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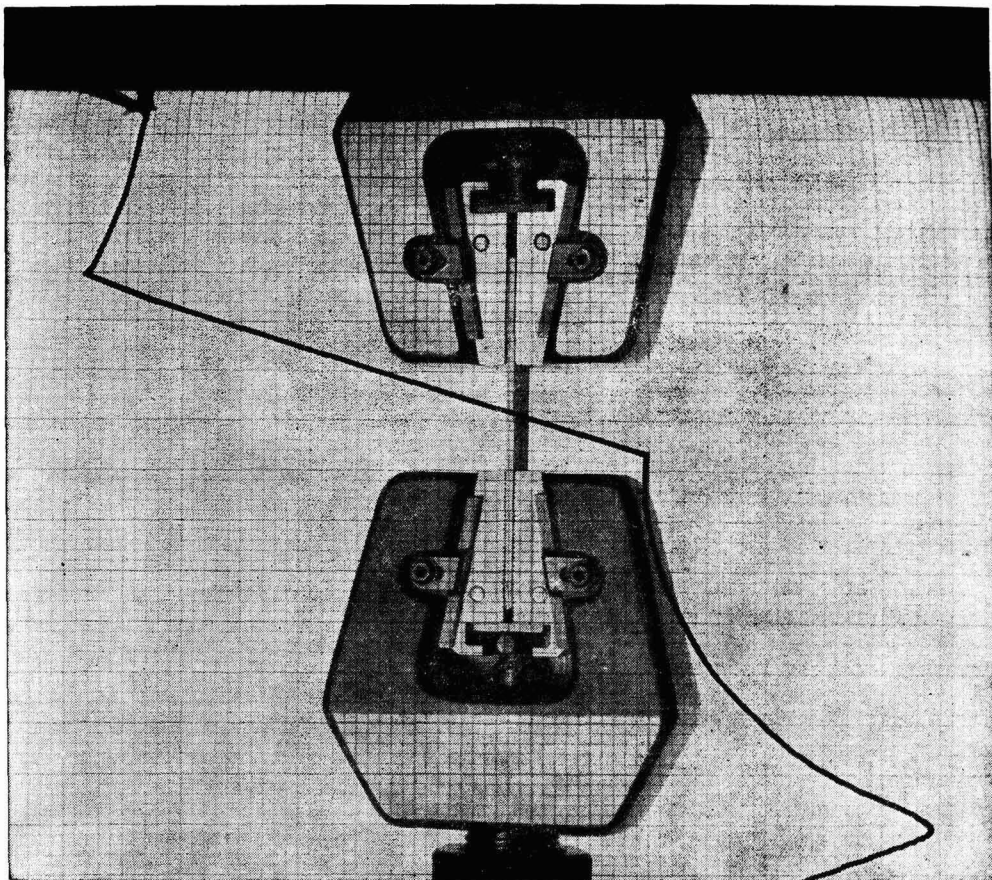
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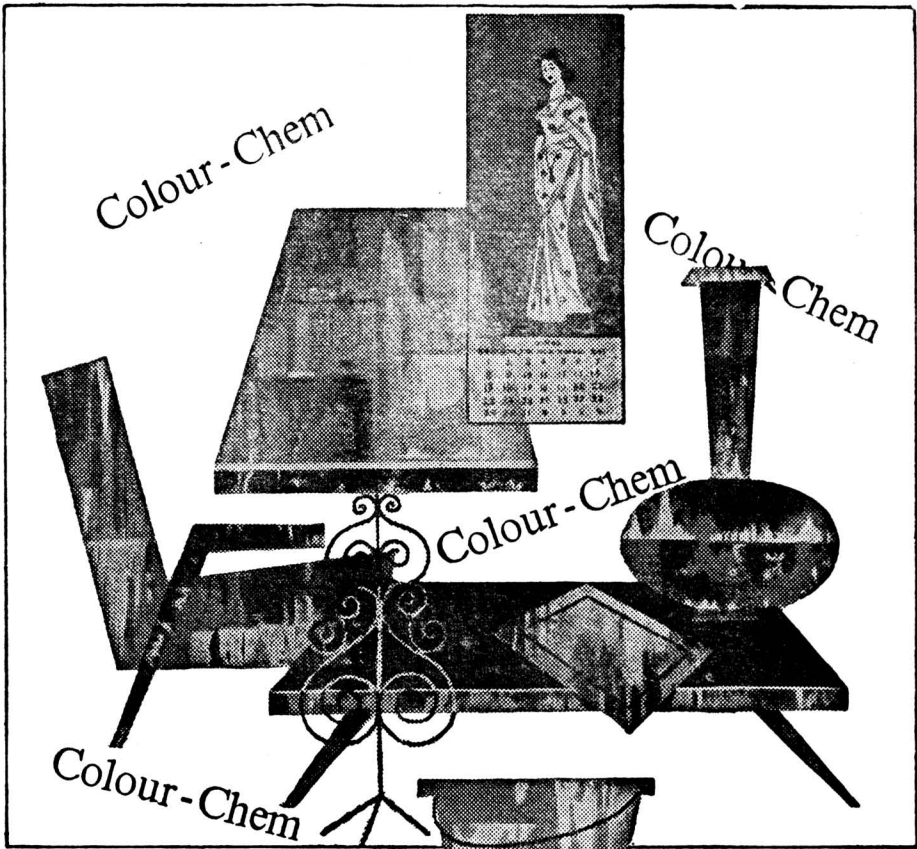
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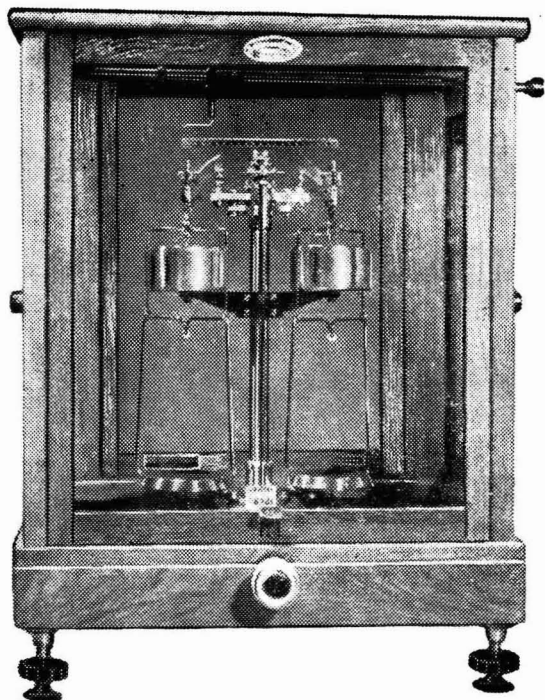
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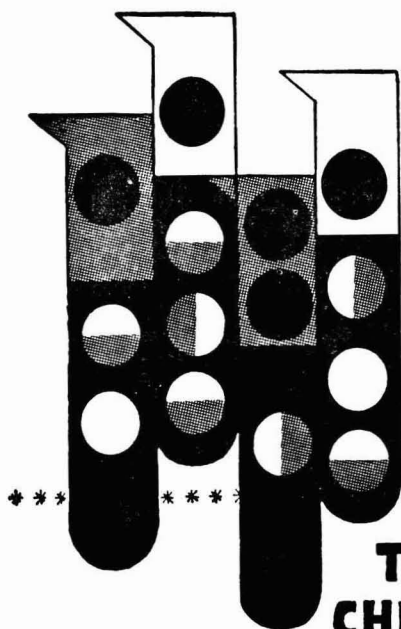
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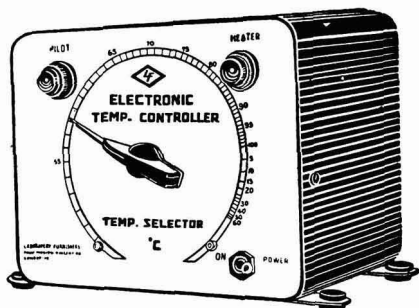
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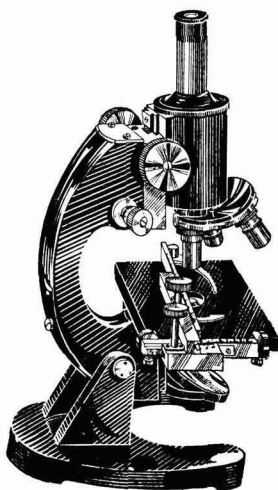


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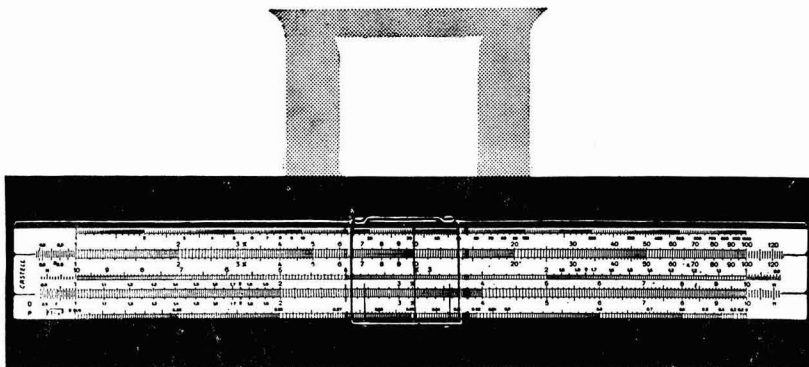
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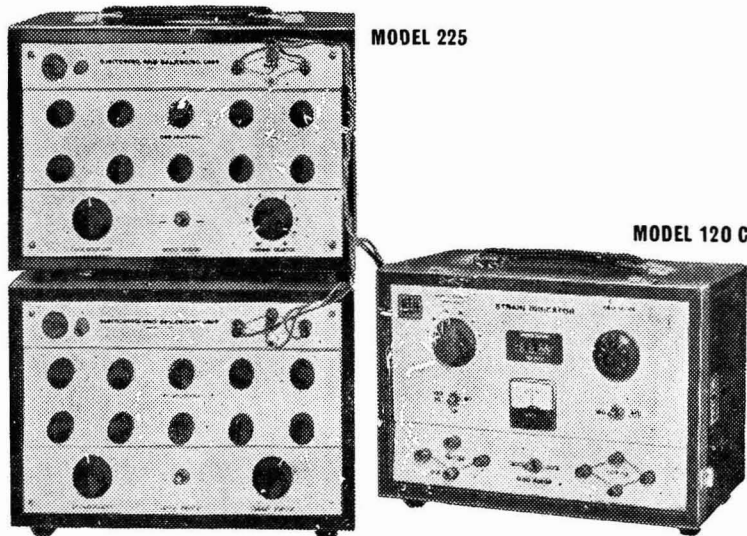
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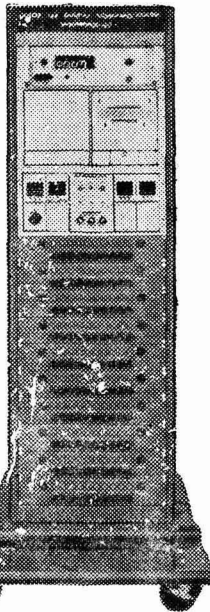
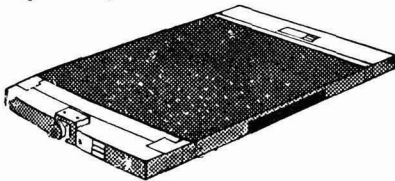
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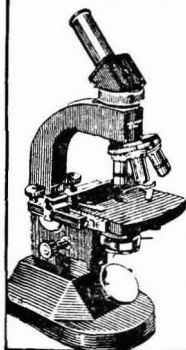
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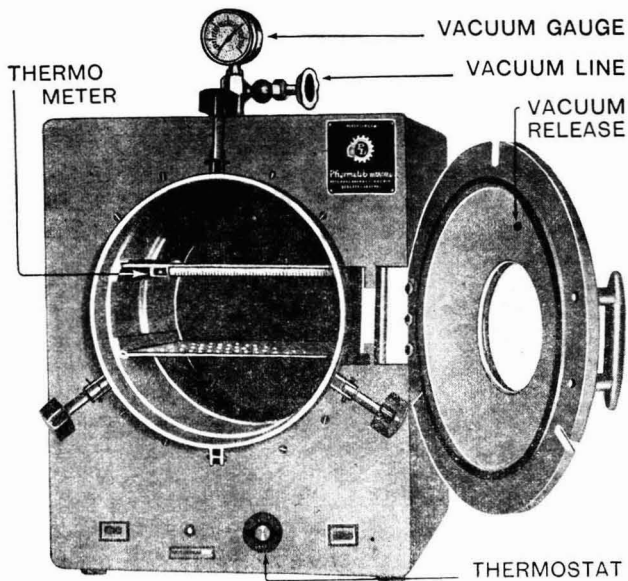
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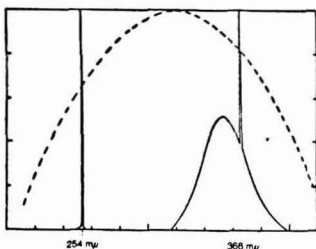
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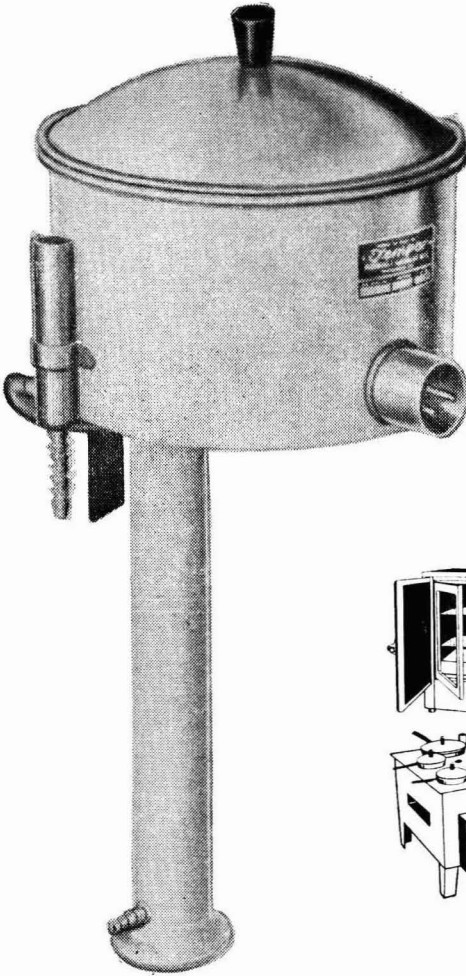
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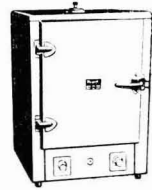
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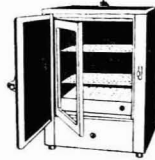
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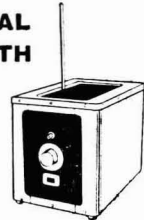
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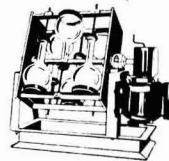
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Current Topics

Nonferrous Metals Technology

AS the premier research establishment in the field of metallurgy in the country, the National Metallurgical Laboratory, Jamshedpur, has, during the past 15 years, done a yeoman's service towards the growth and development of the ferrous and nonferrous industries. An important activity of the laboratory has been to hold, at frequent intervals, national and international symposia on problems of vital concern to the research scientists as well as the industries concerned. These symposia have come to be recognized as excellent media for exchange of information and viewpoints and for identification of problems and fields for investigation in the context of the raw materials available, requirements of industry, and other related considerations. The latest symposium held during 4-7 December 1968 dealt with the important and highly topical subjects 'Development of nonferrous metals technology'.

Among the various industrially important nonferrous metals, India is favourably placed only in respect of aluminium. For others like copper, zinc, tin, lead, antimony, etc., she depends mainly on imports and the import bill for these metals by 1975-76 is likely to go up to Rs 500 crores per annum. It is evident that an all-out effort is needed towards reducing the country's dependence on foreign sources for these metals. The main objectives in this respect should be: (i) raising the status of aluminium as an industrial material and diversifying its utilization; (ii) intensive exploitation of the known reserves of the strategic nonferrous metals like copper, zinc and lead and location of new reserves; and (iii) development of technologies aimed at substitution of imported metals by those available indigenously. In the context of the above objectives, considerable significance attaches to the proposal regarding the establishment of an 'Aluminium cell' at the National Metallurgical Laboratory and the recently launched programme of the Geological Survey of India under the name 'Operation Hard Rock' for conducting air-borne surveys to discover new deposits of the metals copper, zinc and lead. It may also be worth while attempting certain unconventional approaches to the problem of reducing dependence on imports for the scarce metals. A typical approach may be to examine the possibility of part replacement of scarce metals like copper in alloy compositions used in bulk quantities, without impairing the properties of the compositions.

A wealth of information was provided in the sixty and odd papers presented and discussed at the symposium under the following broad heads: (1) Alumina: Its extraction and uses; (2) Physical

metallurgy of aluminium; (3) Scarce and strategic nonferrous metals; (4) Physico-chemical and founding aspects of nonferrous metals and alloys; (5) Utilization of indigenous resources of copper and their extraction techniques; (6) Treatment of wolframite, gold ore, magnetite, titanium, zirconium, niobium and tantalum ores; and (7) Role of nonferrous metals in Indian industries. The deliberation of the symposium focused attention on the imperative need for increasing the indigenous production of the various nonferrous metals and the overall strategy to be adopted for reducing imports by maximizing the exploitation of indigenous resources and development of new alloys to mitigate the shortage of many strategic metals like nickel, tin, cobalt, molybdenum, tungsten, etc.

An appraisal of the current status of the nonferrous metals technology in the country provided by the symposium gives an idea of the contributions of the National Metallurgical Laboratory in tackling a wide range of problems. Typical areas of work undertaken include: upgrading of indigenous nonferrous ores, recovery of metals from ores, development of new techniques for the extraction of metals and development of substitute alloys based on available raw materials. One of the major programmes of work in the field of beneficiation of nonferrous ores relates to manganese ores on which as many as 42 projects have been completed and the results made available to industry. Exhaustive beneficiation studies have been completed on low grade chrome ores, gypsum, kyanite, magnesite, gold ores, uranium ores and tungsten ores. A flotation plant for the beneficiation of low grade graphite ores set up by the Patna State Graphite Co. at Titagarh (Orissa) utilizes the know-how developed by the laboratory.

In the absence of large-scale zinc deposits in the country, the laboratory has paid considerable attention to the recovery of zinc from a variety of industrial wastes, such as zinc dross, zinc ash, flux skimmings and zinc blowings. Based on laboratory studies on the distillation of zinc dross, a vacuum distillation unit with a capacity to distil 150-200 kg. of dross/batch has been designed. Of equal economic importance is the development of know-how for the recovery of electrolytic grade lead from lead scrap and tin from tin scrap.

A project of vital importance to defence effort concerns the reconditioning of magnesium powder of 60-90 per cent magnesium content to a product containing over 90 per cent magnesium. Investigations on the production of magnesium metal by silicothermal reduction of calcium dolomite have been completed and a semi-commercial unit for producing 250 tons of ingot magnesium per annum is being set up by the laboratory.

In view of the limited resources of copper in the country, the possibility of using aluminium conductors for power transmission has been investigated and an aluminium conductor, designed PM-2, has been developed from indigenous electric grade aluminium (purity >99.5 per cent); the conductor possesses better electrical conductivity, higher strength and improved corrosion resistance compared to those currently in use.

The laboratory's achievements to date provide ample evidence of its important role in taking the country nearer the goal of self-reliance in respect

of nonferrous metals. In this endeavour, considerable responsibility rests upon the nonferrous metals industry, which is the ultimate user of the know-how developed. Besides utilizing the facilities and expertise available at the National Metallurgical Laboratory, it may be worth while for the nonferrous metals industry to consider seriously the formation of a cooperative research association, as advocated by Shri Jehangir Ghandy in his presidential address, so that its problems could be tackled on a sound and organized basis.

Nobel Prize Awards, 1968

The Nobel Prize in Physics for 1968 has been awarded to Prof. Luis Alvarez, Associate Director, Lawrence Radiation Laboratory, Berkeley, USA, for his contribution to the development and exploitation of the hydrogen bubble chamber. Though the bubble chamber was originally invented by Prof. Glaser in 1952, it was Prof. Alvarez's work in developing the larger hydrogen bubble chambers that opened the way for the study of interactions of elementary particles on a large scale. Prof. Alvarez has also notable achievements to his credit in the field of fundamental particles.

The Nobel Prize in Chemistry has been awarded to Prof. Lars Onsager of Yale University, USA, for his contributions to thermodynamics and statistical mechanics. Among his outstanding achievements are: (1) the theoretical treatment of the relationships existing between the parameters determining the rates of flow in non-equilibrium systems in a steady state, and (2) calculation of the properties of Ising lattice — a two-dimensional net of points on which are placed two-valued elements (e.g. magnetic poles) capable of interacting with each other. Prof. Onsager's contributions

to the thermodynamics of flow processes are of great practical utility in treating problems involving the maintenance of transport phenomena by the influence of more than one kind of driving force.

The Nobel Prize in Medicine has been awarded jointly to Prof. Robert W. Holley of Cornell University, Prof. H. G. Khorana of University of Wisconsin and Prof. Marshall W. Nirenberg of the National Heart Institute, Bethesda, USA, for their independent work on the unravelling of the genetic code. Prof. Nirenberg demonstrated that a synthetic polynucleotide containing a single type of base, uridylic acid, directs the synthesis of a protein containing a single type of amino acid, phenylalanine. This helped establish that a sequence of three specific nucleotides is required to code for each amino acid in the protein molecule. Prof. Khorana synthesized all the 64 possible trinucleotides and confirmed that the genetic code is read in a linear and consecutive manner and that it is a non-overlapping triplet code. Prof. Holley determined the first complete nucleotide sequence of any nucleic acid — that of transfer RNA.

International Conference on Light Scattering Spectra of Solids, 1968

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THE year 1968 marks the fortieth year of the discovery of the Raman effect* and also coincides with the eightieth year of age of its discoverer†, the world-famous Indian scientist. It was, therefore, a fitting occasion to have an international conference on Raman effect. During the period 1950-60, the subject of Raman spectroscopy was the topic of research only in a few laboratories. In recent years, there has been an unusual revival of interest in Raman effect. This is mainly due to the development of lasers, which have since become invaluable tools for the study of Raman spectra. In view of the increased activity on the subject in many laboratories of the world, the first international conference on Raman spectra of crystals was held in the University of Paris in July 1965‡. The present one is the second in the series. This conference which was co-sponsored by the International Union of Pure & Applied Physics and the US Army Research Office, Durham, was held under the auspices of the New York University during 3-6 September 1968. This conference had a wider scope and was concerned not only with all aspects of Raman effect in solids, but also with the theoretical and experimental aspects of Brillouin and Rayleigh scattering phenomena and their applications to the investigation of the solid state.

Brillouin effect was discovered nearly 46 years ago and Rayleigh scattering very much earlier. Scientific interest in these two topics also was at a low ebb before the advent of lasers. The development of the laser as a source of excitation has revived interest in these topics and many papers have appeared on Brillouin scattering in recent years. The widened scope of the present conference is, therefore, understandable. The conference Secretary was Prof. J. L. Birman of the New York University, while the Chairman of the Planning Committee was Prof. E. Burstein of the University of Pennsylvania. The International Advisory Committee, of which the author was a member, consisted of one member each from USA, India, England, France, Italy, USSR and Canada. Although the organizers had extended special invitations to the discoverers, both Prof. C. V. Raman and Prof. Leon Brillouin, to grace the conference by their presence as distinguished guests, only the latter could accept the invitation and was present for the conference. While the first conference on Raman effect held in Paris in 1965 had 30 delegates, the present one had well over 200 participants from 16 countries, including the USSR.

The proceedings of the conference were held in the lecture hall of the Courant Institute for Mathe-

matics of the New York University near Washington Square. The conference was formally opened by Dr Allen M. Cartter, Chancellor and Executive Vice-President of the New York University. This was followed by a brief review of the conference by Prof. Birman. He also gave a historical review of the theory of Raman scattering starting from Placzek's polarizability theory and ending with the photon-phonon interaction theory of Loudon. The scientific programme was divided into eight sessions; the important points brought out during each session are summarized below.

Phonons and Polaritons

The first session started with an introductory talk by Prof. S. P. S. Porto of the University of Southern California. He described the experimental set-up employed for studying Raman spectra of crystals at different temperatures using laser sources. The most commonly used laser sources are: (1) He-Ne 6328 Å.; (2) A⁺ 4880 Å. and 5145 Å.; and (3) Nd-YAG 1.06 μ. He briefly reviewed the results on the Raman spectra of GaP, TiO₂, MnF₂, FeF₂, quartz and BeO obtained with laser sources. The advantages and disadvantages of using laser sources for Raman excitation were also enumerated.

The properties of long wavelength lattice vibrations, with particular reference to polar phonons, were reviewed by Prof. Loudon of Essex University. The interactions of such phonons with the electromagnetic field leading to the formation of polariton modes were discussed. The theory of light scattering by these excitations was reviewed and formulae were developed for the intensity of first order Raman scattering by a given polariton. This is usually observed only in small angle scattering experiments. From the measured intensity of Raman scattering it is possible to estimate electro-optic coefficients of polar crystals. Stimulated Raman scattering of polaritons forms a potential source of infrared radiations whose frequency can be varied by varying the scattering angle. A couple of papers describing Raman scattering by polaritons in α-quartz and in other polyatomic crystals were also presented.

Phonons

This session was opened by a review talk on light scattering from phonons by Dr F. A. Johnson of the Radar Research Establishment, Great Malvern. Light scattering experiments from phonons are very valuable, as they provide information about phonon energies. However, the couplings to the phonons and the phonon spectrum itself are usually considered to be problems too difficult for first principle calculations and one resorts to classical phenomenological models in both cases. Johnson pointed out that although the models obtained for

*The discovery of the effect was announced on 16 March 1928.

†Sir C. V. Raman was born on 7 November 1888.

‡Report published in *this Journal*, 24 (1965), 609.

the phonon spectrum were more or less successful, the models assumed for the coupling process were in an unsatisfactory state. If one considers the microscopic theories of the phonon spectrum, one would find striking parallels between these and the two phonon scattering tensors. He further showed how one could develop more realistic concepts of both the coupling process and the phonon spectrum. He also pointed out the intimate relationship between two phonon scattering and the electronic terms in the phonon spectrum. This review was followed by a theoretical paper by Dr Hardy and Dr Karo on the interpretation of the second order Raman spectra of NaF, KF, RbF and CsF. Two alternative models for the polarizability tensor have been used. Hardy and Karo showed that the combined density of states idea alone would not satisfactorily explain the relative intensities of the observed peaks in the second order spectra of the alkali halides and it would be necessary to adopt Born and Bradburns' treatment using suitable coupling constants between the ions of the lattice.

Two important papers presented in this session related to the successful recording of the second order Raman spectra of magnesium oxide by Dr Mon from Paris using an argon laser and of lithium fluoride by the author and Dr Narayanan from Bangalore using λ 2537 radiation. The frequency shift of the observed peaks in LiF were in good agreement with the frequencies corresponding to the peaks reported from the inelastic scattering experiments. The author also presented the lattice dynamics calculations of the low frequency transitional lattice modes in a few ionic crystals which exhibit phase transitions. Dr Fray of the Radar Research Establishment group at Great Malvern described in detail the piezoelectric crystal modulated Fabry Perot interferometric technique and pulse integrating circuit developed and successfully employed by them for studies on Brillouin scattering as well as low frequency or lattice Raman scattering.

Another important paper presented in the session was concerned with the Rayleigh and Raman scattering by surface modes in ionic crystals. Rayleigh scattering from liquid and solid surfaces was first observed by Raman and Ramdas as early as 1924. It has been shown from a theoretical standpoint that if the dimension of the sample is of the order of the wavelength, the surface mode scattering is comparable with that of the bulk modes. In crystals which lack centre of inversion, first order Raman scattering from surface modes should appear. The relative intensities of the bulk and surface mode Raman scattering from thin slabs of zinc blende structure have been estimated.

There was an informal discussion on problems and progress in second order Raman scattering. The principal speakers were Prof. Cummins, Dr Worlock, the author, Prof. Porto and Prof. Burstein. There was a general review of the present position of the second order Raman spectra and their interpretation. There was a general feeling that the resolution obtained so far in laser Raman spectroscopy, namely 2 cm^{-1} , was not enough and has to

be further improved. It was pointed out that the starting points of the upward steep rise of the intensity maxima on the long wavelength side and not the points corresponding to the peak intensities themselves correspond to the octaves and combinations of the critical point frequencies. It was further shown that crystal specimens obtained from natural sources as well as those obtained artificially using different crystal growth techniques give identical second order Raman spectra.

Magnons and Other Electronic Excitations

Dr Fleury of the Bell Laboratories gave a review talk on the Raman scattering from magnons or collective excitations in magnetic systems like MnF_2 , FeF_2 , NiF_2 , CoF_2 , etc. He drew attention to the determination of magnon dispersion relation from Raman effect studies and to the existence of magnon-magnon interactions as evidenced from the line shape of the two magnon or second order magnon spectra. The new feature of the experimental results is the persistence of the magnon excitation above the Niel temperature in the paramagnetic phase of the hexagonal RbNiF_3 . Among the ten papers presented during this session, two deserve special mention. One was concerned with the work on Raman scattering from magnons in MnF_2 doped with Ni^{2+} and Fe^{2+} . For each doped crystal, three additional temperature and polarization dependent Raman lines have been observed at temperatures $T \ll 2/3T_N$. The second one refers to the observation for the first time of the spin flip Raman scattering from neutral donors and acceptors in CdS. The applied magnetic field separates the desired scattering of small frequency shift from the Rayleigh scattering. In CdS, the spin flip scattering has a large cross-section, since the exciting line 4880 Å. was very close to the frequency of bound excitation states at donors. There were a few papers on electronic Raman effect in rare earth compounds.

Free Carriers

In a review talk in this session, Dr Wolff of the Bell Laboratories reviewed the classical theory of light scattering from plasmas. He also discussed the changes in the Raman spectra arising from non-parabolicity of electron bands. Experimental results obtained from studies on the Raman spectra from single particle electron and hole excitations in semiconductors, such as GaAs using a 30-watt Nd-YAG laser giving radiations of 1.06μ , were described by Dr Mooradian of the MIT Lincoln Laboratory.

Phonons, Resonance Scattering, Metals and Morphic Effects

In a review talk, Prof. Burstein of the University of Pennsylvania analysed the available data for I_{LO}/I_{TO} and its frequency dispersion. The Raman scattering tensor $\chi^{(1)}$ is separated into a part, $\chi^{(1)ex}$, due to excitations and a part, $\chi^{(1)eh}$, due to free particle-hole excitations, which may have different frequency dispersions. $\chi^{(1)ex}$ will dominate the

scattering process at $\omega_0 \approx \omega_{ex}$. On the other hand, $\chi^{(1)sh}$ will dominate the scattering process at $\omega_0 \ll \omega_{ex}$. The large I_{LO}/I_{TO} in CdS at $\omega_0 \approx \omega_{ex}$ is attributed to the fact that the electro-optic contribution to $\chi^{(1)ex}$ arising from the strong interaction of excitations and LO phonons via the macroscopic electric field is much larger than the atomic displacement contribution arising from deformation potential effects.

Dr Leite of the Bell Laboratories reported the latest experimental results on the resonant Raman effect in CdS and ZnSe. The transverse and longitudinal optical phonon cross-sections exhibit very different frequency dependence. As resonance is approached, TO photons initially display greater enhancement than do LO phonons; however, TO phonon scattering saturates near resonance, while LO scattering does not. Dr Parker of the Westinghouse Research Laboratories reported the observation of Raman scattering by optical modes of metals like Zn, Mg and Bi using Ar ion laser. Zn and Mg exhibited one Raman line each at 75 and 105 cm^{-1} respectively and Bi, two Raman lines at 70 and 97 cm^{-1} . They are in agreement with neutron scattering data. Results obtained on electric field induced Raman scattering in diamond, in cubic perovskite crystals and in InSb were also presented during this session.

Mixed Crystals and Point Defects

Prof. Pershan of Harvard University reviewed the theories of Raman scattering and infrared absorption of mixed crystals and those containing point defects. He showed that the Green's function treatment of the dynamics of crystal lattices containing small but finite impurities was able to satisfactorily account for the various experimental results that have been obtained for different mixed crystals at much larger concentrations. Ten papers were presented during this session dealing with the theoretical and experimental work on the impurity induced Raman scattering in crystals.

Brillouin Scattering

Prof. Leon Brillouin, who predicted the appearance of Doppler shifted components in the light scattering by any continuous medium, gave a brief historical account of how he became interested in the problem as early as in 1914. The First World War delayed the publication of this work. After the war, he had to do the theoretical work afresh and the final paper was published in *Annales des Physique* in 1922. This historical reminiscence was followed by a review talk on the Brillouin scattering of crystals by Prof. Cummins of the Johns Hopkins University at Baltimore, whose group has done pioneering work on the Brillouin scattering spectra of crystals using lasers. He referred to the good work done earlier by the Bangalore group on the same subject under difficult circumstances using ordinary light sources long before lasers came into the picture. Dr Gammon of his group then discussed the polarization selection rules for Brillouin scattering components appearing under the species V_v , H_v , V_h and H_h , originally pointed out by Dr Chandrasekharan from the Indian Insti-

tute of Science, Bangalore. The validity of these selection rules has been demonstrated by the Brillouin spectra of crystal quartz, NH_4Cl , fused quartz, KDP and triglycine sulphate taken with laser excitation by Prof. Cummins and his group. More than eight papers in this session dealt with Brillouin scattering in various types of crystals.

Phase Transitions and Critical Scattering

The last session started with a review talk by Prof. Benedek of MIT. He emphasized the advantages of using Brillouin scattering techniques for investigating the properties of systems near the critical temperature and also of systems possessing other types of transition points. In this connection, he referred to an important paper published by Dr V. L. Ginzberg on the scattering of light near phase transitions in solids in *Physics Uspekhi* (1962). Near the critical point of second order phase transitions, the order parameter describing the system shows very large amplitude fluctuations which relax back to equilibrium ever more slowly as the critical point is approached. Prof. Benedek reviewed the experimental studies of the intensity and spectrum of light scattered near critical points of simple fluids and two component critical mixtures. These provide detailed information on the divergence of the fluctuations and their relaxation times in fluids. Analogous behaviour is observed in solids near second order phase transitions. He gave details of the electronic beat method of measuring extremely small line widths of Rayleigh lines near T_c . Two papers were presented describing the Raman and Brillouin scattering studies on potassium dihydrogen phosphate and also another one on the Raman spectrum of SrTiO_3 .

Polymeric solids are known to undergo a number of relaxational transitions. These transitions involve either changes in the skeletal and/or side group structure and their determination is strongly dependent on the frequency of the detection method and other extrinsic factors. Dr Gayles of the IBM Research Laboratories reported the detection of phase transitions in amorphous solids like plastics in the gigahertz range using Brillouin scattering as a probe. The last paper was on Raman scattering in the three phases of KNO_3 , which was presented by Prof. Balkanski of Paris. He suggested that a close correspondence existed between the normal modes when the crystal undergoes the change from one crystalline structure to another. He has obtained the Raman scattering for a complete phase transition cycle which allows one to follow the Raman active modes during the different phase transitions.

There was a conference dinner and the guest speaker was Dr Robinson, Academic Vice-President of New York University, who had previously held a position as Deputy Scientific Adviser to the President of the United States. He gave a brief outline of the duties and functions of the Scientific Adviser to the President of USA. He said that there is a Scientific Advisory Council consisting of top scientists and engineers outside governmental organizations presided over by the Scientific Adviser, whose function is to review the application of science

to non-scientific areas. There is an Internal Scientific Committee of the Government with heads of Government Scientific Organizations as members and the Scientific Adviser as Chairman to coordinate the work of various scientific programmes and to decide on major policy issues. The Scientific Adviser is the head of the office of science and technology whose function is to evaluate the technical value of every scientific programme financed by the Government. He is also expected to give special assistance to the President on scientific matters.

Dr Robinson then traced the growth of scientific research in universities and the financial support it received from the various organizations of the Federal Government, such as National Institute of Health, National Science Foundation, Atomic Energy Commission, National Aeronautics and

Space Administration, Defence, etc. Under the present system, individual scientific work gets multiple support from different organizations for his research projects. Recently, there has been a cut in the expenditure on scientific research financed by Federal Agencies. This had led to some criticisms in certain quarters. Thinking in the government circles now seems to be on the lines of having one single Department of Science and Technology in the Federal Government for financing scientific research in non-governmental institutions like universities, etc. This is the system followed in the United Kingdom.

The conference ended with a vote of thanks by Prof. Burstein to the organizers and the participants. The proceedings of the conference along with the papers presented are expected to be published in a book form in due course.

Sources & Utilization of Vegetable Oils*

K. T. ACHAYA

Regional Research Laboratory, Hyderabad

AT the annual symposium and convention of the Oil Technologists' Association of India (OTAI) organized by the Western Zonal Branch in Bombay in January 1967, the Executive Council requested some members from Hyderabad to organize the next meet in that city. This also implied that a Southern Zonal Branch of the OTAI with its headquarters at Hyderabad, covering the Southern States of Andhra Pradesh, Kerala, Madras, Mysore and Pondicherry, would have to be organized in the intervening period and that this fledgling would have to bear the organizational burden. The challenge was accepted. The Southern Zonal Branch was formed and its office-bearers chosen, a membership of 125 enrolled and the Twenty-third Annual Symposium and Convention of the OTAI conducted during 9-11 February 1968 at the Regional Research Laboratory, Hyderabad, which is also the zonal headquarters.

The symposium was sponsored by the following bodies: All-India Cottonseed Crushers' Association of India, the Council of Scientific & Industrial Research, the Soyabean Council of America Inc., the Vanaspati Manufacturers' Association of India, DeSmet (India) Pvt Ltd, Godrej Soaps Pvt Ltd, and Tata Oil Mills Co. Ltd. Eight private industries (Amrit Banaspati Co. Ltd, Bombay Oil Industries Pvt Ltd, B.T. Chandranna & Co., Hindustan Lever Ltd, Kusum Products Ltd, Lakshmi Carbons, and Tungabhadra Industries Ltd) made donations towards specific expenses.

*Proceedings of the symposium published in full in *Chemical Processing and Engineering*, Annual No., July 1968.

About 250 participants attended, drawn about equally from industry and research. The discussions were marked by punctuality and point. The sessions were of two types — one for the normal presentation of research papers, and the other devoted to discussion in chosen areas, such as sources of oils, hydrogenation, detergents, and detection of adulteration, based on background material which had been distributed earlier.

Dr G. S. Sidhu, Director of the Regional Research Laboratory, Hyderabad, welcomed the gathering. The President of the Southern Zonal Branch of OTAI, Dr K. S. Murti, pointed out the appropriateness of starting a zonal branch in the oil-seeds-rich southern region and particularly in Hyderabad, and the steps which had been taken in this direction. Lala Kishan Narain, President of the OTAI, drew attention to the shortfalls in oil production in the country and the various potential sources which needed to be made use of, such as cottonseed, rice bran, fish oils and animal fats. He also expressed satisfaction at the growth of the OTAI in recent years through the formation of strong branches earlier in Calcutta, Delhi and Bombay, and now in Hyderabad. The inaugural address was given by K. Brahmananda Reddy, the Chief Minister of Andhra Pradesh. The state led the country in production of groundnut and castor, and took second place in respect of two other important sources of oil, viz. rice bran and safflower. It was also fortunate in having two research centres in oils at Hyderabad and Anantapur, which worked in close collaboration. Through the marvels of

genetic engineering, increased yields of oilseeds crops appeared likely, and he echoed this by coining a slogan for the conference: 'More oil for food and factory'. Dr M. R. Subbaram, Secretary of the Southern Zonal Branch, thanked all those concerned with the symposium, and Dr K. T. Achaya, convener, made a few announcements.

Sources of Oil

'No technical know-how or process, however efficient, is of any value unless the basic raw materials are available in adequate amounts.' Thus, Dr J. S. Aggarwal, co-chairman of the session, introduced the subject, and the chairman, Prof. J. G. Kane, added that 'the price of oil sources is also important'. In the discussions, a vision of plenty was drawn by agricultural scientists and plant breeders, in particular N. S. Maini and Dr L. G. Kulkarni. Against the present oilseeds production of 8.5 million tonnes, an extra one million tonnes of groundnuts annually by 1971 was a certainty under the package plan. The double-cropping programmes under way should yield another two million tonnes, ensuring that the target of 11.4 million tonnes would be more than met. In castor also, a larger outturn was certain, since new short-duration varieties would permit this oilseed to be grown as a second pure crop, which is very undemanding of rain and fertilizer. Of the new oilseeds, the soyabean has been given priority because of its short duration and high return, and about 10,000 tonnes of two varieties of the seed, *Braggs* and *Clark 63*, should be available by 1971. P. V. Gujarathi pointed out that in 10 years, the collection of minor oilseeds by the units of the All-India Khadi and Village Industries Board had risen from 300 to 24,000 tonnes. Various points were made regarding the growing and collection of seeds of khakan, sal, red palm, tobacco, rubber and tung. Synthetic fatty acids from petroleum were mentioned.

Chemistry and Technology of Minor Fats

At two research sessions, with Dr P. S. Raman and Dr D. R. Dhingra in the chair, 15 research papers were presented concerning minor fats. Four papers dealt with the refining, stabilization, colour problem and utilization of sardine oil. It was clear that there was no bar to the use of sardine oil except availability! Several papers from Kanpur, Anantapur and Hyderabad were concerned with technology: decortication of nageswar seed, fluidized-bed drying of neem seed, recovery of fatty acids from kusun oil and techniques for processing watermelon, wild castor and spent ajowan seed for their oils. Analytical characteristics of the seeds or oil of *Albizia labeck* and *A. procera* (sirisi and safed sirisi) and *Pithecolobium dulce* (gorakh imli) were recorded. A novel approach to destroying cyclopropene fatty acids in cottonseed oil was by exposure to light *in vacuo*; its utility in practice was discussed. Fresh data on kusun oil showed that only 40 per cent of the oil consists of glycerides, while it also carries 1.1 per cent of nitrogen in the form of 3,5-dimethyl pyridine 2,6-dicarboxylic acid.

Hydrogenation

From the chair, Dr S. Varadarajan provided useful information on the hydrogenation of oils. Though apparently simple, the hydrogenation reaction was beset with the problems like selectivity of catalysts, specific catalyst forms in terms of the products produced, the texture of hydrogenated products and nutritive value in relation to the fatty acid types produced during hydrogenation. Some of these areas were extended in the discussion. Work being conducted in Hyderabad on the migration of double bonds caused by poisoning of catalysts was described. The analytical control of product composition during the hydrogenation was discussed, and precautions outlined to ensure catalyst life on the one hand and a stable product on the other. Special attention was paid to the hydrogenation of abnormal oils like acidic oils and solvent-extracted oils and work done in Bombay University and in industry was described. It was felt that under Indian conditions, where the cost factor is vital, an important problem may be to study how best to hydrogenate raw oils without prior refining and bleaching, which increased the cost. Problems connected with the use of soyabean oil in hydrogenated products were discussed; it may be necessary to hydrogenate this oil to a higher melting point to achieve the same high storage life associated with vanaspati made from groundnut oil. Moreover, the single criterion of melting point used at present to define the product is probably insufficient for the varying outlets for hydrogenated fats. In advanced countries today, hydrogenated fat is not a single product but a blend of hardened fats with unhydrogenated liquid oils, usually interesterified thereafter to achieve plasticity. Such products are in line with modern nutritional knowledge, since they ensure an adequate level of essential fatty acids. Much discussion centred on catalysts, which are entirely imported. Regeneration of spent catalysts is now practised commercially in India in at least two factories, but import of some fresh catalyst is inescapable. Certain other materials like filter aids are still imported and indigenous development is necessary. The technology of making fatty alcohols is now known in India; two firms are contemplating production, but the small consumption of the product and the rather costly initial equipment are perhaps deterrents.

At the research session on hydrogenation, with Dr S. R. Gupta in the chair, five papers were presented. The first was concerned with the hydrogenation of fatty acids, where catalyst deactivation is economically important, since a rather large amount is required. The preparation up to pilot plant level of mainly tristearin glycerides for use in soap and cosmetic industries starting from castor oil by a two-temperature process was described. Data on poisoning of catalyst activity during the hydrogenation of soaps and of partly-refined neem oil containing residual sulphur suggest that poisoned catalysts possess distinctive characteristics, one of which is the promotion of migration of *cis* double bonds to other *cis* positions. Another paper

described the selective hydrogenation of epoxy to hydroxy groups, leaving ethenoid unsaturation intact through π -complex formation. The chairman remarked on the varied and interesting nature of the research work being done in the country and its industrial potential.

Detergents

S. M. Mistry took the chair at the session devoted to detergents in India, and reviewed the raw material position and the technical knowledge available in the country. He remarked: "There are no serious difficulties in the way of manufacture... since Indian chemists have acquired by experience the ability to do so. The problem is of high cost of manufacture and there does not seem to be any solution to this unless alkylbenzene is removed from the category of petroleum products for excise purposes, and import duty on it is also reduced." In the discussion, it was argued that the question of biodegradability should not be made a limitation at present on detergent production, especially since the cost of a biodegradable product was 25-30 per cent higher than the other. In a couple of years, olefins derived by cracking Barauni wax are likely to be available for the production of alkylbenzenes. The shortcomings of sodium tripolyphosphate as a builder are its tendency to promote the growth of algae, and the relative cost of manufacture of this material and of nitrilotriacetic acid; its possible replacement was examined. Finally, the use of soap-detergent mixtures in the form of bars was considered to be one part of the answer to the shortage of fats in India.

Dr B. C. Subbarao was in the chair when six research papers on detergents were presented. Data were provided on the foaming characteristics of mixtures of soaps and syndets; at the discussion it was pointed out that since foam can be regulated using foam boosters, other properties, such as detergency, were more critical. Three papers furnished a wealth of information on the comparative surfactant evaluation of groups of related products, such as sulphates of varying unsaturation based on ricinoleyl alcohol, structurally-identical alkyl sulphates and sulphonates and sulphated pure mono-glycerides of various fatty acids. The next paper described the direct addition of ethylene oxide to castor oil to yield powerful emulsifiers for water-in-oil systems. Pilot plant work on the production of both saturated and unsaturated fatty alcohols from fatty oils and fatty acids described the use of catalyst promoters to speed up the reaction and catalyst modifiers to retain part of the unsaturation.

Seminar on Detection of Adulteration

As the chairman, Dr M. M. Chakrabarthy, remarked in illustration, 95 per cent of ghee samples received by the Calcutta Corporation are adulterated. The co-chairman, Dr G. Lakshminarayana, reported on the experiences gathered from Indian analysts. As many as 27 adulterants were found, and the extent of sophistication varied widely. Argemone oil, for example, was not reported in more than

one per cent concentration, suggesting contamination rather than true adulteration. The need was for quick, modern, sensitive methods based on chromatographic or colour tests, capable of application to a large number of samples. This theme was continued during the discussions. The ammonium molybdate test for castor oil came in for considerable discussion, and it was thought to be a useful screening test to be confirmed by the more specific thin layer chromatographic method. Tests for the detection of 2.5 per cent of taramira oil in Indian mustard oil, and paper chromatographic tests to detect this order of animal fat in ghee, worked out at the Central Agmark Laboratories were described. Collaborative work at 8 laboratories sponsored by the Central Committee for Food Standards had established that the paper chromatographic method could reveal adulteration with as little as 0.005 per cent of argemone oil.

Following these discussions of analytical experience, eight research papers on the detection of adulteration were presented. One paper discussed the reliability of and the time required for several methods for the detection of argemone oil, and two papers from Anantapur described new colour tests for the detection of karanja and tobaccoseed oils in other oils. Two papers were concerned with the detection of castor oil by the ammonium molybdate test. One of them pointed out the pitfalls of the test and cast doubts on its value. The other paper described experiments to show that an insoluble sulphate was responsible for the turbidity; it was deduced that the test would be answered, first, if a precursor of such an insoluble sulphate were present, and, second, if conditions were also conducive to its precipitation. Three papers described methods for the detection of adulterants in ghee, each based on a different principle, but all utilizing thin layer chromatography. In the discussion of these papers, the role of antimony trichloride in the colour test for karanja oil and possible interference from vitamin A were discussed. It was clearly desirable to thoroughly check as many pitfalls as possible of any new method before it is published, to establish confidence in the test and save subsequent arguments.

Analytical Methods, Oilseed Constituents and Oil Modification

A total of 17 papers describing current researches in the country were presented at two research sessions at which Prof. D. Rebello and R. K. Bhatnagar took the chair. Four papers from Hyderabad were concerned with the accuracy or utility of fat analytical methods, such as the use of permanganate-periodate for oxidation of double bonds, estimation of glycerol as its trimethylsilyl ether, and use of gas-liquid chromatography and nuclear magnetic resonance for the identification of fatty materials. Work from the same laboratory revealed the proportions of the various constituents present in cottonseed phospholipids, in which a fair proportion of gossypol is bound to phosphatidylethanolamine. A paper from Mysore described the production of a high protein sesame oilcake, and two from Kanpur an

examination of the constituents of mahua oil-cake.

Five papers were concerned with epoxidation. Two papers described products obtained by epoxidation of Indian vegetable oils, and another described the preparation of concentrated peracids, and the high degree of epoxidation possible with it. The use of epoxy derivatives of castor oil as plasticizers for PVC resins was described from the Shri Ram Institute, Delhi, and another paper from Aligarh Muslim University traced the stereochemical relationships between the epoxy, bromoacetoxy and dihydroxy derivatives of *cis* and *trans* C₂₂ monoene acids. The modification of oils for use in surface coatings found expression in two papers on urethane oils from Kanpur, and in one from Hyderabad describing the preparation of a large number of vinyl monomers based on undecenoic acid. Modification of fat glycerides was the subject of two papers, one on solvent-interesterification from Calcutta University and the other from Bombay University on the preparation of a cocoa-butter substitute from sal fat.

Indian Oilseeds Economy

F. G. T. Menezes took the chair at a discussion by a panel of experts on the oilseeds economy, whose importance and urgency he underlined. Low production of oil in India from 1965 had necessitated quite large imports from countries like the USA and the USSR. Despite the lifting of the ban on the use of solvent-extracted oil for edible purposes, the response from industry had been rather disappointing. S. Subrahmanyam outlined the steps which had been taken by the Indian Standards Institution in respect of laying down standards for oilseeds and oils. Not only had such measures rationalized the number of categories of any product, but in many cases the formulation of standards had given direction and fillip to commodities in an early stage of their development. Lala Kishan Narain spoke on trading practices. Formerly supply and demand determined oil price, but today a number of other factors, such as government decisions on exports, imports or movement of oilseeds, constantly changing outlets for vegetable oils, and shifts towards sophistication in the habits of the people, all played their part in determining the price structure. G. C. Lahiri of the South Central Railway outlined the principles followed in laying down railway freight rates in respect of oilseed commodities, such as the intrinsic value of the commodity, its stage of manufacture, the care required, the size of the load and naturally the distance travelled. On these considerations, freight on oils was classified into four divisions, and additionally incentives for bulk movement or for export traffic were also given. He saw little scope for further reduction in the already low freight rates for oilseed products. N. Sen spoke about export incentives for oilcakes, with special reference to cottonseed cake. The earlier government incentives of copra import entitlement against cottonseed cake export caused a great spurt in the export of this commodity. After devaluation, the cash incentive scheme was instituted in the expecta-

tion that a lower price for Indian oilcakes would prevail on the world market, but this had not materialized. Even this scheme was withdrawn at the end of 1967. A plea was made for reviving the import entitlement scheme which had proved so effective in the past. Maharajkumar Virendrasingh assessed the effect of imported soyabean oil on the oilseeds economy of the country in recent years. Due to shortages, the price of oils had reached fantastic levels in August 1966 and had only been stabilized by the arrival of imported soyabean oil. Such imports had in his view been one of 'too little too late', since they were made when the prices had already become runaway, and then in insufficient quantities. He argued that even though a record oilseed crop was now expected, there was no occasion for complacency, since the demand would still exceed the supply, and imports of oils available cheaply from elsewhere could play a significant part in stabilizing prices. Dr K. S. Murti spoke on processing efficiency and pointed out how considerable quantities of valuable edible oils could be added to the economy by adopting modern efficient equipment and improved processing techniques at different stages. Such losses occurred, for example, by poor seed storage, by operating old oil expellers, through outdated refining procedures and by inefficient solvent extraction methods. Even available resources of oil still remain untapped, cottonseed oil and rice bran oil being outstanding examples. Any problems that arise were for the industrialists and technologists to tackle. Dr S. Varadarajan gave some thoughtful suggestions on what he considered to be the place of research in the oilseeds economy. Research should aim at increasing the range and variety of raw materials used, in reducing the cost of raw materials and in improving the quality of the products made from fats. Not only was it necessary to produce more oil, but these oils should preferably be of the right type, such as the polyunsaturated fats which are in world demand. An understanding of the basic chemistry involved in every step of handling and processing, such as colour fixation or flavour, must be developed. Prejudice against the use of solvent-extracted oils must be overcome by factual evidence. The specific nutritional requirements for fats under Indian living conditions needed to be garnered. Why should not the fat industry, like the petrochemical industry, produce tailored molecules for specific jobs?

Oilseed Proteins

Dr B. L. Amla spoke at a special evening lecture on the utilization of oilseed proteins in relation to the protein shortage in the country, with its incalculable permanent effects on growth and intelligence. Criteria which scientists and technologists have to bear in mind in formulating products were mentioned. Examples were given of various products based on groundnut protein, such as Indian multipurpose food, products of the *Bal Ahar* type, weaning food, biscuits, protein-enriched wheat flour, macaroni-like products, powder milk substitute, liquid milk extenders and malted milk beverages.

Organizational Changes

Important decisions regarding the future functioning of the OTAI were taken at meetings of the Executive Council and General Body held concurrently. A comprehensive revision of its entire

constitution was set in motion, seeking to reflect organizationally its representative national character. Realizing the importance of having a quality journal in the field, a small committee was formed with Dr S. Varadarajan as convener to outline how best this could be done.

Activation Analysis*

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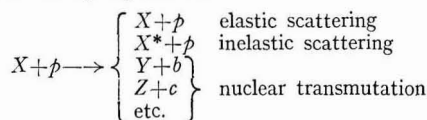
ACTIVATION analysis is a nuclear technique of elemental analysis. An ideal analytical technique should be accurate, precise, specific, non-destructive, fast, economical and universally applicable. Activation analysis satisfies nearly all the above requirements. It has gained much importance in the field of trace analysis as it is the most sensitive method, known at present, for detecting a majority of the elements. The lower limit of detection for most analytical techniques is about 10^{15} atoms. But for activation analysis it is 10^9 atoms (a million times less) for certain favourable cases. This technique is being used in a variety of fields such as agriculture, medicine, geology, criminology, electronics, astronautics, metallurgy, etc. The potential of activation analysis is such that it may assume an importance comparable to that of nuclear power¹.

Activation analysis is developing quite fast at the present time. With the availability of 14 MeV., high flux, low-cost neutron generators, it is becoming routine analytical tool even in many small research laboratories and industrial organizations. Several books¹⁻¹¹ have recently been written on this technique. Numerous review articles exist on this subject, but only a few of them¹²⁻¹⁵ could be referred to due to the limited scope of this paper. At present, on the average one international conference per year is being devoted only to this technique¹⁶⁻¹⁸. (Very recently, the conference on modern trends in activation analysis has been held at the National Bureau of Standards, Washington DC, from 7 to 11 October 1968.) Research papers on this technique are widely scattered throughout the literature of many scientific disciplines. During the last five years about 2000 papers concerned with activation analysis have been published. Very few of these have been referred to here. Interested readers may refer to the above-mentioned books and reviews for a detailed bibliography. Review articles that are published every alternate year in *Analytical Chemistry*, under the heading 'Nucleonics', may serve as a good reference source on activation analysis. In this article, an effort has been made to

explain the technical fundamentals of this technique. Also, a scheme¹⁹ has been presented to solve the practical problems using 14 MeV. neutron generator. To appreciate and use this technique, one requires some knowledge of nuclear physics, nuclear instrumentation and radiochemistry. Constant effort is being made to make this technique completely instrumental so that use of radiochemistry may be avoided even in the case of complex samples.

Basic Principle

Each stable isotope emits its characteristic nuclear radiation on being bombarded by nuclear projectiles. These radiations are different for different projectiles. In activation analysis, the elements, or more precisely the stable isotopes of a sample, are determined by means of these radiations. The sample is bombarded by nuclear projectiles of known energy and type (neutrons, charged particles and gamma rays), produced in a reactor or accelerator. The characteristic nuclear radiations are recorded by a nuclear detector. The elemental composition of the specimen is then determined by analysing the recorded radiations. The basic principle of this technique can be understood by considering the bombardment process. The bombardment process can be represented by the following expression:



where X is the nucleus of an isotope belonging to an element that composes the sample, p is the bombarding nuclear projectile, X^* represents X in excited state, Y and Z are residual nuclei of different elements and b and c are ejected particles of different kinds. Nuclear transmutations are very important for activation analysis; the other two processes, viz. elastic and inelastic scatterings, are not that important for it. It may now be worth while to ask how many kinds of nuclear transmutations are possible in a certain set-up? The answer

*Based on a lecture delivered by the author at the National Physical Laboratory, Delhi, on 5 December 1967.

is obtained by looking into the Q -value table²⁰. It depends upon X , p and energy of p .

Consider any particular nuclear transmutation, say



We know that in a nuclear transmutation, the mass and the charge numbers are conserved along with some other quantities. Therefore, X can be predicted if p , b and y are known. Neutron capture reaction ($X+n \longrightarrow Y+\gamma$) is extensively used in activation analysis. In this transmutation, p is a thermal neutron, b is gamma ray and y may be any nucleus depending upon X . This is not known. The main problem of activation analysis is to identify and measure Y , the residual nuclei. With high energy projectiles more than one type of nuclear transmutation may take place. This gives rise to interference, which may be taken into account in the analysis. The method of taking this into account has been discussed in a later section entitled 'Interferences' towards the end of this article.

Sources of Activation

Neutron flux is the best source of activation, because even thermal neutrons can cause nuclear transformation, whereas high energy charged particles and gamma rays are required to induce nuclear transmutation. In fact thermal neutrons are better than fast neutrons. With thermal neutrons usually only capture reaction (n,γ) is possible. The cross-section of this reaction for heavier nuclei is usually larger. Therefore, with thermal neutrons analysis may be performed with less interference and high sensitivity, specially for heavier elements. With fast neutrons, many reactions (n,p), (n,α), ($n,2n$), (n,d), etc., may be possible, resulting in complicated interferences.

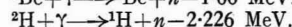
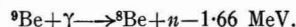
Thermal neutrons — At present reactors are the best sources of high flux thermal neutrons. TRIGA reactors are commercially available. They operate at power levels in the range of 10-1000 kW. and produce usable fluxes in the range of 10^{11} - 10^{13} n/cm.² sec. They can be pulsed and are equipped with a rapid transfer pneumatic tube. They are pulsed, when very short-lived [$\sim 10^{-3}$ /sec.] activities are to be analysed. The pneumatic tube is used for activating samples, where the induced activity of interest has a half-life in the range of seconds to minutes. Such reactors cost in the range of \$ 150,000 to \$ 300,000. The use of reactors is limited to big research establishments because of their high cost.

Fast neutrons — Fast neutron activation is essential for the trace analysis of light elements, because (n,γ) cross-section for these elements is small. They are detected with high sensitivity, using high cross-sections (n,p), (n,α) and ($n,2n$) reactions on them. Fast neutron activation has gained more importance because of the availability of low-cost (\sim \$ 24,000), high flux ($\sim 10^{10}$ n/cm.² sec.) 14 MeV. neutron generators²¹. The main drawback of these generators is that their flux is not steady.

Charged particle activation — Charged particles (proton, ^3He) have also been used as the source of activation. Proton-induced reactions are usually

of high negative Q -value reactions. ^3He ions undergo a number of reactions with light elements in which the energy is released (positive Q -value); hence, little or no additional energy is required to bring about these nuclear reactions once the particle has penetrated the Coulomb barrier of the sample nucleus. But even an 8 MeV. ^3He ion will penetrate only a few mils into the surface of a sample. This major limitation of all the charged particle activation, that the reaction permits only a surface analysis, is advantageous in some instances, e.g. metal surface studies. Recently various aspects of charged particle activation have been explored²²⁻²⁵ and it was found that 9.2 in. cyclotron is very useful for ^3He activation.

Gamma ray activation — This kind of source has limited but selective applications. It is used for the determination of Be and ^2H by the following reaction:



It is also used for the selective excitation of isometric levels.

High energy bremsstrahlung (continuous hard X-rays) produced in electron accelerators are also used for activation with only limited applications²⁶.

Isotopic neutron sources, based on (α,n) and (γ,n) reactions, have also been used for the activation. But the sensitivity with such sources is less²⁷ because of their low flux ($\sim 10^6$ n/sec. cm.²). Transuranic element californium-252 emits 10^9 n/sec. mg. and is, therefore, expected to be a very good source of activation if produced in sufficient quantity in reactor.

Alpha emitter curium-242 too is being used to activate characteristic X-rays. But it has very low penetration and generates heat in the sample.

Identification and Measurement of Activity

In a nuclear transmutation the residual nuclei, Y , are usually radioactive and formed in the excited states. They come to the ground state by emitting prompt gamma rays (in a time $\sim 10^{-10}$ sec.). Residual nuclei can be identified by recording either their characteristic prompt gamma ray spectrum or radioactivity. The former method suffers from the following serious disadvantages²⁸: (1) Details of the prompt gamma ray spectra are not yet known. (2) These spectra are often too complicated and, therefore, difficult to interpret. (3) The counting is done, while the irradiation is on. Therefore, the background is large. This reduces the sensitivity.

Following are the advantages of this method²⁸: (1) Analysis is always non-destructive and quick. (2) Analysis can be performed even if the residual nucleus is not radioactive. (3) Wide range of gamma rays are available for the analysis.

The latter method based on radioactivity measurements does not suffer from the serious disadvantages of the former method, and is, therefore, normally used in actual practice.

The processes by which radionuclides decay are quite varied. The processes of maximum interest from the point of view of activation analysis are those involving beta (electron) and gamma (photon) emissions. The electrons radiated from a given

nuclide are not monoenergetic but exhibit a continuous energy distribution from zero to some maximum energy that is characteristic of the radionuclide. Photon emissions are monoenergetic and give rise to peaks in the gamma ray spectrum. The energies of these photons are characteristic of the radionuclide producing them. The radionuclides may be identified by either beta or gamma counting. The latter method is superior because of the following reasons: (1) It offers double check of peak position and half-life, on the activity under measurements. (2) Source self-absorption and scattering are small. Therefore, comparatively larger samples can be counted and the sensitivity of the analysis can be enhanced. (3) Many radionuclides present in the same specimen may be identified without chemical separation, even if they have very nearly equal half-lives.

In case the irradiated sample is thin and contains only two or three activities, beta counting with Geiger-Müller counter may be adopted for its analysis. However, the gamma counting with NaI(Tl) scintillation spectrometer is adopted, if the irradiated sample is thick and contains many activities. The limit on the number of elements composing the sample that may be analysed without chemical separation (non-destructive) is imposed by the resolution of the spectrometer. NaI(Tl) gamma ray spectrometer has about 8 per cent resolution for 0.662 MeV. gamma ray. Recently developed lithium-drifted-germanium (Li-Ge) detector has less than $\frac{1}{2}$ per cent resolution for this gamma ray. Therefore, by using this detector, it is possible to analyse many more elements than with NaI(Tl) detector (without chemical separation.) But the detection efficiency of the Li-Ge detector is low and it has to be operated at liquid air temperature in conjunction with low noise pre-amplifier. The detection efficiency may be increased by using large volume Li-Ge detectors that are now available.

Even with the use of Li-Ge detector it may not be possible to measure a very weak activity in the presence of a strong activity without chemical separation, specially if the characteristic gamma energy of weak activity is less than that of strong activity, because the full energy peak of the weak activity will be masked by the Compton radiation of the strong activity. However, this limitation may be overcome by such an anticoincidence counting which suppresses the Compton part of the gamma ray spectrum. This may be done by surrounding the Li-Ge detector by NaI(Tl) crystal and recording those events that produce electrical pulses in Li-Ge detector only.

At present NaI(Tl) detectors are being used in most of the activation analysis work, because of the non-availability of large size Li-Ge detectors. Here the Compton part of the gamma ray spectrum is suppressed by putting NaI crystal in a well type CsI crystal. The source is put on the top of NaI crystal. Both the crystals are coupled to the same photomultiplier. NaI pulses are faster than those of CsI. Therefore, if a photon loses its full energy in NaI only, the resulting pulse is faster. But if it loses a part of its energy in NaI and other part in CsI, the composite pulse is slower. The elec-

tronics is so arranged that it rejects the slower composite pulses and records only the faster, full energy pulses. In this way scattered radiation is rejected.

Radiochemical Separation

It is desirable that no radiochemical separation is performed in activation analysis or else it is not non-destructive. But with samples containing many elements, the number of radioactive products may be so large that the activity measurement of a single component becomes almost impossible. In such cases, each activity or a group of activities may be chemically separated and measured. The resolution of the measuring set-up and the ratio of weaker to stronger product activities dictate the need for chemical separation. The lower is this ratio and resolution, the greater is the need for chemical separation.

Chemical separation may be performed before activation (pre-irradiation separation) or after activation (post-irradiation separation). The latter method is mostly adopted because no reagent blank is involved in it. There are many instances where the reagents contain an appreciable quantity of the elements to be determined. If the same reagents are used in pre-irradiation separation, the sought element in both the sample and reagents would become activated and subsequently measured giving wrong information. A post-irradiation separation completely avoids this problem.

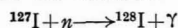
The choice of a separation method depends upon the physical, chemical and nuclear properties of the sought element. Various conventional chemical techniques like precipitation, solvent extraction, distillation, ion exchange, electrodeposition, volatilization, etc., are often employed. The usual difficulties of micro chemistry are eliminated in radiochemical procedure. The loss of activity in the separation process is easily corrected. The two most widely used methods of yield correction are: (1) the addition of isotopic carrier to the sample; and (2) the addition of radiotracer to the sample.

In the first method, a known weight (~ 10 mg.) of stable atoms of the same chemical species as the radioactive atoms is added to the active sample before separation. If this weight is very large compared to the weight of the sought atoms in the sample, the following type of calculation can be used to determine the activity before separation

$$A = A' \frac{W_x}{W'_x} \quad \dots(2)$$

where A is the activity before separation; A' is the recovered activity; W_x is the weight added; and W'_x is the weight recovered.

The use of a radioisotopic tracer in a system is possible when a radionuclide of the sought element is available which is different from the activation analysis product. This is illustrated by the following example. In the analysis of iodine, the ^{127}I isotope undergoes the reaction:



^{128}I decays with a half-life of 25 min. If before the separation of the ^{128}I activity from the sample

a known amount of ^{131}I (half-life 8 days) is added, the following relation is true:

$$A = A' \frac{A_1}{A_2} \quad \dots(3)$$

where A is the activity of ^{129}I before separation; A' is the activity of ^{129}I recovered; A_1 is the activity of ^{131}I added; and A_2 is the activity of ^{131}I recovered.

A series of monographs²⁹ are available on the radiochemistry of elements. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements. These may be very useful for radiochemical separation work.

Quantitative Analysis

The elemental composition of a sample can be qualitatively determined by examining the gamma ray spectrum (peak positions) and the decay curve (half-lives) of the irradiated sample. The quantitative analysis is performed with the help of the following expression:

$$D = \sigma \phi N (1 - e^{-\lambda t}) \quad \dots(4)$$

where D is the rate of disintegration of the characteristic radioactivity just at the end of irradiation, N is the number of nuclides of the particular stable isotope of an element that produces this activity (we want to determine this number), σ is the cross-section for the reaction in which this activity is produced, ϕ is the flux of the nuclear projectiles that bombard the sample, λ ($\lambda = 0.693/\text{half-life}$) is the decay constant of the activity, and t is the duration of irradiation.

The rate of disintegration D is connected to the counting rate by the following equation:

$$D = \frac{A(1+\alpha)}{\theta PC} \quad \dots(5)$$

where A is the counting rate in the full energy peak of the selected gamma ray, α , θ and P are the internal conversion coefficient, branching ratio and the effective full energy peak efficiency of this gamma ray respectively, and C is the source self-absorption and scattering factor.

Quantities σ , λ , α , θ , P and C occurring in Eqs. (4) and (5) can be read from standard tables, charts and sheets³⁰⁻³⁶. The values of A , t and ϕ are measured in each irradiation. Knowing these quantities N can be calculated, which may be converted into grammes by the following expression:

$$m = \frac{N \cdot W}{N_0 \cdot K} \quad \dots(6)$$

where m is mass of the element in gramme; W is atomic weight of the element; N_0 is Avogadro's number ($6.02 \times 10^{23}/\text{mole}$); and K is the fractional isotopic abundance of the given sample nuclide.

Absolute Sensitivity Calculation

The absolute sensitivity has been defined in many ways³⁷. The various definitions differ from each other on the amount of induced activity. According to one of them, the absolute sensitivity is equal to that mass of element which on being irradiated

gives rise to maximum counting rate, which is at least equal to the background of the counting set-up. The term $(1 - e^{-\lambda t})$ in Eq. (4) is called the saturation factor. As the time of irradiation (t) becomes large compared to the half-life of the product nuclide, the saturation factor approaches unity. Therefore, at the saturation time, the counting rate is maximum and is given by:

$$A = \frac{\theta PC}{(1+\alpha)} N \sigma \phi \quad \dots(7)$$

According to the above definition of absolute sensitivity, the maximum counting rate should be at least equal to the background of the counting set-up. We notice from Eq. (7) that it depends mainly upon the cross-section of the reaction, the flux, the background and the efficiency of detection. It is not very difficult to build gamma ray counting set-up with high detection efficiency and low total background of about 2 counts/sec. (ref. 38). One may put some reasonable values of the different quantities in Eq. (7) (actual value of these quantities is read from nuclear tables and sheets) and calculate the minimum value of N that may give rise to actual counting rate of the order of the background. This is illustrated below by taking the following example:

Background = 2 counts/sec.

$$\frac{\theta PC}{(1+\alpha)} = 0.2$$

$$\sigma = 10^{-24} \text{ cm.}^2$$

$$\phi = 10^{12} \text{ neutrons/cm.}^2 \text{ sec.}$$

Then

$$2 = 0.2 \times 10^{-24} \times 10^{12} \times N$$

$$N = 10^{13} \text{ atoms}$$

If these are aluminium atoms, which is mono-isotopic in nature ($K = 1$; $W = 26.98$), then the minimum mass of this element according to Eq. (6) that can be detected is

$$m = \frac{10^{13} \times 26.98}{6.02 \times 10^{23}} = 0.00045 \times 10^{-6} = 0.00045 \text{ } \mu\text{g.}$$

p.p.m. Sensitivity

The parts per million (p.p.m.) sensitivity is defined in the following way:

$$\text{p.p.m. sensitivity} = \frac{\text{absolute sensitivity in } \mu\text{g.}}{\text{mass of the sample}}$$

Therefore, if a sample of 10 g. can be irradiated and counted, then according to the above calculations the minimum mass of the element that can be detected per gramme of the sample is equal to

$$\frac{0.00045}{10} = 0.000045 \text{ } \mu\text{g.}$$

That is the p.p.m. sensitivity of the activation analysis in this case is 0.000045. It should be emphasized that calculated sensitivities can be very misleading since interferences by other activities present and difficulty in counting may cause the actual attainable sensitivities to be much poorer than those predicted. Nevertheless, calculated

values may usefully serve as a guideline. Extensive sensitivity calculations are available both for thermal^{39,40} and 14 MeV. neutrons⁴¹⁻⁴⁴.

Errors

The accuracy of the various quantities that enter in the calculation of *N* is such that the overall accuracy of the absolute activation analysis is not better than ± 15 per cent. The maximum error is on the cross-section ($\sim \pm 12$ per cent). Therefore, there is a need to measure cross-sections with better accuracy. In fact due to large errors in the nuclear parameters required for the calculations of *N* virtually all activation analysis work is done by the comparison method. In this method, each activity induced in the sample is compared with similar activity, induced in the standard of similar size and composition, exactly in the same way as the sample. Because of this comparison all the nuclear parameters get cancelled and the accuracy of the analysis is improved to 1 to 3 per cent. The expression for *m* [Eq. (6)] then takes the following form:

$$m = \frac{\text{activity of the sample} \times \text{mass of standard}}{\text{activity of the standard}}$$

But then the versatility of the technique is reduced in the sense that one will have to know the element he is looking for. Further, this method involves more time and work also, specially if many elements

are to be analysed. At present various aspects of activation analysis are being analysed to improve the accuracy and precision⁴⁵⁻⁴⁹ of the technique.

Interferences

There are two main types of interferences: (1) overlapping of two or more photopeaks, and (2) production of same activity from the activation of different elements or isotopes^{50,51}. The first one occurs whenever one or more other induced gamma ray emitters emit gamma rays of nearly the same energy as that of the induced activity of interest, in statistically significant amounts and where decay does not eliminate them. The closer the two gamma rays are to one another in energy and the greater the counting rate of the interfering activity relative to the one of interest, the greater is the extent of interference. Often such interferences can be minimized by proper choice of irradiation and decay times and by using detector of better energy resolution. Also, a pure photopeak of interest can be obtained by the process of spectrum stripping, that is, subtracting the undesired gamma ray from the sample spectrum. Alternatively, the interfering contribution can be removed mathematically by computer calculation. If the interfering peak is due to activity of a different element, it can be removed by chemical separation.

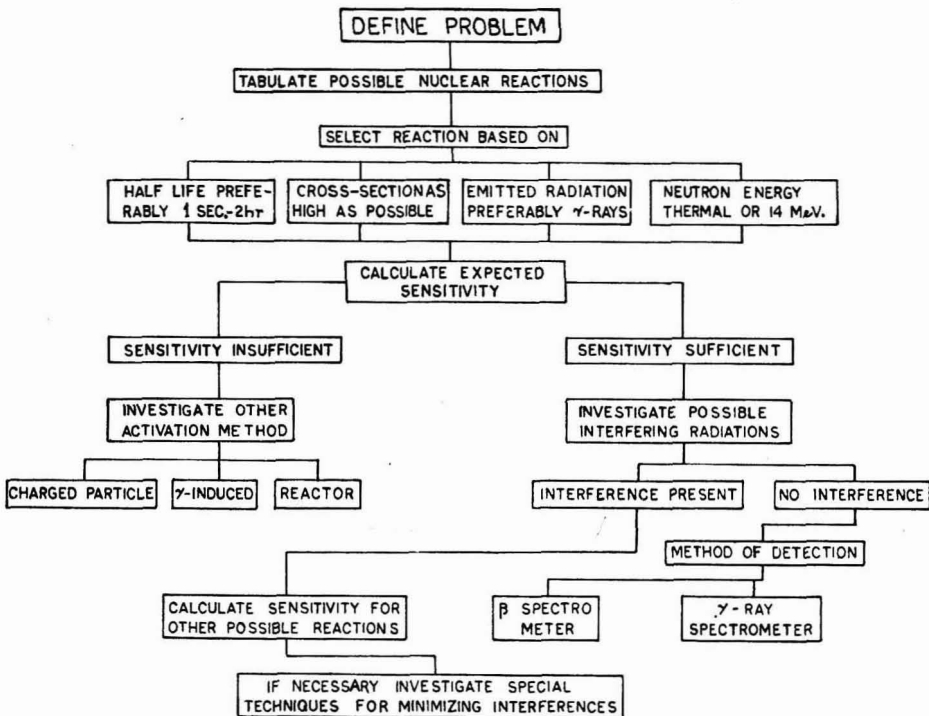


Fig. 1 — Guide chart for establishing the feasibility of neutron activation for a particular analytical problem

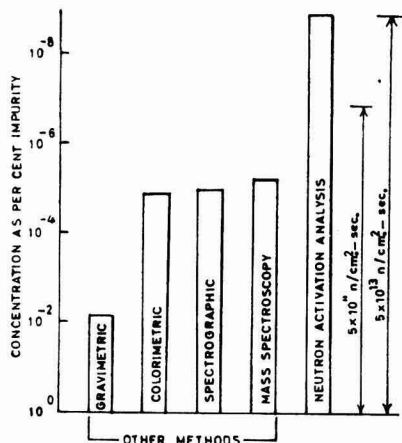
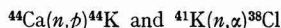


Fig. 2 — Comparison of the sensitivity of neutron activation analysis with other types of analysis [Reproduced from ref. 9]

The second type of interference occurs in high energy activation of samples, containing neighbouring elements. For example, ^{41}Ar is formed both in the activation of both calcium and potassium by the 14 MeV. neutrons from $^{44}\text{Ca}(n,\alpha)^{41}\text{Ar}$ and $^{41}\text{K}(n,p)^{41}\text{Ar}$ reactions. Therefore, it is not possible to say whether both or only one element is present in the sample, from observed ^{41}Ar activity. In such cases one should tabulate other possible reactions [(n,α), (n,p) and ($n,2n$)] on these isotopes (in this case on ^{44}Ca and ^{41}K) the end products of which are radioactive. In the present example they are:



Hence one should look for ^{44}K and ^{38}Cl activities in the irradiated sample in order to remove the ambiguity. If both these activities are present, the sample contains both calcium and potassium. But if only one, say ^{44}K , is present then the sample contains calcium and not potassium.

But if no activation product of potassium other than ^{41}Ar was radioactive (i.e. if ^{38}Cl was stable), then the content of ^{44}Ca would be calculated from ^{44}K activity and the contribution of (n,α) reaction on this much amount of ^{44}Ca , in observed ^{41}Ar activity, would be determined. The excess activity of ^{41}Ar , if any, would be because of the activation of potassium.

Assessment of the Technique

The steps to be followed to establish the feasibility of activation analysis in a given problem are detailed in Fig. 1. It may be noticed that the principal limitations of the activation technique arise from the nuclear properties of an element and not its chemistry.

Activation analysis is an expensive technique. Initial set-up may cost as much as \$ 60,000 if one uses a 14 MeV. high flux neutron generator.

However, because of its high speed this technique may turn out to be not so expensive in the long run, provided a large number of samples are to be handled. In case the bulk of work is not large, one can utilize the expensive components for other interesting studies like mutation, radiation effect, measurements of certain nuclear parameters, production of short-lived isotopes, etc. This justifies the money spent on an activation analysis laboratory.

The sensitivity of activation analysis varies with the flux level, the time used for irradiation, the type of particle used, and the element itself. Fig. 2 shows that activation analysis is potentially more sensitive than other techniques. For those applications which require highly sensitive, rapid and non-destructive analysis, activation analysis may be ideally suited. However, in certain cases other methods may be more useful and convenient. Any improvement in activation analysis will depend upon the further developments in nuclear physics and chemistry. Therefore, it is desirable that activation analysts remain in touch with developments in these areas, particularly nuclear instrumentation.

Summary

Technical fundamentals of activation analysis are discussed under the headings: basic principle, sources of activation, identification and measurement of activity, radiochemical separation, quantitative analysis, absolute sensitivity calculation, p.p.m. sensitivity errors, and interferences. A chart, containing various steps to be followed in a given problem, is given. The relative merits of this technique as compared with other analytical techniques are discussed. It is concluded that for those problems which require highly sensitive, rapid and non-destructive analysis, activation technique may be ideally suited.

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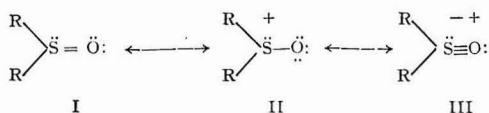
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Coordination Compounds of Sulphoxides

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SULPHOXIDES, with the general formula R_2SO ($R = \text{alkyl or aryl}$), contain a 'soft' sulphur and a 'hard' oxygen^{1,2}, both of which can act as nucleophiles. The S-O linkage in sulphoxides is a semi-polar bond, as revealed by their physical properties such as dipole moment, bond refraction, parachor and force constant determined from infrared spectra^{3,4}. Although there is a controversy regarding the nature of S-O bond⁵⁻⁷, it is now believed that the S-O linkage in sulphoxides consists of a σ -bond over which a $p_\pi-d_\pi$ bond is superimposed⁸⁻¹⁰. The structure of sulphoxides is usually represented as a resonance hybrid of the canonical forms (I-III):



In structure (III), one of the empty d -orbitals of sulphur is used for accepting p_π electrons from oxygen.

Of all the sulphoxides, dimethyl sulphoxide (DMSO) has been largely investigated as a solvent¹¹ and as a reactant in organic and inorganic reactions¹². The role of DMSO as a solvent and as a reaction medium for organic reactions has been reviewed adequately^{13,14}.

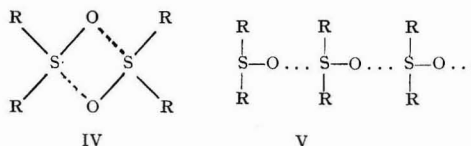
Recently, the physical properties of DMSO and its use as a medium for organic reactions have been reviewed by Martin *et al.*¹⁵, while the stereomutation of sulphoxides by thermal, photochemical and chemical methods has been reviewed by Mislow¹⁶.

Sulphoxides form coordination compounds with transition and non-transition metal ions. The interest in sulphoxides as ligands stems from their dual ability to coordinate, either through oxygen or sulphur. This possibility was first demonstrated by Cotton and Francis¹⁷ in transition metal-DMSO complexes. The purpose of this review is to discuss the donor properties of sulphoxides and the main structural features of the complexes formed. This subject, we believe, has not been reviewed so far.

Physical Properties and Structure of Sulphoxides

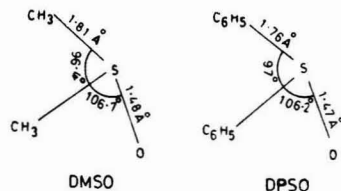
The physical properties of DMSO have been summarized in a recent review¹⁵. Sulphoxides, in general, are basic compounds, having high dielectric constant and fairly large dipole moment (~ 4.0 D). The dielectric constant of DMSO is 48.9, being the highest of all dipolar aprotic solvents¹⁵. These properties make DMSO a good coordinating agent for metal ions.

Sulphoxides associate among themselves forming dimers (IV) at low concentration and polymers (V) at higher concentrations, as revealed by cryoscopic¹⁸ and infrared¹⁹⁻²¹ studies.



The sulphoxides form hydrogen bonds easily with proton donors like water²², alcohols, carboxylic acids and phenols²³, and produce charge-transfer complexes with Lewis acids like iodine²⁴⁻²⁶.

The crystal structures of DMSO^{27,28} and diphenyl sulphoxide (DPSO)²⁹ have been determined by X-ray diffraction. The molecular structure of sulphoxides is essentially pyramidal, with the three bonds formed by sulphur atom being non-coplanar, thus differing from ketones. The sulphur atom is at the apex of the pyramid. Schematic structures of DMSO and DPSO with important bond lengths and bond angles are given below:



The S-O bond length in sulphoxides (1.47-1.48 Å) is shorter than the S-O single bond (1.67 Å), showing its partial double bond character.

Coordination Compounds

General

Although some complexes of DPSO were prepared long time back^{30,31}, DMSO was first employed as a ligand in recent years. Schläfer and Schaffernicht³¹ studied the solubility of many inorganic compounds in DMSO. The solubility of metal salts in DMSO is due to the ease of solvation of cations by this solvent. Lindqvist and Einarsson³² prepared the adducts of $SbCl_5$ and $SbCl_3$ with DMSO and DPSO in 1959, while Muettterties³³ obtained some DMSO complexes of metal tetrafluorides and reported their NMR spectra. Cotton and Francis¹⁷ prepared a large number of DMSO complexes of metal perchlorates and halides in 1960. Their physical properties such as the electronic spectra, magnetic susceptibility and infrared spectra were investigated and

possible structures assigned to some of the complexes. In 1961, Schläfer and Opitz³⁴ reported DMSO complexes of the first transition metal series. In the meantime, many laboratories got interested in the complexes of DMSO. Thus, Drago and his coworkers³⁵ prepared many transition metal halide complexes of DMSO and studied their behaviour in solution by electronic spectra. Selbin and co-workers³⁶ reported a large number of DMSO complexes and their infrared spectra. Weaver and Keim³⁷ investigated the thermal, conductometric and cryoscopic behaviour of DMSO complexes of some of the first transition metal halides and nitrates. DMSO complexes of titanyl, zirconyl, uranyl and thorium perchlorates were prepared and investigated in this laboratory^{38,39}.

Although the early investigations were largely confined to the DMSO complexes, complexes of other sulphoxides like TMSO, PMSO and DPSO have been investigated more recently. Francis and Cotton⁴⁰ prepared TMSO complexes of metal perchlorates and halides and reported their infrared spectra. Drago *et al.*⁴¹ studied the reaction of the ligand with CuCl₂ and PdCl₂. The complexes of DPSO with some divalent metal perchlorates and halides were prepared and investigated by Gopalakrishnan and Patel⁴². At almost the same time, Van Leeuwen and Groeneveld reported the preparation⁴³ and infrared spectra⁴⁴ of DPSO complexes of metal perchlorates and fluoroborates. Later, these workers extended their study to other sulphoxides like TMSO and PMSO⁴⁵. Recently, Currier and Weber⁴⁶ investigated transition metal complexes of DPSO, MPSO, Pr₂SO and Bu₂SO. The complexes of DMSO together with their physico-chemical properties such as S-O stretching frequency, behaviour in solution, probable structure, etc., are given in Table 1. Similar data on other sulphoxide complexes are given in Table 2.

Methods of Preparation of Complexes

The DMSO complexes of metal tetrafluorides like SiF₄ and GeF₄ are prepared by passing the vapours of the tetrafluorides in DMSO dissolved in solvents like ether, acetonitrile and benzene³³. The adducts precipitate out from the solution. The DMSO complexes of other metal compounds are prepared¹⁷ by dissolving them in DMSO, and crystallizing out the complex, after removal of the excess ligand under reduced pressure at 50-60°C. In the preparation of [Cr(DMSO)₆](ClO₄)₃ (ref. 17), the excess DMSO was removed under reduced pressure at 100°C. However, the reaction of some transition metal perchlorates with excess DMSO and subsequent distillation of the solvent led to hazardous explosion³⁸ even under reduced pressure.

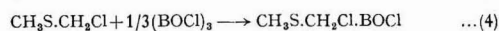
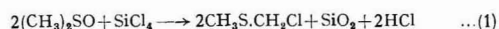
The sulphoxide complexes have also been prepared by dissolving the metal salt in an organic solvent like acetone or ethanol and then adding the required amount of sulphoxide in the same solvent. The complexes can either be crystallized out or precipitated by the addition of an inert solvent^{42,43}. The method is more general and employed in the preparation of many sulphoxide complexes⁴⁵. For the quantitative determination of

sulphoxides in metal complexes, a new method has been developed which is based on the oxidation of sulphoxide to sulphone by acid dichromate¹⁰⁰.

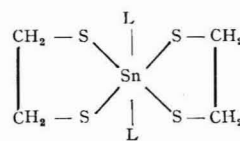
Complexes of Non-transition Elements

The sulphoxide complexes of alkali metal ions, with the exception of LiCl.DMSO¹¹ and KCNS.DMSO⁴⁷, are not known. The alkaline-earth metal perchlorates form weak complexes with sulphoxides, as revealed by their infrared spectra⁴⁴.

Groups IIIb and IVb halides react with sulphoxides giving different products. Cotton and Francis¹⁷ have studied the reaction of DMSO with BF₃, AlCl₃, Al(NO₃)₃ and SnCl₄ and isolated the complexes. Both AlCl₃ and Al(NO₃)₃ form hexa-coordinated complexes, [Al(DMSO)₆]X₃, where X = Cl or NO₃. SnCl₄.2DMSO is an interesting complex, as it possesses great thermal stability, subliming without decomposition at 180°C., and it is also stable towards hydrolysis. The stability of this complex is also indicated by the large lowering in ν_{S-O} (920, 905 cm.⁻¹). Lappert and Smith⁵⁸ have studied the reactions of boron, silicon and tin(IV) halides with dimethyl-, isopropyl-, *t*-butyl-, di-*t*-butyl- and diphenyl sulphoxides. Interaction of the sulphoxide with BX₃ (X = F or Cl) and SnX₄ (X = Cl, Br or I) in methylene dichloride at low temperature precipitates the corresponding complexes, BX₃.L and SnX₄.2L (L = sulphoxide). However, DMSO-BCl₃, DMSO-SiCl₄ and DPSO-SiCl₄ systems differ from the general behaviour, producing chloro-substituted sulphide or its derivatives. The reactions are given as:



Poller and Spillman⁶⁰ have prepared sulphoxide adducts of bis(dithiolato)tin(IV). The far infrared spectra of the complexes show *trans*-octahedral geometry (VI), as revealed by Sn-S stretching frequency. Langer and Blut⁵⁷ have obtained sulphoxide complexes of organometallics of group IVb halides. The tin complexes have the general formula, R_nSnCl_{4-n}.x.DMSO, where R = Me or Ph, n = 1, 2 or 3 and x = 1 or 2. The complexes of organotin halides and Ph₂PbCl₂.2DMSO are prepared without solvolysis in DMSO, DMSO-water mixtures and organic solvents. Organosilicon and germanium halides undergo solvolysis in DMSO



(L = sulphoxide)

VI

TABLE 1 — COMPLEXES OF DMSO

Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.	Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.	
NON-TRANSITION ELEMENTS								
LiCl.DMSO			11	SnCl ₄ .2DMSO	920, 905	<i>cis</i> -Octahedral; possesses great thermal stability; stable toward hydrolysis	17, 57	
KCNS.DMSO			47				58	
BF ₃ .DMSO	938	DMSO → BF ₃	17					
AlCl ₃ .6DMSO		[Al(DMSO) ₆]Cl ₃	17, 36					
AlCl ₃ .2DMSO			11	SnBr ₄ .2DMSO	911, 903	<i>cis</i> -Octahedral	58	
Al(NO ₃) ₃ .6DMSO		[Al(DMSO) ₆](NO ₃) ₃	17	SnI ₄ .2DMSO	924, 904	do	58	
GaCl ₃ .2DMSO			48	SnCl ₂ .2DMSO	920	do	59	
Ga(ClO ₄) ₃ .6DMSO		[Ga(DMSO) ₆](ClO ₄) ₃	36	Sn(DT) ₂ .2DMSO		<i>trans</i> -Octahedral structure	60	
InCl ₃ .3DMSO	945sh, 960, 995	Non-electrolytes in CH ₃ NO ₂ ;	49, 50	PbCl ₂ .1DMSO			36	
InBr ₃ .3DMSO	960, 995	the chloro and bromo		PbBr ₂ .1DMSO			36	
InI ₃ .2DMSO	940, 960sh, 980	complexes are <i>trans</i> -octahedral, while the iodo complex is five-coordinated		PbI ₂ .2DMSO			47	
				Pb(ClO ₄) ₂ .3DMSO			36	
In(NCS) ₃ .3DMSO	955, 980	[In(DMSO) ₆](NCS) ₃	51	PhSnCl ₂ .2DMSO	919	Octahedral	57	
In(NO ₃) ₃ .6DMSO	945	[In(DMSO) ₆](NO ₃) ₃	52	Ph ₂ SnCl ₂ .2DMSO	948	do	57	
In(ClO ₄) ₃ .6DMSO	950	[In(DMSO) ₆](ClO ₄) ₃	53	Ph ₃ SnCl.1DMSO	954	Probably trigonal bipyramidal	57	
TiCl ₃ .2DMSO	930	Monomeric, non-electrolyte in non-aqueous solvent; probably five-coordinated	54, 55	MeSnCl ₂ .2DMSO	928	Octahedral	57	
				Me ₂ SnCl ₂ .2DMSO	944	do	57	
				Me ₃ SnCl.1DMSO	958	Probably trigonal bipyramidal	57	
TiBr ₃ .2DMSO	930			Ph ₂ PbCl ₂ .2DMSO	945	Octahedral	57, 61	
SiF ₄ .2DMSO		<i>cis</i> -Octahedral	33, 56	Ph ₂ PbBr ₂ .2DMSO		do	57, 61	
GeF ₄ .2DMSO		do	33	SbCl ₅ .1DMSO		do	11, 62	
GeCl ₄ .2DMSO	894	do	57	SbONO ₂ .1DMSO		do	63	
SnF ₄ .2DMSO		do	33	Bi(NO ₃) ₃ .3DMSO		do	63	
TRANSITION METALS								
TiF ₄ .2DMSO		Stable towards hydrolysis; <i>cis</i> -octahedral	33	Fe(ClO ₄) ₃ .6DMSO	940	[Fe(DMSO) ₆](ClO ₄) ₃	11, 17	
TiCl ₄ .11DMSO	950		64	Fe(NO ₃) ₃ .6DMSO		[Fe(DMSO) ₆](NO ₃) ₃	11	
TiBr ₄ .11DMSO	910		64	FeCl ₂ .2DMSO			48	
TiO(ClO ₄) ₂ .5DMSO	934	[TiO(DMSO) ₅](ClO ₄) ₂	38	FeI ₂ .4DMSO			17	
(EtO) ₂ TiCl ₂ .DMSO			65	Fe(ClO ₄) ₂ .6DMSO		[Fe(DMSO) ₆](ClO ₄) ₂	9, 17,	
VO(ClO ₄) ₂ .5DMSO	945	[VO(DMSO) ₅](ClO ₄) ₂	66	CoCl ₂ .3DMSO	950	[Co(DMSO) ₆](CoCl ₄) ₂	35	
VOCl ₃ .3DMSO		[VOCl ₃ (DMSO) ₃]	67				17, 35	
VOC ₂ O ₄ .2DMSO	940	[VOC ₂ O ₄ (DMSO) ₂]	68	CoBr ₂ .3DMSO	951	[Co(DMSO) ₆][CoBr ₂]	11	
CrCl ₃ .3DMSO			17	CoBr ₂ .8DMSO		[Co(DMSO) ₆]	11	
CrCl ₃ .5DMSO			11, 69			Br ₂ .2DMSO		
CrBr ₃ .6DMSO			11, 69	CoI ₂ .3DMSO	951	[Co(DMSO) ₆][CoI ₂]	17	
Cr(NO ₃) ₃ .6DMSO		[Cr(DMSO) ₆](NO ₃) ₃	11, 69	CoI ₂ .6DMSO	948	[Co(DMSO) ₆]I ₂	11, 17,	
Cr(ClO ₄) ₃ .6DMSO	928	[Cr(DMSO) ₆](ClO ₄) ₃	11, 69				35	
			34, 69	Co(CNS) ₂ .4DMSO	953	[Co(DMSO) ₄](NCS) ₂	17, 73	
CrCl ₂ .2DMSO		High spin complexes with Cr(II) ion in a distorted octahedral environment	70	Co(CNS) ₂ .3DMSO	950	[Co(DMSO) ₆][Co(NCS) ₄]	17, 73	
CrBr ₂ .3DMSO					Co[N(CN) ₂] ₂ .2DMSO		Polymeric structure with bridged N(CN) ₂ groups	72
CrI ₄ .4DMSO					Co[C(CN) ₃] ₂ .6DMSO		[Co(DMSO) ₆][C(CN) ₃] ₂	72
					Co(NO ₃) ₂ .6DMSO			73
Mn(ClO ₄) ₂ .6DMSO		[Mn(DMSO) ₆](ClO ₄) ₂	71	Co(ClO ₄) ₂ .6DMSO	956	[Co(DMSO) ₆](ClO ₄) ₂	17	
MnCl ₂ .3DMSO		[Mn(DMSO) ₆][MnCl ₄]	11, 17, 35, 69	Co(ClO ₄) ₂ .8DMSO			11	
MnBr ₂ .3DMSO			17	NiCl ₂ .3DMSO	940	[Ni(DMSO) ₆][NiCl ₄]	11, 17,	
MnBr ₂ .2DMSO			48				35	
MnBr ₂ .6DMSO			11	NiBr ₂ .3DMSO		[Ni(DMSO) ₆][NiBr ₂]	17, 35	
MnI ₂ .3DMSO		[Mn(DMSO) ₆][MnI ₄]	17	NiBr ₂ .6DMSO		[Ni(DMSO) ₆]Br ₂	48	
MnI ₂ .6DMSO		[Mn(DMSO) ₆]I ₂	11	NiBr ₂ .8DMSO			11	
Mn(ClO ₄) ₂ .6DMSO	955	[Mn(DMSO) ₆](ClO ₄) ₂	11, 17	NiI ₂ .4DMSO		[Ni(DMSO) ₆]I ₂	48	
Mn(ClO ₄) ₂ .3DMSO.		Obtained from aqueous DMSO	17	NiI ₂ .6DMSO		[Ni(DMSO) ₆]I ₂	11	
4H ₂ O				Ni(NCS) ₂ .4DMSO		[Ni(DMSO) ₄](NCS) ₂	73	
MnBr ₂ .3DMSO.6H ₂ O				Ni(NO ₃) ₂ .8DMSO			11	
Mn[N(CN) ₂] ₂ .2DMSO		Polymeric structure with bridged N(CN) ₂ groups	72	Ni(ClO ₄) ₂ .6DMSO	955	[Ni(DMSO) ₆](ClO ₄) ₂	11, 17	
				Ni[N(CN) ₂] ₂ .2DMSO		Polymeric structure with bridged N(CN) ₂ groups	72	
Mn[C(CN) ₃] ₂ .6DMSO		[Mn(DMSO) ₆][C(CN) ₃] ₂	72				72	
FeCl ₃ .2DMSO	933	Can be sublimed in vacuum at 190°C.; <i>trans</i> -[FeCl ₂ (DMSO) ₄][FeCl ₄]	17	Ni[C(CN) ₃] ₂ .8DMSO			72	
				Ni[C(CN) ₃] ₂ .1DMSO			72	
FeCl ₃ .4DMSO			11	CuCl ₂ .2DMSO	923	[CuCl ₂ .2DMSO] _n	11, 17,	
FeBr ₃ .6DMSO			17				70, 74	

TABLE 1 — COMPLEXES OF DMSO — *Contd*

Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.	Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.
TRANSITION METALS							
CuBr ₂ .3DMSO	broad band 950-1000	Halide-bridged distorted octahedral dimeric structure [CuBr ₂ (DMSO) ₂] _n	11, 17, 70	NbF ₅ .2DMSO		Seven-coordinated complex	76
CuBr ₂ .2DMSO			17, 35, 70	TaF ₅ .2DMSO		do	76
Cu(ClO ₄) ₂ .4DMSO	940		17	NbOCl ₃ .2DMSO		Distorted octahedral	77
Cu(ClO ₄) ₂ .9DMSO			11	TaOCl ₃ .2DMSO		do	77
CuSO ₄ .2DMSO			17	MoOCl ₃ .2DMSO		dc	78, 79
Cu(NO ₃) ₂ .2DMSO			37	MoO ₂ Cl ₂ .2DMSO			78
Cu(NO ₃) ₂ .4DMSO			17, 37	RhCl ₃ .3DMSO			48
Cu(OAc) ₂ .DMSO		Dimeric structure similar to copper(II) acetate hydrate	37	RhI ₃ .2DMSO			48
				Rh(OAc) ₂ .DMSO	1086	Dimeric structure similar to copper(II) acetate; DMSO is S-bonded	80
Cu[N(CN) ₂] ₂ .2DMSO		Polymeric structure with bridged N(CN) ₂ groups	72	PdCl ₂ .2DMSO	1116	DMSO is S-bonded	17
				PdSO ₄ .2DMSO		do	81
Cu[C(CN) ₃] ₂ .6DMSO			72	PtCl ₂ .2DMSO	1157, 1134	do	17
Cu[C(CN) ₃] ₂ .1DMSO			72	Mo ₆ Cl ₁₂ .2DMSO	930		82
CuCl ₂ .PyO.DMSO			75	[Mo ₆ Cl ₉ (DMSO) ₆](ClO ₄) ₄	930		82
CuBr ₂ .PyO.DMSO			75	[Mo ₆ Cl ₉ (DMSO) ₂ (CH ₃ SO ₃) ₄]	930		82
ZnCl ₂ .2DMSO	942		17	[Re ₃ Br ₃ (DMSO) ₃](AsO ₄) ₂	925		82a
ZnBr ₂ .DMSO			17				
Zn(ClO ₄) ₂ .6DMSO	956		17	CdCl ₂ .1DMSO	950		17, 36
Zn(ClO ₄) ₂ .5DMSO	947		46	CdBr ₂ .1DMSO			36
Zn(NO ₃) ₂ .2DMSO	952		17	Cd[N(CN) ₂] ₂ .2DMSO		Polymeric structure with bridging N(CN) ₂ groups	72
Zn[N(CN) ₂] ₂ .0.5DMSO			72				
Zn[C(CN) ₃] ₂ .6DMSO		[Zn(DMSO) ₆][C(CN) ₃] ₂	72	Cd[C(CN) ₃] ₂ .6DMSO			72
ZrF ₄ .2DMSO		Probably <i>cis</i> -octahedral	33	HgCl ₂ .1DMSO			36
ZrCl ₄ .9DMSO	950		64	(HgCl ₂) ₂ .1DMSO			17
ZrBr ₄ .10DMSO	920		64	(HgBr ₂) ₂ .2DMSO			17
ZrO(ClO ₄) ₂ .8DMSO	1024w, 938s	[ZrO(DMSO) ₆](ClO ₄) ₂ .2DMSO	38	Hg(SCN) ₂ .2DMSO			35
ZrO(ClO ₄) ₂ .6DMSO	1144s	DMSO is probably S-bonded	38	Hg(ClO ₄) ₂ .6DMSO			83
HfCl ₄ .9DMSO	950		64	Hg ₂ (ClO ₄) ₂ .3.4DMSO			84
HfBr ₄ .10DMSO	920		64	Hg ₂ (SiF ₆).DMSO. x H ₂ O			84
				Ag(ClO ₄).DMSO	940		85
LANTHANIDES							
LaCl ₃ .4DMSO	998	The chloro complexes are non-electrolytes in acetonitrile, showing a coordination number of seven for all but Y complex	86	La(NO ₃) ₃ .4DMSO	941s	The nitrate complexes are monomeric non-electrolytes in acetonitrile. NO ₃ ⁻ is coordinated to the metal	87
CeCl ₃ .4DMSO				Ce(NO ₃) ₃ .4DMSO			
PrCl ₃ .4DMSO				Pr(NO ₃) ₃ .4DMSO			
NdCl ₃ .4DMSO				Nd(NO ₃) ₃ .4DMSO			
SmCl ₃ .4DMSO				Sm(NO ₃) ₃ .4DMSO			
GdCl ₃ .4DMSO				Gd(NO ₃) ₃ .4DMSO			
YCl ₃ .3DMSO				Y(NO ₃) ₃ .3DMSO			
La(ClO ₄) ₃ .8DMSO	992	The complexes behave as 1:3 electrolytes in nitrobenzene. Perchlorate groups are ionic	88	Ho(NO ₃) ₃ .3DMSO			
Ce(ClO ₄) ₃ .8DMSO	993			Yb(NO ₃) ₃ .3DMSO			
Pr(ClO ₄) ₃ .8DMSO	996						
Nd(ClO ₄) ₃ .8DMSO	995						
Sm(ClO ₄) ₃ .7DMSO	1000						
Y(ClO ₄) ₃ .7DMSO							
ACTINIDES							
ThCl ₄ .3DMSO	960	Monomeric non-electrolyte	89a	UBr ₄ .6DMSO	937		89
ThCl ₄ .5DMSO	942	do	89, 89a	UO ₂ (NO ₃) ₂ .2DMSO			17
ThBr ₄ .6DMSO	948		89	UO ₂ (ClO ₄) ₂ .5DMSO	1026w, 941s	[UO ₂ (DMSO) ₄](ClO ₄) ₂ .DMSO	39, 90
Th(NO ₃) ₄ .6DMSO			17, 90	UO ₂ (ClO ₄) ₂ .4DMSO	1152	DMSO is probably S-bonded	39
Th(ClO ₄) ₄ .12DMSO	1044m, 946s	[Th(DMSO) ₆](ClO ₄) ₄ .6DMSO	38	UCl ₄ .7DMSO	1047m, 942s	[UCl ₄ (DMSO) ₂].2DMSO	89a
Th(ClO ₄) ₄ .6DMSO	1144s	DMSO is S-bonded	38	UCl ₄ .5DMSO	940		89a
ThCl ₄ .8DMSO			89a				
ThCl ₄ .10DMSO							

TABLE 1 — COMPLEXES OF DMSO — *Contd*

Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.	Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.
ACTINIDES							
UCl ₄ .3DMSO	960	Monomeric non-electrolyte	89, 89a, 90	NpCl ₄ .7DMSO	1047m, 942s	[NpCl ₄ (DMSO) ₅]. 2DMSO	89a
PaCl ₄ .5DMSO	940		89a	PuCl ₄ .3DMSO	965		89a, 90, 91
PaCl ₄ .3DMSO	950		89a	PuCl ₄ .7DMSO	1050m, 945s	[PuCl ₄ (DMSO) ₅]. 2DMSO	89a
NpCl ₄ .3DMSO	962		89a				
NpCl ₄ .5DMSO	945		89a				

TABLE 2 — COMPLEXES OF SULPHOXIDES OTHER THAN DMSO

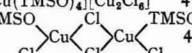
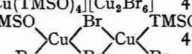
Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.	Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.
NON-TRANSITION ELEMENTS							
Mg(ClO ₄) ₂ .6DPSO	1012	[Mg(DPSO) ₆](ClO ₄) ₂	43, 44	Ph ₃ SnCl.DTM	990		92
Mg(ClO ₄) ₂ .6PMSO	992	[Mg(PMSO) ₆](ClO ₄) ₂	45	SnI ₄ .2DTM	948		92
Mg(ClO ₄) ₂ .6TMSO	985	[Mg(TMSO) ₆](ClO ₄) ₂	45	(TDTD)	1028, 1021		92
Ca(ClO ₄) ₂ .7DPSO	1012-1035b	[Ca(DPSO) ₆](ClO ₄) ₂	43, 44	Ph ₂ SnCl ₂ .TDTD	937	Ligand acts as a bidentate	92
Ca(ClO ₄) ₂ .6PMSO	1023	[Ca(PMSO) ₆](ClO ₄) ₂	45	PhSnCl ₂ .TDTD	966, 948		92
Ca(ClO ₄) ₂ .6TMSO	1010-1030b	[Ca(TMSO) ₆](ClO ₄) ₂	45	SnI ₄ .TDTD (CDTD)	937, 1026, 1015, 997, 980		92
BF ₃ .TMSO			40	Ph ₂ SnCl ₂ .CDTD	1026, 1010, 997	Ligand is monodentate. The complexes are monomeric	92
BCl ₃ .Pr ⁿ Bu ^t SO	913		58	PhSnCl ₃ .CDTD	1023, 960, 940	5-coordinated	
BCl ₃ .Bu ⁿ SO	919		58	SnI ₄ .CDTD	1020, 950		
BCl ₃ .DPSO	887		58	SbCl ₅ .1DPSO		Octahedral	93
Al(ClO ₄) ₃ .6DPSO	942	[Al(DPSO) ₆](ClO ₄) ₃	43, 44				
Al(ClO ₄) ₃ .6TMSO	950b	[Al(TMSO) ₆](ClO ₄) ₃	45				
SnCl ₄ .2DPSO	937, 913	<i>cis</i> -Octahedral	58				
Sn(DT) ₂ .2DES0			60				
SnCl ₄ .2DPSO (DTM)	1021		59				
Ph ₂ SnCl ₂ .2DTM	957		92				
			92				
			92				
TRANSITION METALS							
TiO(ClO ₄) ₂ .5DPSO	990, 975, 955	[TiO(DPSO) ₅](ClO ₄) ₂	94	Co(BF ₄) ₂ .6TMSO	962	[Co(TMSO) ₆](BF ₄) ₂	45
VO(ClO ₄) ₂ .5DPSO	965	[VO(DPSO) ₅](ClO ₄) ₂	94	CoCl ₂ .3TMSO	965	[Co(TMSO) ₆][CoCl ₄]	40
VOCl ₂ .3DPSO	980, 975	[VOCl ₂ (DPSO) ₃]	94	CoBr ₂ .3TMSO	966	[Co(TMSO) ₆][CoBr ₄]	40
Cr(ClO ₄) ₃ .6DPSO	930	[Cr(DPSO) ₆](ClO ₄) ₃	95	CoBr ₂ .6TMSO	967	[Co(TMSO) ₆][Br ₂]	40
Mn(ClO ₄) ₂ .6DPSO	983	[Mn(DPSO) ₆](ClO ₄) ₂	42, 43, 44	CoI ₂ .3TMSO	965	[Co(TMSO) ₆][CoI ₄]	40
Mn(ClO ₄) ₂ .6PMSO	978	[Mn(PMSO) ₆](ClO ₄) ₂	45	CoI ₂ .6TMSO	963	[Co(TMSO) ₆][I ₂]	40
Mn(ClO ₄) ₂ .6TMSO	965	[Mn(TMSO) ₆](ClO ₄) ₂	45	Co(NCS) ₂ .4TMSO	972	[Co(TMSO) ₆](NCS) ₂	40
Mn(BF ₄) ₂ .6DPSO	991	[Mn(DPSO) ₆](BF ₄) ₂	43, 44	Co(ClO ₄) ₂ .6Pr ⁿ SO	972	[Co(Pr ⁿ SO) ₆](ClO ₄) ₂	46
Mn(ClO ₄) ₂ .6PMSO	950	[Mn(PMSO) ₆](ClO ₄) ₂	46	Co(ClO ₄) ₂ .6Bu ⁿ SO	973	[Co(Bu ⁿ SO) ₆](ClO ₄) ₂	46
Mn(ClO ₄) ₂ .6Pr ⁿ SO	982	[Mn(Pr ⁿ SO) ₆](ClO ₄) ₂	46	Ni(ClO ₄) ₂ .6DPSO	982	[Ni(DPSO) ₆](ClO ₄) ₂	42, 43, 44
Mn(ClO ₄) ₂ .6Bu ⁿ SO	972	[Mn(Bu ⁿ SO) ₆](ClO ₄) ₂	46	Ni(BF ₄) ₂ .6DPSO	982	[Ni(DPSO) ₆](BF ₄) ₂	43, 44
Fe(ClO ₄) ₃ .6DPSO	931	[Fe(DPSO) ₆](ClO ₄) ₃	44, 95	Ni(SbCl ₆) ₂ .6DPSO	979	[Ni(DPSO) ₆][SbCl ₆]	43, 44
Fe(ClO ₄) ₃ .6PMSO	924	[Fe(PMSO) ₆](ClO ₄) ₃	45	Ni(FeCl ₄) ₂ .6DPSO	982	[Ni(DPSO) ₆][FeCl ₄]	43, 44
Fe(ClO ₄) ₃ .6TMSO	920b	[Fe(TMSO) ₆](ClO ₄) ₃	40	Ni(ClO ₄) ₂ .6PMSO	976	[Ni(PMSO) ₆](ClO ₄) ₂	45
FeCl ₃ .2TMSO		Can be sublimed in vacuum at 170°C.	40	Ni(BF ₄) ₂ .6TMSO	962b	[Ni(TMSO) ₆](BF ₄) ₂	45
				Ni(ClO ₄) ₂ .6TMSO	962	[Ni(TMSO) ₆](ClO ₄) ₂	45
				Ni(BF ₄) ₂ .6TMSO	962b	[Ni(TMSO) ₆](BF ₄) ₂	45
				Ni(ClO ₄) ₂ .6Pr ⁿ SO	982, 950	[Ni(MPSO) ₆](ClO ₄) ₂	46
				Ni(ClO ₄) ₂ .6Bu ⁿ SO	968	[Ni(Pr ⁿ SO) ₆](ClO ₄) ₂	46
				Ni(ClO ₄) ₂ .6Bu ⁿ SO	974	[Ni(Bu ⁿ SO) ₆](ClO ₄) ₂	46
FeCl ₃ .2DPSO		[FeCl ₃ (DPSO) ₄][FeCl ₄]	96	NiCl ₂ .3TMSO	971	[Ni(TMSO) ₆][NiCl ₄]	40
Fe(ClO ₄) ₂ .6DPSO	987	[Fe(DPSO) ₆](ClO ₄) ₂	46	NiBr ₂ .4TMSO	970	[Ni(Br ₂ (TMSO)) ₄]	40
Fe(ClO ₄) ₂ .6PMSO	947	[Fe(PMSO) ₆](ClO ₄) ₂	46	NiI ₂ .4TMSO	945	[NiI ₂ (TMSO) ₄]	40
Fe(ClO ₄) ₂ .6Pr ⁿ SO	975	[Fe(Pr ⁿ SO) ₆](ClO ₄) ₂	46	CuCl ₂ .2TMSO	937	[CuCl ₂ (TMSO) ₂]	40
Co(ClO ₄) ₂ .6DPSO	980	[Co(DPSO) ₆](ClO ₄) ₂	42, 43, 44, 46	3CuCl ₂ .4TMSO	933	[Cu(TMSO) ₄][Cu ₂ Cl ₆]	41
Co(BF ₄) ₂ .6DPSO	980	[Co(DPSO) ₆](BF ₄) ₂	43, 44	CuCl ₂ .TMSO	941	TMSO  TMSO	41
Co(ClO ₄) ₂ .6PMSO	975	[Co(PMSO) ₆](ClO ₄) ₂	45				
Co(ClO ₄) ₂ .6TMSO	965	[Co(TMSO) ₆](ClO ₄) ₂	40, 45				
Co(ClO ₄) ₂ .6PMSO	950	[Co(MPSO) ₆](ClO ₄) ₂	46	3CuBr ₂ .4TMSO	937	[Cu(TMSO) ₄][Cu ₂ Br ₆]	41
Co(SbCl ₆) ₂ .6DPSO	978	[Co(DPSO) ₆][SbCl ₆]	43, 44	CuBr ₂ .TMSO	925	TMSO  TMSO	41
Co(FeCl ₄) ₂ .6DPSO	984	[Co(DPSO) ₆][FeCl ₄]	43, 44				
Co(BF ₄) ₂ .6PMSO	974	[Co(PMSO) ₆](BF ₄) ₂	45				

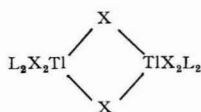
TABLE 2—COMPLEXES OF SULPHOXIDES OTHER THAN DMSO — *Contd*

Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.	Complex	$\nu_{S=O}$ cm. ⁻¹	Remarks	Ref.
TRANSITION METALS							
Cu(ClO ₄) ₂ .4DPSO	948	[Cu(DPSO) ₄](ClO ₄) ₂	42, 43,	Zn(ClO ₄) ₂ .6MPSO	987(949)	[Zn(MPSO) ₆](ClO ₄) ₂	46
			44	ZnCl ₂ .2DPSO	997	Monomer in nitrobenzene	42
Cu(BF ₄) ₂ .6DPSO	948, 1012	[Cu(DPSO) ₆](ClO ₄) ₂ [CuL ₆] ²⁺ (L = DPSO, PMSO, TMSO) is distorted octahedral	43, 44	ZrO(ClO ₄) ₂ .6DPSO	950		94
Cu(ClO ₄) ₂ .6PMSO	988, 955	[Cu(PMSO) ₆](ClO ₄) ₂	45	Re ₃ Cl ₉ .3TMSO	910		97
Cu(ClO ₄) ₂ .6TMSO	988, 948	[Cu(TMSO) ₆](ClO ₄) ₂	45	Re ₃ Cl ₉ .3DPMSO	936		97
Cu(BF ₄) ₂ .6TMSO	986, 947	[Cu(TMSO) ₆](BF ₄) ₂	45	Re ₃ Cl ₉ .3BzSO			97
Cu(DPSO) ₄ (acetone) ₂ (BF ₄) ₂	945		44, 45	PdCl ₂ .2TMSO	1127, 1140sh,	Ligand is S-bonded	40
Cu(BF ₄) ₂ (DPSO) ₄	948	[Cu(DPSO) ₄](BF ₄) ₂	44, 45	PdCl ₂ .2DPSO	1068	do	42
CuCl ₂ .2DPSO			95	PtCl ₂ .2TMSO	1075, 1087,	do	40
Cu(ClO ₄) ₂ .4PMSO	940	[Cu(PMSO) ₄](ClO ₄) ₂	45		1130,		
Cu(ClO ₄) ₂ .4TMSO	930b	[Cu(TMSO) ₄](ClO ₄) ₂	45		1140,		
Cu(BF ₄) ₂ .4TMSO	930b	[Cu(TMSO) ₄](BF ₄) ₂	45		1155		
Zn(ClO ₄) ₂ .6DPSO	987	[Zn(DPSO) ₆](ClO ₄) ₂	42, 43, 44, 46	CdCl ₂ .1DPSO	1048	do	42
Zn(BF ₄) ₂ .6DPSO	988	[Zn(DPSO) ₆](BF ₄) ₂	43, 44	Cd(ClO ₄) ₂ .6DPSO	1050	do	42
Zn(ClO ₄) ₂ .6PMSO	975	[Zn(PMSO) ₆](ClO ₄) ₂	45	HgCl ₂ .1DPSO	1050	do	42
Zn(ClO ₄) ₂ .6TMSO	960-970	[Zn(TMSO) ₆](ClO ₄) ₂	45	Hg ₂ (ClO ₄) ₂ .2.6DPSO	904		84
Zn(ClO ₄) ₂ .6Pr ^{II} ₂ SO	976	[Zn(Pr ^{II} ₂ SO) ₆](ClO ₄) ₂	46	Hg ₂ (ClO ₄) ₂ .4Pr ^{II} ₂ SO	940		84
LANTHANIDES				ACTINIDES			
La(ClO ₄) ₃ .6DPSO	}	[Ln(DPSO) ₆](ClO ₄) ₃	98	Th(ClO ₄) ₄ .6DPSO			94
Ce(ClO ₄) ₃ .6DPSO				UCl ₄ .3DPSO		99	
Pr(ClO ₄) ₃ .6DPSO				UO ₂ (ClO ₄) ₂ .4DPSO	970	[UO ₂ (DPSO) ₄](ClO ₄) ₂	94
Nd(ClO ₄) ₃ .6DPSO				UO ₂ (ClO ₄) ₂ .5TMSO		[UO ₂ (TMSO) ₅](ClO ₄) ₂	90
Sm(ClO ₄) ₃ .6DPSO				UO ₂ (NO ₃) ₂ .2TMSO		[UO ₂ (TMSO) ₂ (NO ₃) ₂]	90
Gd(ClO ₄) ₃ .6DPSO							
Y(ClO ₄) ₃ .6DPSO							
Ho(ClO ₄) ₃ .6DPSO							
Yb(ClO ₄) ₃ .6DPSO							

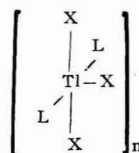
yielding ill-defined oxide or hydroxide complexes. Most of the organotin halide complexes possess octahedral coordination except when the Lewis acid character of the organotin halide is lessened and the steric hindrance of methyl or phenyl substituents prohibits the formation of octahedral structure. This happens in the case of triphenyl tin chloride, and trimethyl tin chloride mono-DMSO complexes. The stability of the complexes seems to decrease in the order SnCl₄.2DMSO > PhSnCl₃.2DMSO > Ph₂SnCl₂.2DMSO > Ph₃SnCl.1DMSO, as indicated by the increasing S-O stretching frequency and decreasing melting point in the series. Trimethyl and triethyl tin chloride and triethyl lead chloride take one TMSO forming five-coordinated complexes. Trigonal bipyramidal structures have been proposed for these complexes¹⁰¹. A large number of complexes of the type, Ar₃SnX.RR'SO [Ar = phenyl or *p*-chlorophenyl, X = Cl or NCS], have been prepared by Boehringer Sohn¹⁰². The complexes show bactericidal and fungicidal activity with low plant toxicity. The structural details regarding the complexes are not known.

The sulphoxide complexes of In(III) and Tl(III) have received considerable attention in recent years. Carty and Tuck⁴⁹⁻⁵³ have prepared DMSO complexes of In(III) perchlorate, nitrate and halides. The perchlorate and nitrate complexes contain the cation

[In(DMSO)₆]³⁺, while the halide complexes are neutral, as indicated by electrical conductance in nitromethane solution. The iodo complex, InI₃.2DMSO, is probably five-coordinated, while the other In(III) complexes are octahedral. In(III) halide complexes show two S-O stretching frequencies around 960 and 990 cm.⁻¹ and this has been attributed to the low molecular symmetry of the ligand in the complex. Five-coordinated TlCl₃.2DMSO has been prepared by Cotton *et al.*⁵⁴. The complex is monomeric in tetramethylene sulphone and non-conducting in acetonitrile. Johnson and Walton⁵⁵ have reported InCl₃.3DMSO and TlBr₃.2DMSO. The far infrared spectra of TlCl₃.2DMSO and TlBr₃.2DMSO show a strong band around 400 cm.⁻¹, which has been assigned to Tl-O stretch. The complexes may have either of the structures, (VII) or (VIII) in the solid state.



VII



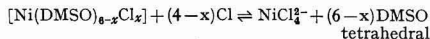
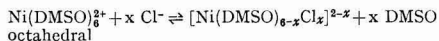
VIII

Among the Vb group elements, $SbCl_5$ and $SbCl_3$ are known to form complexes with sulphoxides. Lindqvist and Einarsson⁸² have obtained 1:1 complexes of $SbCl_5$ with DMSO and DPSO. The crystal structure of $SbCl_5 \cdot DMSO$ reveals an octahedral structure, with oxygen coordination of the ligand⁸³. Straub *et al.*⁸³ have found that some metals, which do not react with N_2O_4 in acetonitrile, react in DMSO medium. The greater reactivity in the latter has been attributed to the good coordinating ability of DMSO both towards N_2O_4 and the metal ion. Thus, antimony and bismuth produce $SbONO_2 \cdot DMSO$ and $Bi(NO_3)_3 \cdot 3DMSO$ respectively. Al, Si, Sn, As and Se show little or no tendency to react with N_2O_4 in DMSO medium.

Complexes of Transition Metals

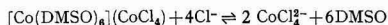
The sulphoxide complexes of 3d-transition metal ions have been well investigated. The interest in these complexes arises from the fact that the partially filled 3d-levels of the metal ion are perturbed on complex formation. The properties arising from the perturbation, the d-d electronic transitions and the magnetic properties, act as convenient probe into the stereochemistry of the complexes. The sulphoxide complexes of transition metal perchlorates, fluoborates, halides and nitrates are prepared and studied extensively. Usually, the perchlorate and fluoborate complexes contain the maximum number of ligands, while the halides and nitrates take relatively less number of donor molecules. This is due to the fact that the tetrahedral perchlorate and fluoborate anions show little or no tendency for coordination, while the halide ions are strongly coordinating. The nitrate falls somewhere in between the perchlorate and halides in their coordinating tendency. The coordination tendency of an anion dictates, to a large extent, the nature of the complex formed with neutral monodentate ligands like sulphoxides.

The 3d-transition metal perchlorate complexes of DMSO, investigated by Cotton and Francis¹⁷ and Schläfer and Optiz⁸⁴, are octahedral with the general formula, $[M(DMSO)_6](ClO_4)_n$, where $M = Cr(III), Fe(III), Mn(II), Co(II), Ni(II)$ or $Zn(II)$ and $n = 2$ or 3. The recently prepared $[Mn(DMSO)_6](ClO_4)_3$ conforms to this general rule⁷¹. The complexes of metal halides like $CoCl_2 \cdot 3DMSO$, $NiCl_2 \cdot 3DMSO$, etc., show magnetic moments which are root mean square of octahedral, $M(DMSO)_6^{2+}$, and tetrahedral, MCl_4^{2-} , ions. The reflectance spectra of the complexes have been found to be a superposition of the electronic spectra of $M(DMSO)_6^{2+}$ and MCl_4^{2-} ions. From these data, the cobalt and nickel chloride complexes have been formulated as $[M(DMSO)_6](MCl_4)^{17}$. From a study of the electronic spectra of $MCl_2 \cdot 3DMSO$ [$M = Mn(II), Co(II)$ and $Ni(II)$] in nitromethane, Meek *et al.*⁸⁵ have arrived at a similar conclusion. However, it has been observed that the nature of species present in solution is highly complex. The following equilibria have been proposed for $NiCl_2$ when dissolved in DMSO:

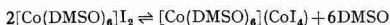


The formation of tetrahedral species is favoured at higher temperatures or in the presence of a solvent with low dielectric constant.

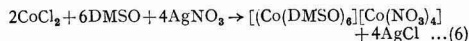
In the case of $[Co(DMSO)_6](CoCl_4)$, the addition of chloride ions favours the formation of $CoCl_4^{2-}$,



revealing thereby that chloride is a better coordinating agent than DMSO. Iodide is a poorer coordinator than chloride. When $[Co(DMSO)_6]I_2$ is dissolved in nitromethane, both DMSO and I^- compete for coordination, establishing the following equilibrium:



The copper(II) halide complexes, $CuCl_2 \cdot 2DMSO$ and $CuBr_2 \cdot 2DMSO$, have been formulated as $[Cu(DMSO)_4](CuX_4)$ in solution⁸⁵. However, a recent study of these complexes, along with the corresponding Cr(II) complexes, has revealed a different situation⁷⁰. The electronic spectra of $CuCl_2 \cdot 2DMSO$ and $CuBr_2 \cdot 2DMSO$ are quite different from those of $CuCl_4^{2-}$ and $CuBr_4^{2-}$. The pale greenish-yellow $CuCl_2 \cdot 2DMSO$ in ethanol, DMSO and nitromethane changes to bright yellow, characteristic of $CuCl_4^{2-}$, on the addition of Cl^- ions. Similar change in colour is observed with $CuBr_2 \cdot 2DMSO$ complex. As there is no similarity in the electronic spectra of $CuCl_4^{2-}$ and $CuCl_2 \cdot 2DMSO$, the structure $[Cu(DMSO)_4](CuX_4)$, proposed by Meek *et al.*, is ruled out, at least in solution. The X-ray powder diffraction studies of $CrCl_2 \cdot 2DMSO$, $CrBr_2 \cdot 3DMSO$ and $CuCl_2 \cdot 2DMSO$ reveal that they are isomorphous. $CrBr_2 \cdot 3DMSO$ and $CuBr_2 \cdot 3DMSO$ give a fairly complex infrared spectrum in the region 950-1000 cm^{-1} , indicating that DMSO exists in more than one chemical environment. The high spin magnetic moments at room temperature and the visible reflectance spectra reveal distorted octahedral coordination for $CrCl_2 \cdot 2DMSO$, $CrBr_2 \cdot 3DMSO$ and $CrI_2 \cdot 4DMSO$. Halide-bridged polymeric structures have been suggested for $MX_2 \cdot 2DMSO$ [$M = Cr(II)$ or $Cu(II)$; $X = Cl$ or Br] and $MBr_2 \cdot 3DMSO$ [$M = Cr(II)$ or $Cu(II)$] complexes. Straub *et al.*¹⁰³ have prepared hexakis(DMSO)cobalt(II)-tetranitratocobaltate(II) in acetonitrile medium by the reaction:

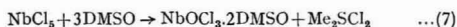


The large cation, $[Co(DMSO)_6]^{2+}$, seems to stabilize the large tetranitrate anion, $[Co(NO_3)_4]^{2-}$, in the crystal lattice. The cation has an octahedral structure, while the anion possesses a tetrahedral structure, as revealed by the electronic spectrum of the complex.

Recently, a new series of DMSO complexes of divalent transition metal cyanamides and tricyanomethylides, having the general formula $M[N(CN)_2]_2 \cdot 2DMSO$ and $M[C(CN)_3]_2 \cdot (6, 8 \text{ or } 1)DMSO$ [$M = Mn, Co, Ni, Cu, Zn$ or $Cd(II)$] respectively, have been investigated by Köhler⁷². The complexes are generally prepared by dissolving the metal dicyanamide or tricyanomethylide in dry DMSO and precipitating the complexes by the

addition of CCl_4 or benzene. In general, tricyanomethylides take six ligands per metal, forming hexa-coordinated complexes, $[\text{M}(\text{DMSO})_6][\text{C}(\text{CN})_3]_2$, although $\text{Ni}[\text{C}(\text{CN})_3]_2 \cdot 8$ or 1DMSO and $\text{Cu}[\text{C}(\text{CN})_3]_2 \cdot 6$ or 1DMSO are also reported. The dicyanamide complexes usually contain two ligands per metal ion. In 10^{-2} to 10^{-3}M solutions of DMSO , both dicyanamide and tricyanomethylide complexes form $[\text{M}(\text{DMSO})_6]^{2+}$ cations. The infrared spectra of solid tricyanomethylide complexes show one $\nu(\text{C}\equiv\text{N})$ at 2175 cm^{-1} , indicating uncoordinated $\text{C}(\text{CN})_3$ groups, whereas those of dicyanamide complexes give two $\nu(\text{C}\equiv\text{N})$ around 2200 and 2250 cm^{-1} , revealing coordination of dicyanamide groups to the metal. The metal ion in the dicyanamide complexes of Mn, Co and Ni seem to have octahedral coordination, as revealed by electronic spectra and magnetic moments. A polymeric structure with bridging $\text{N}(\text{CN})_2$ groups has been suggested for these complexes.

Schläfer and Wille⁶⁴ have prepared complexes of Ti, Zr and Hf tetrachlorides and tetrabromides containing 9 to 11DMSO molecules and it is not known whether all the DMSO molecules are coordinated to the metal. The DMSO complexes of titanyl and zirconyl perchlorates along with those of thorium(IV) and uranyl(VI) perchlorates have been investigated^{68,69}. The X-ray powder diffraction studies indicate that the zirconyl and thorium perchlorate complexes belong to the hexagonal crystal system⁶⁹. Fairbrother *et al.*^{76,77} have studied the reactions of niobium and tantalum pentahalides with DMSO and DPSO. The reaction of pentachloride and pentabromide with sulphoxides involves the abstraction of oxygen atom from the sulphoxide, forming the corresponding metal oxytrihalide and halogen substituted sulphide. The oxyhalide then coordinates with the sulphoxide giving its complex. The overall reaction can be represented as follows:

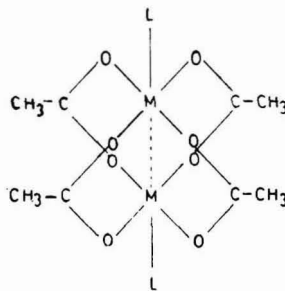


The metal complexes are characterized by chemical analysis, melting point and infrared spectra. The reaction of pentafluorides of Nb and Ta with DMSO, on the other hand, yields stable 1:2 adducts with DMSO⁷⁶, having the formula $\text{MF}_5 \cdot 2\text{DMSO}$ ($\text{M} = \text{Nb}$ or Ta). These complexes are probably seven-coordinated. MoCl_5 reacts similar to NbCl_5 , yielding the green complex, $\text{MoOCl}_3 \cdot 2\text{DMSO}$ ⁷⁸. The complex shows two weak bands at $13,800$ ($\epsilon = 19.0$) and $22,700\text{ cm}^{-1}$ ($\epsilon = 9.4$) corresponding to ${}^2B_2 \rightarrow {}^2E$ and ${}^2B_2 \rightarrow {}^2B_1$, respectively in a C_{4v} field⁷⁹.

Preparation and characterization of a series of nonhalo trirhenium(III) complexes, $\text{Re}_3\text{X}_9 \cdot 3\text{L}$ ($\text{X} = \text{Cl}$ or Br and $\text{L} = \text{phenyl-}, p\text{-tolyl-}, \text{benzyl-},$ or tetramethylene sulphoxide), have been reported by Cotton *et al.*⁹⁷. These complexes give fairly strong electronic absorption bands at about $13,000$ ($\epsilon = 500$), $19,500$ ($\epsilon = 1500$) and $22,300\text{ cm}^{-1}$ ($\epsilon = 800$). These electronic transitions seem to arise from Re_3X_9 group. Several $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ and $\text{Re}_3\text{Br}_9 \cdot 3\text{L}$ complexes are isomorphous and probably isostructural. The sulphoxide complexes of molybdenum, $\text{Mo}_6\text{Cl}_{12} \cdot 2\text{DMSO}$, $[\text{Mo}_6\text{Cl}_8 \cdot 6\text{DMSO}](\text{ClO}_4)_4$ and $[\text{Mo}_6\text{Cl}_{12} \cdot 2\text{DMSO} \cdot 4\text{CH}_3\text{SO}_3]$, have been studied by

Cotton and Curtis⁸². In these complexes, six ligands are coordinated to each $[\text{Mo}_6\text{Cl}_8]^{4+}$ unit. The infrared spectra of the Re and Mo complexes studied by Cotton and coworkers show oxygen-coordination of the ligand. Although both Re and Mo belong to higher transition series, they behave as class (a) rather than class (b) acceptors towards sulphoxides.

Rhodium(II) acetate forms 1:1 complex⁸⁰ with DMSO for which the dimeric structure (IX) is assigned.

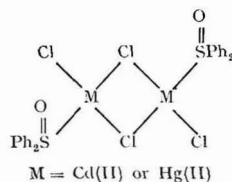


$\text{M} = \text{Cr}(\text{II}), \text{Cu}(\text{II})$ or $\text{Rh}(\text{II}), \text{L} = \text{H}_2\text{O}, \text{DMSO}$ or any monodentate ligand

IX

It has been suggested that the sulphur of DMSO is the donor atom in the rhodium acetate complex, as the S-O stretch occurs at 1086 cm^{-1} . The complexes of Pd(II) and Pt(II) chlorides with sulphoxides are most interesting, since the coordination of the ligand through sulphur has been well established in these cases.

The sulphoxide complexes of Zn(II), Cd(II) and Hg(II) (d^{10} ions) have been studied. Hexa-coordinated Hg(II) complexes, although rare, have been obtained by Carlin *et al.*⁸³. The complexes have the general formula $[\text{HgL}_6](\text{ClO}_4)_2$, where $\text{L} = \text{DMSO}, \text{TMSO}$ and TSO . Infrared spectra of the complexes show oxygen-coordination. The corresponding DPSO complex, however, could not be prepared. The DMSO complexes of Zn, Cd and Hg halides¹⁷ and mercuric thiocyanate⁸⁵ are known, in all of which DMSO is bonded through oxygen. The reviewers⁴² prepared $\text{CdCl}_2 \cdot \text{DPSO}$ and $\text{HgCl}_2 \cdot \text{DPSO}$, in which coordination through sulphur has been suggested from the infrared spectra. The dimeric structure (X) is proposed for the complexes:



$\text{M} = \text{Cd}(\text{II})$ or $\text{Hg}(\text{II})$

X

The infrared spectrum of $[\text{Cd}(\text{DPSO})_6](\text{ClO}_4)_2$ indicates sulphur-coordination ($\nu_{\text{S-O}} = 1050\text{ cm}^{-1}$), while

the corresponding Zn(II) perchlorate ($\nu_{S-O} = 995$ cm^{-1}) shows oxygen-coordination. It seems that Zn(II) behaves as class (a) acceptor, while Cd(II) and Hg(II) act as class (b) acceptors towards DPSO⁴².

An interesting Ag(I) complex, $\text{Ag}(\text{DMSO})(\text{ClO}_4)$, has been obtained. It shows an enantiomorphic solid phase transformation at 91°C., the enthalpy of transition being ~ 2.2 kcal./mole. The S-O stretch at 941 cm^{-1} indicates oxygen-coordination⁸⁵, although Ag(I) is known to be mostly a class (b) acceptor.

Complexes of Lanthanides and Actinides

Krishnamurthy and Sundararajan⁸⁸ have reported the preparation, infrared spectra, electrical conductance and molecular weight of DMSO complexes of La, Ce, Pr, Nd, Sm, Gd and Y perchlorates. The first four take 8DMSO molecules, while the rest, 7 ligands per metal ion. Infrared spectra of the complexes reveal that all the DMSO molecules are oxygen-coordinated and the perchlorate groups have tetrahedral symmetry. The molecular weight in freezing water shows complete dissociation of the complexes, while in freezing nitrobenzene, they dissociate into $[\text{Ln}(\text{DMSO})_n]^{3+}$ and 3ClO_4^- ions. Ramalingam and Sundararajan^{86,87} have investigated the DMSO complexes of lanthanum chlorides and nitrates, having the formula $[\text{Ln}(\text{DMSO})_n\text{X}_3]$, where $n = 4$ for light lanthanides and $n = 3$ for heavy lanthanides and $\text{X} = \text{Cl}^-$ or NO_3^- . The nitrate groups are coordinated to the metal, as revealed by the infrared spectra. The nitrate and halocomplexes are monomeric and almost non-conducting in acetonitrile, thus exhibiting coordination numbers of eight in lighter lanthanides and seven in heavier lanthanides and yttrium. The DMSO complexes of lanthanum perchlorates, having the general formula $[\text{Ln}(\text{DMSO})_n(\text{ClO}_4)_3]$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Y}, \text{Ho}$ or Yb), have also been investigated by the same authors⁸⁸. The electrical conductance, cryoscopic molecular weight and infrared spectra indicate a coordination number of six in all the complexes. The lower coordination number in DMSO complexes is perhaps due to the bulky nature of the ligand. In general, all the trivalent lanthanides behave as class (a) acceptors towards sulphoxides.

Among the actinides, the DMSO complexes of Th(IV) to Pu(IV) and dioxouranium(VI) have been mainly investigated. The DMSO complexes of thorium and uranyl perchlorates having the composition, $\text{Th}(\text{ClO}_4)_4 \cdot 12\text{DMSO}$ and $\text{UO}_2(\text{ClO}_4)_2 \cdot 5\text{DMSO}$, have been prepared^{88,89}. Edwards and Stritar⁹⁰ have considered that all the five DMSO molecules in the uranyl complex are coordinated, while Krishnan and Patel⁸⁹ have shown by the DTA and infrared spectral studies that four ligands are coordinated and one DMSO is lattice-held. The thorium and uranyl complexes, on heating around 180°C., lose the lattice-held ligand molecules, yielding $[\text{Th}(\text{DMSO})_6](\text{ClO}_4)_4$ and $[\text{UO}_2(\text{DMSO})_4](\text{ClO}_4)_2$ respectively. In the latter complex, bonding of the ligand seems to occur through sulphur of DMSO, as revealed by the infrared spectra. The DMSO complexes of tetravalent thorium, uranium and

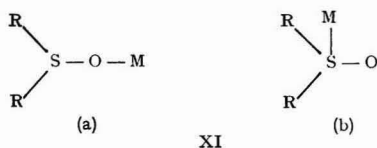
plutonium have been studied by Balakrishnan *et al.*⁹¹. The thorium(IV) nitrate complex, $[\text{Th}(\text{DMSO})_6](\text{NO}_3)_4$, is diamagnetic, while uranium(IV) and plutonium(IV) chloride complexes, $[\text{M}(\text{DMSO})_3\text{Cl}_4]$, are paramagnetic, with magnetic moments of 2.78 and 1.80 B.M. respectively at room temperature. This suggests that the unpaired electrons are in 6*d* and 5*f* levels respectively. From the decrease in the S-O stretch in the infrared spectra, the relative order of stability of the complexes has been given as $\text{Pu}(\text{IV}) > \text{U}(\text{IV}) > \text{Th}(\text{IV})$. The DMSO complexes of U(IV) and Th(IV) perchlorides and tetrabromides have been prepared from the corresponding tetrahalides or their methyl cyanide complexes, $\text{MX}_4 \cdot 4\text{CH}_3\text{CN}$, in acetone⁸⁹. The tetrachloro complexes, $\text{UCl}_4 \cdot 3\text{DMSO}$ and $\text{ThCl}_4 \cdot 5\text{DMSO}$, are non-conducting in nitromethane and monomeric in boiling acetonitrile, indicating coordination numbers of 7 and 9 respectively. The electrical conductance of the tetrabromo complexes in nitromethane increases with dilution. The vacuum thermal decomposition of the thorium complexes yields ThOCl_2 and ThOBr_2 at 450° and 400°C. respectively, while the uranium chloride complex decomposes to U_3O_8 , without giving any intermediate product. The uranium bromide complex gives an intermediate product, $\text{UO}_2\text{Br}_2 \cdot \text{DMSO}$, at 140-170°C. and finally a mixture of U_3O_8 and UO_2Br_2 . In these complexes, the coordination of the ligand occurs through oxygen of the sulphoxide. The infrared spectrum of the intermediate complex, $\text{UO}_2\text{Br}_2 \cdot \text{DMSO}$, however, has not been recorded. Recently, Bagnall and coworkers^{89a} have prepared DMSO complexes of tetrachlorides of Th, Pa, U, Np and Pu. The complexes of the general formula, $\text{MCl}_4 \cdot 7\text{DMSO}$ ($\text{M} = \text{U}, \text{Np}$ or Pu), have been obtained from hot DMSO, while complexes of the composition $\text{MCl}_4 \cdot 5\text{DMSO}$ ($\text{M} = \text{Th}$ to Np) and $\text{MCl}_4 \cdot 3\text{DMSO}$ (Th to Pu) are produced from acetone medium. The tris- and pentakis- complexes of Th and U are non-electrolytes in nitromethane and monomeric in acetonitrile. The infrared spectra of tris- and pentakis- complexes exhibit the S=O stretching frequency at 950 cm^{-1} , revealing oxygen-coordination of the ligand. In the $\text{MCl}_4 \cdot 7\text{DMSO}$ complexes, two ligand molecules are not coordinated.

Physico-chemical Investigations

Infrared Spectra and Molecular Structures of the Complexes

DMSO complexes—DMSO in vapour phase¹⁰⁴ shows a strong absorption band near 1100 cm^{-1} and, in neat⁹⁶ or CH_3NO_2 solution¹⁰⁵, near 1050 cm^{-1} . This band has been assigned to S=O stretching fundamental vibration. However, the normal coordinate analysis of DMSO and the calculation of potential energy distribution among the normal modes of vibration show that there is a considerable mixing of vibrational modes. The so-called S=O stretching mode at ~ 1050 cm^{-1} actually contains only half of the true S=O character and the rest is associated with rocking modes of methyl groups. A complete assignment of infrared bands of DMSO and its deuterated analogue, $\text{DMSO}-d_6$, has been made by Horrocks and Cotton¹⁰⁴.

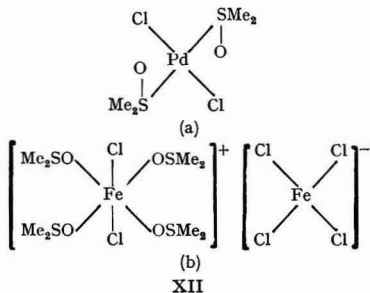
As already mentioned, in sulphoxide complexes, either sulphur or oxygen can be the donor to the metal. An infrared spectral study of the complexes can help distinguishing between the two possibilities. Cotton *et al.*¹⁰⁶ have discussed the effect of both the types of coordination on the infrared spectra. The coordination of sulphoxide through oxygen (XIa) would result in two opposing effects: (i) the kinematic coupling of S-O and M-O oscillators, which would lead to an increase in the S=O stretch, as compared to that of the free ligand; and (ii) a decrease in the $d_{\pi}-p_{\pi}$ bond order of S-O which would decrease the S=O stretch. Usually, the effect (ii) predominates over (i) and hence an overall decrease in S=O stretch is observed on oxygen-coordination. On the other hand, coordination through sulphur (XIb) would increase the $d_{\pi}-p_{\pi}$ donation and consequently increase the S-O stretch.



However, in these considerations, the mass effect of the acceptor atom and the 'back-bonding' from the filled metal d_{π} -orbitals to the vacant $3d_{\pi}$ -orbitals of sulphur have not been taken into account.

In the infrared spectra of most of the DMSO complexes, it is found that the band around 1050 cm^{-1} observed for the free ligand disappears, giving place to a new band around 950-1000 cm^{-1} . Cotton *et al.*¹⁰⁶ have assigned this band to S=O stretch of the coordinated DMSO and attributed the lowering to the oxygen-coordination of the ligand. However, in two of their complexes, $\text{PdCl}_2 \cdot 2\text{DMSO}$ and $\text{PtCl}_2 \cdot 2\text{DMSO}$, the S=O stretch occurs as a strong band at about 1115 and 1150 cm^{-1} respectively. This increase in $\nu(\text{S}=\text{O})$ is ascribed to sulphur-coordination in Pd(II) and Pt(II) complexes. The predictions regarding sulphur- and oxygen-coordination in DMSO complexes are well borne out by infrared spectral data and later confirmed by X-ray crystal structure determinations of $\text{PdCl}_2 \cdot 2\text{DMSO}$ and $\text{FeCl}_3 \cdot 2\text{DMSO}$ ¹⁰⁷⁻¹⁰⁹.

$\text{PdCl}_2 \cdot 2\text{DMSO}$ has a *trans*-square-planar structure (XIIa) with sulphur-coordination, the S-O bond length in the complex (1.475 Å) being slightly shorter than that of free DMSO (1.513 Å).^{107,109}



The complex $\text{FeCl}_3 \cdot 2\text{DMSO}$ is a dimer (XIIb) containing a *trans*-octahedral $[\text{FeCl}_2(\text{DMSO})_4]^+$ cation and tetrahedral $[\text{FeCl}_4]^-$ anion. The DMSO is coordinated through oxygen and consequently the S-O bond length (1.541 Å) is significantly longer than that in the free DMSO (1.513 Å).^{107,108} The corresponding DPSO complex having the composition $\text{FeCl}_3 \cdot 2\text{DPSO}$ is assigned a similar structure on the basis of electrical conductance and molecular weight determination in nitrobenzene⁹⁶.

Until recently, there was an ambiguity regarding the assignment of S-O stretch in DMSO complexes. The infrared spectra of the complexes show two strong bands, one at about 940-950 cm^{-1} and the other, 980-1010 cm^{-1} . Cotton *et al.*¹⁰⁶ have assigned the former band to S=O stretch in the DMSO complexes and the latter to methyl rock, although the possibility of coupling between the two modes is recognized from normal coordinate analysis of the ligand¹⁰⁴. The assignment of Drago and Meek¹⁰⁵ is just the reverse of that of Cotton *et al.*¹⁰⁶. Drago and Meek have pointed out that in the DMSO complexes, as the band at $\sim 1000 \text{ cm}^{-1}$ approaches the one around 950 cm^{-1} , the intensity of the latter increases. Further, the position of the band around 1000 cm^{-1} varies with the metal ion, while that around 950 cm^{-1} remains fairly constant. These observations have led Drago and Meek¹⁰⁵ to the assignment of the latter band to methyl rock. They have also noted that the increase in intensity and the broadening of the 950 cm^{-1} band may be due to the "borrowing of intensity" by coupling between the two modes of vibration. The extent of coupling increases as the frequencies come closer.

The controversy regarding the S=O stretch in DMSO complexes has been settled by studying the infrared spectra of deuterated complexes, $\text{UCl}_4 \cdot 3\text{DMSO}-d_6$ and $\text{UCl}_4 \cdot 5\text{DMSO}-d_6$, and their non-deuterated analogues^{89a}. The band around 950 cm^{-1} does not shift in deuterated and non-deuterated complexes. This band is, therefore, assignable to S=O stretch in complexes, supporting the assignment of Cotton *et al.*¹⁰⁶.

The deformation modes of CH_3 group of DMSO in the region 1290-1440 cm^{-1} are not much affected on complex formation¹⁰⁶. The C-S stretching frequencies at 660 and 690 cm^{-1} increase on oxygen- as well as sulphur-coordination. In the oxygen-bonded complexes, these bands are generally weak. However, this does not serve as a criterion to distinguish between the oxygen- and sulphur-coordination in sulphoxide complexes¹⁰⁶.

Selbin and coworkers³⁶ have investigated the infrared spectra of many DMSO complexes and from the decrease in the S=O stretch ($\sim 950 \text{ cm}^{-1}$ band) found that the stability of metal-oxygen bond increases in the following order: $\text{Hg} < \text{Ni} < \text{Mn} < \text{Co} < \text{Fe} < \text{Cd} < \text{Pb} < \text{Cu(II)} < \text{Al} < \text{Ga} < \text{Fe(III)}$.

According to Carrier and Weber⁴⁶, such a series cannot be given much importance in view of the complicated nature of $\nu(\text{S}=\text{O})$ in DMSO complexes.

DPSO and other sulphoxide complexes — The infrared spectra of all the sulphoxides⁴²⁻⁴⁶ show a strong band in the region 1025-1050 cm^{-1} , which is assigned to S=O stretch. As a result of self-association²³,

the position of this band in a given sulphoxide varies slightly depending on the medium. In oxygen-coordinated sulphoxide complexes, the S=O stretch is lowered. The infrared spectra of TMSO and its complexes, studied by Francis and Cotton⁴⁰, show essentially the same behaviour as DMSO complexes. Pd(II) and Pt(II) chlorides form sulphur-bonded and other transition metal ions oxygen-bonded complexes with TMSO. The infrared spectra of DPSO complexes of some metal perchlorates and chlorides have been studied by Gopalakrishnan and Patel⁴². The S=O stretch of DPSO occurs at 1045 cm.⁻¹ and this is lowered by about 50-70 cm.⁻¹ in most of the complexes, except those of Cd(II), Hg(II) and Pd(II). In the latter complexes, the S=O stretch occurs at 1045-1050 cm.⁻¹, without undergoing any significant shift from that of the free ligand. The infrared spectra of DPSO and its oxygen- and sulphur-bonded complexes are given in Figs. 1 and 2 respectively. It is suggested that the DPSO in Cd, Hg and Pd complexes is sulphur-bonded, while in other complexes it is oxygen-bonded. It is significant to note that the DMSO complexes of Cd(II) and Hg(II) are only oxygen-bonded, which indicates that DPSO shows greater tendency to coordinate through sulphur than DMSO. This may be associated with the electron-withdrawing tendency of phenyl groups, which would facilitate the back-donation of non-bonding *d*-electrons of class (b) acceptors (Cd, Hg, Pd, etc.) to the vacant *d*_π-orbitals of sulphur⁴².

Infrared spectral studies of DPSO, TMSO and PMSO complexes of many divalent and trivalent metal perchlorates and metal fluoroborates have been recently reported^{44,45}. The S=O stretch indicates coordination of the ligand through oxygen in all

the cases studied. Carrier and Weber⁴⁶ studied the infrared spectra of some octahedral transition metal perchlorate complexes of di-*n*-propyl-, di-*n*-butyl-, diphenyl-, and methyl phenyl sulphoxides. In the first three ligands, as there is no possibility of S=O stretch coupling with any other ligand vibration, the decrease in S=O stretch on complex formation is taken to represent the strength of metal-ligand bond. The following order of stability for the metal-sulphoxide complexes is obtained from the S = O stretch⁴⁶: Ni(II) ~ Co(II) > Fe(II) ~ Mn(II) ≥ Zn(II). The stability series similarly obtained for the ligands from their respective metal complexes is as follows: Bu₂SO > DPSO > Pr₂SO⁴⁶; TMSO > PMSO > DPSO⁴⁵.

It appears that the stability series obtained for the 3*d*-metal ions parallels the Irving-Williams stability series¹¹⁰. However, Van Leeuwen and Groeneveld⁴⁵ attribute the series to the variation in electronegativity of the metal ions.

Structural features from infrared spectra — From the infrared spectra of ZrO(ClO₄)₂.8DMSO, Th(ClO₄)₄.12DMSO and UO₂(ClO₄)₂.5DMSO, Krishnan and Patel^{38,39} have found both oxygen-coordinated and lattice-held DMSO molecules in the complexes. During the thermal treatment of the complexes, the lattice-held DMSO is lost around 185°C., yielding new complexes, in which sulphur-coordination of DMSO is suggested from their infrared spectra. The spectra of [UO₂(DMSO)₄](ClO₄)₂.DMSO and [UO₂(DMSO)₄](ClO₄)₂ are given in Fig. 3. The recently prepared actinide complexes MCl₄.7DMSO (M = U, Np and Pu) show two S=O stretching frequencies at 950 and 1045 cm.⁻¹, indicating respectively the presence of both coordinated and lattice-held DMSO in the complex^{88a}.

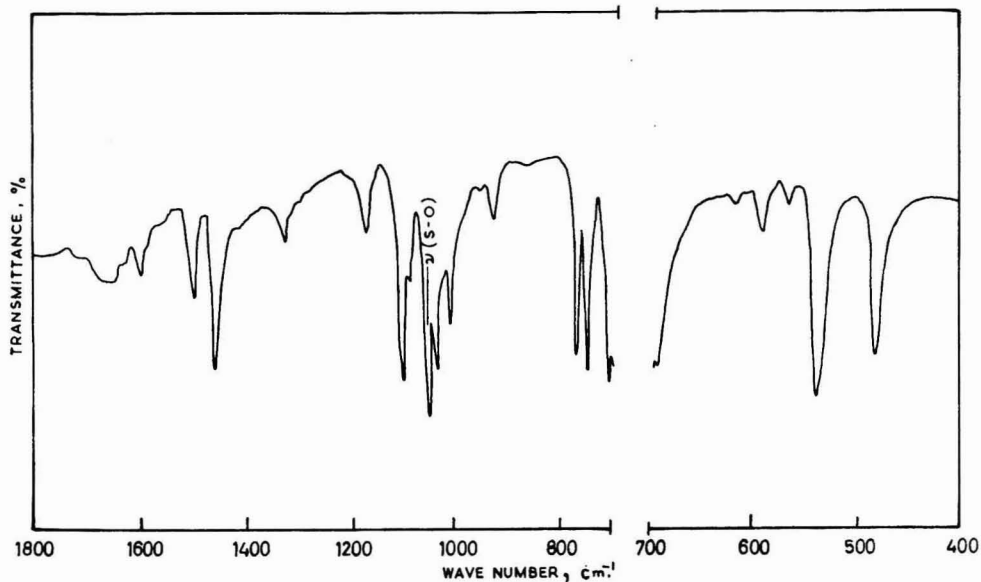


Fig. 1 — IR spectrum of DPSO

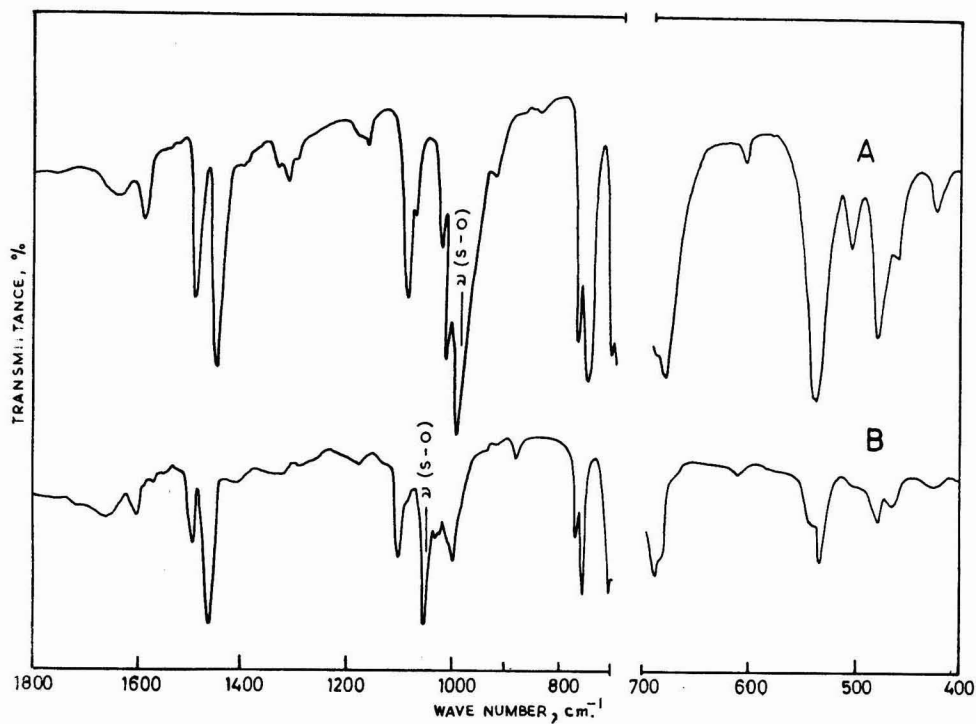


Fig. 2 — IR spectra of (A) ZnCl₂.2DPSO and (B) CdCl₂.DPSO

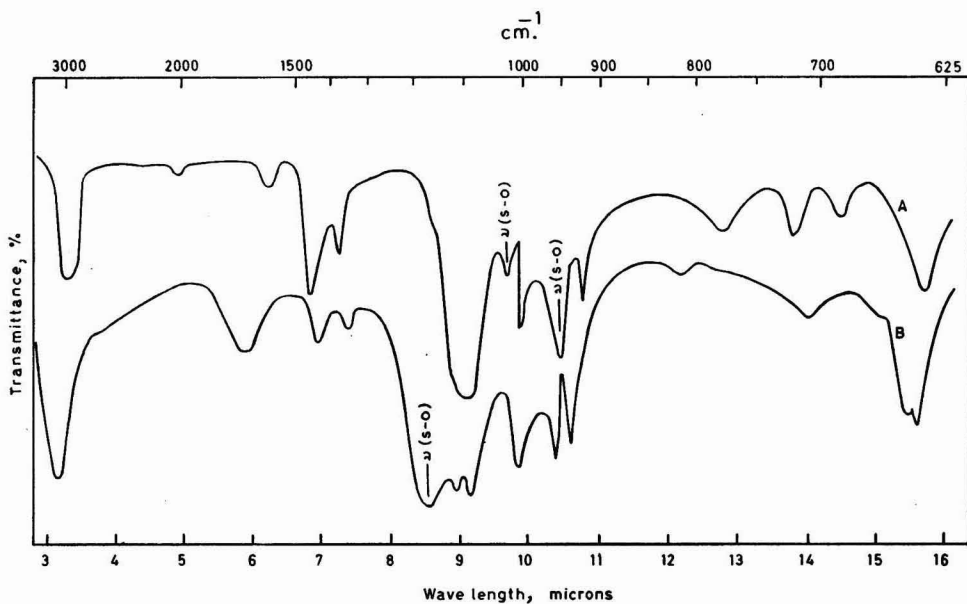
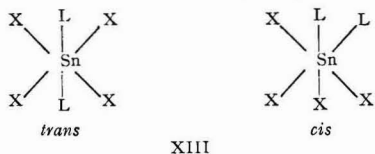


Fig. 3 — IR spectra of (A) UO₂.5(DMSO)(ClO₄)₂ and (B) UO₂.4(DMSO)(ClO₄)₂

The stereochemistry of $\text{SnX}_4 \cdot 2\text{DMSO}$ ($X = \text{Cl}, \text{Br}$ or I) and $\text{SnCl}_4 \cdot 2\text{DPSO}$ has been assigned from their infrared spectra⁶⁸. The complexes can have either *cis*- or *trans*-structures (XIII).



The coupling of two S-O stretching modes through the metal atom would give rise to symmetric and antisymmetric modes. In the *trans*-complex, the former mode would be infrared inactive, whereas in the *cis*-complex both would be infrared active. The presence of two S-O stretching bands at about 905 and 920 cm^{-1} in $\text{SnX}_4 \cdot 2\text{L}$ ($L = \text{DMSO}$ and DPSO) complexes indicates a *cis*-octahedral structure. The infrared spectra of *cis*- and *trans*-dithian disulphoxide complexes have been studied recently⁹². The complexes of the *trans*-ligand show only one $\nu(\text{S}=\text{O})$ at $\sim 950 \text{ cm}^{-1}$, whereas those of the *cis*-ligand show two $\nu(\text{S}=\text{O})$ at 950 and $\sim 1020 \text{ cm}^{-1}$. This observation reveals that the *cis*-ligand acts as a monodentate, while the *trans*-ligand is a bidentate.

Van Leeuwen and Groeneveld⁴⁵ have observed two S-O stretching modes in the hexa-coordinated copper(II) complexes of the type $[\text{CuL}_6]^{2+}$ ($L = \text{TMSO}, \text{PMSO}$ and DPSO), a strong band around 940 cm^{-1} and a fairly weak one around 1000 cm^{-1} . The appearance of two bands in these seemingly octahedral complexes is ascribed to Jahn-Teller tetragonal distortion of the octahedral $[\text{CuL}_6]^{2+}$ ion. The strong band arises from the strongly coordinated ligand molecules in the square plane and the weak band from the weakly coordinated axial ligands.

Far infrared spectra — Johnson and Walton⁴⁸ have studied the far infrared spectra (500-265 cm^{-1}) of fifteen DMSO complexes. The bands observed in the region 460-420 cm^{-1} are associated with M-O stretch. However, these bands are unlikely to be pure M-O stretch, since coupling with other ligand vibrations such as $\delta(\text{C-S-O})$, $\nu(\text{C-S})$, etc., is possible. The sulphur-bonded DMSO complexes, $\text{PdCl}_2 \cdot 2\text{DMSO}$ and $\text{PtCl}_2 \cdot 2\text{DMSO}$, also give a band in the region 400-450 cm^{-1} . It is, therefore, not possible to distinguish between sulphur- and oxygen-bonding from the far infrared spectra. The infrared spectra of some complexes having the general formula, $[\text{M}(\text{DMSO})_6]^{n+}(\text{ClO}_4)_n$, have been studied¹¹¹ with special emphasis on the region 600-200 cm^{-1} . A band assignable to metal-oxygen stretching vibration appears in the region 444-415 cm^{-1} for the divalent transition metal complexes, while for the Cr(III) complex, it appears at 529 cm^{-1} . The M-O frequency order observed is: $\text{Cr(III)} > \text{Ni(II)} > \text{Co(II)} > \text{Zn(II)} > \text{Fe(II)} > \text{Mn(II)}$.

In the oxygen-bonded DPSO complexes of transition metal perchlorates, a band around 400-435 cm^{-1} is assigned to M-O stretching mode⁴². The frequency of this band in the complexes varies as follows: $\text{Mn(II)} < \text{Co(II)} \sim \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$.

The far infrared spectra of monomeric $\text{InX}_3 \cdot 3\text{DMSO}$ ($X = \text{Cl}, \text{Br}$) complexes have been studied by Adams *et al.*¹¹² with a view to determining the stereochemistry of the complexes. The complexes can exist either as *cis* or *trans* form. The *trans*-complex, with local symmetry C_{2v} , is expected to give three infrared active $\nu(\text{In-X})$ bands, while only two are expected for the *cis*-isomer. The complexes actually give three $\nu(\text{In-X})$ bands in the range 300-350 cm^{-1} revealing the *trans*-structure. The strong doublet near 450 cm^{-1} is assigned to In-O stretching mode in the complexes.

Electronic Spectra and Magnetic Moments of Complexes

Cotton and Francis¹⁷ and Schläfer and Optiz³⁴ have recorded the electronic spectra of the first transition metal complexes of DMSO. The spectra of the sulphoxide complexes of metal perchlorates are similar to those of the other octahedral weak field complexes such as $\text{M}(\text{H}_2\text{O})_6^{n+}$. The magnetic moments also indicate the high spin nature of the complexes¹¹³. Schläfer and Optiz³⁴ have determined the spectrochemical splitting factor, D_q , and the Racah parameter, B' , for DMSO complexes from the electronic spectra of $\text{M}(\text{DMSO})_6^{n+}$ and compared the data with those of H_2O . Meek *et al.*¹¹⁴ have studied the electronic spectra of octahedral DMSO and TMSO complexes of Ni(II), Co(II) and Cr(III) and obtained D_q and β for these ligands. The electronic spectra of DPSO complexes of Cr(III), Co(II), Ni(II) and Cu(II) perchlorates have been studied by Gopalakrishnan and Patel⁴² and the D_q and β for the ligand determined. Recently, similar information on octahedral Co(II) and Ni(II) complexes of DPSO, MPMSO, TMSO and PMSO have been obtained both in the solid state and in solution by Van Leeuwen and Groeneveld¹¹⁵. The D_q and B' for some of the sulphoxide ligands together with water for the first transition metal complexes are given in Table 3.

The data given in Table 3 indicate that all the sulphoxides studied provide comparatively weaker crystal field (D_q) than water. However, the decrease in the Racah parameter, B , which represents the interelectronic repulsion energy of the metal ion in

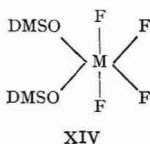
TABLE 3 — D_q AND B' FOR SOME 3d METAL SULPHOXIDE AND AQUO COMPLEXES

Ligand	Metal ion:					
	Cr ³⁺	Fe ³⁺	Mn ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺
	D_q (cm^{-1})					
DMSO ⁸⁴	1587	1250	710	850	781	1190
TMSO ^{114,115}	1575	—	—	830	775	—
DPSO ⁴²	1580	—	—	840	780	1175
H ₂ O ⁸⁴	1740	1370	780	930	850	1260
	B' (cm^{-1})					
Free ion	1030	1100	960	970	1080	—
DMSO ⁸⁴	680	660	780	~825	920	—
DPSO ⁴²	—	—	—	~825	920	—
TMSO ^{114,115}	—	—	—	~825	918	—
H ₂ O ⁸⁴	750	770	790	~950	940	—

the complexes, is more with sulphoxides than with water. Thus, water exerts higher crystal field than sulphoxides, as revealed by the D_q , whereas the sulphoxides are more 'nephelauxetic' (covalent), as indicated by the Racah parameters. Among the sulphoxides, it is difficult to draw any conclusions regarding their relative donor ability from D_q and B' values. Van Leeuwen and Groeneveld¹¹⁵ have proposed the following series from the D_q values of Ni(II) complexes: $H_2O > PMSO > TMSO > DMSO > DPSO$. On the other hand, the nephelauxetic ratio, β , ranges from 0.84 to 0.87 in all the sulphoxide complexes of Ni(II), indicating that the nephelauxetic effect of different sulphoxides is almost the same.

NMR and ESR Spectra of Complexes

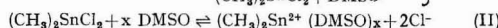
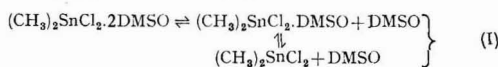
NMR spectroscopy has been employed for the characterization of *cis-trans* isomers and for the study of solution behaviour of some complexes. The ^{19}F magnetic resonance spectra of $TiF_4 \cdot 2DMSO$ and $SnF_4 \cdot 2DMSO$ at $-30^\circ C$. give two triplets of equal intensity, which indicate two types of fluorine environments of equal population. The data can be reconciled with a *cis*-octahedral structure (XIV) for the complexes³⁸. However, only a single fluorine resonance is observed at higher temperatures, indicating rapid dissociation of the complex making all the fluorines equivalent.



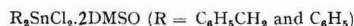
The proton magnetic resonance spectrum of $Al(DMSO)_6(ClO_4)_3$ in anhydrous DMSO, studied by Thomas and Reynolds¹¹⁶, reveals mainly two peaks, the prominent one for the bulk and the smaller one for the coordinated solvent at 25 cps downfield from the bulk solvent peak. The intensity of the peak due to coordinated DMSO is directly proportional to the concentration of the complex in the solution. The solvation number of $Al(III)$ has been calculated from the ratio of the line intensities of the coordinated and the bulk solvent using Swinehart and Taube's method¹¹⁷. The calculated solvation number is around six. Recently, the same workers¹¹⁸ have studied the proton resonance of $[Ni(DMSO)_6](ClO_4)_2$ and $[Co(DMSO)_6](ClO_4)_2$ in DMSO. The spectrum of each of the complexes at $40^\circ C$. shows one peak which is downfield by 463 and 585 cps respectively from the central proton peak of pure DMSO. Further, the first order rate constant for the exchange of coordinated and bulk solvent has been determined as functions of the concentration of Ni(II) (0.026-0.13M) and the temperature (16-43°C.). The energy of activation for the exchange of DMSO (~ 8 kcal. mole⁻¹) is lower than that for CH_3OH (15.8 kcal. mole⁻¹) and H_2O (11.6 kcal. mole⁻¹) in their corresponding Ni(II) complexes. The difference has been attributed to the lack of hydrogen bonding in DMSO, unlike

CH_3OH and H_2O . Assuming that the shifts in proton resonance of the coordinated solvent from the bulk solvent are contact shifts, the coupling constants for Ni(II) and Co(II) complexes obtained by the method of Happe and Ward¹¹⁹ are 1.9×10^6 and 1.2×10^6 cps respectively. The contact shifts are explained on the basis of metal electron delocalization on the ligand orbitals.

The NMR spectra of DMSO complexes of organotin halides, prepared by Langer and Blut⁵⁷, have been investigated by Kitching¹²⁰. In $CHCl_3$ solution, it has been found that the coupling constant J_{Sn-CH_3} is considerably higher for $(CH_3)_2SnCl_2 \cdot 2DMSO$ (~ 85 cps) than that for $(CH_3)_2SnCl_2$ (~ 70 cps). The coupling constant for $(CH_3)_2SnCl_2$ increases very much in DMSO medium (~ 110 cps). The data seem to indicate the following equilibria in $CHCl_3$ (I) and DMSO (II):



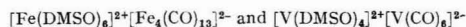
Similar measurements have been made on complexes having the formula



Relatively little work has been done on the ESR spectra of sulphoxide complexes. Lohmann and coworkers¹²¹ have studied the ESR spectra of chlorides of Mn(II), Fe(III), Cu(II) in DMSO and other non-aqueous solvents. In the case of $FeCl_3$ in DMSO, the formation of $[FeCl_4]^-$ species is indicated. This corroborates with the findings of Cotton *et al.*¹⁰⁸ that $FeCl_3 \cdot 2DMSO$ exists as $[FeCl_2(DMSO)_2][FeCl_4]$. The ESR spectrum of crystalline $CuCl_2 \cdot 2DMSO$ has been studied by Reddy and Srinivasan¹²². The observed g -values, $g_1 = 2.021 \pm 0.005$ and $g_{||} = 2.421 \pm 0.005$, indicate an ionically bound Cu(II) in the complex. The g_1 value is very close to the free spin value, which seems to indicate that the coordination around Cu(II) ion departs from a square-planar configuration with a distortion towards tetrahedral symmetry. The ESR spectrum of $[Cu(DPSO)_4](ClO_4)_2$ has also been studied¹²³. The data indicate an essentially ionic bonding between the metal and the ligand with Cu(II) in tetragonal environment.

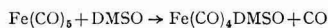
Reactions of Sulphoxides with Metal Carbonyls

The reaction of a metal carbonyl with an n -electron donor like DMSO can be brought about by either thermal or photochemical methods. The thermal reactions of $Fe(CO)_5$ and $V(CO)_6$ with DMSO in benzene have been studied by Hieber and coworkers^{124,125}. The reaction products as characterized by chemical analysis and electrical conductance are:

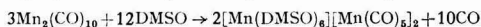


The photochemical substitutions of metal carbonyls or their derivatives with electron donors have been reviewed by Strohmeier¹²⁶ who has carried out pioneer work in this field. In general, two fundamental types of reactions have been observed.

(i) Substitution reaction: In this reaction, one or more CO groups of the metal carbonyl are replaced by the electron donor.



(ii) Base reaction: In this case, the metal carbonyl disproportionates producing metal carbonylates.



In both the type of products, sulphoxides coordinate to the metal through oxygen.

Conclusion

Although a variety of sulphoxides — aliphatic, aromatic and cyclic — have been employed as co-ordinating agents to the metal ions, very little work has been done with bidentate sulphoxides as ligands. The conditions under which oxygen- and sulphur-coordination of sulphoxides occurs to metal ions are not clearly established. Further work on these lines will be interesting.

Summary

Coordination compounds of non-transition, *d*-transition, lanthanide and actinide elements with sulphoxides as ligands have been reviewed. The preparation, physico-chemical investigations and the molecular structures of the complexes, as revealed from their infrared, electronic, nuclear magnetic resonance and electron spin resonance spectral studies, are discussed. The nature of oxygen- or sulphur-coordination in sulphoxide complexes is discussed on the basis of hard and soft donors and acceptors. Sulphoxides, in general, have a strong tendency to coordinate through oxygen in almost all complexes, except when the class (b) character of the metal ion is very prominent. Thus, Rh(II), Pd(II), Cd(II), Pt(II) and Hg(II) form complexes by coordination through sulphur.

Acknowledgement

The authors thank Prof. M. R. A. Rao for his interest and going through the manuscript. One of them (J.G.K.) thanks the Council of Scientific & Industrial Research, New Delhi, for the award of a senior fellowship.

Abbreviations Used

DMSO = dimethyl sulphoxide, $(\text{CH}_3)_2\text{SO}$
 DESO = diethyl sulphoxide, $(\text{C}_2\text{H}_5)_2\text{SO}$
 PrⁿSO = *n*-propyl sulphoxide, $(\text{C}_3\text{H}_7)_2\text{SO}$
 BuⁿSO = *n*-butyl sulphoxide, $(\text{C}_4\text{H}_9)_2\text{SO}$
 TMSO = tetramethylene sulphoxide, $(\text{CH}_2)_4\text{SO}$
 PMSO = p-pentamethylene sulphoxide, $(\text{CH}_2)_5\text{SO}$
 MPSO = methyl phenyl sulphoxide, $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{SO}$
 DPSO = diphenyl sulphoxide, $(\text{C}_6\text{H}_5)_2\text{SO}$
 BzSO = benzyl sulphoxide, $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SO}$
 ToSO = *p*-tolyl sulphoxide, $(p\text{-CH}_3\text{-C}_6\text{H}_4)_2\text{SO}$
 TSO = thioxane oxide
 DTM = dithian monosulphoxide
 TDTD = *trans*-dithian disulphoxide
 CDTD = *cis*-dithian disulphoxide
 DT = ethane-1,2-dithiolate
 ν = stretching vibration
 δ = bending vibration

D_q = spectrochemical splitting factor
 B = Racah parameter for gaseous metal ion
 B' = Racah parameter for the metal ion in the complex
 β = B'/B , nephelauxetic ratio

Note Added in Proof

Recently, the crystal structures of some complexes containing DMSO as a ligand have been determined. McPartlin and Mason¹²⁷ have solved the crystal structure of dichlorobenzylacetophenone-bis(DMSO) iridium(III). The iridium(III) ion has a distorted octahedral coordination, with two sulphur atoms from DMSO molecules, two chlorides and one oxygen and one carbon from the benzylacetophenone moiety. The two DMSO molecules are *cis* to each other and coordinate through sulphur atom. Langs *et al.*¹²⁸ have reported the crystal structure of dinitrato-bis(DMSO) palladium(II). The complex is approximately square-planar. The DMSO molecules are sulphur-bonded and they are *cis* to each other. The nitrate groups are monodentate. This structure is to be contrasted with that of $\text{PdCl}_2(\text{DMSO})_2$ which contains *trans*-DMSO¹⁰⁹. The Pd-S bonds in the nitrate complex are non-equivalent (2.231 and 2.253 Å.), which are significantly shorter than the equivalent bond lengths of 2.300 Å. observed in *trans*- $\text{PdCl}_2(\text{DMSO})_2$. In accordance with the *cis* structure of the nitrate complex, two $\nu(\text{S}-\text{O})$ frequencies are observed at 1136 and 1157 cm^{-1} . The related $\text{PtCl}_2(\text{DMSO})_2$ also shows two $\nu(\text{S}-\text{O})$ at 1134 and 1157 cm^{-1} , on the basis of which a *cis* structure is suggested for this complex. The crystal structure of *cis*-dichloro-*cis*-bis(DMSO)-*trans*-dimethyl tin(IV), determined by Isaacs *et al.*¹²⁹, shows a regular octahedral coordination around tin with *cis*-coordination of both the two chloro and two DMSO ligands, the latter coordinating through oxygen. The three crystal structures provide ample support to the thesis that DMSO coordinates through sulphur whenever the metal atom is 'soft' and through oxygen when the metal atom is 'hard'.

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REVIEWS

UNIFIED CIRCUIT THEORY IN ELECTRONICS AND ENGINEERING ANALYSIS by J. W. Stead & C. G. Mayo (Illiffe Books Ltd, London), 1965. Pp. 174. Price 42s.

The study of the behaviour of linear physical systems with general inputs (steady state and non-steady state inputs) is an important aspect of circuit theory. A number of mathematical techniques such as the Laplace transforms, the symbolic calculus, the Fourier integrals and transforms, the convolution integrals, and the operational calculus are available for study and analysis of linear physical systems. Of these, the Laplace transform method of converting the set of integro-differential equations of the physical system into a set of algebraic equations and the subsequent use of the inverse transforms for obtaining the final solutions is the one most commonly used.

In the present book the authors have developed the technique of Heaviside operational calculus to study and analyse the linear physical systems with general inputs. They have also compared the methods of operational analysis with other methods of analysis, bringing out the relative advantages.

The book consists of eighteen chapters and five supporting appendices. It may be broadly divided into two parts. The first part, which consists of Chapters 1-5, gives an introduction to the operational calculus of Heaviside and outlines the methods of determining the response of linear networks to general inputs. It also brings out the use of partial fractions and Heaviside shift theorems in the analysis of networks.

The second part of the book is essentially mathematical in its content. It begins with Chapter 6, which briefly mentions the various methods of approach for creative understanding of circuit problems. The next chapter discusses the step and impulse functions and paves the way for the fundamental integral transforms discussed in the following chapter (Chapter 8). The two subsequent chapters consider the inverse transforms, the generalization of shift theorems, the convolution integral and the question of convergence.

The responses of linear systems to sinusoidal inputs and arbitrary periodic inputs form the subject matter for Chapters 11 and 12. Chapter 13 extends the case for arbitrary periodic inputs into the case of infinite period and, thus, goes into the concept of Fourier integrals. The 'metrical' form of the Fourier integral as well as the approaches due to Bromwich and Van der Poll are discussed.

The general principles of feedback and servo mechanisms, the stability criteria in these systems and the use of operational calculus for the solution of feedback problems form the subject matter for Chapter 14. Chapter 15 compares operational calculus with symbolic and transform calculus and brings out the advantages of the first one, particularly the quick and direct way in which it gives

the results. Chapter 16 attempts to coordinate the ideas of previous chapters by the concepts of vectors and tensors, and Chapter 17 deals with coherence and continuity.

The last chapter, which is very useful, summarizes the important results discussed earlier. The five appendices of the book give useful additional details on partial fraction techniques, evaluation of polynomials, use of matrices, etc.

The authors have succeeded in bringing out clearly that the operational calculus due to Heaviside is a powerful technique in the analysis of linear physical systems and that it has the advantages of simplicity and direct approach leading to a clearer understanding of practical problems. The book would, therefore, be worth while for engineering students as well as for practising engineers interested in the analysis of linear physical systems.

D. L. SUBRAHMANYAM

PHYSICAL METHODS IN INORGANIC CHEMISTRY by Russell S. Drago (Reinhold Publishing Corporation Inc., New York, and Affiliated East-West Press Pvt Ltd, New Delhi), 1968. Pp. xviii+430. Price Rs 22.00

This is an Indian edition of an American text on physical methods in inorganic chemistry, dealing mainly with the spectroscopic methods. The book is of introductory character and is divided into two parts. Part I contains an elementary treatment of atomic structure and chemical bonding including ligand field theory. Part II covers a cursory chapter on molecular symmetry followed by general introduction to spectroscopy and various spectroscopic methods — electronic, vibration and rotation, nuclear magnetic resonance, nuclear quadrupole resonance, electron paramagnetic resonance and Mössbauer. Lastly, a chapter on mass spectrometry is also included. The principles, applications and limitations of the spectroscopic methods are discussed. The chapters on electronic, infrared and Raman, NMR and ESR spectroscopy will be helpful to those engaged in research work in inorganic chemistry. In addition, the six appendices dealing with magnetic properties of transition metal compounds, some selected character tables, Tanabe Sugano diagrams, methods for the calculation of Dq and β for octahedral and tetrahedral complexes, normal vibration modes for common structures and conversion of chemical shift data will be useful for ready reference.

The typographical mistakes present in the American edition are unfortunately carried over in the present edition also. A short account of instrumentation and techniques of all the spectroscopic methods would have been a desirable addition to the book.

Part II of the book can be recommended for the M.Sc. course in chemistry in universities. The book is written in a very clear and straightforward manner. A collection of exercises at the end of

each chapter will enable the student to understand and apply the subject matter described in the text while the list of references will enable him to explore the thrills of spectroscopic methods.

C. C. PATEL

SUBSTITUENT EFFECTS IN ORGANIC POLAROGRAPHY
by Peter Zuman (Plenum Press Inc., New York), 1967. Pp. xvi+384. Price \$ 17.50

This book is intended primarily for the physical organic chemists and presents an original attempt to meet greater and greater need for a unified presentation of the ever-increasing mass of experimental observations in the field of organic polarography. The author has developed a mathematical treatment of half-wave potentials of organic substances by using various forms of linear free energy relationships. The general validity of such relationships is substantiated by the fact that so far they have been shown to apply to the half-wave potentials of over 600 benzene derivatives, over 100 heterocyclic compounds and over 100 polycyclic substances, references to which are given here.

The general equation indicating a measure of the influence of the substituents on the half-wave potential of a system has the form $\Delta E_{1/2} = P + M_{\pi} + S$, where P represents the shift in half-wave potential, resulting from the change in polar activation energy increment; M_{π} , the shift in the half-wave potential due to change in the mesomeric (resonance) energy increment; and S , the shift in half-wave potential due to change in the total steric energy increment, the polar P , steric S and mesomeric M_{π} effects often being independent variables. Besides separating quantitatively the effect of polar, steric and mesomeric substituent effects, its special forms may be used not only to predict the half-wave potentials of the substances that have not been studied so far, but also to distinguish the type of mechanism.

The smallness of number of half-wave potentials known in the reaction series studied is a real obstacle. While the present author has remarkably succeeded in stressing the experimental conditions which must be observed for valid polarographic studies of organic structural problems, he has not stuck to the composition and stereochemistry of the transition state in his concept of 'mechanism'. This limitation is, however, quite general in polarography and does not reduce the utility of studies suggested by the author. It surely brings home the fact that the book is an outcome of an attempt, more to systematize the existing knowledge rather than to write an original treatise.

The polarographic behaviour of organic substances based on correlations between the polarographic half-wave potentials and their Hammett constants forms the basis of a unified classification system. The text is divided into nine chapters. The first two chapters include introduction and mathematical derivation of the general equation. The rest seven chapters, in succession, are devoted to benzene derivatives, monocyclic heterocyclic compounds, reaction series in which the electroactive group is directly attached to an alkyl or aryl substituent, effects of substituents in polycyclic heterocyclic

compounds, effects of substituents in quinonoid compounds and alicyclic systems.

Dr Zuman has aptly used his rich experience in making the subject matter readily intelligible to the reader. At places it is full of thought-provoking remarks. The book has about 115 diagrams and 66 tables and it is a compendium of polarographic information which would command a pride position in the personal book-shelf of every serious student of polarography, engaged in active research. The book has excellent printing and is remarkably free from errors.

H. L. NIGAM

CHEMISTRY AND INDUSTRY: APPLICATION OF BASIC PRINCIPLES IN RESEARCH AND PROCESS DEVELOPMENT edited by D. G. Jones (Clarendon Press, London), 1967. Pp. ix+217. Price 20s.

The purpose of this book is to show to young chemists how the chemistry they have learnt is applied in the chemical industry. This object has been achieved adequately by reviewing the stages in the development of a process and showing how understanding of chemical principles is involved at every stage to culminate in the successful manufacture of a chemical product. However, in effect, the book has proved that the knowledge of physical science, viz. chemistry, physics and mathematics, combined with social sciences like economics and full understanding of engineering principles is essential for the profitable development of a chemical process.

Besides an introduction, the book has seven chapters and an index. In the brief introduction, the editor, D. G. Jones, a Deputy Chairman, Imperial Chemical Industries Ltd, Heavy Organic Chemicals Division, sets out to define the object of the book and how the contributors have tried to achieve it. He concludes, significantly, that a success piece of process development will be the outcome of many disciplines.

Chapter I, 'The importance of physical chemistry', is written by A. E. Brown, Manager, Physical Chemistry Section, Research Department, Imperial Chemical Industries Ltd, Heavy Organic Chemicals Division. The basic considerations of a chemical process, viz. the equilibrium constant of a reaction, the reaction mechanism and the problem of separation are discussed adequately with examples. However, it is too much to swallow a remark like "It could, with some force, be argued that process chemistry throughout the whole range of research development and production consists simply in the application of principles of physical chemistry".

Chapter II, 'The chemistry of some organic processes', is authored by G. H. Twigg, Senior Adviser to the Controller of Research, B.P. Chemicals (UK) Ltd. The importance of determining reaction mechanisms is discussed. They enter into two of the main features of an industrial process, the rate and efficiency of the reaction. To illustrate the point, the mechanism of cumene-phenol process, oxidation of acetaldehyde, the Wacker acetaldehyde process and the oxidation of paraffins have been discussed.

'The chemistry of some inorganic processes' is the title of Chapter III written by J. Manning

of the University of New Castle-upon-Tyne. The importance of inorganic processes has been illustrated in this chapter by considering in some detail (1) the manufacture of ammonium sulphate from anhydrite and ammonia and (2) the oxidation of ammonia to give nitric acid.

Chapters IV and V have been devoted to the development of a process and have been authored jointly by H. M. E. Steiner and W. L. Seddon, the former from the University of Manchester and the latter, Technical Director, Petrocarbon Developments Ltd. The chapters are concerned with various aspects which are to be studied for designing, and for safe and efficient operation of a plant for producing a chemical product. Some of the topics covered are stoichiometry, thermodynamic and transport properties, kinetics, catalysis, optimization, products and coproducts formation, separation and purification, reactor design, materials of construction, etc.

The economics of chemical processes have been discussed in Chapter VI by A. Mott, Commercial Development Manager, Berk Ltd, and R. N. Quartano, Director, Heywood-Temple Industrial Publications. The chapter deals with the evaluation of chemical projects in order to determine at what cost the product is produced and whether the sales realization is enough to cover all costs.

P. V. Youle, Head of Central Investigation Group, Imperial Chemical Industries Ltd, Heavy Organic Chemicals Division, and part-time professor of Systems Engineering, University of Lancaster, has written the last chapter on process investigation of a chemical plant. The author has made a systems analysis of a paraxylene plant and laid down criteria on what to put into good experimentation for improving the plant operation.

This book, containing the contributions of experts with intimate personal knowledge of the areas of process development on which they have written, is truly exciting to read. There is much to learn in these few pages for all those who have anything to do with the development of a process from the laboratory to the successful operation of a production plant which makes profit.

N. R. KULLOOR

ANALYSIS OF INDETERMINATE FRAMEWORKS by N. M. Thadani (Orient Longmans Ltd, Bombay), 1967. Pp. 226. Price Rs 25.00

In this book, the author has presented the Kani method from first principles in a form that will appeal to the design engineer. The two main advantages of the Kani method are: (i) it involves only simple arithmetical operations, and (ii) the

method is general enough to be applicable to frames of all configurations loaded in any manner.

Chapter I is devoted to introducing some basic concepts. Important relations between bending moments and deformations are reviewed in Chapter II. Frames without sway are dealt with in Chapter III to be followed by continuous beams and frames in Chapter IV. Chapter V is devoted to symmetrical frames subjected to symmetrical loading (no side-sway). Frames subjected to side-sway but not acted upon by horizontal loads are discussed in Chapter VI. Chapter VII is exclusively devoted to the study of multi-storey frames subjected to lateral loads. Frames with unequal column lengths receive attention in Chapter VIII. Frames with through columns, which one comes across occasionally in practice, receive adequate treatment in Chapter IX. Other chapters are devoted to beams on elastic supports and influence lines.

The appended tables giving fixed-end moments and end-slopes are assembled in a convenient form for ready reference.

The book is characterized by extreme clarity of presentation throughout. The many worked out examples given in the book make it an ideal book for self-study.

Some examples are in the FPS system while others are in the MKS system. It may be an advantage to use the MKS system throughout in subsequent impressions of the book.

G. S. RAMASWAMY

PUBLICATIONS RECEIVED

HIGH ENERGY COLLISIONS OF ELEMENTARY PARTICLES by R. J. Eden (Cambridge University Press, London), 1968. Pp. xi+298. Price 55s. or \$ 9.50

INTRODUCTION TO MODERN OPTICS by Grant R. Forwles (Holt, Rinehart & Winston Inc., New York), 1968. Pp. x+304. Price \$ 11.95

AN INTRODUCTION TO FLUID DYNAMICS by G. K. Batchelor (Cambridge University Press, London), 1968. Pp. xvii+615. Price 75s. or \$ 13.50

THE PHILOSOPHY OF QUANTUM MECHANICS by D. I. Blokhintsev (D. Reidel Publishing Co., Holland), 1968. Pp. viii+132. Price Dfl. 32

BOTANICO-PERIODICUM HUNTIANUM edited by George H. M. Lawrence, A. F. Günther Buchheim, Gilbert S. Dantel & Helmut Dolezal (Hunt Botanical Library, Carnegie-Mellon University, Pittsburgh), 1968. Pp. 1063. Price \$ 30.00

GENERAL ENTOMOLOGY by M. S. Mani (Oxford and IBH Publishing Co., Calcutta), 1968. Pp. xii+501. Price Rs 18.00

Flat holograms for 360° view of an object

Conventional holograms present a three-dimensional image of only a limited angular view of an object. Earlier, the only way to obtain 360° view of an object, i.e. as if the object were being examined by the viewer moving around it in a full circle, was based on cylindrical holograms. In this method the object has to be surrounded by the film which is exposed by illuminating the object through the ends of the cylinder. The finished hologram can only be viewed without distortion by illuminating it in the same way. Besides, the resulting cylindrical holograms are larger than the object and are not very convenient for handling.

These disadvantages are overcome in a new technique for producing a succession of 3-D images of an object through 360°. This technique developed at the Bell Telephone Laboratories, USA, can achieve the effect of a cylindrical hologram simply if the viewer moves his head from side to side in front of a flat hologram.

To make a flat hologram with a 360° view, vertical strips of the photographic plates are exposed sequentially from left to right across the plate. A narrow slit in a mask in front of the plate allows only one strip to be exposed at a time. Each narrow strip is a complete hologram of one view of the object. The first view is exposed with the slit at the extreme left of the plate. The object is then rotated slightly, the mask is translated by one slit width to the right and another exposure is taken. Eventually, the entire plate is exposed and the object rotated through 360°.

These flat holograms which can be viewed with a monochromatic filler and a strong white light source can be incorporated with advantage in text-books, etc., providing a convenient way of presenting three-dimensional views of objects of complex structures [*Bell Lab. Record*, 46 (No. 3) (1968), 100].

Stronger magnets with rare earths

New permanent magnet materials which contain samarium or

NOTES & NEWS

cerium have been developed at the Bell Telephone Laboratories, USA. The new materials are based on compounds of cobalt, copper and either samarium or cerium.

These compounds have a very large magnetic saturation and a large degree of magnetic anisotropy. The new materials have much higher intrinsic coercive forces than any known materials of comparable magnetic properties. This high resistance for demagnetization is obtained in conventional materials only by casting or sintering them from powder. However, such alloys are hard and brittle and cannot easily be machined.

The new magnets are cast by melting in appropriate moulds, measured quantities of solid cobalt, copper, iron and either of the rare earth elements on a water-cooled copper hearth in an arc furnace filled with argon gas. The resulting materials are then magnetized.

The coercive force of these materials varies with the copper content in the system. In their high coercive force and the ease of fabrication, the new materials have advantage over the available materials used to make permanent magnets [*Bell Lab. Record*, 46 (No. 7) (1968), 240].

Microwave temperatures as colours

A new method, using liquid crystals, has been developed for viewing microwaves and changes in them in real time. In the new process, the microwave pattern is converted into a pattern of hot and cold areas on a membrane; these temperature variations are then converted into variations of colour by the use of liquid crystals.

The liquid crystals which are neither liquid nor crystal exhibit some properties of both states; they scatter light of different colours as their temperature is varied over a range of about 3°C.

The first model of the new real time detector consists of a 6 in. diameter Mylar membrane

stretched over a plastic holder. The membrane (about 0.002 in. thick) is covered with a thin metalized film to give it a surface conductivity of about 400 ohms per sq. in. The liquid crystals in a fast evaporating solvent are sprayed on to the membrane; after the evaporation of the solvent a coating of waxy liquid crystals is left behind. When the microwaves fall on the membrane, distinct oval concentric bands of colour appear as soon as the microenergy is increased to about 20 mW. As the temperature changes from high to low values, the colours change from blue to red via green, yellow and orange. A power spread of 7 db. results in a colour transition from blue to red. The process is reversible and, therefore, changes in the field can be monitored continuously.

The real time detector can find use in microwave holography, in the design of different microwave components, etc. [*New Scientist*, 39 (1968), 344; *Electronics*, 41 (No. 13) (1968), 118].

International years of the active sun

The International Geophysical Year (1957-58) was followed by the International Quiet Sun Year (1964-65). Now that the sun is entering another active period (1968-70), the solar-terrestrial scientists are beginning to carry out a programme of coordinated observation of solar activities and the title 'International Years of the Active Sun (IASY)' has been adopted for this period.

Under the IASY, a number of distinct projects, each broad enough to be justified as either a routine but essential monitoring programme or as especially appropriate to the period of maximum solar activity, have been proposed. The projects are as follows.

Monitoring of solar-terrestrial phenomena — It will supply much of the routine information needed for all other projects and will include plans for observation, at

least once each 24 hr, of slowly varying phenomena on the sun (e.g. sunspots and the magnetic field); nearly continuous monitoring for the more abrupt solar events; and the regular observations of geomagnetic variations, the ionosphere, auroras, airglow and cosmic rays.

Proton flares — Thirty-six scientific problems concerning flares have been listed for this programme which envisions designating a two-week period some time in 1969 for a short, intensive spell of investigations on an active proton centre on the sun which is very likely to evolve.

Disturbances in the interplanetary magnetic field configuration — This project includes observations relating to the origin, nature and the effects of disturbances of the interplanetary magnetic field.

Determination of the characteristics of the magnetosphere — The main aim of this project is to discover how to relate observations made from satellites and from ground instruments of the behaviour of the fields, plasma and particles in the magnetosphere and the adjacent interplanetary space.

Conjugate point experiments — If a geomagnetic field line forms a closed loop linking the northern and southern hemispheres, many effects (e.g. whistlers, auroras, very low frequency emissions, etc.) can be detected on the ground almost simultaneously in opposite hemispheres at the conjugate points at which the line intersects the earth's surface. The project aims at investigating these phenomena.

Electric fields in the magnetosphere — Several techniques that can help overcome the difficulties in measuring the fields are now being developed and this project hopes to carry out their inter-comparison.

Magnetic storms and polar disturbances — The programme aims at the improvement of magnetic observations at ground stations and rapid transmission of micro-filmed data to the world data centres.

Low latitude auroras — This programme calls for equipping present tropical airglow observatories with sensitive photoelectric photometers with which many barely subvisual auroras which occur could be detected.

Basic structure and dynamics of the upper atmosphere — The region of the atmosphere between the areas covered by meteorological rockets and by satellites (i.e. about 60-200 km.) is not adequately studied. Many important dynamic processes take place in this region. This programme aims to attack these problems.

Ion chemistry of the D and E regions — This project has been selected by specialists as deserving greatly increased research effort during the solar maximum. Detailed measurements, carefully coordinated simultaneously in both space and time during a relatively small number of selected occasions, will be carried out.

Sudden atmospheric disturbances — The programme is based on the determination, at various heights in the ionosphere, of the effects of soft X-ray radiations from solar flares on the ionosphere.

A new solar lake

A small (80×40 m.) lake with a peculiar hydrographic pattern has been discovered about 200 km. south of the port of Elat on the Red Sea [*Nature, Lond.*, **218** (1968), 860]. The lake has no open connection with the sea. Its sub-surface temperature is very high; the increase in temperature in the uppermost 1.5 m. is from 16° to 40°C. At a greater depth, the temperature increases to 48°C., coming down at the bottom (depth 5 m.) to slightly below 40°C. The salinity of the lake also shows a gradient, increasing from 42.6 g. of chlorine/litre at the surface to 90.7 g./litre of chlorine at the bottom.

This is clearly an example of a meromictic lake (of which there are only a few in the world) where a bottom water mass of high density (also called monimolimnion) is adiabatically isolated from the upper low density layer. A greenhouse effect is produced in which the monimolimnion accumulates heat from solar radiation.

In the case of the Elat Lake, the cool surface layer results from the inflow of sea water seeping through sand, while the high salinity may have resulted from natural accumulation through evaporation or it may be the residue of an old salt pan. The lake has a con-

siderable future in relation to desalination plants and low energy turbines in the Elat area in which both energy resources and fresh water are scarce.

One-step synthesis of adenine

In view of the increasing demand of adenine, a convenient one-step synthesis of adenine under pre-biotic conditions has been evolved using commercially available formamide and phosphorous oxychloride. A mixture of formamide and phosphorous oxychloride (1:2 mole ratio) was heated at 120°C. in a sealed vessel for 15 hr. The reaction mixture, after dilution with a large volume of water, was percolated through a column of active charcoal. After being washed with water, the column was eluted with 30 per cent ammonia and the elute evaporated to yield 40-50 per cent of practically pure crystals of adenine calculated on the basis of formamide used. If the above reaction is carried out in an open vessel, a large quantity of ammonium chloride separates, sublimes and condenses on the surface of the wall of the vessel and no adenine is produced [*Chemistry Ind.*, (1968), 1117].

Static method for determining blood yield stress

An improved method for determining blood yield stress independent of blood viscometry has been developed by using the settling technique [*Nature, Lond.*, **216** (1967), 1121]. In the existing methods, the yield stress is determined by extrapolating to zero shear rate from viscometry at higher shear rates. But the results are of doubtful value in view of the fact that blood does not seem to have a yield stress if sufficiently low shear rates are achieved.

In the new method, a capillary tube of inside diameter about 0.20 cm. is finely tapered to an inside diameter of 30 μ and the tip is broken to allow the tube to be filled with the liquid. This tapered tube is filled with blood and sealed at the bottom with clay and allowed to stand in a vertical position for 5-10 min. In this time, settling of cells is observed in a certain diameter above which no

settling occurs. This diameter represents the yield diameter (D_y). It is essential to note the first break in structure and to avoid trapping bubbles in the blood which disrupt the suspension structure. If allowed to stand too long, the cell suspension structure may slip and cause secondary breaks. The yield stress is calculated from the equation

$$\tau_y = \frac{(g)(\phi)(\rho_c - \rho_p)D_y}{4 \cos \theta}$$

where ρ_p is plasma density; ρ_c , cell density; D_y , yield diameter; τ_y , yield stress; g , gravitational constant; ϕ , volume fraction of red cells; and θ , the angle of taper which is very small in the drawn capillary tubes so that $\cos \theta = 1$.

The density difference between plasma and cells is determined by the copper sulphate method by noting the solution densities which just suspend plasma and centrifuged cells. This density can be measured to 0.001 g./ml. by this method. The density difference ($\rho_c - \rho_p$) does not change substantially for a relatively larger range of temperature and remains nearly constant. The density difference error is within 4 per cent. The yield diameter is measured by using a low power microscope with a graded eyepiece. A drop of immersion oil on glass tube aids the measurement.

Clonal growth of rabbit cells — A new technique

A new technique for the study of the clonal growth of cells, taken directly from rabbit, has been developed. The technique involves the preparation of a single cell suspension from the choroids of adult rabbit eyes using pronase digestion, gentle pipetting and centrifugation. This technique has yielded plating efficiencies averaging 40-50 per cent.

The nutritive medium, F_{12} , supplemented with 5 per cent fetal bovine serum and 10 per cent rabbit serum (F12FB5R10), stored frozen in the laboratory, without calcium, magnesium, iron, zinc and linoleic acid, which are added from concentrations just before the medium is to be used. The sera are also added just before the medium is used. The final medium can be

stored frozen, but storage in liquid form for more than 3 days should be avoided. The saline used for digestion contains NaCl, KCl, CaCl_2 , MgCl_2 , NaH_2PO_4 , glucose, NaHCO_3 and phenol red at the same concentrations as in medium F_{12} . The saline is adjusted to pH 7.3 with 0.1N HCl before use. Pronase (Calbiochem) 0.1 mg./ml. is dissolved in a simpler saline consisting of NaCl, KCl, NaH_2PO_4 , glucose and phenol red, all at F_{12} concentration and adjusted to pH 7.3 with 1.0N NaOH. Pronase is warmed to 37°C. in water-bath prior to use.

For the preparation of cell suspension from the choroids of adult female rabbit, intact eye balls, removed within minutes after killing the rabbits by cervical dislocation, are rinsed with sterile saline and cut into hemispheres such that one half contains all the retina and choroid, while the iris and cornea remain in the other half. The neural retina is gently peeled off and discarded. The choroid is gently pushed off the sclera. The choroid and adhering retinal epithelium are rinsed off of extra blood cells by treating with saline and cut into small pieces in a petridish containing 5 ml. of 0.1 mg./ml. pronase and incubated at 37°C. for 10-20 min. After incubation, the contents of the dish are gently pipetted to free adhering cells from chunks. The larger segments are separated by drawing the suspension into a vertically held pipette, allowing the fragments to settle into the tip of the pipette and gently discharging them into a minimum volume of suspension. The remaining cell suspension is discharged into a centrifuged tube containing 2 ml. of complete medium. The fragments are then digested for one additional minute in a second 5 ml. of pronase, pipetted gently and combined with the first cell suspension in the centrifuge tube. The combined suspension is centrifuged at 1200 r.p.m. for 30 sec. and then at 400 r.p.m. for 30 sec. to remove the tissue fragments. The cells are resuspended in 10 ml. of complete serum containing the medium and again centrifuged. This process is repeated and the cells are counted in a haemocytometer. The resulting suspension consists primarily of single cells

from choroid and red blood cells. The cell suspension is diluted with the complete medium to a final concentration of 1000 cells/ml. in a sterile test tube and 0.1 ml. of dilute suspension is added into each dish, resulting in an inoculum of 100 cells/dish. Inoculated petridishes are incubated at 37°C. for 7-10 days in a regulated atmosphere of 5 per cent CO_2 in air saturated with water vapours. Prior to the inoculation the petridishes are equilibrated under the same condition. After the incubation the medium is removed and colonies are fixed with 10 per cent formalin and stained with 0.1 per cent crystal violet for 10 min. Macroscopic colonies are counted and the plating efficiency is calculated as the percentage of inoculated cells which give rise to the colonies. The macroscopic colonies are estimated to have 500-1000 cells, suggesting a generation time of the order of 18 hr. Optimum clonal growth of rabbit choroid cells is obtained in the presence of a mixture of fetal bovine and rabbit serum [*J. Cell Physiol.*, **70** (1967), 275].

Central Fuel Research Institute, Dhanbad

The annual report of the Institute for 1967 highlights its work on the survey, assessment, preparation and utilization of coal. The fabrication of a formed coke pilot plant (12 tons/day) for the production of hard briquette coke from non-coking coal was completed and studies on the feasibility of production of formed coke from the lignite available in Thailand were undertaken. Laboratory and pilot plant blending tests were carried out for the selection of blends to be used in the Bokaro, Bhilai and Rourkela steel plants. Causes for the low yield of ammonia at the Durgapur steel plant and for the low yield of gas in the coke ovens of the Durgapur Projects Ltd have been ascertained.

In the Parbatpur block of Jharia coalfield (Seam XIII and above) coals suitable for metallurgical coke have been found. Strongly caking coal (20-25 per cent ash) has been found in the Mahal block.

Coal beneficiation studies and guarantee tests have been carried out for the NCDC, Hindustan

Steel Ltd, Durgapur Projects Ltd and Bokaro Steel Ltd. A statistical analysis of the performance of the public and private sector washeries in India has been taken in hand.

Water-resistant pellets suitable for domestic use have been prepared from coking coal and char fines using various inorganic and organic binders in a drum type pelletizer. Sufficiently strong shaped formed coke briquettes were prepared in a low pressure briquetting plant. Studies have been successfully carried out on the production of pig iron using varying proportions of formed coke (both fluxed and non-fluxed) from non-coking coals, iron ore and limestone.

Studies have been taken up on the production of electrode carbon from coal and petroleum coke. Encouraging results were obtained from the use of two semi-anthracite samples from Jammu and Kashmir, for the production of electrodes. The evaluation of optimum operational variables for the pilot plant production of active carbon has been carried out. The product has shown high gas adsorption property.

Methanation studies have been carried out for the production of a high calorific value gas from synthesis gas; 94 per cent conversion of CO-H₂ mixture in the feed gas has been obtained with a catalyst developed at the Institute. For the production of hydrogen from purified synthesis gas, a two-stage CO conversion unit has been operated with two different catalysts developed at the Institute and nearly 100 per cent conversion of CO has been achieved.

Design calculations for the different units of a slag bath gasifier (coal throughput 70 kg/hr) have been completed. An underfeed stoker suitable for installation in vertical boilers has been designed and fabricated; its performance has been found to be satisfactory.

Investigations on the conversion of organic sulphur in gases to H₂S, in the presence of an iron based catalyst, have shown that with hydrogen as carrier gas for organic

sulphur, the conversion efficiency lies between 94 and 99 per cent, while the corresponding range with low temperature carbonization (LTC) gas is between 77 and 94 per cent.

Using a catalyst, developed at the Institute and allowing higher contact time, more than 99 per cent conversion of anthracene to anthraquinone has been achieved. The Institute method for preparing resins (used as binders for hardboards) from tar acids and formaldehyde has been improved to have wider industrial applications.

The possibility of using LTC tar fractions for the recovery of benzol from coke oven has been explored. Different fractions of LTC tar have been tried and these have been found to possess benzol adsorption characteristics comparable to those of wash oils derived from high temperature tars. The recovery potentials of Neyveli lignite tar constituents like tar acids, tar bases and alkyl naphthalenes, currently in demand in the fine chemicals industry have been assessed. A process for the production of 4-cyanopyridine, an imported pharmaceutical chemical, from three different raw materials, viz. γ -picoline, 2,4-lutidine, and 2,4,6-collidine, has been developed. A process for the isolation of α - and β -methyl naphthalenes from drained naphthalene oil has been developed.

Studies have been undertaken on the preparation of plant hormones from different tar fractions containing naphthalene, alkyl-naphthalene, β -naphthol; a method for the preparation of polymeric surfactant from coal tar products has been developed. The surfactant prepared compares favourably with the commercial surfactant Flocal T/254.

Investigations have also been carried out on the production of (i) synthetic petroleum from high sulphur Assam coals by hydrogenation with simultaneous extraction of sulphur; (ii) organic fertilizer from lignite and coal by simultaneous oxidation and ammoniation; (iii) building materials from fly ash; and (iv) germanium from coal ash.

Information Sciences

Launched by the American Elsevier Publishing Co. Inc., New York, this new quarterly journal publishes papers (including some tutorial or expository in nature) in the general area of the information sciences. Emphasis is on work of deep conceptual significance and may be either experimental or theoretical or both. Annual subscription is \$ 24.00.

Announcements

■ *The Twenty-first Annual Scientific Meeting of the Palaeobotanical Society* will be held during 21-23 January 1969 at Birbal Sahni Institute of Palaeobotany, Lucknow. Further details can be obtained from the Registrar of the Institute.

■ *Unesco Science Prize* — The first \$ 3000 Unesco Science Prize for the year 1968 has been awarded to Prof. Robert Simpson Silver, James Watt Professor of Mechanical Engineering, University of Glasgow, UK, inventor of the multi-stage flash distillation process used in desalinating sea water.

■ *A Summer School in Thin Film Technology* will be held in the Department of Applied Physics, Andhra University, Waltair, during 15-30 April 1969. The topics to be covered include Vacuum coating equipment; Methods of preparation of films; Ellipsometry; Test equipment design and fabrication for study of film properties; Applications of thin films in various fields; and Preparation and performance evaluation of thin film products like full reflectors, beam splitters, interference filters, antireflection coating. Provision is made for practical demonstration and training. Candidates sponsored by universities, research institutions and industry will be admitted to the school. Full particulars may be had from the Head of the Department of Applied Physics, Andhra University, Waltair. The last date for applications is 15 February 1969.

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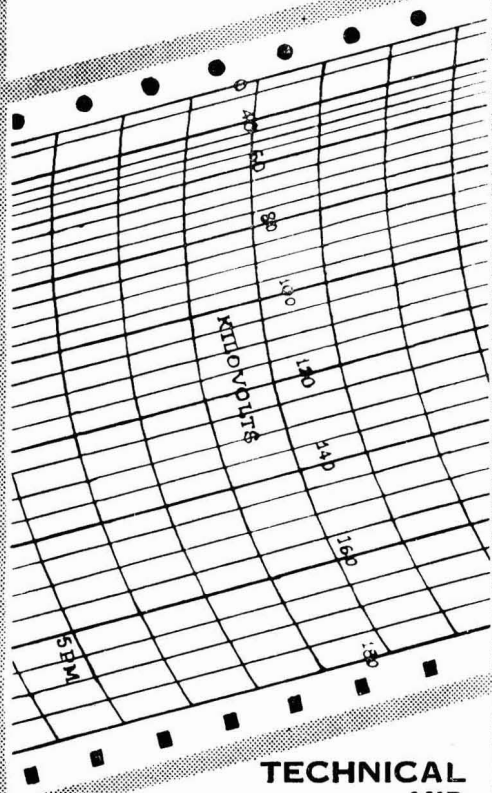
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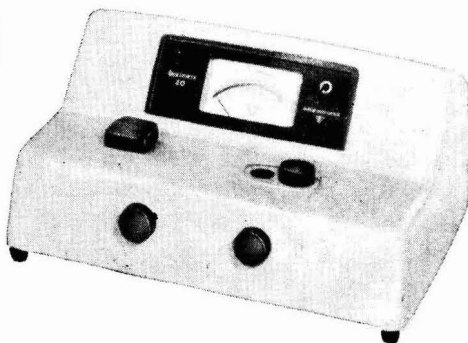
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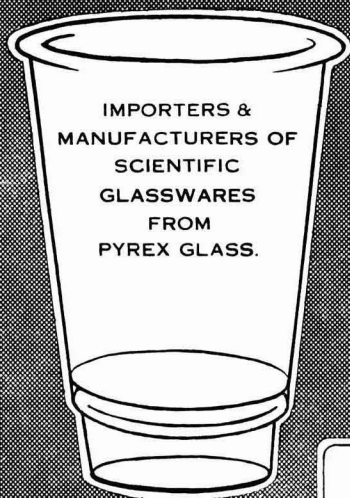
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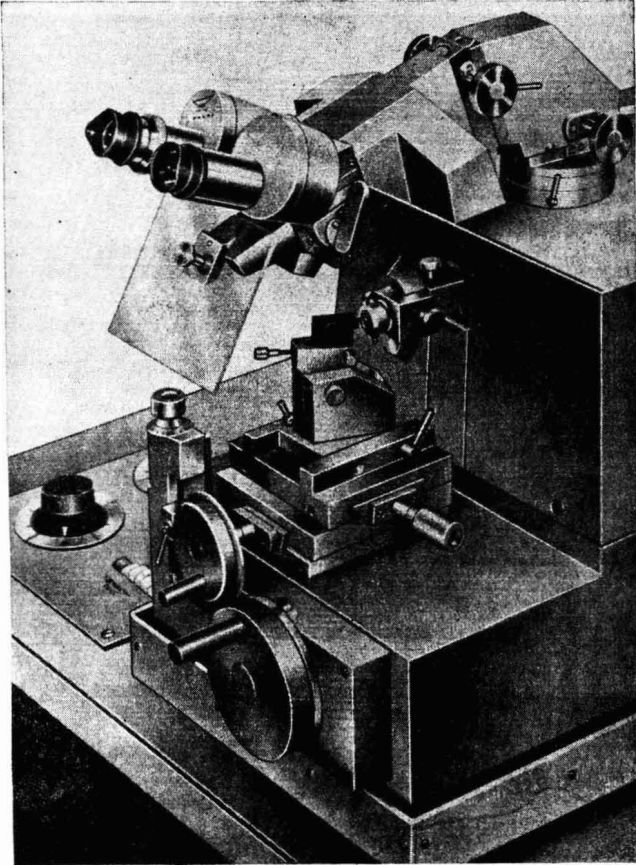
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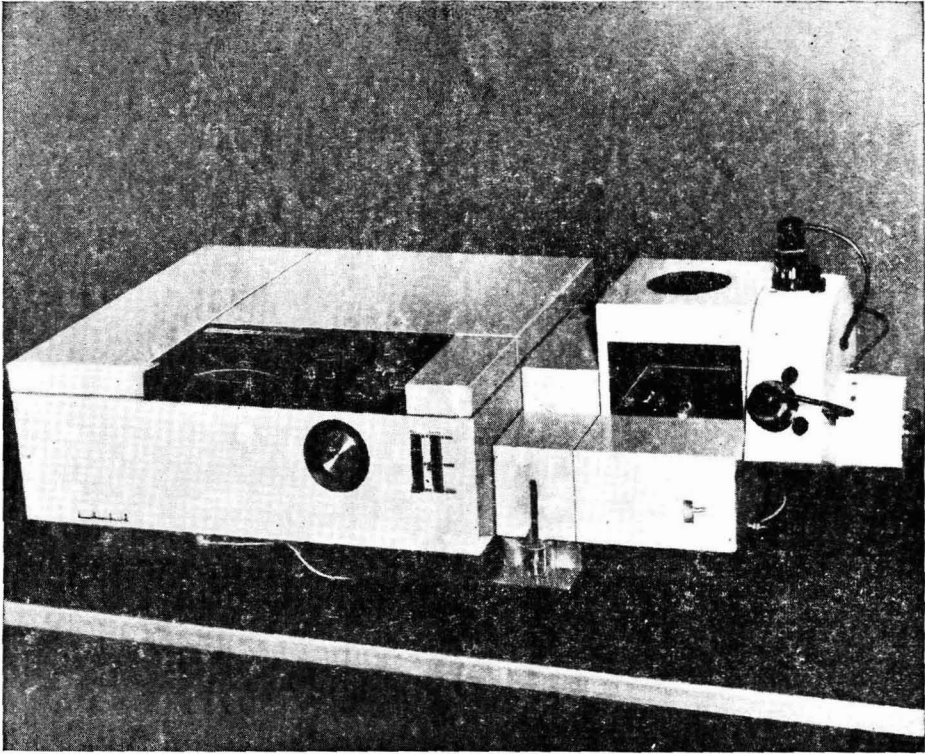
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