown Barrett Ltd., and as a private consultant, Dr. Andrews joined Ivon Watkins Ltd. in 1955. In 1958 he became Works Director and in 1960 a director of Watkins Gardinol Chemicals Ltd. At the time of his death he was Works Director of Ivon Watkins-Dow Ltd.

Dr. Andrews was appointed to the D.S.I.R. Council in 1936 and later to the Defence Scientific Advisory Council. He was a member of the Auckland University College Council from 1946-1955 and was its representative on the Council of Massey Agricultural College from 1953. When Massey College became the new Massey University of the Manawatu he was appointed to the new Council as the Governor-General's representative, and became its first Chancellor. To the task of developing an agricultural institution into a full university he brought a background of both arts and sciences, a keen appreciation of the needs of the community, and a sympathetic, very likeable personality to the resolution of many of the differences of opinion in such a new venture.

His interest in the N.Z. Institute of Chemistry goes back to its formation. He was secretary of the Auckland Chemical Society before it merged into the N.Z.I.C. He became a Fellow of the Institute in 1936, and was President in 1945. In 1964 he arranged a large gathering of Institute members and other chemists in New Plymouth. He was a principal speaker at the Conference in Wellington in 1966 just before his death.

The sympathy of the N.Z.I.C. is extended to his widow and his five children.

INDUSTRIAL DEVELOPMENT IN NEW ZEALAND *

J. C. Andrews

MY TASK this evening is to review our industrial position and to stimulate some thought as to its future development. In discussing this topic I would like you to relate my remarks to two basic factors which control our activities—people and money. Without an adequate supply of both it is impossible not only to make progress but to maintain our present position. Sometimes it is possible for these two factors to work against each other to some extent, and we should be careful to avoid conflicts. Again, it is possible to waste both or use them inefficiently.

As a country we have had our successes and our failures. We have used our favourable agricultural climate to great advantage and have used it as a corner stone upon which to base the high standard of living which we now enjoy. The problem facing us today is, can we maintain this state of affairs? I feel confident that we can provided we are prepared to make a renewed effort. Conditions have changed and are likely to change much more rapidly in the future. A new approach is needed if we are to have the conditions we all desire.

At this stage it is necessary to define our objective. What sort of a place do we want New Zealand to be? I would imagine that we want it to be a pleasant place to live in, where all its inhabitants can enjoy a high standard of living. In achieving this end we have probably been more successful than practically any other country in the world; but without wishing to appear an apostle of doom, I suggest that the time has arrived for us to examine our position critically in the light of modern conditions. To do this we must sum up the present state of affairs.

The basis of our economy to date has been agriculture and there can be no doubt that agriculture must remain the most important economic factor Such an attitude is quite unrealistic in a modern society. In spite of our large exportable surplus of agricultural products we are having difficulty in maintaining a satisfactory trade balance. We must use our ingenuity to overcome this precarious position. It will not be easy and will not come quickly and all sections of the community must make their contribution.

Some of the factors contributing to our present position are—

1. Uncontrolled prices in the world markets for our exportable surpluses. The prices of wool, butter, cheese and milk fluctuate, and as they constitute approximately 95 percent of our overseas earning power the economy is unduly sensitive to such changes.

2. There is a real opportunity for us to increase the added value of our exportable surplus, in some cases preparing it in a form which will attract a wider market. This has not been exploited to the full.

3. Our international commitments have grown considerably. There is a drain on our overseas exchange to meet interest charges on loans, another drain to satisfy royalties and the dividends of overseas capital, and a further drain to help certain undeveloped countries—to say nothing of the brain drain. I am sure all would agree that drains are a necessary adjunct of modern civilisation but like anything else they can be overdone.

Let us now consider what natural resources New Zealand possesses and how far we have been able to use these.

New Zealand is blessed with an almost ideal temperate climate with a well distributed rainfall. The main area consists of two narrow islands with no land far from the sea, so that extremes of temperatures are avoided. It should therefore be ideally suited climatically for agricultural production. On the other hand, the mountainous

*This is the text of an address given to the Canterbury Branch of N.Z.I.C. early in 1966.

nature of the land mass and the low natural fertility of the soil impose handicaps. Where the land is capable of farming, the lack of fertility has been overcome by supplying the necessary nutrients to the soil either by natural means, e.g. nitrogen through clovers, or by the addition of fertiliser in the form of superphosphate, etc. Gradually a pattern of farming has emerged based on the production of grass. On this we support an increasingly vigorous animal industry, the main products of which are wool, meat, butter and cheese. We should consider whether this approach to the exploitation of our agriculture is basically sound, or whether we look for a greater diversification in our agricultural produce with the object of achieving greater stability in the return for our exports. For example, it has been demonstrated that sugar beet can be grown successfully. At present we import all our sugar, but the day may come when not only will it be profitable, but also essential, that we produce at least some of our sugar requirements.

Most fruits and vegetables grow well and small quantities are being exported. Can such export trade be increased? There is some evidence that it can. The recent export of strawberries, which a few years ago would have been considered impractical, is now a reality on a small scale, due to the speed of modern transport.

We are not self sufficient in our production of cereals. Is this always to be the case or can we improve this situation by renewed effort?

Our main agricultural products — meat, butter and cheese — are all relatively expensive foodstuffs and consequently have limited markets. I feel that our markets of the future will lie with the countries bordering the Pacific Ocean. Most of these are unable to pay an economic price for these products. We have relied largely on the British market but we should realise that this market must become less attractive as time goes on. Britain's entry into the Common Market is only a matter of time and when she does this the problems of marketing our traditional products will increase. We should meet the challenge and find methods of preparing our products to meet the requirements of other markets such as in South East Asia. I believe it should be possible to produce a high quality margarine-type product at a price satisfactory to such markets, if we undertake the necessary work. There is a great need for low priced protein in these areas. It is an almost inexhaustible market and it reflects great credit on the Dairy Research Institute that they have appreciated this need, and have produced experimentally a high protein biscuit, based on milk protein. It is unlikely, however, that such a product alone can either meet the demand or solve our own problems. I would say that there is still a great need for a cheap, tasteless protein. Grass is our main crop. Can we obtain it from this source?

In marketing our products it is essential that we present them in the most acceptable form which will require the minimum amount of subsequent processing. This makes the product easier to sell and gives us the best return per unit of raw product. I am sure there are considerable opportunities in this area. Could we not process more of our wool crop at least to a further stage? Or could we not do more in the presentation of our meat, butter and cheese? If we sell products in metric countries, do we pack to their accepted weights and measures? Perhaps all of you can think of other projects worthy of investigation in this area.

A great deal of work has been done in the research establishments of the Universities and Government to increase the productivity of our land. Spectacular results have been achieved by these agencies over the years. But how well have they been applied in practice? I feel there still exists great scope for our present knowledge to be better applied.

The fishing industry could be well described as an underdeveloped industry, yet it is one which should well repay further investigation at all levels — knowledge of

movements of the fish population off our shores, modern methods of harvesting and improved processing of the product. These factors are just beginning to be looked at and should yield valuable results in time. In these investigations, shellfish should not be overlooked. The cultivation of good quality oysters should not be beyond us. Are other shellfish such as mussels worthy of further investigation?

Great stress has always been placed on the need to make two blades of grass grow instead of one, but just as spectacular is the known fact that in New Zealand certain trees grow twice as fast as they do in other countries. This latter fact has been the basis of our rapidly developing forestry industry. Just as this country is adapted to the production of fats and proteins, so it is adapted to the production of cellulose, a material of great value in the modern world and one capable of transformation into a number of useful products. The industry is now making strides in the utilisation of our exotic forests and a healthy export trade is developing. The recent free trade agreement between Australia and New Zealand should benefit this industry.

A number of by-products arising from the main industry offer a potential source of wealth. For example, Forest Products Limited are producing vegetable terpentine. Utilisation of tall oil must develop in time. Cellulose is the basis of rayon and cellulose film and could be a future extension of the industry, or could come from some other source of cellulose.

Our local flax has had a chequered career and has difficulty in competing with synthetics in the cordage industry. However, research and development has enabled the Foxton mills to produce a hard wearing range of floor coverings at prices competitive with other materials in the low price bracket. Perhaps this native plant still holds a definite potential.

It may well be that some other native plant has an industrial potential if properly investigated. Again, it may be possible to introduce into New Zealand a plant that could provide us with an additional product. Some have been introduced and tested. This should be a continuing process as species by selection and breeding can sometimes be so improved as to become economic crops.

When we turn to consider our mineral wealth the picture is not so bright. Surveys to date have not shown that New Zealand is well endowed with mineral resources. Some are known and some still remain to be discovered. It is necessary to see that they are exploited to the best advantage of the country as a whole.

If we can logically look at heat and power as mineral resources, it will be seen that we are reasonably well endowed with coal, natural gas and hydroelectric stations. While our known coal deposits are neither limitless nor of very high quality, they have provided us with fuel in the past, and will so provide us in the future. They could also be a source of certain chemicals. Indeed, some are of the opinion that our reserves of coal should be husbanded against such a requirement and that we should derive our heat from other sources. There may be some truth in this if other forms of energy become readily available. Natural gas has been discovered in reasonable quantity in Taranaki, and further exploration for gas and oil goes on. Natural gas is an excellent source of heat and a starting point for chemical industry. It would seem that gas utilisation in New Zealand will be in the form of energy and would do much to balance the energy draw-off to the North Island through the power cable across Cook Strait.

Most of our power is hydroelectric, though small amounts are obtained from coal stations and from geothermal sources. Hydroelectric power is still capable of development. All electric power is controlled by the state and many discussions have taken place as to the price at which such power should be made available to industry. To raise a question, I wonder what effect it would ultimately have on government revenue if power was made available to indus-

try either free or for a nominal charge. It would surely be a great incentive to some industries and could result in greater company tax returns. So far, no substantial deposits of crude oil have been found. Exploration is still continuing and attention is now being concentrated on the coastal shelf. Exploration rights cover an area approximately half the total land mass of New Zealand. The perfection of off-shore drilling techniques makes exploration of this area possible. Power is undoubtedly a basic requirement of all industry.

The development of an iron and steel industry now seems certain. If handled to the best advantage it could have far-reaching effects on the future development of industry. Apart from the prime production of iron and steel, the shapes to be produced and the use to be made of them gives an opportunity for considerable development in the engineering and allied industries.

Another metal of considerable value to New Zealand is aluminium, and the possible establishment of a plant in Southland could also bring important results. Recently there has been considerable interest aroused by the discovery of copper ore deposits on islands off the Auckland coast. In the early days copper was mined at Kawau Island. If the new deposits can be proved as to quantity and quality the production of copper could be reinstated and could prove a valuable asset. Many other metallic ores have been found in small quantities in New Zealand but have not been of sufficient magnitude to make any substantial contributions to the country, apart from the early exploitation of gold. This does not mean that the search should not go on.

It should not be forgotten, however, that apart from metalliferous ores, many other possibilities exist in the form of clays, etc. Limestone deposits occur widely and are exploited for agricultural purposes. But many classes of clay are found in New Zealand and some have been exploited for the production of a range of ceramic products such as bricks, pipes, whiteware and crockery. Certain clays are valuable for various purposes in industry, e.g., filling of paper, carrier for insecticides. Suitable sands for the production of glass have been found and we now have plants producing blown ware and sheet glass. Siliceous limestone is used extensively for the production of cement.

While not necessarily exhaustive I think I have shown that minerals do contribute considerably to our welfare and that there is still a potential for further contributions. For example, when the iron industry is well established it may be possible to do something with the titanium and vanadium associated with the iron sands.

Turning now to the chemical industry, the only basic chemical we produce in quantity is sulphuric acid. It is, however, dependent on imported sulphur and owes its existence to the large use of superphosphate. Chlorine and caustic soda are produced in relatively small plants for the pulp and paper industry. A simple petroleum refinery is operating at Marsden Point near Whangarei. Although a few plants are operating to produce certain chemicals from intermediates, the chemical industry, as known in many other countries, does not exist. The main barrier to the development of a comprehensive chemical industry lies in the small market available here and the difficulty of competing with large overseas operations. But it has been said with some truth, that as time goes by civilisation tends to lean more and more heavily on the organic chemical industry. Its products enter into all phases of our daily life, and most are imported. It therefore constitutes a challenge to us to do whatever is possible to achieve local production. Some chemists and chemical engineers are concerned about this state of affairs and the chemical engineering department of Canterbury University has been active in studying this problem. I believe that a possible solution in some cases may be found in plant miniaturisation. For example, small plants for the production of sulphuric acid and DDT are cases in point.

The greatest resource we possess is people. New Zealand has no need to be ashamed of the quality of her people, many of whom have contributed significantly both to the progress of New Zealand itself and to mankind as a whole. On the other hand, we do lack quantity to support the effort necessary if we are to enjoy a good standard of living and make full use of the opportunities ahead of us. In addition, it should be realised that there are changes of emphasis occurring, due mainly to the increased rate of technological advances. The demand for skills, as opposed to physical labour, increases and calls for a continual review of our education system, not only to meet this situation, but to achieve more nearly the potential of every member of the population.

The pattern of employment is also undergoing continual change. In the New Zealand Purchasing Journal for March 1966 some interesting figures are given to illustrate what has happened over the past ten years—

	1955-1965 *Change of Employment*	1955-1965 *Change in Production Volume*
Primary Industry	--8%	39%
Manufacturing	34%	75%
Power	17%	120%
Building	20%	35%
Services	31%	38%
OVERALL INCREASE ...	23%	48%

These figures indicate that the productive capacity of the first two groups, Primary Industry and Manufacturing, is increasing at a greater rate than the Building Industry and Services, while Power production has shown a spectacular increase in output per unit of labour. It also means that the proportion of the population required under each heading is subject to considerable variations and indicates that our educational system should be sufficiently flexible to meet changing requirements.

A certain academic departing from this city has referred to New Zealand as a "faceless society". While I may have some sympathy for his outburst, I am glad that he did not go so far as to refer to us as a "brainless society". I think that what he meant was that we have not shown the initiative and vigour that we might have done. No doubt this was due to a number of causes with which you are no doubt familiar — two wars, a depression and a 'she'll be right' attitude. There seems to be a growing realisation that our neglect of the country's educational needs of the past must be overcome. The pointers in this direction are—

The recent stimulus for greater mental discipline from primary to tertiary education, the three-year course for teachers, the creation of the technological institutes and the long overdue provision of university facilities.

Apart from university trained personnel, there is a great shortage of tradesmen and technicians who constitute the action force of the community to carry out the creations of the university graduate. The rewards for both classes are inadequate. Both spend some years obtaining the necessary training at more or less subsistence levels. Until the country recognises these skills and abilities with adequate margins, we will not attract sufficient people to equip themselves to undertake such work. This shortage of technicians is slowly being recognised by the establishment of technological institutes. But without the necessary incentive of an adequate margin of reward the effectiveness of these institutes and apprenticeships will be seriously curtailed. It is now essential that we recognise skills and abilities to make possible their achievement by a percentage of the population greater than has been the case in the past. This is an investment for the future. If we do not take action now, we will be faced with ever increasing shortages of competent citizens. This is a world-wide problem. At a recent U.K. Conference on Productivity, Technology and Change reported in Chemistry & Industry 1998, 1965, it was stated that there could be a shortage of 200,000 competent people in 1970. Each

year sees less manual labour and more skills required in almost every human activity.

Finally, I should like to say a few words on the relationship of the university with industry. This has been the subject of some comment in the Journals of recent date. Professor J. K. Feibleman (Nature, Volume *209*, 122 (1966)) suggests that Science satisfies the need to know and Technology the need to do. He goes on to say that "Since the 17th Century we have learned that by doing it is also possible to satisfy knowing. We learn by doing but only if we have an adequate technology. The Universities are the major contributors to knowing (Scientia) and Industry of doing. The two must work together if progress is to be made." But perhaps the most significant contribution was made by Dr. C. S. Marvel in his Perkin Medal address when he referred to the "Symbiotic Relationship between the Universities and Industry." This was also highlighted by the President of the American Chemical Society in a message in Chemical & Engineering News, January 3, 1966. The first paragraph of Dr. Marvel's address is, to my mind, an admirable summary of the position.

"There is sometimes a feeling among chemists that the interests of the university teachers and the industrial chemists are in conflict. Some university professors feel they are to some extent exploited by industry since their fundamental research results are sometimes used as a basis of money making developments for which the professor receives no direct return. This may occasionally happen, but it is not frequently the case. The university man is, in general, rather well cared for by society and allowed a great deal of freedom in his work. The industrial chemist is at times inclined to feel the university man is too far detached from reality in his research and is more interested in advancing himself than in teaching students or advancing chemistry. It is my view that the interests of the two groups are so closely interwoven that anything that is good for one group will also be good for the other. Neither group is living parasitically on the other, but they grow together in a symbiotic relationship."

I believe it would do both universities and industry good to devise methods of interchange of both ideas and personnel so that a proper symbiotic relationship is developed here. I must compliment the University of Canterbury in making a move in this direction, as this gathering tonight proves. Remember, knowledge has little value if it is not used.

I shall feel rewarded if I have been able to stimulate first discussion and then action, in the overall development of our resources; or in other words, give a facelift to New Zealand society, so that we can look at ourselves again with some confidence for the future.

BOOK REVIEW[1]

Methods in Microanalysis, Volume II, "Wet Combustion and Catalytic Methods in Microanalysis", being microchemical research papers of A. P. Terent'ev and J. Körbl, translated by K. Gingold and edited by J. A. Kuck. Gordon and Breach, New York 1965, 412 pages, $21 (U.S.).

This volume is a translation of selected papers of Professor A. P. Terent'ev of Moscow University and Juri Körbl of the Analytical Department, Research Institute for Pharmacy and Biochemistry, Prague, and their students. The most notable contribution of Terent'ev and his group is contained in a series of papers giving experimental details of wet combustion methods for the determination of the elements in organic, organometallic and polymeric materials. Another series of papers which relates to the use of gas volumetric methods in organic analysis contains various methods for the determination of active hydrogen and for microhydrogenation. The valuable work of Körbl and his associates at Prague on the preparation and uses of the extremely active combustion catalyst, the decomposition product of silver permanganate, is contained in a further series.

Because of its specialised nature this book will have a limited circulation. However, it is a very useful book to the research microanalyst for it gives full experimental details of methods and techniques which previously were readily available only in abstract form.

A. D. Campbell.

THE CHEMISTRY OF THE INERT GASES *

C. J. Wilkins
Chemistry Department, University of Canterbury

MY CHIEF qualification for lecturing on this topic seems to be that for nearly twenty years I was amongst those who declared the unreactivity of these elements. Yet, perhaps it is for this very reason that the Branch Committee has given me this opportunity to make amends. There was something comfortable about being able to say that this entire group of elements refused to form chemical bonds. It was in accord with the 8-*n* rule for the valencies of the non-metals towards hydrogen and towards atoms of their own kind. Certainly this rule does not hold for combination with atoms of high electronegativity; but, after all, the atoms of the inert gases have no unpaired electrons in the ground state, they have higher ionisation potentials than elements of any other group and the energies for $p \rightarrow d$ electron promotion within the valence shell are high, ranging from 13.8 e.v. for argon to 9.9 e.v. for xenon as compared with 6.6 e.v. for production of the sp^3 valence state of carbon.

Earlier Investigations

Ramsay examined the behaviour of these gases towards most of the chemical elements and common reagents. Along with Raleigh he established their molecules to be monatomic. The early evidence on their behaviour towards fluorine, however, was less satisfactory. When Ramsay visited Paris in March 1895 to lecture before the Société Chimique de Paris on his researches on argon he took with him samples of the gas. Travers[1] records that one of these was handed to Moissan "who was to experiment with argon and fluorine", but there exists no published report of the result. Later investigations have confirmed that the two elements do not combine, but the situation seems to have been accepted without question by most chemists.

With the recent discovery of compounds of the inert gases, it is of interest to review the ideas and experiments on the possibility of compound formation during the intervening years. We need not elaborate here on the well-established clathrates formed by the inert gases through entrapping of their atoms within ice or quinol lattices. These products merit classification as compounds in so far as the compositions approach a limiting stoichiometry and only the one crystalline phase is present with the entrapped molecules playing a definite role. By occupying a cavity of suitable size in the host lattice, these molecules contribute to the total van der Waals forces, but no primary valence forces are involved.

In 1924 von Antropoff suggested, on the basis of the trends within the periodic table, that the heavier inert gases would be the most likely to combine with halogens. He subsequently reported indications that argon and krypton combined with chlorine when the gases were subjected to an electric discharge. Ruff and Menzel in 1933 — a year of remarkable activity in the field — were unable either to confirm this result or to obtain evidence of combination even with fluorine. This interest in possible fluorides prompted the Italian chemist Oddo to publish correspondence he had initiated with Ramsay nearly forty years before, suggesting the possibility of the formation of fluorides. Ramsay had apparently felt at the time that the experiments suggested by Oddo were impracticable. Again in the same year Pauling[2] in a paper on "The Constitution of the Antimonates" in which he was surveying the composition and structure of oxyanions made a remarkable prediction in writing "Xenic Acid, H_4XeO_6, should form salts such as Ag_4XeO_6 and AgH_3Xe0_6." It was at Pauling's suggestion, too, that Yost and

*Based on a lecture delivered to the Canterbury Branch, April, 1966.

Kaye[3] made experiments with xenon and fluorine, as well as with krypton and fluorine. In passing an electric discharge through a xenon-fluorine mixture they must have come very close to success but were unable to adduce positive evidence of combination. Writing in 1963 with infectious good humour after the isolation of the xenon fluorides, Yost[4] said ". . . Albert Kaye (then a graduate student) and I tried without success to bring about reaction between xenon and both chlorine and fluorine; this was thirty years ago at the California Institute of Technology. In some ways conditions were very favourable for carrying out the experiments at that time; there were no redundant administrators, safety officers, or editors to bother us or to suggest delicious sins that we might be tempted to commit. We were on our own throughout. We constructed our own apparatus, blew our own glass, and used cast-off Ford coils as a source of high potentials.

On the other hand, our sole supply of xenon was some 200 c.c. at less than one-half atmosphere pressure which had been kindly loaned to us by Dr. Frederick John Allen of Purdue. Furthermore, we had to construct and operate our own (temperamental) fluorine generator; only visionary scholars ever dreamed then of sometime being able to buy this gas compressed in cylinders." There the matter rested until the discovery of the first undoubted xenon compound in 1962.

Compounds of Xenon

Dr. Neil Bartlett of the University of British Columbia investigating the chemistry of the volatile and very reactive platinum hexafluoride encountered an impurity which was found to have the composition PtO_2F_6. This compound was no ordinary oxy-fluoride for its isomorphism with $KSbF_3$ and $NO^+OsF_6^-$ established it as being dioxygenyl hexafluoroplatinate(V), $O_2^+PtF_6^-$. Bartlett reasoned that if platinum hexafluoride was a sufficiently strong oxidising agent to remove an electron from molecular oxygen, it might well do the same with other molecules having similar ionisation potential and which were not susceptible to fluorination. The xenon molecule whose first ionisation potential (12.13 e.v.) is almost exactly the same as that of oxygen fulfilled the requirement. In an elegantly designed experiment platinum hexafluoride and xenon were introduced into two bulbs separated by a glass 'break seal'. When the xenon, at the higher pressure, was allowed to flow into the red platinum hexafluoride vapour the result was dramatic, for there appeared a yellow mist which settled onto the walls of the vessel. A true chemical compound had formed spontaneously at room temperature. This first experiment, briefly reported[5] in June 1962, indicated a 1:1 combining ratio, but subsequent experiments showed variability with the molar ratio PtF_6:Xe rising as high as 2:1. Even higher combining ratios obtained with ruthenium hexafluoride at the U.S. Argonne National Laboratory (where the metal hexafluorides had first been prepared) suggested that fluorination of xenon to produce simple fluorides might also be taking place .Experiments with fluorine and xenon were immediately fruitful.[6] When the two gases in molar ratio 5:1 were heated to 400° in a nickel vessel, xenon tetrafluoride was obtained in high yield. On the other hand, when a mixture of fluorine and xenon was exposed to ultra-violet radiation the difluoride was the main product. With thermal activation at high pressures and with a high fluorine:xenon molar ratio, yet a third compound, the hexafluoride, was obtained. There is some evidence too, of an octafluoride. It happens also, that crystals of composition XeF_3 can be condensed from the mixed vapours of the difluoride and tetrafluoride, but this phase represents a lattice compound containing equal numbers of the two molecular species.

The xenon fluorides[7] are all crystalline solids exerting appreciable vapour pressures at ordinary temperatures. Like most covalent fluorides their liquid range is short. While the small symmetrical molecules pack neatly in a crystal lattice, their low polarisability

means that van der Waals forces within the liquid are low. Not unexpectedly, the compounds are all active fluorinating agents, the violence of the reaction increasing from the di- to the hexafluoride. The lower fluorides can be stored in dry silica vessels but the hexafluoride converts silica to silicon tetrafluoride. Other important types of reactions include complex formation and hydrolysis. Xenon difluoride reacts with the pentafluorides of arsenic, antimony, niobium and tantalum to give derivatives of composition $Xe(MF_6)_2$. These compounds may contain Xe-F-M bridges, but their structure has yet to be settled. Xenon hexafluoride is readily soluble in anhydrous hydrogen fluoride, giving a highly conducting solution. The very broad F^{19} band in the n.m.r. spectrum of this solution indicates rapid fluorine exchange. Xenon difluoride on the other hand, though moderately soluble in hydrogen fluoride, does not give a conducting solution.

Hydrolysis products vary, not only from fluoride to fluoride, but also according to whether reaction occurs with water or alkali. The difluoride is decomposed slowly by water, but rapidly by alkali, essentially according to the equation

$$2XeF_2 + 2H_2O \rightarrow 2Xe + O_2 + 4HF.$$

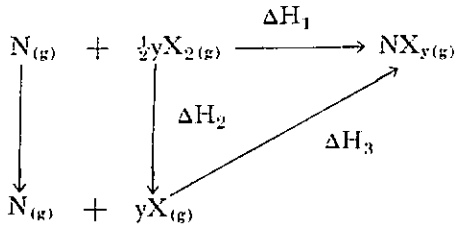
A transitory yellow colour of an unidentified intermediate appears during the alkaline hydrolysis. The tetrafluoride yields about one-third of its xenon as xenontrioxide through self-oxidation upon reaction with water. The hexafluoride gives the trioxide in high yield, but limited amounts of water give the intermediate oxyfluoride $XeOF_4$. The ease with which xenon trioxide is produced through hydrolysis of the fluorides is a source of difficulty and danger, because the oxide is an extremely unstable compound liable to spontaneous detonation with a violence said to be comparable with TNT.

Self-oxidation of xenon VI to xenon VIII occurs under alkaline conditions and from such solutions perxenates, e.g. hydrates of Na_4XeO_6 whose composition accords with that predicted by Pauling, have been isolated. Treatment of perxenates with sulphuric acid leads to the liberation of small amounts of xenon tetroxide. Identification of this tetroxide was entirely dependent upon mass spectrometry, a technique which has been widely applied in xenon chemistry. It enables quick assay of volatile reaction products and identification even of minor or transitory constituents.

The isolation of these compounds has naturally prompted examination of how far the range of inert gas compounds can be extended. Efforts to produce xenon chlorides have been unsuccessful, but radon and krypton tetrafluorides and krypton difluorides have been reported. The radon compound is formed through combination of the elements at 400°. It may well be intrinsically more stable than the xenon analogue, but its investigation and its properties are complicated by the intense radio-activity associated with radon. The krypton compounds on the other hand are less stable than the xenon analogues. Krypton tetrafluoride arises when an electric discharge is passed through the gases at low temperature. The formation of krypton difluoride has been demonstrated using a matrix isolation technique. A mixture of krypton and fluorine was condensed on a salt window at liquid nitrogen temperature and the mixture subjected to ultraviolet radiation. New bands which arose in the infra-red spectrum of the matrix as a result of this treatment were closely similar to the spectrum of xenon difluoride and thus afforded evidence for the formation of an analogous unstable krypton compound.

If the bonds formed by xenon are of ordinary covalent type and not fundamentally different from those formed by other elements, we should expect that for series of compounds such as SbF_3, TeF_4, IF_5, XeF_6 the plot of a bond property such as bond strength against atomic number would give a smooth curve. This proves to be the case.[7a] For Xe-F, bond energy values of 30-32 kcal per mole have been obtained from measurement of the enthalpy changes

when xenon fluorides react with ammonia. For Xe-O, a value of 20 kcal has been obtained from the enthalpy of decomposition of the trioxide. From the thermochemical cycle for the combination of an inert gas (N) with $\frac{1}{2}y$ molecules of a diatomic gas X_2

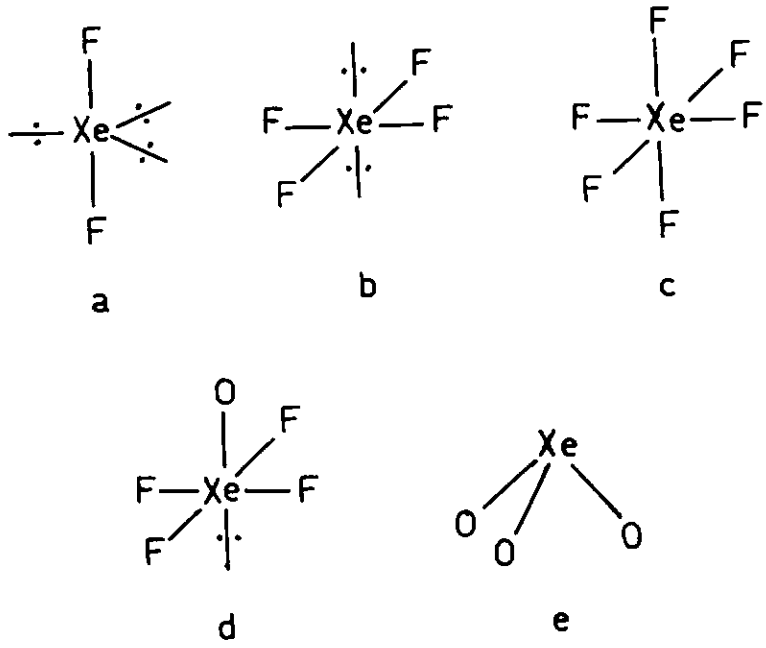


it will be seen that if $|\Delta H_3| > |\Delta H_2|$ then the enthalpy of formation of the compound, ΔH_1, will be negative; that is if $E_{N\text{-}X} > \frac{1}{2}E_{X\text{-}X}$ then the formation of the compound from the elements will be an exothermic process. For fluorine, $\frac{1}{2}E_{X\text{-}X} = 18.3$ kcal, and for oxygen, $\frac{1}{2}E_{X\text{-}X} = 59.2$ kcal (X-X here referring to the "double" bond in the oxygen molecule). It is evident therefore that the xenon fluorides will be exothermic compounds, but that xenon trioxide will be highly endothermic (about 90 kcal per mole). For a possible xenon-chlorine bond, we may suppose that in line with the relative values for covalent chlorides and fluorides of other elements $E_{Xe\text{-}Cl}$ will have about two-thirds the value of $E_{Xe\text{-}F}$. Hence because $E_{Xe\text{-}Cl}$ (approximately 20 kcal) is less than $\frac{1}{2}E_{Cl\text{-}Cl}$ (= 29 kcal) the formation of any xenon chloride from the elements would be endothermic. It can be estimated that for the reaction $Xe_{(g)} + Cl_{2(g)} \rightarrow XeCl_{2(g)}$, the entropy increase at 25° would contribute a further 3-4 kcal towards the free energy *increase* attending the process[8]. The presence of the entropy term in the relation $\Delta G = \Delta H - T\Delta S$ means incidentally that for a compound of marginal thermodynamic stability, the chances of success in its preparation will be greater, the lower the temperature. The first ionisation potential of krypton is 1.9 e.v. greater than that of xenon. The precise effect of this on the energy of a Kr-F as compared with an Xe-F bond is arguable, but it could amount to 15 kcal. If this be so, the krypton fluorides would certainly be of doubtful thermodynamic stability, as the difficulty in their preparation suggests.

The full range of methods for structure determination has been brought to bear on xenon compounds. Crystal structures have been examined by X-ray and neutron diffraction, and molecular structures in the vapour phase by electron diffraction. Infrared and Raman spectra have provided evidence on molecular symmetry and bonding. Xenon difluoride has a linear molecule with $l_{Xe\text{-}F} = 1.96$A, the tetrafluoride is square planar with $l_{Xe\text{-}F} = 1.94$A, while the trioxide is trigonal pyramidal with the very short bond length 1.75A and bond angles close to 100° (fig. 1). The tetragonal pyramidal structure of $XeOF_4$ has been assigned by comparison of its infrared and Raman spectra with the tetrafluoride spectra. The oxyfluoride gives bonds corresponding to all the stretching and bending modes of the tetrafluoride, thus indicating a similar square planar arrangement of the halogens. Additional infrared bands arise from the Xe-O bond directed towards the apex of the pyramid. The structure of xenon hexafluoride is of unusual interest because the molecular orbital and valence bond-hybridisation theories would predict respectively, regular and irregular octahedral configurations. But practical difficulties arising from the high reactivity of the compound have delayed finality. Electron diffraction and infrared evidence which suggests some departure from regular octahedral symmetry may be suspect, due to impurities.

Bonding in Xenon Compounds

Any interpretation of the bonding in the xenon fluorides[7] must necessarily take account of the completely filled p orbitals of the xenon, its predisposition to combine with even numbers of fluorine atoms, and the stereochemistry of the compounds. Three types of approach to the problem may be considered.



(a) The linear XeF_2 molecule with three electron pairs in the equatorial plane. (b) Square planar XeF_4. (c) XeF_6. Unless the seventh electron pair (not shown) be in the spherically symmetrical but energetically unfavourable 6*s* orbital there would be a departure from regular octahedral symmetry. (d) The tetragonal pyramidal (pseudo-octahedral) $XeOF_4$ molecule. (e) XeO_3, trigonal pyramidal as for IO_3^-.

1. *The valence bond-hybridisation theory.* As applied to XeF_2 where the xenon has a ten electron valence shell, the necessary orbitals would be provided by hybridisation of the p_z and d_{z^2} orbitals to link the two fluorines in diametrically opposite directions. The remaining three pairs of non-bonding electrons would be accommodated in sp^2 hybrids disposed symmetrically in the equatorial plane. (This same geometry would be anticipated, whether the approach be based primarily on hybridisation or on minimisation of electron pair repulsions in the valence shell.) The interpretation can be extended to XeF_4 where sp^3d^2 octahedral hybrids are invoked to accommodate the six pairs of electrons in the valence shell. For XeF_6, however, there is a complication associated with the seventh electron pair which would be expected to disturb the symmetry of the octahedron.

It has been argued that *d* orbital hybridisation is unlikely due to the large energy separation between the *p* and *d* sub-shells. Attachment of atoms of high electronegativity, however, undoubtedly reduces this energy separation and is commonly stated in other cases, e.g. SF_6, to facilitate hybridisation of outer *d* orbitals.

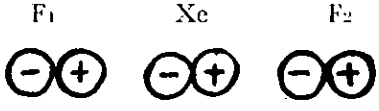
2. *The valence bond resonance model.* This theory[9] considers the contributing canonical forms $F^-Xe^+—F$ and $F—Xe^+F^-$. The electrostatic energy for the creation of the charged particles Xe^+ and F^- within an ionic lattice will be given by

$$I(Xe) - A(F) - e^2/d$$

where I(Xe) is the ionisation potential of xenon, A(F) is the electron affinity of fluorine and e^2/d the decrease in potential energy when the charged particles take up positions a distance *d* apart. Substituting the appropriate values for these three terms, 12.1, 3.6, and 6.7 e.v. respectively, the resultant energy is 1.7 e.v. This energy intake is likely to be more or less balanced by the covalent bond

in the other half of the molecule along with the "resonance energy". The structure is, therefore, energetically feasible, but the analysis does show that the development of such a structure will be critically dependent upon the ionisation potential of the inert gas—as indeed the experimental evidence on the instability of the krypton fluorides would bear out.

3. *Molecular orbital theory.* As applied by Rundle[7b] this uses a $5p$ orbital of xenon for overlap in diametrically opposite directions with p orbitals of fluorine atoms to give three-centre molecular orbitals. The ways in which these orbitals



can be combined to give mutually independent linear combinations are

$$\psi_{nb} = \tfrac{1}{2}\psi(F_1) - \frac{1}{\sqrt{2}}\psi(Xe) + \tfrac{1}{2}\psi(F_2)$$

$$\psi_{nb} = \frac{1}{\sqrt{2}}\psi(F_1) + 0\psi(Xe) + \frac{1}{\sqrt{2}}\psi(F_2)$$

$$\psi_{b} = \tfrac{1}{2}\psi(F_1) + \frac{1}{\sqrt{2}}\psi(Xe) + \tfrac{1}{2}\psi(F_2)$$

By squaring and adding coefficients in each vertical and horizontal column we can check that each atomic orbital has been used just once and that each molecular orbital holding two electrons is normalised to unity. ψ_b giving an increased electron density between the atoms, is a bonding orbital, and conversely ψ_{ab} is anti-bonding. ψ_{nb}, which does not significantly alter this electron density, is non-bonding. As regards electron occupancy, ψ_b and ψ_{nb} will both contain two electrons, so that each xenon atom has $2 \times \left(\frac{1}{\sqrt{2}}\right)^2 = 1$ electron in its vicinity and that each fluorine has $2 \times (\frac{1}{2})^2 + 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 = 1\frac{1}{2}$ electrons (statistically) in its vicinity. Hence we see that the model indicates the development of formal charges analogues to those of the valence bond resonance model. Both theories too, can be extended to the higher fluorides and, contrary to the valence bond-hybridisation theory, would predict regular octahedral symmetry for the hexafluoride.

It must be pointed out that none of these interpretations is new in principle. Nor is the problem new, but the discovery of xenon compounds has directed attention afresh to the inability of valence theory to predict the behaviour of valence shells containing more than six pairs of electrons. After all, XeF_6 is isoelectronic with the IF^-_6 and TeF_6^{2-} ions whose unknown structures have not attracted as much attention as the novel xenon compounds. Nevertheless, the structure of XeF_6 as a neutral molecule could remain more significant than those of the isoelectronic ions which might be subject to lattice distortion. Precise information as to whether or not it is regular octahedral could provide grounds for rejecting one or other of the theoretical interpretations.

Retrospect

The history of the investigation of the inert gases is not without a broader significance relevant to the development of chemistry at large. Valence theory had been unable to provide clear guidance as to whether these elements would form chemical bonds. With the accumulation of negative results it had become almost a tradition that the elements were completely unreactive, but to its credit, the world of chemistry quickly adjusted itself to the discoveries that have given xenon so interesting a place. Circumstances leading to the eventual discovery of xenon compounds developed from the chance observation of PtO_2F_6, but it is more important to observe that the work was brought to fruition only through diligent examination of this compound and a scholarly assessment

of the significance of its existence. When once the way to the xenon fluorides was signposted the experimental work was greatly assisted by technical developments which made the elements more readily available than at the time of the earlier investigations and improved the means for the manipulation of such reactive compounds.

The belated discovery of xenon compounds in an era when so many laboratories are generously equipped with a wide range of instrumental facilities led to a heavy concentration of work in this novel field with about 100 communications appearing during the first year. Understandably enough, numerous unsolved problems remain—as for example, those relating to bonding, to the properties of xenon hexafluoride, and to unstable oxygen compounds—but perhaps to no greater extent than in many comparable fields of chemistry.

References

1. Travers,, "A Life of Sir William Ramsay", Arnold, London, 1956, p. 146.
2. Pauling, L., J.Amer.Chem.Soc., 1933, *55*, 1895.
3. Yost and Kaye, J.Amer.Chem.Soc., 1933, *55*, 3890.
4. Yost, "Noble Gas Compounds", Hyman, Ed., Univ. of Chicago Press, 1963, p. 21. (This publication contains the proceedings of a conference held at the Argonne Laboratory in April 1963.)
5. Bartlett, N., Proc.Chem.Soc., London, 1962, 218.
6. Claassen, Selig, and Malm, J.Amer.Chem.Soc., 1962, *84*, 3593.
7. As examples of important reviews the following are cited:
   (a) Bartlett, N., Endeavour, 1964, *23*, 3.
   (b) Greenwood, N., Education in Chemistry, 1964, *1*, 116.
   (c) Malm, Selig, Jortner, and Rice, Chemical Reviews, 1965, *65*, 199.
   (d) Holloway, Progress in Inorganic Chemistry, Vol. VI, p. 241.
8. Dasent, W. E., Nonexistent Compounds", Dekker, New York, 1965, p. 143.
9. Coulson, J.Chem.Soc., London, 1964, 1442.

THE REGISTRY

The following applicant was elected to the Fellowship at the November Council meeting:

LESTER, Patrick, F.R.I.C., Technical Correspondence Institute, Wellington (Tutor).

The following were elected as Associates:

BEANLAND, Eric, M.Sc.(Lond.), A.R.I.C., Chemistry Division, D.S.I.R., Private Bag, Petone (Scientist).

BURNS, Neil George, M.Sc.(Victoria), W. D. and H. O. Wills (N.Z.) Ltd., Petone (Assistant Chemist).

EDWARDS, George David, B.Sc.(Hons.)(Otago), Laminex Industries Ltd., P.O. Box 16-063, Christchurch (Works Chemist).

FERGUSON, Allan Ross, B.Sc.(Hons.)(Victoria), Fruit Research Division, D.S.I.R., Private Bag, Auckland (Scientist).

GALLOP, Donald John, M.Sc.(Victoria), Wilson's N.Z. Portland Cement Co. Ltd., Whangarei (Chief Chemist).

GARSIDE, John Herbert, B.Sc.(Hons.), Ph.D. (Lond.), A.R.I.C., Central Institute of Technology, Petone (Tutor).

GORDON, Gerard James, M.Sc.(Victoria), Guardian Cement Co. Ltd., Westport (Chief Chemist).

HANSEN, Sydney Brian, B.Sc., Technical Correspondence Institute, Wellington (Tutor).

HOLEY, David, Unilever (N.Z.) Ltd., Private Bag, Petone (Industrial Chemist).

KITTO, George Barrie, M.Sc.(Victoria), Ph.D. (Brandeis), Dept. of Chemistry, University of Texas, Austin, Texas (Assistant Professor).

KNOX, Bruce Stanley, B.Sc., Postgraduate School of Obstetrics and Gynaecology, National Women's Hospital, Auckland (Research Biochemist).

MOLLOY, Leslie Francis, M.Sc.(Victoria), Soil Bureau, D.S.I.R., Private Bag, Lower Hutt (Scientist).

PLUIJMERS, Catrinus Bernadus, J. Wattie Canneries Ltd., P.O. Box 439, Hastings (Chemist).

RICHARDS, Kenneth Eric, B.Sc.(Hons.)(Exeter), Ph.D.(Keele), Chemistry Dept., University of Canterbury, Christchurch (Lecturer).

SIMPSON, Wallace Harley, B.Sc., Wilson's N.Z. Portland Cement Co. Ltd., Whangarei (Assistant Chemist).

TURNER, Roscoe Cameron, B.Sc.(Lond.), Shell Oil (N.Z.) Ltd., Wellington (Chemist).

Resignation

M. G. RUMSBY accepted with regret.

Leave

N. J. PEET—two years with remission of subscription.

BOOK REVIEWS

Mathematics and Statistics for Chemists. C. J. Brookes, I. G. Betteley and S. M. Loxston. Published by J. Wiley and Sons, London 1966, 418 pages, price $A6.35.

This comprehensive text covers most of the mathematical manipulations required in chemical studies. A certain amount of prior knowledge is required by the reader and hence the book is not for the beginner but for the chemist with a good basic grounding in trigonometry and algebra. The text is designed to lead the reader confidently towards more difficult forms of mathematical manipulations. It has a large number of worked examples as well as problems and answers. There are several excellent chapters on statistics and their use in practical problems. Of particular interest is the chapter on the design of experiments so that maximum information can be obtained.

This is not a book that one can sit down and browse through. It requires concentrated reading —usually in conjunction with pencil and paper. If approached in this manner much useful information can be obtained on the application of mathematics to chemical problems.

P. C. RANKIN.

The Chemistry of the Carbonyl Group, edited by Saul Patai. John Wiley & Sons Ltd. (Interscience), London 1966, English price 220/-.

This book is the second in a series of advanced treatises dealing with the chemistry of functional groups under the editorship of Saul Patai ("The Chemistry of the Alkenes" was published in 1964). The first chapter of the present book deals with physico-chemical aspects and bonding in the carbonyl group. The following six chapters are concerned with the synthesis of carbonyl compounds including a discussion of the biochemical formation of carbonyl groups. The later chapters deal with methods of analysis, basicity of carbonyl compounds and typical reactions (oxidation, reduction, condensation, decarbonylation, etc.). The two final chapters are concerned with the photochemistry of carbonyl compounds and the chemistry of thioketones. Two chapters, "Equilibrium additions to carbonyl groups" and "Synthesis and uses of isotopically labelled carbonyl compounds" did not materialise in time to meet publication deadlines.

The book has both an author and subject index and over 3,000 references are given. There is no doubt that the volume will be useful to chemists generally as a reference work although its price will limit its purchase to libraries. R. W. HAY.

The Concept of Energy, by D. W. Theobald, E. and F. N. Spen Ltd., London 1966, 192 pages, 42/-.

This book is essentially a short treatise on energy written from the point of view of the historian and the philosopher of science and perhaps for the physicist with a philosophical turn of mind. Mechanical energy, thermal energy, energy in the field and the quantum of energy are discussed in succession and the book concludes with chapters on the conservation of energy and energy, grammar and existence. The treatment is too theoretical and philosophical to make much impact on the majority of chemists and to the chemist who is primarily an experimentalist it will have no appeal at all. However, honours students with a more theoretical turn of mind will no doubt find that it makes interesting and valuable reading.

B. D. ENGLAND.

Chemical Transport Reactions, by H. Schafer, University of Munster, translated by H. Frankfort. Academic Press, New York and London (1964), 161 pages, price $6.80 (U.S.).

The term 'chemical transport reaction' will probably be unfamiliar to many chemists, although the concept will not. Thus, the carbonyl method of refining nickel metal makes use of a typical chemical transport reaction. A volatile compound is produced from involatile starting materials, and then transported in the gas phase to a region where the physical conditions are so changed, that a further reaction ensues which results in the deposition of an involatile product.

The stated aim of the author is to direct the attention of inorganic chemists to the proved usefulness and potential applications of these reactions. He provides a clear account of some suitable experimental techniques and a simplified theoretical treatment of the subject which is shown to be adequate for many purposes. The major part of the book is devoted to discussing specific transport reactions which have been carefully chosen to illustrate the sort of problems which can be tackled. The reactions described are conveniently indexed in tabular form at the end of the book.

The present edition, which appeared in 1964, is a revised translation of a book first published in German in 1962. Even so, about a third of the references are dated 1961 or later.

The translation is good in that it appears to be scientifically accurate, and is for the most part easy to follow. However, many of the sentences seem to have kept rather too closely in form to the German original.

This monograph should be a worthwhile addition to many libraries. In particular, it contains a lot of data which are not assembled elsewhere, and which would often be difficult to obtain without considerable facility with translation from the German.

C. G. POPE.

Peptide Synthesis, by M. Bodzansky and M. A. Ondetti. Interscience, New York 1966, price £4/5/6 (N.Z.).

This is a concise (250pp) and useful survey of current methods of peptide synthesis somewhat along the lines of an article in "Organic Reactions". About half the book is devoted to a summary of protection techniques, coupling methods and ways of detecting racemisations. The remainder consists of a short but useful chapter on the tactics of synthesis—which is the best way to fit possible fragments together, and a larger section giving specific examples of the application of previously described principles. Examples in this latter section include descriptions of the synthesis of small molecules like bradykinin as well as more substantial operations such as the full synthesis of insulin.

J. N. Smith.

Principles of Chemical Equilibrium, by Kelso B. Morris, Reinhold and Chapman and Hall, London 1966, 114 pages, 10/6. One of Reinhold's Series: Selected Topics in Modern Chemistry.

This book, like others in the series, is aimed at the freshman chemistry student. It is divided into three chapters dealing respectively with Heterogeneous Equilibrium and the Phase Rule, Non-ionic Chemical Equilibrium and Ionic Chemical Equilibrium. About half the book is devoted to ionic equilibria.

The approach is uneven, very traditional and, in the reviewer's opinion, likely to confuse the student and direct his thinking into the wrong channels. There is virtually no attempt to unify the three main themes: to the author they seem to be three distinct branches of chemistry in which progress is made by applying three different sets of empirical rules.

One of the major tasks of the University teacher of Physical Chemistry is to separate the ideas of thermodynamics and kinetics, these often having been already sadly mixed up by traditional school derivations of the equilibrium constant expression by kinetic methods. The better school and Stage I texts now avoid this trap but this book states the time honoured Law of Mass Action without qualifications and uses it to deduce that K is a constant at constant temperature with no indication that the deduction is valid only for a one-stage process. The diagram on page 26 implies that reaction speed is a linear function of time and introduces the term "inhibitor catalyst" with no explanation. Just what is an inhibitor catalyst! Le Chatelier's principle is sketchily treated with no indication that the effects of pressure and temperature are fundamentally different insofar as only temperature, in an ideal system, affects the equilibrium constant.

In the section on aqueous solution the Lowry-Bronsted definition of acids and bases is never mentioned. Consequently there is no indication that the process labelled hydrolysis of acetate ion is really the dissociation of the weak base, CH_3COO^-.

Altogether this book is an unnecessary addition to the literature of chemistry.

B. D. England.

Chemical Energy, by Lawrence E. Strong and Wilmer J. Stratten, Reinhold and Chapman and Hall, London 1966, 115 pages, 10/6. One of Reinhold's series: Selected Topics in Modern Chemistry.

This small paperback is essentially an introduction to Chemical Thermodynamics suitable for the advanced Stage I student and also readable with profit by Stage II and III students. It is a modern treatment insofar as the aim is to use thermodynamics to interpret physical and chemical changes rather than to present the logical foundations of the subject. The Carnot Cycle is not mentioned at all and reversible processes receive only a sketchy treatment. On the other hand there is a good deal of interpretation of ΔH values in terms of bond strengths in products and reagents and of ΔS values in terms of changes in randomness in the species concerned in the reaction. In the reviewer's opinion this is a thoroughly sensible way to write a book of this kind.

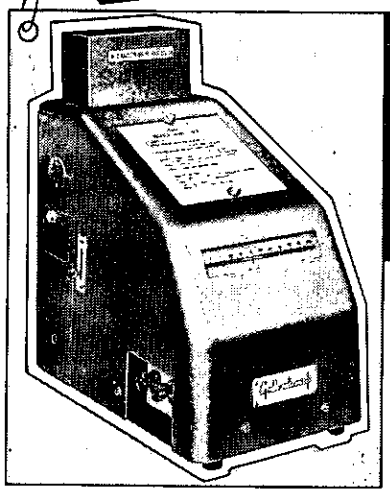
The authors make considerable use of enthalpy diagrams of the type for which Chemical Systems, the CBA text, is justly famous and these add greatly to the students' understanding of this subject. However, the authors never seem to explain the significance of the two different types of arrows that they use in these diagrams. There is also much emphasis on actual thermodynamics data with many tables of thermodynamic functions for related reactions with interpretations of the observed differences. This should correct a tendency among those whose education in thermodynamics has been too pure to regard such data as being ordained by the Almighty and therefore impossible to interpret in terms of the changes that are going on at a molecular level.

The book can be recommended to anyone who wishes to use thermodynamic data to understand chemistry rather than to enquire into the logical foundations of the subject.

B. D. England.

Advanced Laboratory Instruments

BY Gallenkamp



Gallenkamp FLAME ANALYSER

For faster, more accurate determinations of Sodium and Potassium

- **Accurate reading in 5 sec.**
- **Negligible cross-interference between elements**
- **Virtually rust-proof burner/atomiser assembly**
- **Tropicalised photocell**
- **Immediate operation, no warming up**
- **Operates on town or most commercial gases**
- **Ready accessibility of interior for cleaning and servicing**

Applications

Sodium and potassium determinations in:
Biochemical samples, pharmaceuticals, cosmetics, foods
Plant and animal tissues
Fertilisers, soils, water, oils
Cement, glass, ceramics and many other materials

PERFORMANCE: Sodium 2 ppm (0.087 mE/l) for full scale deflection. Potassium 5 ppm (0.125 mE/l) for full scale deflection. Sample uptake rate: 4 ml/min. Minimum volume for one reading: 0.5 ml (for accurate results, the average of several readings should be taken). Repeatibiliy: 1%.

Each £122.10.0 Ask for details.

Gallenkamp

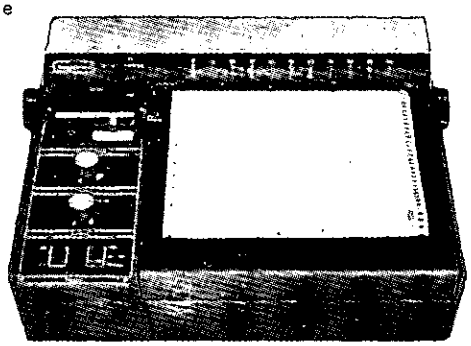
LONDON
Technico House · Christopher Street · London · E.C.2

Appointed distributor :
Geo. W. Wilton & Co. Ltd.,
Box 9071, Newmarket, Auckland.
Box 367, Wellington.

uj nou yeni new*

No matter how you say it, the Beckman Ten-Inch Laboratory Recorder is *new* . . . the newest in high performance recording instrumentation. It has been specifically designed for the analytical laboratory — by the company that knows laboratory instruments. Its performance specifications allow it to speak any language — Ultraviolet and Infrared Spectrophotometry, Gas Chromatography, pH, etc.

The Recorder translates rapidly and accurately. It scans the full 10-inch scale in less than 0.5 seconds. Pen zero can be set to any point on the scale. It's accurate to ±0.25% for linear recording. Seven chart speeds may be instantly selected with finger tip control. Three calibrated input spans — 1, 10, and 100 mv — permit a wide range of applications. For convenience, all major controls are on one accessible panel, and mounting accessories are available for any laboratory need.



*For the record — "new" is in Hungarian, Rumanian, Turkish.

For more information on the linear or linear-log model, see your local Beckman Sales Engineer. Or write for Data File LR-166.

Beckman® INSTRUMENTS, INC.

WATSON VICTOR LTD.

AUCKLAND
WELLINGTON
CHRISTCHURCH
DUNEDIN

WATVIC

Printed by David F. Jones Ltd.