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July 1967

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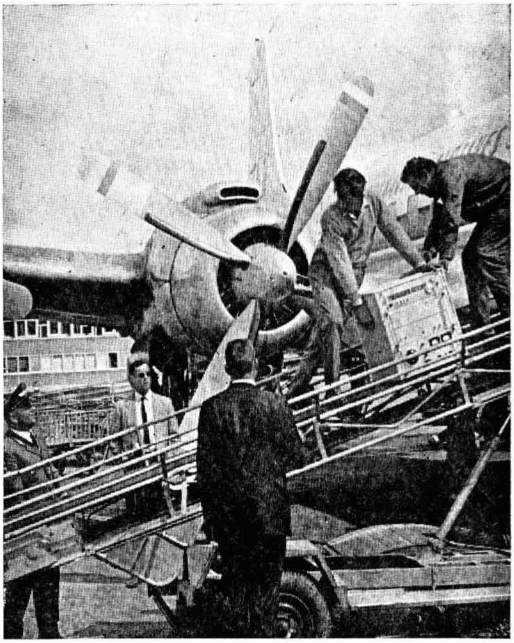

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CONTENTS

For Index to Advertisers, see page A21


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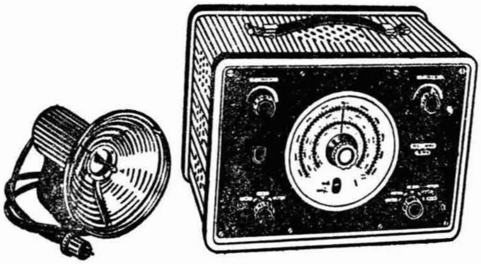

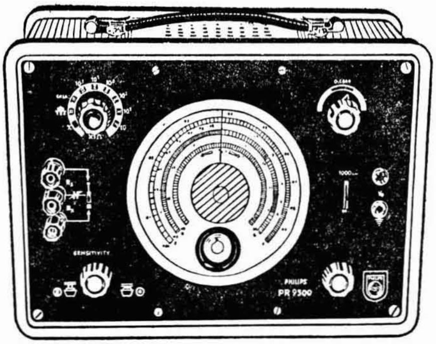

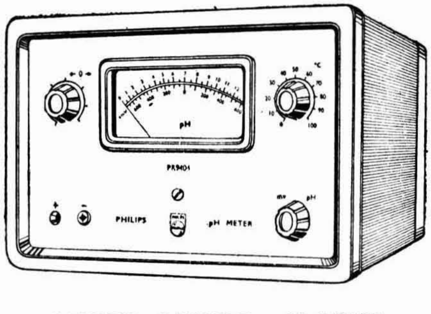

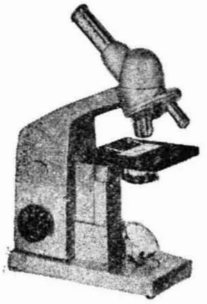

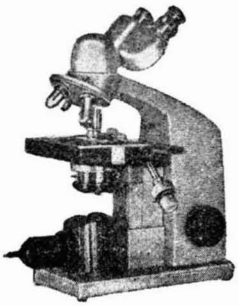

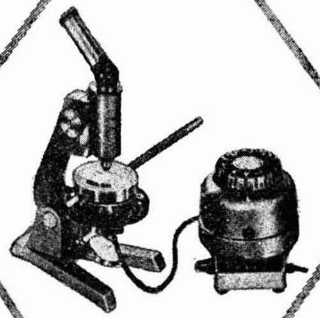

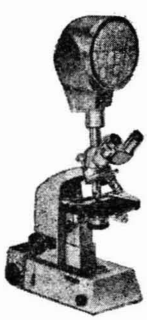

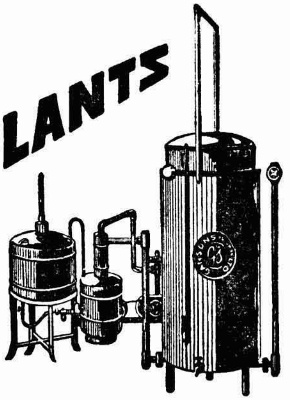

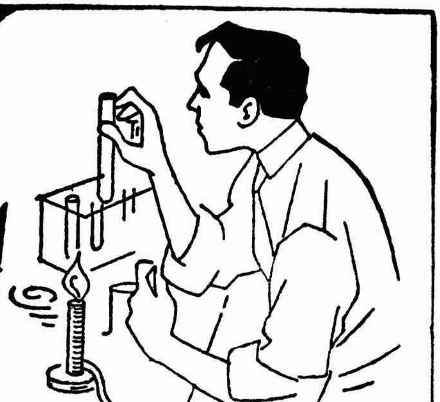

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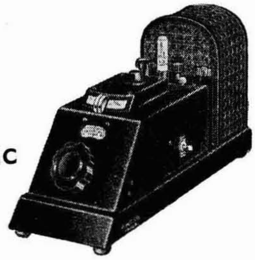

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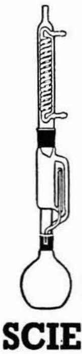

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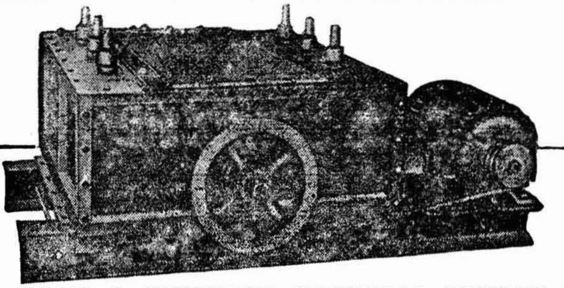

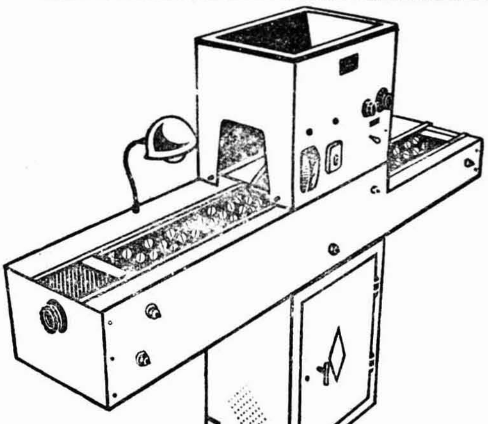

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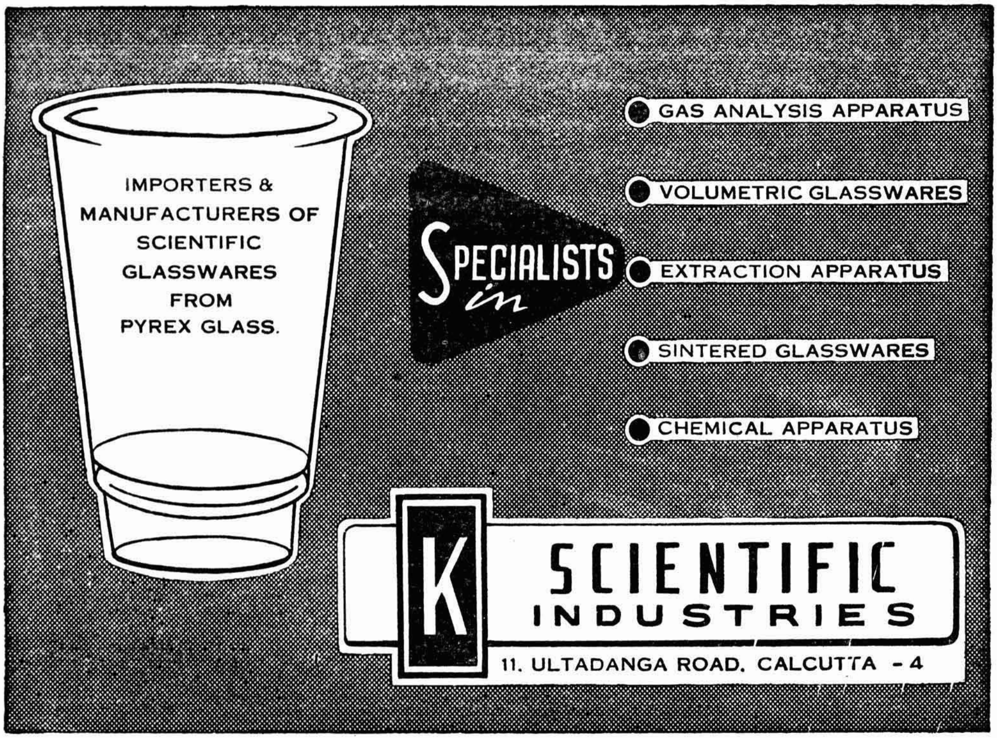

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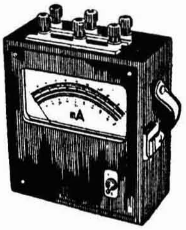

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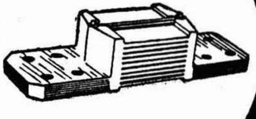

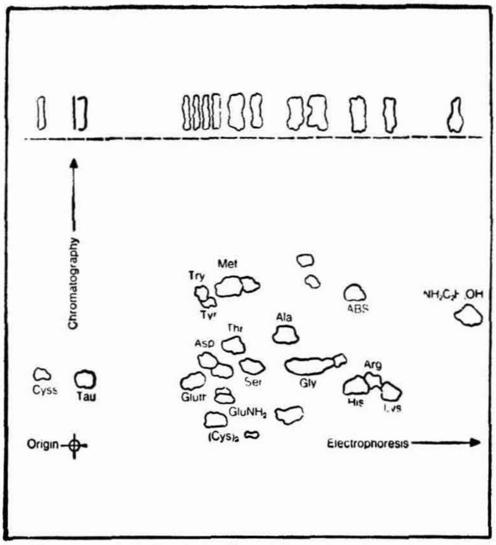
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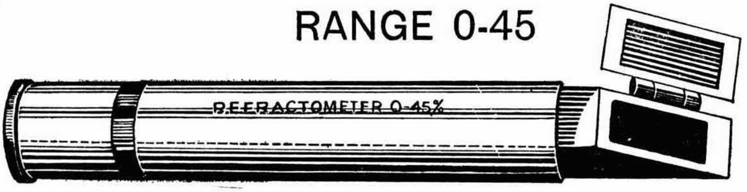

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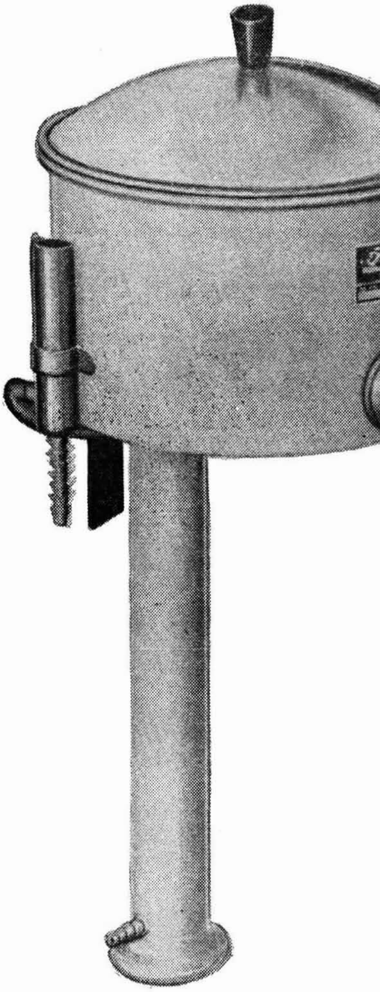

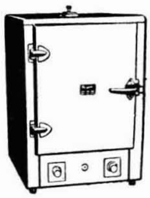

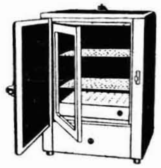

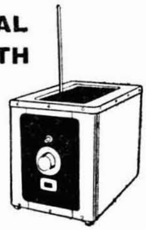

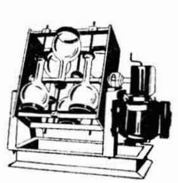

Current Topics

Scientific Periodicals in India

A REPORT* published by the Research Survey & Planning Organization of the Council of Scientific & Industrial Research deals with the growth of scientific and technical periodicals in the country since 1820 up to 1964. The survey covers the following aspects: (i) age of journals, (ii) distribution by subject, category, language and discipline, (iii) periodicity, (iv) coverage in abstracting periodicals, (v) subscription and circulation, (vi) time lag in publication of research communications, (vii) publication difficulties, etc. The data are based on replies received in response to a questionnaire.

Prior to 1947 there were less than 200 scientific and technical periodicals published in the country, of which 132 were research periodicals. In 1964 there were 607 periodicals, of which 426 were research periodicals; periodicals published by the learned societies, government agencies and others constitute 43, 24 and 33 per cent respectively.

Most of the periodicals published in the country today are in the English language, the number in the Indian languages being about 70; more than 50 per cent of the periodicals in the Indian languages are in Hindi. With the exception of a single periodical in Hindi, there are no research periodicals in the Indian languages, most of them being general or popular science periodicals. There are no periodicals in the Indian languages dealing with mathematics, physics, chemistry, botany and zoology, though there are a number of them in agricultural and medical sciences.

The survey draws attention to the lack of bibliographic, abstracting and review periodicals in specialized fields. Also, there are few periodicals dealing with the interaction of science, technology, industry and society, and with organizational, sociological and economic problems of science. The report also points out the need for a weekly or fortnightly periodical for quick publication of brief research communications. Difficulties encountered by editors and publishers are detailed, particularly paucity of funds for periodicals published by learned societies, lack of publication facilities, etc.

Since collecting the data for the report in 1964, some of the above lacunae have been filled. The *Indian Science Abstracts* published since January 1965 by INSDOC is a welcome beginning and INSDOC may very well undertake the job of publishing bibliographic and abstracting periodicals in specialized fields, provided there is a demand for such services. The need for a fortnightly journal for quick publication of brief research communications is being met by *Current Science* since January 1964. However, a more important requirement of the scientists in the country is perhaps a current awareness journal of the type of *Current Contents*. It may be worth while to make a selection of the most important journals in different areas which are regularly consulted by scientists in the country, the journals obtained by air and their contents pages speedily distributed.

The importance attached to review journals as essential tools for research workers is evident from two recent reports from USA and UK. The American Chemical Society will be issuing from January 1968 a new journal, *Accounts on Chemical Research*, comprising invited critical reviews by research workers of recognized accomplishment. The main objective of these reviews will be to place recent developments in perspective, both as to their connections with earlier work and their probable future significance. A similar facility, announced by the British Chemical Society, will be in the form of " Specialized Reports " reviewing the progress in limited areas of chemistry by experts. These are important developments and the possibilities of starting such publications in India should be explored.

Among the difficulties encountered by the publishing agencies, particularly learned societies, the major ones are paucity of funds, and inadequate publication and printing facilities. The cost of journals published by learned societies is higher because, as indicated in the report, their circulation is small and consequently their cost of production per unit is very high. This difficulty can perhaps be overcome if the learned societies pool their resources and set up common facilities which could provide editorial, production, sales and distribution, and other services.

Publication of scientific and technical periodicals of high standard is not only an expensive but also a highly specialized job, and the services of devoted workers both at the editorial and reviewer levels are essential. The problem of qualified and trained editors has to be tackled vigorously, and the standard of reviewing of papers by research workers, who act as referees, has to be raised. There is urgent need for a more rigorous weeding out of sub-standard research communications, both at the origin as well as at editorial and reviewer levels. This responsibility lies largely with the senior research workers in the country and the editors.

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*Rahman, A., Sen, N. & Sen Gupta, K. N., *Scientific journals in India — A study of their characteristics, Survey Report No.* 10 (Research Survey & Planning Organization, CSIR, New Delhi), 1967, pp. 52.

Report on the US Patent System

R. B. PAI

Patent Unit, Council of Scientific & Industrial Research, New Delhi 1

THE US President's Commission for modernization of the Patent System presented its Report[1,2] last November. The report deals not only with US patent reform but also with international patent matters. It acknowledges the unique service rendered by the patent system in stimulating the creative work of inventors and scientists and in translating the 'fire of genius' into commercially useful products and processes and expresses the view that the system is capable of continuing to provide an incentive to research, development and innovation.

Early Publication

An important function of the patent system is to bring about a speedy public disclosure of scientific and technological inventions. The system acts as a clearing house where the latest inventions would be readily available to the public properly classified and indexed. At present, US patent specifications are printed and published simultaneously with the sealing of the patent which may take up to five years or more after filing. The commission, therefore, recommends a new system of early publication of the application whereby pending applications will be published 18-24 months after filing, or promptly after allowance or appeal, whichever comes first. But an applicant may request even earlier publication. The report thus stresses the advantages of early publication which could prevent needless duplication of work, promote additional technological advances based on the information disclosed and apprise entrepreneurs of their potential liability.

Optional Deferred Examination

The introduction of an optional deferred examination system is recommended. This would enable official examination to be deferred for five years at the option of the applicant. Even a deferred application will be promptly inspected for formal matters and then published, but no prior art search will be made before a full examination is requested.

Any party, without being required to disclose its identity, may initiate an examination upon request and payment of fee.

Optional deferred examination is justified on the ground that it involves a wastage of examination, resources of the patent office to devote substantial effort to applications having little value. The applicant and his competitors are in the best position to select out applications which should be subjected by the patent office to prove novelty.

The Dutch Patents Act, 1963, provides for deferred examination, and the principle is also embodied in the draft European patent law of the EEC[3].

Ex parte Disposal of Prior Art Cited by the Public

After publication of the application, the public is to be given an opportunity to cite prior art to the patent office in a way which is inexpensive and does not reveal the identity of the party citing the references. Such prior art will be considered *ex parte* by the patent office. The applicant will be given an opportunity to rebut the determination or to narrow down the scope of the claim.

Another recommendation seeks to provide an *ex parte* administrative procedue for cancellation of claims which are clearly unpatentable. The procedure will be faster and less costly than court proceedings. Within three years of issuance of a patent, a third party can, upon payment of a relatively high fee, cite prior art and ask the patent office to review the validity of claims.

Twenty-year Term for Patents

The commission's view is that the term of a patent should be 20 years after its earliest effective US filing date, as against 17 years from the date of issuance at present.

The suggestion that the life of a patent should be 20 years is in contrast to the provision of the Indian Patents Bill, 1965, now lapsed, which sought to curtail the term of patents to 14 years from the present 16-year term and also sought to reduce the term to 10 years for food and drugs patents.

The following are some of the US commission's recommendations which will bring the US practice into closer conformity with most foreign systems.

First Come First Served

The report calls for a basic change in filing procedures based on the 'first to file' idea. Under current law, priority goes to the first person to invent. The new rule would abolish this principle. When two or more persons separately apply for a patent on the same invention, the patent would be issued to the one who is first to file his application. The reason is that the first to file is apt to be the inventor who first appreciated the worth of the invention and promptly acted to make the invention public. This would bring US practice into harmony with that prevailing in almost all other industrial nations.

Preliminary Application

There would be no grace period. For instance, at present, a US patent application may be filed within one year of publication. This is suggested to be abolished. Instead, it is proposed to have a preliminary application, which would only consist of a written description of the invention permitting filing even by a person having no special knowledge of patent law. An application complying with the present formal requirements must be filed within 12 months of the earliest preliminary application relied on.

Assignee Applications

The formalities for filing applications are to be simplified by permitting the owner of the patent rights to sign and file the necessary papers. Thus, either the inventor or the assignee may file and sign the applications, and omission of an inventor's name or the inclusion of the name of a person not an inventor, without deceptive intent, can be corrected at any time.

The foregoing principles that the patent should go to applicant to file first, that the application should be able to secure a filing date by filing a preliminary patent application and that either the inventor or the assignee should be able to file and sign both preliminary patent and complete applications are already there in the Indian Patents Act.

The present US practice of allowing an applicant to serially file continuing applications for an unlimited period and maintain his invention in secrecy is to be thoroughly revised.

Infringement by Importation

The suggestion that importation into the US of a product made abroad by a process patented in the US should be considered patent infringement, would bring the US law in line with Indian law in this matter.

Secrecy Delays

The term of a patent whose issuance has been delayed by reason of the application being placed under secrecy order shall be extended for a period equal to the delay in the issuance of the patent after notice of allowability. Some such protection was sought to be granted in this country by a clause of the Indian Patents Bill, 1965, by way of special provisions with regard to applications which got held up as they had references to atomic energy and now stand lapsed due to no fault of the applicants on the ground that the maximum period allowed under the present act has expired.

Standing Advisory Body

The commission is of the view that in a time of rapid development the patent system needs continuous review in the light of the nation's changing needs and the capacity of the system to respond to these needs. The institution of a standing advisory body composed of members with varied patent experience representing the principal areas served by the patent system has been recommended. Such a council would continually diagnose the health of the patent system and prescribe remedies in a quadrennial report.

International Action

The commission has urged that the United States should take a position in favour of the proposed revision[4] of the Paris Convention to include " Inventors' Certificates " for priority purposes. The USSR which joined the convention in July 1965, and some Eastern European member countries of the convention, issue Inventor's Certificates as well as Patents. According to the proposed revision, the date of an application for an inventor's certificate in one country would be recognized for priority purposes in all convention countries.

The commission's recommendations cover several other matters including government patent policy, reduction of litigation costs, patent office staffing, housing and financing, information retrieval, and international collaboration in the patent field. Particular emphasis is laid on the formation of regional patent system groupings, cooperative searching and mutually recognized patents as developments in the direction of achieving the ultimate goal of a universal patent.

Bills based on and incorporating many of the recommendations of the commission have been introduced in the US legislature[5].

References

1. *To promote the progress of . . . useful arts in an age of exploding technology* (Superintendent of Documents, Government Printing Office, Washington), 1966.
2. *Summary of the report on the patent system of the commission appointed by the President of the United States of America — Industrial property — 6th year, No. 1, January* 1967 (UN Bureau for the Protection of Intellectual Property, Geneva), 1967, 22.
3. LJUNGMAN, S., *Trends and harmonization of patent legislation of Europe — Lecture course on industrial property* (UN Bureau for the Protection of Intellectual Property, Geneva), 1965, 55.
4. *International convention for the protection of industrial property — Proposal for amending article* 4 *of the convention*, S/2 (Govt of Sweden and UN Bureau for the Protection of Intellectual Property, Geneva), 1966.
5. *Official Gazette of the United States Patent Office* (Commissioner of Patents, Washington DC), 1967.

Ninth International Conference on Coordination Chemistry

C. C. PATEL

Department of Inorganic & Physical Chemistry, Indian Institute of Science, Bangalore 12

NEARLY 850 chemists, interested in different aspects of coordination chemistry, met on 3 September 1966 in Zürich, Switzerland, to celebrate the birth centenary and pay homage to the late Prof. Alfred Werner, the pioneer of structural coordination chemistry. On this occasion, the first Werner gold medal was presented to Prof. J. C. Bailer (Jr), University of Illinois, Urbana, USA, for his contributions to modern coordination chemistry. Prof. G. Schwarzenbach, Federal Institute of Technology, Zürich, spoke on 'Werner and his accomplishments'. Prof. Bailer delivered a lecture on 'Advances in the stereochemistry of coordination compounds since Werner', while Prof. L. Horner, University of Mainz, Germany, spoke on 'Stereochemistry of organic compounds of the V group elements'.

The venue of the Ninth International Conference on Coordination Chemistry was St Moritz-Bad, in the picturesque valley of Swiss Alps from 5 to 8 September. From nearly 430 abstracts submitted, 190 papers were accepted for presentation at the conference. After a plenary lecture by an eminent coordination chemist daily, except on the third day when two plenary lectures were delivered, the conference got split into four parallel sessions for presentation and discussion of the papers. The following plenary lectures were delivered: (1) Prof. F. A. Cotton (Cambridge, USA) — Structure and bonding in metal carbonyls and related compounds; (2) Dr C. K. Jørgensen (Cologny, Switzerland) — Fractional charges, integral oxidation states and the nephelauxetic effect in the five transition groups; (3) Dr L. Malatesta (Milan, Italy) — Some aspects of the chemistry of iridium; (4) Dr K. B. Yatsimirskii (Kiev, USSR) — Spectral, thermodynamic and kinetic characteristics of rare earth complexes; (5) Dr D. H. Busch (Columbus, USA) — Macrocyclic complexes of transition metal ions; and (6) Dr A. D. Wadsley (Melbourne, Australia) — Composition, coordination and valency in lattice compounds.

The plenary lectures along with those delivered at the Werner Birth Centenary Celebrations are to be published in a special volume of the *Helvetica Chimica Acta*.

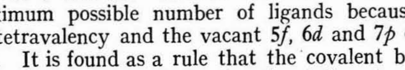
From the papers presented at the conference, one gets the impression that chemists are not lagging behind the physicists in the use of modern experimetal techniques for studies on coordination compounds. Nuclear magnetic resonance, electron spin resonance, Mössbauer spectroscopy, X-ray diffraction, etc., are being increasingly used by the chemists. There is a trend to classify the metals into groups A and B, the ligands as hard and soft, and correlate the stability of the complexes formed and the substitution reactions in terms of these classifications. Ligands with sulphur donor atoms are being increasingly used for complexation and so are the ligands with more complex nature.

Advances in Coordination Chemistry

It is difficult to point out the notable advances since the Eighth International Conference on Coordination Chemistry held in Vienna, Austria, two years ago. However, over half a dozen papers deserve special mention.

Electronic spectral and X-ray diffraction evidences are provided by Gray (California Institute of Technology, Pasadena, California) and Stiefel (Columbia University, New York) for trigonal prismatic structures of 6-coordinate complexes, formed by unsaturated bidentate sulphur donor ligands of the type benzene-1,2-dithiolate. Over a dozen such complexes of five different metals (V, Cr, Mo, W and Re) and four sulphur ligands have been prepared. These complexes are of fundamental importance, since so far only octahedral complexes with 6-coordination are known. The structure of $Re(S_2C_2Ph_2)_3$ has been solved by X-ray diffraction and is found to have a near perfect trigonal prismatic array of sulphur donor atoms. Chernyaev *et al.* (Institute of General & Inorganic Chemistry, Academy of Sciences, USSR, Moscow) have prepared thorium complexes with coordination numbers varying from 6 to 12, with the exception of 7 and 11. Thorium coordinates with the maximum possible number of ligands because of its tetravalency and the vacant *5f*, *6d* and *7p* orbitals. It is found as a rule that the covalent bonds between thorium and the functional ligand atoms are not equivalent. Evidences for temperature dependent dynamic Jahn-Teller effect in hexammine copper halides have been provided by electron spin resonace and X-ray diffraction studies carried out by Harkema *et al.* (Technische Hogeschool Twente, Enschede, Netherlands). At room temperature both the bromide and iodide complexes are cubic while the chloride is tetragonal. The transition temperatures for Jahn-Teller deformation of the hexammine copper complexes from cubic to tetragonal are: chloride 45-50°C., bromide 0-5°C., and iodide −90° to −100°C.

New bond isomers have been observed in Pt(II) complexes of acetylacetone by Nakamoto and Behnke (Illinois Institute of Technology Centre, Chicago). These isomers have been characterized by infrared spectra.



(a) (b) (c)

The type (b) has given two stereoisomers having yellow and green colours. Mixed type of bond isomers in the same molecule are also observed.

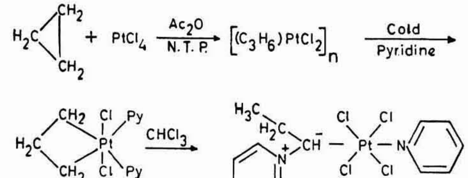
Effects of coordination of oxyanions such as carbonate, nitrate, phosphate, sulphate and perchlorate on their infrared frequencies have been interpreted from normal coordinate analyses by Britzinger (Basle University, Switzerland) and Grassman and Hester (University of York, England).

Wolfsberg-Helmholz modified MO calculations have been employed to obtain energy levels in certain tetrahedral tetroxo ions CrO_4^{2-}, MnO_4^-, MnO_4^{2-} and MnO_4^{3-} by Oleari *et al.* (University of Padova, Italy).

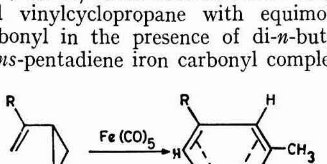
The papers presented at the conference can be classified as follows: (i) Organo-metallic compounds, (ii) Complexes of non-transition metals, (iii) Transition metal chemistry, (iv) Electronic and infrared spectra, (v) Complex compounds of ligands with H, B, P, As, Si, Ge, S and Se as donor atoms, (vi) Stereochemistry, (vii) X-ray crystal structure, (viii) Transition metal complexes of special interest, and (ix) Miscellaneous. Although an attempt has been made at classification of the papers, one will find that many of the papers can be grouped in more than one class. The research papers were presented in 4 days in four parallel sessions. It is, therefore, not possible to do justice to all the papers in a review like this. An attempt has been made here to give only the salient points in each group of the papers, that too from the subjective point of view.

Organo-metallic Compounds

Considerable progress has been made in the chemistry of compounds containing the metal-carbon bonds, from both the synthetic and structural aspects, and also from the numerous substitutional reactions carried out using these compounds. Modes of attachment of C_3 residues of cyclopropane to transition metals are described by Gillard *et al.* (University of Sheffield, UK). They have established the following reactions:

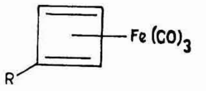


Sarel and Ben-Shoshan (Hebrew University, Jerusalem, Israel) have observed that on refluxing activated vinylcyclopropane with equimolar iron pentacarbonyl in the presence of di-*n*-butyl ether gives *trans*-pentadiene iron carbonyl complexes:



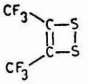
where R = phenyl, *p*-anisyl, *p*-chlorophenyl or cyclopropyl. The structures of the end products are assigned by infrared and NMR spectra.

Cyclobutadiene iron tricarbonyl complex has been prepared by Pettit *et al.* (University of Texas, Austin, USA) by reaction of $Fe_2(CO)_9$ with *cis*-3,4-dichlorocyclobutene. As in ferrocene, electrophilic substitution on the cyclobutadiene ring of the complex can be effected to produce



($R = COCH_3, COOH, CH_2Cl$, etc.). The cyclobutadiene iron tricarbonyl decomposes rapidly by electron transfer oxidizing agents such as Ce^{4+}, releasing free cyclobutadiene, which can be utilized *in situ* for other synthesis.

Reactions of bis-(trifluoromethyl) dithietene (a) with cyclopentadienyl metal carbonyls have been studied by King and Bisnette (Mellon Institute, Pittsburgh) and the compounds having the general formula $[C_5H_5MS_2C_2(CF_3)_2]_n$ [$n = 2$, M = V, Cr or Mo; (b) $n = 1$, M = Co or Ni] are reported. The reaction with $C_5H_5W(CO)_2NO$ in boiling methyl cyclohexane gives a dark green compound $C_5H_5W[S_2C_2(CF_3)_2]_2$ (c), while the major product in the reaction with $C_5H_5W(CO)_3H$ is $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ (d).



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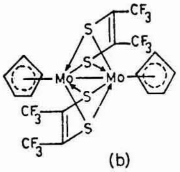

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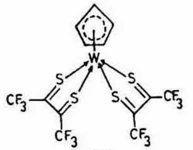
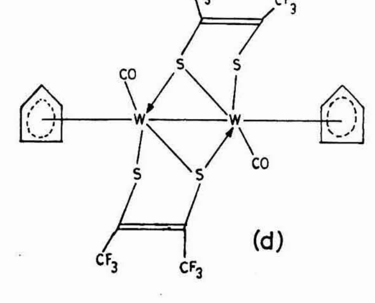


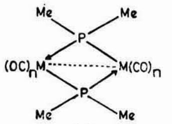
(c)



(d)

Electron diffraction studies on gaseous cyclopentadienyl (Cp) complexes of Fe, Mn, Pb and Sn (MCp_2) have been carried out by Almenningen *et al.* (University of Oslo, Norway). Whereas in iron and manganese complexes, the cyclopentadienyl rings are parallel to each other, they make an angle of 45° in lead and tin complexes. Pavlik and Klikorka (Institute of Chemical Technology, Pardubice, Czechoslovakia) have shown that the basicity of the ferrocene nucleus increases as ferrocene $<$ ethylferrocene $<$ 1,1′-diethylferrocene. It is further shown that the electronic structure of ferrocene changes on protonation, $[C_{10}H_{10}FeH]^+$.

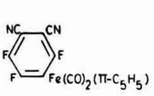
Thompson (Petrochemical & Polymer Laboratory, ICI Ltd, The Heath, UK) has described the reactions of some dinuclear carbonyl complexes containing phosphido bridges (e) with reagents such as halogens, phosphines and reducing agents. The role of solvents in these reactions is also noted.



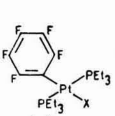
(e)

I, M=Mo; n=4
II, M=Fe; n=3

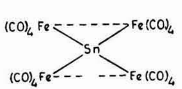
Bruce *et al.* (University of Bristol, UK) have prepared many fluoroaromatic-metal complexes (f) by reacting metal carbonyls with substituted perfluorobenzenes. The fluorocarbon derivatives (g) have also been made by treating complexes of zerovalent Ni, Pd and Pt with fluoroalkyl iodides. Reactions of iron carbonyl with tin compounds have yielded several new compounds with metal-metal bonds, as revealed by X-ray diffraction (h).



(f)



(g)

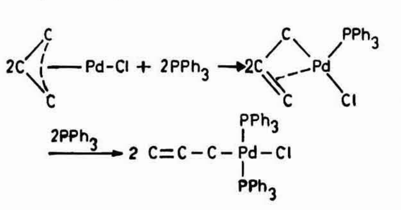


(h)

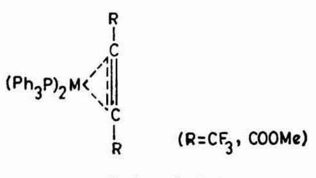
Titanium and zirconium compounds of the type $(C_5H_5)_2M(YR)_2$ [Y = S or Se and R = aryl, alkyl, H or bifunctional ring closing group] have been prepared by reducing $(C_5H_5)_2MCl_2$ with RYH by Köpf *et al.* (University of Wurzburg, Germany).

Sneeden (Monsanto Research SA, Zürich) has prepared sigma-bonded organo-chromium compounds of the formula $R_nCrCl_{3-n}(S)_x$ [R = aryl, aralkyl or alkyl, S = solvent molecules] and studied their stability and reactivity. These compounds act as potential sources of radicals and carbanions.

Powell and Shaw (University of Leeds, UK) have employed X-ray diffraction and PMR to show that some double bonding ligands like PPh_3 convert bridged halogeno-π-allylic palladium(II) complexes into σ-allylic complexes:



New acetylenic complexes of Pd and Rh(O)



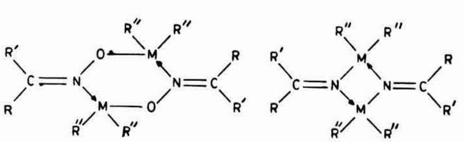
(R = CF_3, COOMe)

have been prepared by Maitlis *et al.* (McMaster University, Hamilton, Canada) and their structures assigned by IR and PMR spectra.

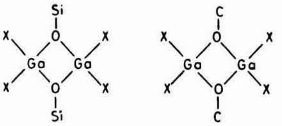
Diorganozinc compounds, R_2Zn, have been used by Noltes (Institute for Organic Chemistry, TNO, Utrecht, Netherlands) to get a variety of compounds having the formula RZnY (Y = a ligand with a functional atom O, S, N, P or As). Rapid exchange of ethyl groups between EtZnY and Et_2Zn has been indicated by NMR.

Complexes of Non-transition Metals

A large number of 6-coordinated indium complexes of F^-, OH^-, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{3-}, $P_2O_7^{4-}$ and $[Fe(CN)_6]^{4-}$ have been prepared and their physicochemical properties are studied by Deytschman (Institute of General & Inorganic Chemistry, Academy of Sciences, USSR, Moscow). Adducts of indium halides and thiocyanate with neutral ligands like pyridine, DMSO, 1,10-phenanthroline, etc., are prepared by Sowerby *et al.* (University of Nottingham, UK). Compounds of azomethine $[(RR'C=N)_nMX_{3-n}]$ and oxyazomethine $[(RR'C=NO)_nMX_{3-n}]$ of B, Al, Ga, In and Tl (X = alkyl, Cl or NMe_2) have been subjected to infrared, NMR and X-ray diffraction by Jennings *et al.* (Durham University, UK). The complexes are generally dimerized forming four- or six-membered ring structures, metal being 4-coordinated.



Mögele (Siemens-Schuckertwerke AG, Erlagen, Germany) has prepared gallium mono- and dihaloalkoxide, $XGa(OR)_2$ and $X_2Ga(OR)$. These compounds are found to be dimeric like gallo-siloxanes:



Gallo - siloxan Gallo - alkoxide

The halogens in the compounds can be replaced by alkyl groups, as

$$X_2GaOR + 2LiR \longrightarrow R_2GaOR + 2LiX$$

Smith and Wallbridge (University of Sheffield, UK) have dealt with the stoichiometry and relative stability of alkyl derivatives of aluminium with the general formula $(R_2AlX)_n$, where X = halogen, H, CN, etc., n = 2, 3 or 4. They have also studied adducts of $(Et_2AlX)_n$ with pyridine, trimethylamine and tetrahydrofuran. The acceptor tendency is found to increase as $R_2AlF < R_2AlCl < R_2AlBr < R_2AlI$, based on competitive displacement reactions.

Huber *et al.* (Technische Hochschule, Aachen, Germany) have prepared compounds of the type R_2MOX_2 [R = alkyl or aryl group, M = Ge, Sn, Pb(IV); HOX = 8-hydroxyquinoline] and determined their dipole moments. They have also prepared halogen containing compounds of similar type and characterized them by physico-chemical studies. The coordinating tendency is found to increase markedly as: $MR_4 < R_3MX \ll R_2MX_2 < RMX_3 < MX_4$. Schröder *et al.* (C.H. Boehringer Sohn, Ingelheim, Germany) have studied 5-coordinated crystalline complexes of triaryl- and trialkyl-tin halides with ligands having $\geqslant N \rightarrow O$, $\geqslant P = O$ and $>S=O$ groups as donors. A stability series of triorgano-tin adducts is given as: $Ph_3Sn \gg Me_3Sn > Et_3Sn > (iso\text{-}Pr)_3Sn \geqslant Pr_3Sn > Bu_3Sn$. The stability of the complexes with respect to the anions is: $NCS \gg Cl > Br > I$.

Transition Metal Chemistry

Complexes of heavier transition metals have not received as much importance as those of the 3*d* transition metals. Chromium(II) complexes of ethylenediamine (en) and diethylenetriamine (dien) have been prepared by Earnshaw *et al.* (Battersea College of Technology, London) and their magnetic and spectral properties are investigated. Influence of an anion on the configuration of nickel diamine complexes is discussed by Fargo *et al.* (Bedford College, London). Electronic spectral studies indicate that $[Nien_2(OH_2)_2](ClO_4)_2$ has *trans*-configuration while $(Nien_2(OH_2)_2](BPh_4)_2$ has *cis*-configuration (BPh_4 = tetraphenyl borate). Nickel complexes of 2-methyl-1,2-diaminopropane with different halide ions give a variety of coloured isomers.

Investigations on complexes of *o,o'*-dihydroxy azo dyes with chromium(III) are described by Idelson *et al.* (Polaroid Corporation, Cambridge, Mass., USA). It is observed that complexed dyes have higher light stability than the uncomplexed dyes. Optically active free dyes do not show Cotton effect whereas the complexed dyes show the effect in their optical rotatory dispersion curves.

Metal nitrosyl species in complexes has been variously represented as $M^-(NO)^+$, $M^0(NO)^0$ and $M^+(NO)^-$. To establish the type of the species, the nitrosyl compounds of iron and cobalt have been prepared by Feltham and Silverthorn (University of Arizona, USA) using *o*-phenylenebis-dimethylarsine(das) to stabilize the metal-nitrosyl moiety. Cobalt compounds of the type $[CoClNO(das)_2]^+$ are found to contain $(NO)^-$ coordinated to Co^{3+}. The best model for $[FeBrNO(das)_2]^+$ is suggested to be $Fe^{3+}NO^-$. These conclusions are based on infrared and electronic spectral studies. Mašek (Heyrovsky Institute of Polarography, Prague, Czechoslovakia) has studied the oxidation-reduction properties of coordinated nitrosyl group in $[M(CN)_5NO]^{n-}$ (M = Fe, Mn, Cr, V and *n* varies from 2 to 5) polarographically. NO^+ is found to be reduced in three irreversible steps:

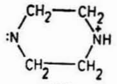
$$NO^+ \longrightarrow NO$$
$$NO \longrightarrow NO^-$$
$$NO^+ \longrightarrow NH_2OH$$

König (H. C. Ørsted Institute, Copenhagen, Denmark) and Madeja (University of Greifswald, Germany) have studied magnetic properties of a series of iron(II) bis-(1,10-phenanthroline) complexes of the type $[Fe\ phen_2X_2]$, where X = Cl^-, Br^-, OCN^-, etc. When X = NCS^- or $NCSe^-$ (N-bonded), the magnetic properties of the complexes show α spin-state equilibrium between $^5T_2$, the ground state for a high spin complex, and $^1A_1$ state, the ground state for a low spin complex. This equilibrium is supported by the temperature dependence of infrared and electronic spectra of the complexes. Analogous compounds of iron with 2,2'-dipyridyl and 4,7-dimethyl-1,10-phenanthroline have also been investigated. A Mössbauer study of some of the complexes is also carried out.

Mainly, complexes of neutral or negatively charged ligands have been studied so far. Quagliano and Vallarino (Florida State University, Tallahassee, USA) have investigated the donor properties of a number of positively charged ligands, with nitrogen as a donor of a primary, secondary and tertiary amine or an aromatic heterocyclic base such as

$:NH_2(CH_2)_3\overset{+}{N}(CH_3)_3$

(1)



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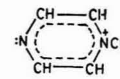
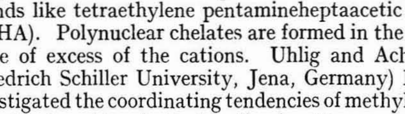


(3)

Such ligands (L) form solid complexes with dipositive metals of the 3*d* series, Ag(I), Pd(II) and Pt(II): $M(L^+)X_3$, $M(L^+)_2X_4$, $M(L^+)_4X_6$ and $M(L^+)_6(ClO_4)_8$ where X = Cl^-, Br^-, I^-, NO_3^- or ClO_4^-. The stereochemistry of the complexes depends on M^{II}, L and X. The positive charge has a marked effect on the coordinating ability of the ligands. Work on positively charged ligands with sulphur, arsenic or phosphorus as a donor atom is expected to yield interesting results.

Stability Constants

The trend is to determine the stability constants of complexes with bulky polydentate ligands. The formation of polynuclear complexes with EDTA and its higher homologues has been studied by Anderegg (Federal Institute of Technology, Zürich, Switzerland) by determining their stability constants using *p*H titration method. Mercury(II) complexes are found to be dimeric. Martell and Bohigian (Illinois Institute of Technology, Chicago) have determined the stability constants of Mg^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+} and La^{3+} complexes of multidentate ligands like tetraethylene pentamineheptaacetic acid (TPHA). Polynuclear chelates are formed in the presence of excess of the cations. Uhlig and Achilles (Friedrich Schiller University, Jena, Germany) have investigated the coordinating tendencies of methylenephosphonic acids of ethylenediamine like



$$^-HO_3PCH_2N^+H_2CH_2-CH_2-N^+H(CH_2-PO_3H^-)(CH_2-PO_3H_2)$$

with transition metals of the 3*d* series by the potentiometric method.

The donor-acceptor properties of arsenic(III) has been studied by Pettit and Royston (University of Leeds, UK) by preparing a series of complexes of substituted phenyl-di(carboxymethyl) arsines, with silver(I) and measuring their stability constants.

Stability constants of silver, cadmium, copper and zinc complexes of substituted pyridines, anilines and benzoic acids have been correlated with Hammett's σ-factor by da Silva *et al.* (Institute of Superior Technology, Lisbon, Portugal). Uranyl complexes of *d*- and *l*-aspartic acids (HA) have shown the existence of three species $UO_2(HA)_2$, $UO_2(A_2)^{2-}$ and $UO_2(OH)H_2^{3-}$ by Lai and Wey (Cheng Kung University, Tainan, Taiwan, China). The laevo complexes are stronger than the dextro complexes.

Studies carried out by Dove and Hallett (University of Nottingham, UK) on polymeric silver cyanide in liquid hydrogen fluoride have shown protonation, forming $(AgNCH)^+$. The reactions of Fe^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+} with dichloro- and monofluoroacetic acids have been studied potentiometrically by Pajdoweski and John (University of Wroclaw, Poland). Solvent and inductive effects have been investigated spectrophotometrically.

Substitution Reactions

Transition metal complexes of condensation products of 1,3-diiminoisoindoline and heterocyclic amines and imines undergo ligand reactions, which include protonation, alkoxylation and hydrolysis of the imino group [Robinson *et al.* (Olin Matheson Research Centre, New Haven, Connecticut, USA)]. These reactions are often accompanied by rearrangement.

The effect of coordination on the oxidation and reduction reactions of coordinated nitro group of $Co(NH_3)_n(NO_2)_{6-n}^{n-3}$ complexes has been studied by Beck and Dozsa (József Attila University, Szeged, Hungary). Kinetics and mechanism of substitution reactions of substituted bis-(ethylenediamine) cobalt(III) complexes in nonaqueous media have been investigated by Asperger *et al.* (University of Zagreb, Yugoslavia).

Electronic and Infrared Spectra

Schäffer and Glerup (University of Copenhagen, Denmark) have attempted to give a rough intensity rule for the spin-allowed transitions of $3d^3$ and $3d^6$ metal complexes. The intensity is shown to depend on the ligands rather than the substitutional distortion in the complexes; for example, hexammine complexes have practically the same intensity as chloropentammines, even though the latter complexes have no centre of symmetry. The dependence of the intensity on the ligands is in accordance with the hyperchromic series of Yamada and Tsuchida.

Selbin *et al.* (Louisiana State University, Baton Rouge, USA) have obtained the electronic spectra of low symmetry oxovanadium(IV) complexes. Their interpretation of the $d \longleftrightarrow d$ transitions differs from that proposed by Ballhausen and Gray on the basis of MO calculations.

Nyholm and Wooliams (University College, London) have studied the spectral and magnetic properties of $[MO_4]^{2-}$ anions of Mn, Tc and Re(VI). Infrared spectra show a considerable amount of double bonding in MO bonds; while their electronic spectra are difficult to interpret because of a number of bands and charge transfer absorptions, especially in TcO_4^{2-} and ReO_4^{2-}. However, the 12,000 $cm.^{-1}$ band in MnO_4^{2-} is assigned to a $d \longleftrightarrow d$ transition ($e \rightarrow t_2$).

Sen (Jadavpur University, Calcutta) has attempted to interpret the ultraviolet spectra of metal-biguanide complexes, with the help of simple LCAO-MO calculations for biguanide and the perturbation of the energy levels of biguanide by the metal *d*-orbitals. The shift of the spectral bands is explained on the basis of the assumed structures of the complexes.

The infrared spectra of the complex compounds have been studied mainly to know the coordination of ligands to the metal, the structure of the complexes and substitution as well as solvent effects and to determine force constants. Work in the far infrared region is gaining in importance as most of the metal-ligand bond frequencies occur in that region.

The force constants of $Au(CN)_2Cl_2^-$, $AuCl_4^-$ and $Au(CN)_4^-$ and of isoelectronic species $Co(CN)_6^{3-}$ and $Cr(CO)_6$ are calculated using the general quadratic valence force field by Jones (University of California, Los Alamos, USA). The significance of the force constants obtained is discussed.

Infrared and Raman spectra of aqueous solutions of dialkyl gold ions have been investigated by Tobias *et al.* (University of Minnesota, Minneapolis, USA). $[(CH_3)_2Au]^+$ indicates *cis*-configuration with an appreciable covalent bond character for $Au\text{-}OH_2$ group. Infrared spectra of perfluoromethyl phosphorus and arsenic complexes of transition metals of the type $Mn_2(CO)_8E(CF_3)_2X$ [$E = P$ or As, $X = I$, SCF_3, etc.] and $[Fe(CO)_3P(CF_3)_2]_2$ by Grobe (Technische Hochschule, Karlsruhe, Germany). The carbonyl group frequencies are assigned after Cotton. The ligand series based on substituents on P and As is given and structures are assigned to the complexes.

A ligand series obtained from the V=O stretching frequency of oxovanadium(IV) complexes having the same symmetry has been shown to parallel the nephelauxetic series by Patel and Sathyanarayana (Indian Institute of Science, Bangalore). A similar series for uranyl complexes, from the asymmetric stretching frequency of UO_2^{2+}, is also shown to compare well with the nephelauxetic series rather than the spectrochemical series.

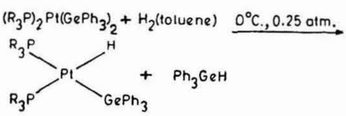
The infrared spectra of the addition compounds of substituted bis-salicyaldehyde ethylenediamine copper complexes have enabled Tanaka (Saga University, Japan) to arrange in a series the substituents in the order of complexing tendencies. The series depends on the nature of the solvents.

The spectra of cobalt(III) ammine complexes have been studied in the near infrared region (0·7-2·5 μ) by Kondo and Jørgensen (Cyanamid European Research Institute, Cologny, Switzerland). Far infrared spectra of hexahalo metal complexes of the type $(MX_6)M'_2$ [$MX_6 = PtCl_6$, $SnBr_6$, $IrCl_6$, etc., $M' = K$, Cs, NH_4^+, etc.] have been studied by Debeau (Laboratoire des Recherches Physiques, Sorbonne, France) while those of Se, Te and Sn(IV) by Straughan (University of Newcastle-upon-Tyne, UK). Cleare and Griffith (Imperial College, London) have also investigated far infrared spectra of hexammine and nitrosyl complexes of group VIII metals.

Complex Compounds with H, B, P, As, Si, Ge, S and Se Donor Atoms

Hydrogen Donor

Ginsberg (Bell Telephone Laboratories, Murray Hill, New Jersey, USA) has reported $[ReH_9]^{2-}$ and $[TcH_9]^{2-}$ in which metal atoms are coordinated by hydrogen only. M_2ReH_9 [$M = K^+$, Na^+, Li^+ or $(alkyl)_4N^+$] reacts with a number of mono- and di-tertiary phosphines and arsines in the absence and presence of solvents (alcohols and ethers), yielding several new complexes with Re-H bond. Infrared and NMR spectral evidences are used for the assignment of structures. Glockling (University of Durham, UK) has prepared complexes containing Pt-H and Pd-H bonds by



Both the platinum and palladium complexes take up hydrogen from molecular hydrogen.

Boron Donors

Nöth and Schmid (Münich University, Germany) have prepared $(CO)_4CoBX_2$ (a), $R_3P(CO)_3CoBX_2$ (b), $(PF_3)_4CoBX_2$ (c), $(diphos)_2Co(BX_2)_2$ (d), $(diphos)_2CoYBX_2$ (e) and $(diglyb)_2(R_3P)CoBX_2$ (f) [diphos $= Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2$ or $o\text{-}C_6H_4(PMe_2)_2$, diglyb $= Ph_2B$ substituted dimethylglyoximate]. Complexes (a), (b) and (c) are prepared by reacting a suitable boron halide with an alkali metal salt of cobalt hydride. The complex (d) can be prepared by

$$2(diphos)_2CoH + 2ClBPh_2 \longrightarrow (diphos)_2CoCl_2 + (diphos)_2Co(BPh_2)_2 + H_2$$

The complex $(diphos)_2Co(BPh_2)_2$ is used for synthesis of many new metal-diphenylboranes, the Ph_2B group being transferred as an anion,

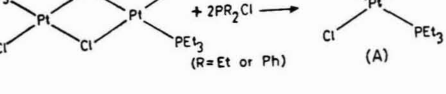
$$(diphos)_2Co(BPh_2)_2 + 2BrMn(CO)_5 \longrightarrow (diphos)_2CoBr_2 + 2Ph_2BMn(CO)_5$$

$$(diphos)_2Co(BPh_2)_2 + 2ClAuPPh_3 \longrightarrow (diphos)_2CoCl_2 + 2Ph_2BAuPPh_3$$

The metal-boron σ-bond strength is enhanced by dp-π bonds, the electrons being furnished by the metal atom. NMR shifts due to electron withdrawing and donating groups at cobalt atom are also investigated.

Phosphorus Donors

Chatt and Heaton (University of Sussex, Brighton, UK) have prepared some interesting hydroxyphosphine and other complexes with Pt-P bond:



When A is recrystallized from HCl containing aqueous acetone, *cis*-$[PtCl_2(PR_2OH)(PEt_3)]$ is produced, which on treatment with methanolic sodium methoxide yields $[Pt_2Cl_2(PR_2O)_2(PEt_3)_2]$. In this dimeric complex, (PR_2O) groups are bridging and the chlorine atoms are terminal. If the end atoms are replaced by the strongly bridging SEt groups, rearrangement occurs and $[Pt_2(SEt)_2(PR_2O)_2(PEt_3)_2]$ is obtained with PR_2O as terminal groups. The structures of various products were determined by infrared and NMR spectroscopy.

Germanium and Silicon Donors

Glockling (University of Durham, UK) has devised the following methods to produce complexes with M-Ge bonds:

$$\underset{(cis\text{- and }trans\text{-})}{(R_3P)_2PtCl_2} + Ph_3GeLi \longrightarrow \underset{(cis\text{- and }trans\text{-})}{(R_3P)_2Pt(GePh_3)_2} \quad \ldots(1)$$

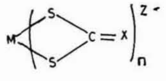
$$cis\text{-}(R_3P)_2PtCl_2 + (Me_3Ge)_2Hg \longrightarrow trans\text{-}(R_3P)_2PtCl(GeMe_3) + Hg + Me_3GeCl \quad \ldots(2)$$

$$\pi\text{-}C_5H_5(CO)_3MoNa + R_3GeBr \longrightarrow \pi\text{-}C_5H_5(CO)_3MoGeR_3 \quad \ldots(3)$$

Silyl complex with M-Si can be obtained using reaction (2) with trialkyl silyl in place of trialkyl germanyl. With the exception of $Et_4N[Au(GePh_3)_2]$, stable metal-metal bonded complexes are formed when the transition metal is bonded to π-bonding ligands. Germanyl complexes of Ag, Cu and Pd(II) have also been prepared. The thermal stability of the complexes depends on the coordination number of the transition metals in the complexes. The thermal fragmentation of $\pi\text{-}C_5H_5(CO)_3MoGeEt_3$ has been studied by a mass spectrometer, which indicates Mo-Ge bond intact in its fragments. A variety of chemical reactions on M-Ge complexes is investigated.

Sulphur and Selenium Donors

Ligands with sulphur donors are receiving increased attention. Falkler and Coucouvanis (Case Institute of Technology, Cleaveland, USA) have prepared metal complexes of unsaturated 1,1-dithiols of the type



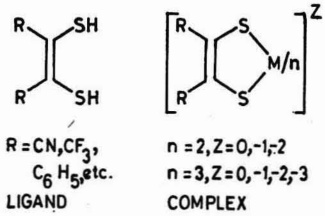
where $X = S$, $C(CN)_2$, $CHNO_2$, $C(CN)(C_6H_5)$, etc. Ni(II), Pd(II) and Pt(II) form square planar complexes while Cr(III) forms octahedral complexes. Some of these complexes, particularly those with $X = CHNO_2$ and $C(CN)(C_6H_5)$, undergo electrochemical oxidation to a new species. Complexes such as $M(S_2CS)_2^{2-}$ are oxidized irreversibly and form $M(S_3CS)_2$ species which undergo reversible oxidation. Another interesting aspect of the complexes of 1,1-dithiols is that on reaction with SCN^- and S_8, sulphur may be inserted into the M-S bond, forming $M(S_3CN)_2^{2-}$ complexes, which contain a 5-membered chelate ring. However, triphenylphosphine extracts the sulphur from the chelate to form triphenylphosphine sulphide and the original complex. The reduction of planar $Cu(i\text{-}MNT)_2^{2-}$, [i-MNT = $S_2CC(CN)_2^{2-}$] by bromide gives the unusual cluster anion, $Cu_4(i\text{-}MNT)_3^{2-}$. The electronic spectral properties of the complexes are described.

Structure of $Ni(dtp)_2$ (dtp = *o,o'*-diethyldithiophosphate) has been determined by Fernando (University of Arizona, Tucson, USA) by X-ray single crystal study. Adduct formation of $Ni(dtp)_2$ with pyridine, quinoline, etc., is discussed from structural point of view. Polarographic and infrared data of $Ni(dtp)_2$ and its adducts are also discussed. Gould and Taylor (University of Edinburgh, UK) have described isomorphous complexes of Ni(II) and Pd(II) with 2-mercaptoethanol and its analogues. Structures are discussed from X-ray diffraction studies.

Spectral (IR and UV), magnetic, conductivity and X-ray diffraction studies on complexes $[ML_2(NCS)_2]$ of Co, Ni, Mn and Cd(II) thiocyanates with substituted thioureas (L) have been carried out by Puglisi *et al.* (Facultad de Ciencias Exactoes y Naturales, Buenos Aires, Argentina), with particular reference to their stereochemistry.

Cotton *et al.* (Massachusetts Institute of Technology, Cambridge, USA, and University of Sheffield, UK) have studied dithiocyanate ($C_2N_2S_2^{2-}$) complexes, $[MC_4N_4S_4]^{2-}$ (M = Cu, Ni, Pd, Pt) and $[MC_6N_6S_6]^{3-}$ (M = Co, Tl). The crystal and molecular structure of $[(C_6H_5)_4As]_2[NiC_4N_4S_4]$ are described. A large number of new complexes of dithiooxamides and substituted dithiooxamides with Cu, Ni and Co have been prepared and studied by Peyronel *et al.* (University of Modena, Italy).

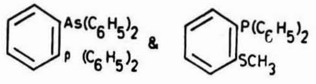
Hoyer *et al.* (Karl Marx University, Leipzig, GDR) have prepared complexes of Pd, Cu, Ni, Co, Zn and Pb with substituted dithiolate.



Polarographic, thermal and electronic spectral studies have been carried out. The X-ray crystal structure of $[Ni(ebt)_2]^0$ (ebt = *cis*-ethylene bis-thiolate) shows square planar coordination for Ni.

Mixed Donors: P, As, S and Se

Meek *et al.* (Ohio State University, Columbus, USA) have studied complexes of polydentate ligands containing P, As, S and Se donors. They determined the coordinating tendency of a series of ligands, containing two different donor atoms, for example, the tetradentate ligands $P(o\text{-}C_6H_4SeCH_3)_3$ and $P(o\text{-}C_6H_4SCH_3)_3$. These ligands form trigonal bipyramidal complexes with Ni(II), whereas arsine homologues do not. $As(o\text{-}C_6H_4AsPh_2)_3$ forms 5-coordinate complexes with Ni, Pd and Pt(II); but when one of the arsenic is replaced by sulphur, the new ligand, $As(o\text{-}C_6H_4AsPh_2)_2\text{-}(o\text{-}C_6H_4SCH_3)$ forms a 5-coordinate complex with Ni(II) but not with Pd(II). The tridentate ligands $C_6H_5P[CH_2CH_2CH_2\text{-}As(CH_3)_2]_2$ and $C_6H_5P[o\text{-}C_6H_4SCH_3]_2$ form trigonal bipyramidal complexes with Ni(II) and square planar complexes with Pd(II). The two bidentate ligands



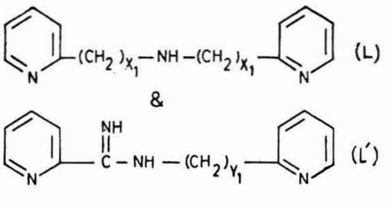
form 5-coordinate complexes, having the formula $[M(ligand)_2X]^+$, M = Ni or Co. Electronic spectral studies are made on all these complexes.

Stereochemistry

The main interest in the stereochemistry of inorganic complexes has been penta-coordination, and centres round the synthesis of some new complexes, mainly of 3*d* transition metals, the factors that promote penta-coordination and the arrangement of ligands. The penta-coordinated compounds of transition metals are not so rare as it was once thought to be.

Orioli *et al.* (University of Florence, Italy) have discussed the stereochemistry of 5-coordinated, high spin, 3*d* metal complexes. Bulky and polydentate ligands favour the formation of high spin complexes of the type [M(Me$_6$tren)Br]Br, [Me$_6$tren = $N\{(CH_2)_2N(CH_3)_2\}_3$, M = Cr through Zn]. According to these authors, 5-coordination is attained as a result of steric effects, shape of the ligands and packing forces in the solid state. The stability of trigonal bipyramidal or square pyramidal configuration is determined by the nature of the metal-ligand bond, ligand-ligand repulsions and crystal field stabilization energy in addition to the factors already mentioned. Meek *et al.* (Ohio State University, Columbus, USA), however, attribute the formation of trigonal bipyramidal or square pyramidal complexes to the electronic nature of the ligand atoms rather than the symmetry of the polydentate ligands. This is inferred from a study of a series of 5-coordinate complexes of Ni and Co(II) with polydentate ligands, containing As, P, S and Se functional atoms, like $P[(CH_2)_3As(CH_3)_2]_3$, $As[(CH_2)_3As(CH_3)_2]_3$, $P(o\text{-}C_6H_4SCH_3)_3$, $P(o\text{-}C_6H_4\text{-}SeCH_3)_3$, $C_6H_5P[(CH_2)_3As(CH_3)_2]_2$, etc. Yamada *et al.* (Osaka University, Japan) have prepared 5-coordinate Co(II) complexes of Schiff's bases, by introduction of a molecule of pyridine or picoline in the fifth position. The ligand field is considered to play an important part in deciding the coordination number of cobalt.

Nelson and Rodgers (Queen's University, Belfast, Ireland) have described low and high spin 5-coordinate complexes of iron(II) with tridentate amines,



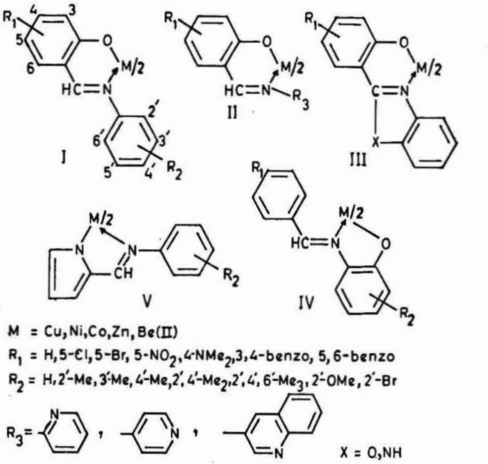
When $X_1 = 1$ and $Y_1 = 1$, both L and L′ form low spin iron(II) complexes of the type $[FeL_2]X_2$ (X = halide, NCS, etc.). Shortening or lengthening the saturated chain, linking the terminal pyridyl groups of L, decreases the ligand field strength and favours the formation of spin-free complexes of iron(II). When $X_1 = 0$, the ligand L acts as a bidentate, forming 6-membered chelate rings. When $X_1 = 2$, only one molecule of the ligand coordinates to the metal ion, forming MLX_2 complexes [M = Mn, Co, Ni, Cu, Zn(II)], some of the complexes being high spin 5-coordinate complexes. $NiLBr_2$ has a trigonal bipyramidal configuration and is found to be isomorphous with $CoLBr_2$ and $CuLBr_2$ by X-ray powder diffraction.

Oxovanadium(IV) complexes of mono- and bidentate ligands have been studied by Patel and Sathyanarayana (Indian Institute of Science, Bangalore). These compounds are found to be 5- or 6-coordinated. When two or all the four positions in the square plane are occupied by a bidentate ligand/ligands, the complexes are generally penta-coordinate with rectangular pyramidal structure. Non-bulky monodentate ligands form hexa-coordinate complexes, while bulky ligands form 5-coordinate complexes. The nature of the complexes and the attainment of a particular configuration are discussed.

It is already pointed out in the section on advances in coordination chemistry, that some unsaturated bidentate ligands containing sulphur donors form 6-coordinate transition metal complexes, which have a trigonal prismatic structure instead of the usual octahedral structure.

Certain peculiarities in the stereochemistry of thorium have come to light as a result of X-ray crystal studies of certain acido and neutral complexes by Chernyaev *et al.* (Institute of General & Inorganic Chemistry, Academy of Sciences, USSR, Moscow). Thorium can have coordination numbers 6, 8, 9, 10 and 12. Different coordination numbers can be had with the same ratio of thorium to ligand. Various types of coordination polyhedra are possible for the same coordination number. For example, in 9-coordinated complex, $K_4[Th(SO_4)_4(H_2O)_2]$, four sulphato groups are bridging, one is a bidentate and one is a monodentate. They have prepared 8-coordinated thorium complexes of urea: $[Th.4\ urea.4H_2O]X_4$ (X = Cl, Br, I, NO_3, NCS); $[Th.6\ urea.2H_2O]X_4$ (X = Cl, Br, I, NO_3); and $[Th.8\ urea]X_4$ (X = Cl, Br, I). The 8-coordinated thorium is also supposed to be present in aquo isothiocyanate complexes ranging from $[Th(NCS)_4.4H_2O]$ to $Me_4[Th(NCS)_8].2H_2O$. Nine-coordination for thorium has been established in $C(NH_2)_3Na[Th(SO_4)_3.3H_2O]$.-2-$3H_2O$ and $K_4[Th(SO_4)_4.2H_2O]$. In the guanidine complex, only bridging bidentate sulphato groups are present. The X-ray analysis of thorium tetraformate, $[Th(OOCH)_4.2H_2O].H_2O$, has shown ten-coordinate thorium. The maximum coordination number of twelve for thorium is found in guanidine hexa-acetate, $[C(NH_2)_3]_2[Th(OOC.CH_3)_6]$, the thorium atom being bonded to twelve acetate oxygens arranged cyclically.

Osipov and Minkin (Rostov on Don State University, Rostov on Don, USSR) have investigated the effect of substitution on the stereochemistry of the following complexes from dipole moment and magnetic properties:



Chelates (I) and (V) in solution give square planar ⇌ tetrahedral conformational equilibrium which depends on the structure of the ligands. Complexes (III) and (IV) assume tetrahedral configuration of chelate rings in solution and the solid state. Complexes (II) attain tetrahedral configuration in solution and octahedral in the solid state.

Crystal Structure

The determination of structures of complexes by X-ray diffraction of single crystals has gained popularity in the last few years. These studies have been helpful in making some generalizations about the molecular structures.

Ethylenediamine complexes of nickel(II), $Nien_2XX'$ [X, X′ = NO_2, NCS, Cl, Br, I, ClO_4], have been studied by X-ray diffraction by Porai-Koshits *et al.* (Institute of General & Inorganic Chemistry, Academy of Sciences, USSR, Moscow). They have correlated the chemical structure with the nature of the ligands: (1) complexes $Nien_2X_2$ (X = ClO_4^-, $AgBr_2^-$) are diamagnetic and the cation $[Nien_2]^{2+}$ is square planar; (2) nitro compounds, $Nien_2NO_2X$, are paramagnetic and have *trans*-octahedral configuration. These compounds are monomeric if X = NO_2, Cl, Br; but polymeric with chains of $[Nien_2NO_2]^+_\infty$ if X = ClO_4^-, BF_4^-; (3) halogeno complexes, $Nien_2XX'$ (X, X′ = Cl, Br, I), have dimeric *cis*-structures of cations $[en_2NiX_2Nien_2]^{2+}$; and (4) thiocyanato compounds $[Nien_2NCSX]$ have *cis*-octahedral structures: monomeric if X = NO_2, Cl, Br and dimeric $[en_2Ni(NCS)_2Nien_2]^{2+}$ if X = I^-, ClO_4^-.

Kellerman and Lingafelter (University of Washington, Seattle) have prepared four isomorphous complexes, $Ni(en)_2(AgI_2)_2$, $Ni(en_2)(AgBrI)_2$, $Ni(en)_2(AgBr_2)_2$ and $Cu(en)_2(AgBr_2)_2$. The crystals are monoclinic. The structure of $Ni(en)_2(AgBr_2)_2$ by single crystal X-ray diffraction shows planar coordination of nickel, in agreement with its diamagnetic character. However, the anion is not discrete; instead of a linear $AgBr_2^-$ expected, a polymeric chain in which silver is tetrahedrally coordinated by bridging bromide ions is observed.

Complexes of pyridine-2-carboxamide (PiaH), $C_5H_4NCONH_2$, of nickel(II), $Ni(pia)_2.2H_2O$ (a) and $Ni(piaH)_2Cl_2.2H_2O$ (b) have been prepared by Saito *et al.* (University of Tokyo and Nagoya University, Japan), and their crystal structures are determined. The former is orthorhombic while the latter is monoclinic. Complex (a) is *trans* square planar, where the ligands are bonded to the metal through the nitrogens. The blue complex (b) is ionic and the cation $[Ni(piaH)_2(H_2O)_2]^{2+}$ has octahedral configuration. The ligand molecules occupy *trans*-positions by means of oxygen and nitrogen atoms of the pyridine ring.

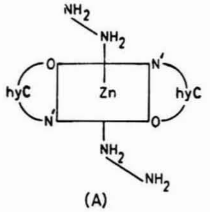
Three sets of hydrazincarboxylic acid ($hyC = HN_2'-NH-COO$) complexes of transition metals have been prepared and their X-ray crystal structures studied by Braibanti *et al.* (University of Parma, Italy):

(1) $M(N_2H_4)_2hyC_2$ (monoclinic), M(II)=Mn, Co, Ni, Zn

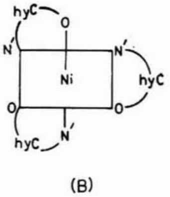
(2) $(N_2H_5)[MhyC_3].H_2O$ (monoclinic), M(II)=Fe, Co, Ni, Zn

(3) $K[MhyC_3]$ (trigonal), M(II)=Fe, Co, Ni, Zn

The crystals of each set are isostructural. The zinc compound has the structure (A). The crystal structure of the nickel complex of set (2) shows an anionic chelate of type (B).



(A)

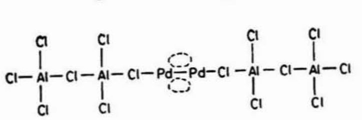


(B)

The complexes of set (3) contain anions $[MhyC_3]^-$ of *cis* type, analogous to those of set (b), as deduced from symmetry considerations.

Bokij (Institute of Radio Engineering & Electronics, Academy of Sciences, USSR, Moscow) has synthesized a number of complexes of the type $K[PtNH_3Cl_3]$, $K[PtC_2H_4Br_3]H_2O$, etc., and has shown by X-ray diffraction that the inter-atomic distances depend on the *trans* effect and that the distances are larger with more labile ligands.

Allegra (Institute of Industrial Chemistry of Central Polytechnic of CNR, Milan, Italy) has determined the crystal and molecular structures of two bis-arene-metal complexes. Metal to benzene coordination and shortest Pd-Pd distances are the novel features of these complexes. Complex (A) has a structure in which two parallel benzene rings act as a bridge between a pair of bonded Pd atoms:



(A)

The second complex (B) has the formula $Pd_2Al_2Cl_8(C_6H_6)_2$ and is related to (A), from which $AlCl_3$ end groups are removed. Compound (A) is triclinic and has one molecule per unit cell, whereas compound (B) is monoclinic with two molecules per unit cell.

The stereochemistry of the binuclear ethylene diamine tetraacetato (= A) dimolybdate(VI) anion of $Na_4[O_3MoAMoO_3].8H_2O$ has been determined by X-ray analysis, carried out by Hoard *et al.* (Cornell University, Ithaca, USA). The sodium salt has a monoclinic unit cell with two formula units per unit cell.

A heteropoly electrolyte with a new structure for the anion $[H_hM^{m+}O_6X^{x+}O_4W_{11}O_{30}]^{-(14-m-x-h)}$ is established by Baker *et al.* (Georgetown University, Washington). This structure is a modification of the well-known 'Keggin unit'. Octahedrally coordinated M^{m+} replaces just one of the 12 W's of the Keggin structure and X^{x+} occupies the central tetrahedral cavity. The following combinations were found in different anions:

	M	X
(1)	Co^{2+}	Si^{4+}
(2)	Co^{3+}	H_2^{2+}
(3)	Ga^{3+}	H_2^{2+}
(4)	Co^{2+}	Co^{2+}
(5)	Co^{2+}	Co^{3+}

Oxidation states, geometry of the coordination and the electronic interactions have been confirmed by spectra for cobalt complexes. An interesting thermal behaviour is also investigated by X-ray diffraction.

Transition Metal Complexes of Special Interest

Complexes by Sulphur Dioxide Insertion

Wojcicki *et al.* (Ohio State University, Columbus, USA) have prepared sulphinato complexes of cyclopentadienyliron dicarbonyl as:

$$C_5H_5Fe(CO)_2Cl + RSO_2Na \xrightarrow[27°C.]{CH_3OH} C_5H_5Fe(CO)_2SO_2R + NaCl$$

$$R = C_6H_5,\ p-C_6H_4CH_3$$

$$C_5H_5Fe(CO)_2R + SO_2 \xrightarrow{-40°C.} C_5H_5Fe(CO)_2SO_2R$$

$$R = CH_3,\ C_2H_5,\ CH_2C_6H_5,\ C_6H_5,\ p\text{-}C_6H_4CH_3$$

Sulphinates of cyclopentadienylmolybdenum tricarbonyl and of manganese pentacarbonyl have also been prepared by reacting the corresponding alkyls with liquid sulphur dioxide. The PMR and infrared spectra suggest strong metal-sulphur π-bonding. Several nucleophilic substitutions on $Mn(CO)_5SO_2R$ have also been investigated.

Oxygen Carriers

Vaska (Clarkson College of Technology, Potsdam, New York) has studied the factors that determine the reversible oxygenation of transition metal complexes. The study is based on the reactions of the type given by an oxygen carrier complex:

$$[IrCl(CO)(Ph_3P)_2] + O_2 \rightleftharpoons [O_2IrCl(CO)(Ph_3P)_2]$$

The role of the constituents of $[IrCl(CO)(Ph_3P)_2]$(I) in the reversible oxygenation process has been examined. For example, $[RhCl(CO)(Ph_3P)_2]$, which is isostructural with Ir complex, shows no measurable oxygen uptake. Another interesting feature of the $[IrX(CO)(Ph_3P)_2]$ complexes is that the rate of oxygenation depends on X, the halide in solution; the bromo and iodo complexes react twice and eight times respectively that of the chloro complex. The iodo complex undergoes oxygenation even in the crystalline state. The presence of CO in the complex is essential to maintain the reversibility of the oxygenation reaction. All four ligands in the parent compound can be displaced by two molecules of bisphosphine. The bisphosphine complex cation of $[Ir(Ph_2\text{-}PCH_2CH_2PPh_2)_2]Cl$ adds readily molecular O_2, CO, SO_2, H_2, HX and related molecules to form five- and six-coordinate adducts and these are more stable toward dissociation than the corresponding adducts of the neutral Ir(I) complex. The effects of oxygen pressure, temperature, solvent, the presence of inhibitors, etc., on the reversible oxygenation process of the parent compound have also been studied.

Nitrogen Fixation

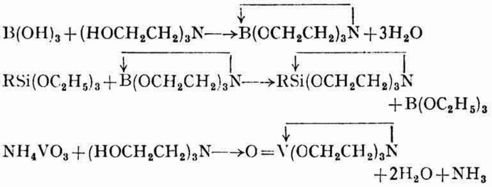
Enzymes are known to fix molecular nitrogen under ordinary conditions because of the formation of π-complexes with transition metals like molybdenum, iron, etc., present in the enzymes. This led Vol'pin and Shur (Institute of Organoelement Compounds, Academy of Sciences, USSR, Moscow) to believe that the activation of molecular nitrogen might be possible during the formation of complexes with metals. For this, they have studied the behaviour of nitrogen towards transition metals capable of forming complexes with olefins, carbon monoxide, acetylene and other unsaturated compounds. It was found that a number of salts and complexes of chromium, molybdenum, tungsten, iron and titanium, on reacting with RMgX, RLi, R_3Al, $LiAlH_4$, $Mg+MgI_2$, etc., fix nitrogen at room temperature. Many Ziegler catalysts are also found to react with nitrogen. Cyclopentadienyls, acetylacetonates and phosphinic complexes of transition metals also bind nitrogen under mild conditions.

Complexes of Elementary Nitrogen

Allen and Senoff (University of Toronto, Canada) have prepared ruthenium complexes containing elementary nitrogen, $[Ru(NH_3)_5N_2]X_2$ ($X = Cl^-, Br^-, I^-, PF_6^-, BF_4^-$). The complexes are diamagnetic, consistent with spin-paired d^6 ruthenium(II). The infrared spectra show a strong, sharp band at about 2150 $cm.^{-1}$, assigned to the N_2 stretch, which is lower by about 200 $cm.^{-1}$ from that observed for molecular nitrogen. The N_2 molecule seems to be linearly coordinated rather than π-bonded.

Atranes

The intra-complex cyclic inorganic esters and alcoholates of triethanolamine and its derivatives are called ' atranes ' by Voronkov *et al.* (Academy of Sciences of Latvian SSR, Riga). They have the general structure $Y_{n-3}\,M(OCH_2CH_2)_3N$, where M is an n-valent metal or a metalloid [B, Si, Ge, Sn, Ti, V, Mo, W, etc., Y is an organic or inorganic substituent]. Atranes can be prepared by reactions of the types:



$$B(OH)_3 + (HOCH_2CH_2)_3N \longrightarrow B(OCH_2CH_2)_3N + 3H_2O$$

$$RSi(OC_2H_5)_3 + B(OCH_2CH_2)_3N \longrightarrow RSi(OCH_2CH_2)_3N + B(OC_2H_5)_3$$

$$NH_4VO_3 + (HOCH_2CH_2)_3N \longrightarrow O{=}V(OCH_2CH_2)_3N + 2H_2O + NH_3$$

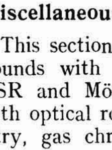
Atranes possess high dipole moments (5-10·5D), attributed to the presence of a M ← N bond and its high polarity.

Miscellaneous

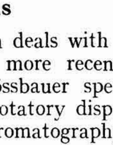
This section deals with studies on complex compounds with more recent techniques like NMR, ESR and Mössbauer spectroscopy. It also deals with optical rotatory dispersion, recoil atom chemistry, gas chromatography and photochemistry of complex compounds.

Nuclear Magnetic Resonance

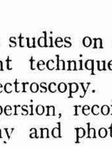
This technique is mainly employed for the study of geometrical isomers. Acetylacetone (acac) and benzoylacetone (bzac) complexes of titanium and zirconium(IV) have been studied by Fay *et al.* (Cornell University, Ithaca, USA). $Ti(acac)_2X_2$, $Ti(bzac)_2X_2$, $Zr(acac)_2X_2$ and $Zr(acac)_3X$ are 6-coordinated, monomeric in benzene and non-electrolytes in nitrobenzene. Low temperature proton NMR spectra of $Ti(acac)_2X_2$ in CH_2Cl_2 reveal it to be *cis*-geometrical isomer (I) from its methyl resonance lines, whereas $Ti(bzac)_2X_2$ complexes are consistent with the presence of an equilibrium mixture of *cis*-isomers (II), (III) and (IV)



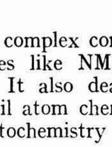
I



II



III



IV

The greater stability of the *cis*-isomers is due to stronger metal-ligand π-bonding in them. $Zr(acac)_3X$ are 7-coordinated and show only a single methyl resonance line in proton NMR spectra. These complexes undergo a rapid rate process which averages the environments of the non-equivalent methyl groups.

The NMR and infrared spectra of bis-acetyl acetonato titanium(IV) dialkoxides, $Ti(acac)_2X_2$ (X=Cl or alkoxide), have been studied by Bradley and Holloway (Queen Mary College, London). They are *cis*-octahedral complexes. The infrared and NMR data suggest π-electron donation from the acac groups to vacant d-orbitals of Ti and this factor stabilizes the *cis*-isomer relative to the *trans*. Kinetics of the ligand rearrangement has also been studied by determining the line broadening of the acac methyl proton resonance with temperature.

Proton magnetic resonance spectra of cobalt ammine complexes have been studied in trifluoroacetic acid medium by Yoneda and Morimoto (Wakayama University, Japan). $Co(NH_3)_6^{3+}$ and $CoNO_2(NH_3)_5^{2+}$ give only a single peak whereas $CoCl(NH_3)_5^{2+}$ and $CoH_2O(NH_3)_5^{3+}$ give peaks for both *cis*- and *trans*-configurations of ammine groups. In the latter complexes the minor peak appears in the high field side of the major, indicating that the protons of the *trans* NH_3 are more shielded than those of the *cis* NH_3. The structures of $Coen_2^{3+}$ and $Cotren_3^{3+}$ are discussed from NMR spectral bands.

The NMR spectra of adducts of metal(II) acetylacetonates and trifluoro- and hexafluoroacetylacetonates (TFAA and HFAA) with pyridine, pyridine N-oxide and related ligands have been studied by Horrocks *et al.* (Princeton University, USA). In the acetylacetonate complexes, there is a labile equilibrium between the coordinated and uncoordinated ligands. In the corresponding adducts of TFAA and HFAA, a decrease in the ligand exchange rate between the coordinated and the uncoordinated ligands is observed by PMR spectra.

The ^{19}FNMR spectra and chemical shifts of fluorides of V, Nb, Ta, Mo and W have been studied at room and low temperatures and their structures discussed by Buslaev *et al.* (N.S. Kurnakov Institute of General & Inorganic Chemistry, Moscow, and Radium Institute, Leningrad).

Phosphorus-phosphorus spin coupling and phosphorus-metal (P-M) bonding in coordination compounds have been investigated by King *et al.* (Iowa State University, Ames, USA). To know the nature of P-M bond, a new experimental approach is developed involving the study of ^{31}P-^{31}P spin coupling constants (J_{pp}) in disubstituted complexes as a function of ligand strengths and coordination geometry. The constants are determined for a number of carbonyl complexes with $P(OCH_2)_3CCH_3$(L) and $P[N(CH_3)_2]_3$(L′) ligands. For the disubstituted complexes of L, the order for J_{pp} is $Fe > Mo > W > Cr > Ni$. According to the geometry, the order is *trans*-trigonal bipyramidal > *trans*-octahedral > tetrahedral and that within O_h symmetry $Mo > W > Cr$. They have also investigated ^{19}F resonance spectra of *trans* and *cis* complexes of Mo and W having the general formula $M(CO)_4(PF_3)_2$. The possible relationship between P-P coupling and P-M bonding is discussed.

Evidences for *trans* effects in octahedral ruthenium(II) and iridium(III) complexes by infrared and NMR spectra and rates of substitution studies are provided by Jenkins *et al.* (University of Leeds, UK). Ligands like CO, PR_3, AsR_3 and hydride have very large *trans* effects and cause *trans* groups to be labilized, whereas Cl^- and Br^- have low *trans* effects. Complexes of the type $[IrCl_nX_{3-n}L_3]$ and $[IrCl_nX_{3-n}L_2(CO)]$ ($n = 1$-3, X = anionic ligand and L = PR_3 or AsR_3) give strong bands for Ir-Cl in the far infrared region. The frequencies of these bands depend very much on the ligands in the *trans*-positions and very little on the ligand in the *cis*-position. The same holds for RuCl frequencies in complexes of the type $[RuXCl(CO)_nL_{4-n}]$ ($n = 1$, 2). Rates of substitution parallel bond weakening effects of *trans*-ligands. In PMe_2Ph complexes of Ir(III) and Ru(II), when the two PMe_2Ph are in mutual *trans*-positions across the metal atom, the methyl resonance shows that the methyls couple equally with both the ^{31}P nuclei, indicating 'virtual' coupling. This arises as a result of strong P-P coupling across the metal atom. When two PMe_2Ph are in mutual *cis*-positions, doublet methyl resonance only are observed, showing that the two P nuclei must couple less strongly. In 'virtual' coupling, nuclear spin-spin interaction is transmitted via valency electrons.

Electron Paramagnetic Resonance

This technique has been used for varied type of studies of paramagnetic complexes.

This technique has been employed by Fujiwara and Nagashima (University of Tokyo, Japan) for studying the distribution of cupric ions when coprecipitated with various diamagnetic metal oxinates. It is found that Zn, Cd, Hg and Mg oxinates form a homogeneous solid solution with copper oxinate, while Ca, Sr, Ba and Ag oxinates do not. In the former, the hyperfine structure of Cu^{2+} ions is retained in the EPR spectra, suggesting that the dipolar interactions are not strong enough to destroy the nuclear-electron hyperfine interactions of Cu^{2+} ions. The broad spectrum in the latter is similar to that of other cupric salts, indicating two different phases in the solid system.

The ESR spectra of oxovanadium(IV) complexes have been studied by Rogers (Michigan State University, USA) and Kuska (University of Akron, USA). The data are employed for calculating a set of molecular orbital coefficients. A correlation, based on the ESR and optical spectral data of these complexes, aids in assigning energy levels for the optical spectra.

The ESR studies are carried out on pyridinium tetrachlorodimethoxomolybdate(V), $C_5H_6N[Mo(OCH_3)_2Cl_4]$ and other similar complexes by McClung *et al.* (Michigan State University, USA). The methoxo complex in ethanol gives the same ESR spectrum as the ethoxo complex in ethanol. If the methoxo complex is dissolved in dimethyl sulphoxide, the ESR spectrum slowly changes but the addition of excess chloride causes the reappearance of the original spectrum. This indicates that the chlorides from the complex are displaced by DMSO and the latter are replaced in the presence of excess chloride. Infrared and electronic spectral studies are also carried out on the complexes.

Voorst (University of Amsterdam, Netherlands) and Hemmerich (University of Basel, Switzerland) have shown by ESR and optical spectra that one electron chemical reduction of $Na_2[Fe(CN)_5NO]$ in aqueous solution by $Na_2S_2O_4$ gives two *p*H-dependent species: a brown one at *p*H 7 and a blue one at *p*H 4. An equilibrium mixture of both the species occur at *p*H 5-6:

$$\underset{\text{brown, stable}}{[Fe(CN)_5NO]^{3-}} + H^+ \rightleftharpoons \underset{\text{blue, slowly hydrolysing}}{[Fe(CN)_5NOH]^{2-}}$$

The blue species is stable when prepared in absolute DMF by reduction of $Na_2[Fe(CN)_5NO]$ with metallic sodium. It is found from the ESR data of the single crystal of the parent complex that p_x and p_y orbitals of nitrogen are mainly involved in the MO of the unpaired electron. This suggests that the principal axis of NO does not coincide with the principal axis of the $Fe(CN)_5$ pyramid.

The nature of the metal-metal bond and the metal-ligand bond in some binuclear copper complexes, $[Cu(pno)(H_2O)Cl_2]_2$ and $[Cu(pno)_2Cl_2]_2$, (pno = pyridine-N-oxide) has been investigated by Gordon *et al.* (University of Maryland and the National Bureau of Standards, Washington DC) by EPR and optical spectra.

Mössbauer Effect

Mössbauer spectra of iron(III) trisdithiocarbamates $[Fe(R_2NCS_2)_3]$ and nitrosyl iron(III) bisdithiocarbamates $[Fe(NO)(R_2NCS_2)_2]$ (R = alkyl or benzyl) have been studied by Frank and Abeledo (Faculty of Natural Sciences, Buenos Aires, Argentina). The variation in the magnitude of quadrupole interaction is correlated with the magnetic moments of the complexes. At room temperature, all the complexes exist in an equilibrium mixture of high and low spin iron nuclei. High spin d^5 complexes have a spherically symmetric electronic configuration which does not contribute to the electric field gradient at the iron nucleus, whereas the non-spherical electron configuration of low spin d^5 complexes gives rise to an appreciable gradient at the nucleus. It is, therefore, possible to establish the contribution of each of the magnetic forms in the equilibrium. The isomer shifts in $[Fe(NO)(R_2NCS_2)_2]$ complexes are found to increase with the inductive effect of the substituents R on dithiocarbamate.

Mössbauer spectra of isonitrile and phenanthroline complexes of iron are investigated by Fitzsimmons (Birkbeck College, London). The *cis-trans* isomers of $Fe(CN)_2(CNR)_4$ have been measured and a 2:1 quadrupole splitting ratio for *trans: cis* isomers has been obtained. Ways of correlating Mössbauer data with other physical measurements are discussed.

Burger (L. Eötvös University, Budapest, Hungary) has investigated back coordination in oxime chelates of $3d^5$-$3d^{10}$ transition metals by equilibrium measurements, infrared absorption, magnetic susceptibility and Mössbauer effect studies. For example, the low spin dimethyl glyoxime complexes of both iron(II) (d^6) and iron (III) (d^5) give nearly the identical isomer shifts in the Mössbauer spectra, showing practically the same *s* electron density at iron nuclei of both the complexes. The *s* electron density at the nucleus is determined by the number of *s* electrons and by the shielding effect of *d* electrons. Since both d^6 and d^5 iron complexes give similar *s* electron density, the back coordination may occur, thus decreasing the *d* electron density of iron(II).

Optical Rotatory Dispersion (ORD)

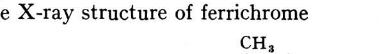
Factors responsible for contributing to ORD are investigated and correlation of absolute configuration of complex structure with ORD is being attempted. Gallais and Haraldsen (Faculty of Sciences, Toulouse, France) have determined the specific and molecular rotations of $Ni(CO)_4$, $Fe(CO)_5$, $Ni[P(OCH_3)_3]_4$, $Ni(PCl_3)_4$ and $Ni(CO)_n[P(OCH_3)_3]_{4-n}$ ($n = 1$, 2 and 3) at 18-20°C. using 5780 A. mercury radiation. All these π-complexes have exceptionally high diamagnetic rotation. The increase in rotation is related to the change in the Ni-P bond.

The influence of ring conformation on the optical activity of tris-diamine cobalt(III) and platinum(IV) complexes has been investigated by Mason *et al.* (University of East Anglia, Norwich, UK). The optical activity of chelated complex ions is due to two stereochemical factors — the configuration of the chelate rings about the metal ion and the conformation of each of the chelate rings. These two stereochemical factors contribute additively to the sign and magnitude (1) of the strong charge transfer circular dichroism band of the chelated diamine cobalt(III) complexes near 2200 A. and (2) of the molecular rotation of tris-diamine platinum(IV) complexes at 5890 A.

The optical rotatory dispersion of copper complexes of a number of amino acids $[A = RCH(NH_2)\text{-}COO^-]$ has been studied by Hare *et al.* (State University of New York, Buffalo). Two types of complexes CuA^+ and CuA_2 are formed. Both the types of complexes show Cotton effect in their ORD curves. The Cotton effect amplitude for CuA_2 depends on the R group. The ORD data are interpreted in terms of an equilibrium between two conformers — one with the R group in a quasi-axial position and the other in a quasi-equatorial orientation of the chelate ring.

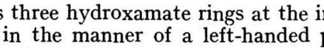
The additivity of the spiral and vicinal contributions to the optical activity has been studied for Co(III) complexes of ethylenediaminediacetate ion (EDDA) with alanine or propylenediamine (Pn) and of 2,2′-diaminobiphenyl by Douglas *et al.* (University of Pittsburgh, USA). They have also studied hexakis-(2-aminoethanethiolo) tricobalt(III) complex, which is chromatographically separated into a *meso* and two optically active forms. The central cobalt in this complex is coordinated by the other two octahedral cobalt(III) complexes through sulphurs. The complex shows strong optical activity due to the spiral arrangement of the chelate rings of the two outer cobalt atoms of the complex.

Bürer (Federal Institute of Technology, Zürich) and Gulyas (Argonne National Laboratory, USA) have studied ORD of iron and chromium(III) polyhydroxamates,



$$M(O\overset{R}{\overset{|}{C}}\overset{R'}{\overset{|}{N}}O)_3\ [R' = -(CH_2)_3 -\text{link to cyclohexapeptide}]$$

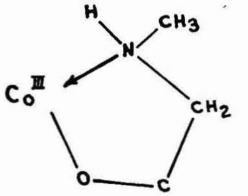
Since X-ray structure of ferrichrome



$$A[M = Fe^{3+},\ R \text{ is } CH{=}\overset{CH_3}{\overset{|}{C}}-CH_2-COOH]$$

which has three hydroxamate rings at the iron atom arranged in the manner of a left-handed propeller, is known, the authors have attempted at correlation of absolute configuration with ORD and circular dichroism (CD). Sargeson (Australian National University, Canberra) has studied CD and

ORD for conformational analysis of $(Coen_2sarcosine)^{2+}$, where Co-sarcosine is



The recemization and deuteration rates of the sarcosine complex are also investigated.

Recoil Atom Chemistry

Ionescu and Rusi (Institute of Atomic Physics, Bucharest, Rumania) have studied the influence of chemical constitution and symmetry of complexes on the annealing process of recoil atoms. They irradiated crystals of ferric cupferronate, potassium tris-oxalatoferrate and nickel(II) and cobalt(III) hexammines and determined the retention values. Octahedral complexes exhibit greater retention values than coplanar and sandwich complexes investigated by other workers. The thermal annealing of recrystallized samples is similar to that of non-recrystallized ones, suggesting that some of the entities created on irradiation are retained in solution and carried to the recrystallized solids as defects.

Photochemistry

Wasgestian and Schläfer (University of Frankfurt-am-Main, Germany) have studied the photoaquation of $[Cr(NH_3)_5Cl]^{2+}$:

$$[Cr(NH_3)_5Cl]^{2+} + H_2O \xrightarrow{h\nu} cis\text{-}[Cr(NH_3)_4Cl(H_2O)]^{2+} + NH_3$$

whereas the thermal aquation occurs as

$$[Cr(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Cr(NH_3)_5H_2O]^{3+} + Cl^-$$

Muraveiskaya *et al.* (Institute of General & Inorganic Chemistry, Academy of Sciences, Moscow) have investigated the action of visible and ultraviolet radiation on reactions of geometrical isomers of $[Pt(IV)am_2(NO_2)_2X_2]$ (am = NH_3, NH_2CH_3, en/2; X = Cl, Br). A new type of photo-chemical reaction — isomerization of asymmetrical $[PtamNO_2amXNO_2X]$ into symmetrical $[Pt(amNO_2)_2X_2]$ — has been discovered.

Gas Chromatography

This is an important technique in the separation and study of volatile coordination compounds. Sievers *et al.* (Aerospace Research Laboratories, Wright-Patterson AFB, Ohio, USA) have employed this technique for the separation of lanthanons employing the complexes formed with 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione [H(fod)] and 2,2,6,6-tetramethyl-3,5-heptanedione [H(thd)]. The fod complexes are more volatile than other known compounds of lanthanons. The trend in gas chromatographic retention of fod and thd complexes parallel the lanthanide contraction, the complexes of the larger ions being retained longer in the column. The effect of the structure of the ligand on the volatility of Cr(III) complexes of the type $Cr(ROC{-}CH{-}COR')_3$ has also been examined. The ease of elution on a poly(dimethylsiloxane) column increases in the order: $R,R' = C(CH_3)_3, C(CH_3)_3 < CH_3, CH_3 < C(CH_3)_3, C_3F_7 < CH_3, CF_3 < C_3F_7, CF_3 < C_2F_5, CF_3 < CF_3, CF_3$. The incorporation of fluorocarbon moities facilitates the elution and volatility of the complexes. This trend holds with complexes of both the transition and representative metals.

Acknowledgement

The author is thankful to Dr D. N. Satyanarayana for his cooperation during the preparation of this report.

International Conference on Spectroscopy

N. A. NARASIMHAM

Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 74

THE First International Conference on Spectroscopy in India was held in Bombay from 9 to 18 January 1967. The conference was organized by the Department of Atomic Energy, India, and co-sponsored by the International Unions of Astronomy (IAU), Chemistry (IUPAC) and Physics (IUPAP). Over 300 delegates attended the conference. Nearly 80 of them came from 12 countries, including USA, France, UK, Canada, USSR and Japan.

Inaugurating the conference, Vikram A. Sarabhai, Chairman, Atomic Energy Commission, recalled the significant contributions of spectroscopy and their applications to technology, solid state physics, plasma physics and allied fields. He referred to the notable contributions by Indian spectroscopists, the Evershed effect, the brilliant work of Meghnad Saha on thermal ionization and the contributions of C. V. Raman to the understanding of molecular spectra. H. N. Sethna, Director of the Bhabha Atomic Research Centre, speaking next, stressed the importance of international symposia which provide an excellent forum to scientists to exchange information and results of their investigations and to coordinate research programmes. R. K. Asundi, Chairman of the Organizing Committee, who presided on the occasion, read out messages from R. S. Mulliken, who was to have inaugurated the conference but could not undertake the journey due to pressing events that required his presence in USA, and from P. Swings, Chairman of the International Astronomical Union.

The conference was held for eight days. The morning sessions were devoted mainly to 30 invited lectures and were given at the Bombay University Club House. The afternoon sessions were devoted to about 115 contributed papers of 10-20 min. duration. These were presented in two parallel sessions at the Tata Institute of Fundamental Research. The subjects dealt with during the individual sessions included: (i) Spectra of atoms and of molecules of astrophysical interest, (ii) Diatomic spectra, (iii) Electronic spectra of polyatomic molecules, (iv) Infrared and Raman spectra and theory of molecular vibrations, (v) Radio frequency and microwave spectra including ESR and NMR, (vi) Solid state spectra, lasers, spectral studies of plasmas and other related topics.

J. Lecomte gave the first invited lecture of the conference on ' The measurement and applications of the infrared refractive indices for liquids and solids ' and was followed by an account of rare earth spectra by Charlotte Moore-Sitterly. Some of the interesting invited lectures that followed on subsequent days related to ' Soft X-ray spectrum of the sun as observed from satellites and rockets of USSR ' by S. Mandelstam, ' The absorption spectrum of interstellar material ' by G. H. Herbig and ' New molecular absorption spectra of ionized molecules (C_2^- and H_3^+) observed in flash discharges ' by G. Herzberg. C. A. Coulson gave an invited talk on ' The shape and size of an excited polyatomic molecule '.

There were nearly 30 papers dealing with spectra of diatomic molecules. One of them was by I. Kovacs, who had interpreted the rotational fine structure of diatomic molecules in terms of spin-orbit, spin-spin and rotation-spin interactions as well as the non-diagonal terms of the centrifugal term which were also to be taken into account. A. E. Douglas presented some new forbidden spectra observed in oxygen-like molecules, NF and NCl. K. Dressler gave convincing evidence for interpreting several of the singlet states of N_2 to only a few excited valence states, $^1\Sigma_u^+$ and $^1\pi_u$, with each state accounting for a very long vibrational progression of absorption bands.

High resolution spectra of polyatomic molecules have not been as well studied as that of diatomic molecules. This is mainly due to the complexity of the electronic spectrum of polyatomic molecules. K. K. Innes and J. H. Callomon presented excellent accounts of the fine structure analysis of formaldehyde, S-tetrazine, pyrazine, N_2O^+ and C_2N_2, while A. D. Walsh and S. Leach reported on gross structure studies on vacuum ultraviolet spectra of tetrachloroethylene and fluorescence spectrum of benzyl radicals respectively.

About 30 papers were presented on infrared and Raman spectra, and on the theory of molecular vibrations. R. C. Lord described a high resolution infrared spectrometer and discussed low frequency vibrational spectra in four-membered ring compounds and in quasi-linear molecules. H. L. Welsh gave an interesting account of pressure-induced infrared absorption and bound states of van der Waals molecules, particularly of H_2 in foreign-gas mixtures. H. H. Nielsen discussed the anomalies in the intensity distribution of vibration-rotation lines in the spectra of polyatomic molecules and P. Shorygin on the Raman resonance spectra.

Some 30 papers were presented on radio frequency and microwave spectra including ESR and NMR spectra. C. C. Lin gave an account on the investigations of line widths of microwave spectral lines and E. Hirota on rotational isomerism and internal rotation. M. T. Rogers and C. A. McDowell discussed ESR spectral studies of radicals, while W. A. Anderson and J. G. Powles discussed NMR spectra. Other interesting topics covered in the conference related to solid state spectra, particularly the papers by M. Balkanski and his group, new and improved techniques of instrumentation by B. Vodar and coworkers, plasmas by O. H. Theimer and A. von Engel, lasers by J. R. Singer and multi-photon processes in quantum electronics by A. M. Prohorov.

There was a one-day special symposium held in honour of R. K. Asundi on 10 January 1967. Several leading spectroscopists presented on this occasion important and original contributions in fields in which Asundi had made significant contributions and with which he was closely associated during the past nearly 40 years.

On all the days of the conference there were lively discussions both during the sessions and outside in the lobbies, and the beautiful lawns of the Tata Institute of Fundamental Research. The conference provided the unique opportunity to workers of different institutions in India to meet some of the eminent spectroscopists and discuss with them problems of common interest.

Seminar on Biochemical Engineering: Training & Research

T. K. GHOSE

Department of Biochemical Engineering & Food Technology, Harcourt Butler Technological Institute, Kanpur 2

A SEMINAR on Biochemical Engineering: Training and Research was organized by the Department of Biochemical Engineering & Food Technology, Harcourt Butler Technological Institute (HBTI), Kanpur, during 25-28 January 1967 with some financial assistance from the University Grants Commission. Biochemical engineering is a new emerging discipline covering such areas as fermentation, food processing and waste disposal, and the seminar was organized with a view to bringing together experts connected with teaching, research and development in the fields of food and fermentation technology and waste treatment so that they could hold discussions on the needs of a biological science-based engineering discipline in the country and give guidance for developing a sound training programme in biochemical engineering in the light of the recent advances made in biology, microbiology, biochemistry, chemical engineering, food processing, fermentation and waste treatment. In spite of the short notice of only 14 weeks given to the participants, the response from academic, research and industrial sectors was quite encouraging. The seminar was well attended and about 65 participants (including biochemical engineering and food technology students of the Jadavpur University and HBTI) took part. Prof. A. E. Humphrey (University of Pennsylvania, USA), a renowned authority in biochemical engineering and who is greatly responsible for promoting biochemical engineering thinking in various parts of the world, participated in the seminar. A significant feature of the seminar was an ' open session ', at which the results of discussions at different sessions were presented before a select general audience.

The inaugural session started on 25 January with a welcome address by Dr C. R. Mitra, Director, HBTI. The theme of the seminar was set forth through two keynote speeches delivered by Prof. A. E. Humphrey on ' Future of biochemical engineering ' and by Prof. T. K. Ghose on ' Biochemical engineering — Its present status and our task ahead '. The first technical session (8 papers), presided over by Prof. D. V. Rege (Bombay University), was devoted to the topic ' Interaction of biochemical engineering in the development of food processing industry in its total range from conventional to unfamiliar foods in India '. The second technical session (11 papers), presided over by Prof. A. E. Humphrey, was concerned with ' Current and future research in biochemical engineering — fermentation systems '. The third session (7 papers) was to have been presided over by Prof. W. W. Eckenfelder (Jr) (University of Texas, Austin, USA), but for unavoidable reasons he could not be present, and Dr T. R. Bhaskaran (All India Institute of Hygeine & Public Health, Calcutta) took the chair. The papers presented at this session were devoted to ' Current and future research in biochemical engineering — waste disposal systems '. The fourth session (6 papers), presided over by Prof. T. K. Ghose (HBTI), was concerned with ' Academic programme for training biochemical engineers '.

The discussions during the technical sessions were extremely useful and at the concluding session held on 28 January recommendations formulated by the chairmen of all the sessions were presented, discussed and adopted in the form of 12 resolutions dealing with biochemical engineering education, training, text-books and research.

The seminar, the first of its kind to be held in India, served to point out the need for a broad-based undergraduate biochemical engineering programme to be pursued in the universities and engineering institutions involving physical, biological and engineering sciences, and suggested measures for evolving a basic pattern of research in a developing country like India. The delegates were of the opinion that there is urgent need for organizing biochemical engineering as an independent discipline in the universities and higher institutes of technology, and that engineering education must include biological environment. It was resolved that for the purpose of academic training only a few centres of excellence should be entrusted with the programmes, and specialization in food processing, fermentation and waste treatment should be taken up at the postgraduate level. The delegates also felt that instead of having a large number of specialized undergraduate courses, it would be better and more economic to have a broad-based undergraduate biochemical engineering course which will take care of all the major operations involved in the processing of biological materials including foodstuffs, and waste treatment. The need for intensive research in the aforesaid areas and for producing suitable text-books on biochemical engineering was stressed.

Optical Centres in Alkali Halides: Part I—Electron Excess Centres & Colloidal Centres*

S. C. JAIN & S. RADHAKRISHNA
Solid State Physics Division, National Physical Laboratory, New Delhi 12

THE alkali halides are an important class of ionic crystals and the understanding of basic processes in these crystals has led to new experimentation and new theoretical investigations in many branches of solid state physics. A brief survey of centres responsible for absorption in the ultraviolet or the visible region of the spectrum in these crystals is presented in this review. We designate these centres as optical centres to distinguish them from those which give rise to absorption in other regions, e.g. microwave or X-ray regions. Optical absorption due to electron excess centres and colloidal centres will be discussed in this part, and that due to *Z* centres in the second part.

Electron Excess Centres

The alkali halide crystals show an extraordinarily wide region of optical transparency. Typical absorption curve of a good sodium chloride crystal is shown in Fig. 1(a) (ref. 1). Fig. 1(b) shows the sodium chloride crystal structure. It can be seen from the figure that there is almost no optical absorption in the crystal from about 1600 to 50000 A. The fundamental absorption in LiF crystal starts much farther in the ultraviolet and that in KI starts somewhat at longer wavelengths. However, the real crystals obtainable in the laboratory do not conform to the ideal structure shown in Fig. 1(b). Temperature dependent electrical conductivity and other experimental data show that crystals have a variety of defects which influence their physical properties in a remarkable way. At best we can hope to produce crystals with controlled number of known defects and study quantitatively the influence of these defects on the properties of ionic crystals.

It is the purpose of this survey to review the various optical absorption bands introduced in an otherwise transparent region in alkali halides and to discuss the nature of the centres responsible for these bands as we understand them today.

The first peak near 1600 A. of the fundamental absorption band shown in Fig. 1(a) is associated with the excitation of electrons from the halide ion. Any perturbation caused by the defects in the crystal is likely to effect the energy of this excitation. Delbecq *et al.*[2] made very detailed and systematic study of the perturbations caused by a negative ion vacancy and by an *F* centre, which is an electron trapped at a negative ion vacancy. The crystals containing negative ion vacancies and *F* centres show additional absorption bands in the neighbourhood of, and on the long wavelength side of, the fundamental absorption band. The bands, called α and β bands respectively, are shown in Fig. 2(a) for KI. On partially bleaching the crystal by illumination with the *F* light at low temperature, it is observed that the decrease in β band is proportional to the decrease in the *F* band. The α band at 238 mμ is observed after bleaching the crystal optically at liquid nitrogen temperature. On warming the crystal to room temperature, both the β and the *F* bands are restored to their original value and the α band disappears. The strict proportionality of β band with *F* band suggests that this band is directly connected with the *F* centre. The α band may be connected either with the *F'* centres which are formed by illuminating the crystal at low temperature or with anion vacancies from where the electrons are ejected. Since the α band has also been observed in X-irradiated crystal in which *F'* band was not appreciable, the band must be connected with the presence of anion vacancies. The fact that the band disappears on warming the crystal to room temperature and migration and association of vacancies take place

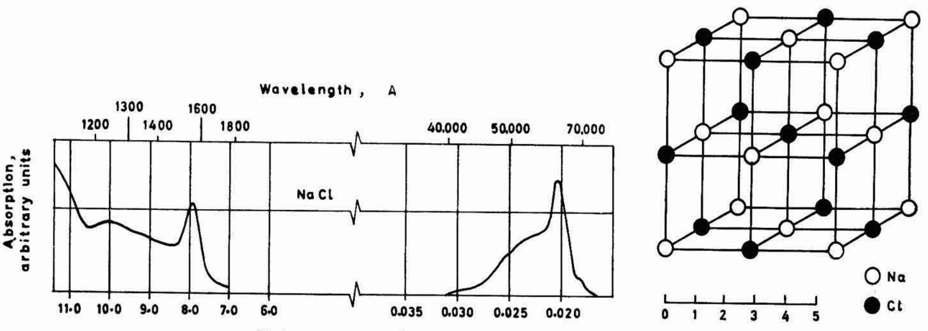


Fig. 1—(a) The ultraviolet and infrared spectrum of an alkali halide crystal [After J. H. Schulman & W. D. Compton, *Colour centres in solids* (Pergamon Press, Oxford), 1963]. (b) The structure of the NaCl type alkali halides

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*Paper presented at the convention organized by the Physical Research Committee of the Council of Scientific & Industrial Research, at the Banaras Hindu Universtiy, Varanasi, in March 1967.

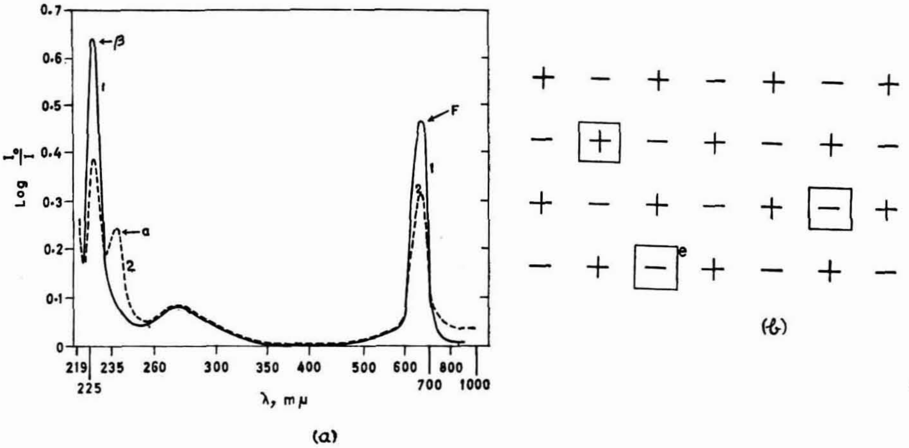

Fig. 2 — (a) The relationship between *F*, *F'*, α and β bands [Curve 1: spectra of additively coloured KI; and curve 2: after irradiation with *F* light. After M. Delbecq, P. Pringsheim & P. Yuster, *J. chem. Phys.*, **19** (1951), 574]. (b) Positive ion vacancy, negative ion vacancy and an *F* centre (an electron captured at a negative ion vacancy) are shown. α and β bands are due to perturbed exciton absorption in the neighbourhood of the negative ion vacancy and the *F* centre

shows that only isolated vacancies must be responsible for this band. Thus Delbecq *et al.*[2] were able to give conclusive evidence that the α and β bands are due to the electronic transitions from the anion to the cation in the neighbourhood of the anion vacancies and the *F* centres respectively. Similar 'Greek' bands have been observed due to mercury-like impurities in alkali halides[3].

The typical optical absorption bands introduced in KCl crystals by additive colouration are shown in Fig. 3 (Sootha, G. D., unpublished data). The crystal, after being rapidly quenched to room temperature from the colouring temperature, was bleached by optical light for about 30 min. to make the *R*, *M* and *N* bands prominent. If the crystal is not bleached optically, it mainly contains the *F* band and a very small amount of the *M* band. The *F* centres responsible for the 560 mμ band in KCl have been the subject of extensive study during the last 30 years. It is not necessary to discuss in detail all the features of *F* centres in this survey as recent excellent reviews are available on the subject[4-6]. However, we would like to make a brief mention of some of the recent work done at the National Physical Laboratory which has revealed some new and interesting features of these centres.

The *F* centre [Fig. 2(b)] is an electron trapped at a negative ion vacancy. Since the negative ion vacancy behaves as a positively charged point at longer distances and since the potential that the electron experiences at large distances is coloumbic, the electron is bound to the vacancy and has infinite number of excited states. Since about 90 per cent of the oscillator strength is associated with the transition from the ground to the first excited state, the absorption due to higher excited state is extremely small. However, the absorption due to the excited state has been studied recently by Luty[7]. The behaviour of *F*

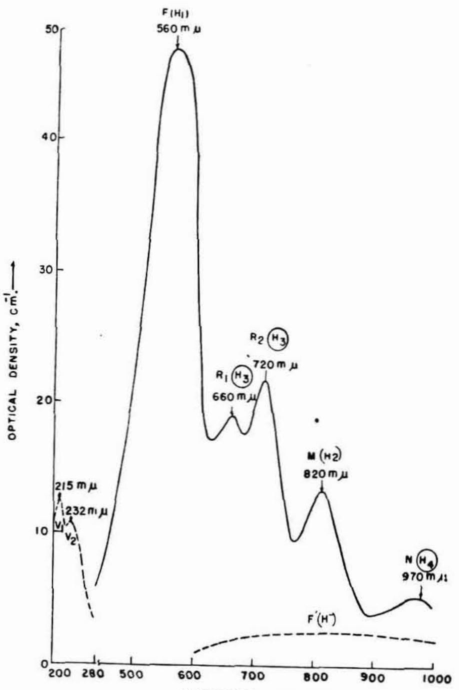

Fig. 3 — The *F* and *F* aggregate bands in an additively coloured crystal of KCl obtained after optically bleaching the crystal [The figures in brackets indicate the analogous hydrogen-like examples. The molecule of 3 and 4 hydrogen atoms is not known. This is indicated by putting H_3 and H_4 in full circles. The position of the *V* and *F'* bands are also shown in the figure by dashed curves]

centres in an irradiated crystal is somewhat different from that in additively coloured crystal. Jain and Mahendru[8] have studied extensively the optical and thermal stability of *F* centres in X-irradiated highly pure KCl crystals.

In Fig. 4 are shown the thermoluminescence results in highly pure X-irradiated KCl crystals. Curves 1-10 are for different times of X-irradiation starting from 30 min. to 24 hr. It will be seen from the figure that for each curve there are two thermoluminescence peaks. Crystals containing more than one or two parts per million of background divalent impurity show additional thermoluminescence peaks at lower temperature. Crystals which were plastically deformed or rapidly quenched showed a thermoluminescence peak at 270°C. It can be seen from the figure that for short times of X-irradiation, the first peak at 135°C. is the only prominent peak. As the time of irradiation increases, the second peak increases rapidly and after about 14 hr of X-irradiation (curve 9) the peak at 190°C. becomes so large that the first peak appears only as a small shoulder. This shows that the apparent number and position of thermoluminescence peaks depend sensitively upon the background impurity, heat and mechanical treatments and the time of X-irradiation. It is no wonder that the thermoluminescence work of earlier workers showed such a wide discrepancy.

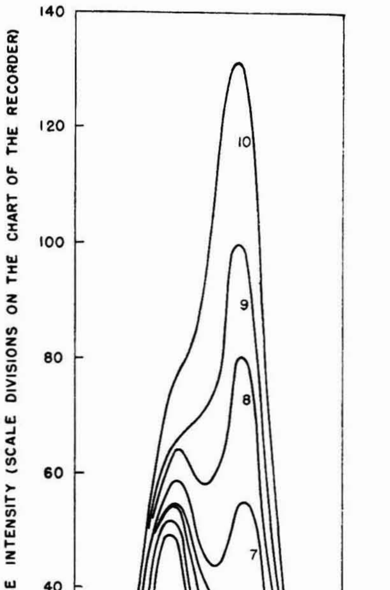

Fig. 4 — Growth of the *F* band and the thermoluminescence with the time of X-irradiation [The periods for which X-irradiation were done were 30 min., 1 hr, 2 hr, 3 hr, 5 hr, 7 hr, 10 hr, 14 hr, 17 hr and 24 hr respectively for curves 1-10. After S. C. Jain & P. C. Mahendru, *Phys. Rev.*, **140** (1965), 957]

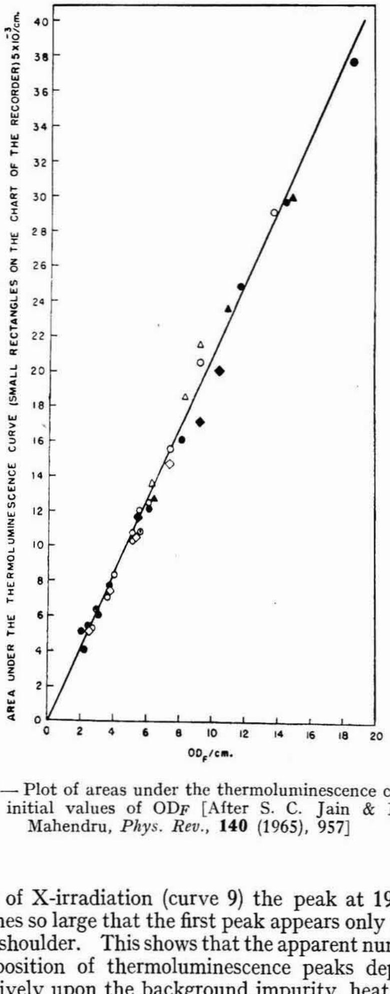

Fig. 5 — Plot of areas under the thermoluminescence curves versus initial values of OD$_F$ [After S. C. Jain & P. C. Mahendru, *Phys. Rev.*, **140** (1965), 957]

In Fig. 5 the total area under the thermoluminescence peaks in Fig. 4 is plotted as a function of optical density at the *F* peak before heating the crystal to induce thermoluminescence. The straight line plot between the total area and the total optical density at *F* peak shows that the total area under both thermoluminescence peaks is proportional to the total number of *F* centres initially present in the crystal.

The rate of growth of *F* centres as a function of time of X-irradiation was also studied by the authors. The curve indicated the usual two-stage growth. Using the method developed by Mitchell *et al.*[9], the two stages were separated and the number of *F* centres produced in the first stage and the second stage were calculated separately. The points showing the area under the first peak as a function of number of *F* centres produced in the first stage and the area under second peak as a function of the number of

F centres produced in the second stage for different times of X-irradiations plot smoothly on the same straight line, showing the proportionality separately between the thermoluminescence areas of the two peaks and the numbers of *F* centres produced in the first and the second stages. This shows conclusively the interesting result that the *F* centres produced in the first stage colouration bleach at lower temperatures giving rise to the first thermoluminescence peak, and the *F* centres produced in the second stage bleach at higher temperatures giving rise to second thermoluminescence peak. Since the constant of proportionality is the same in both the cases quantum efficiency of production of photon by ionized electron remains the same in both the cases. All *F* centres give rise to one bell-shaped optical absorption band, but for thermal bleaching they can be divided at least in two groups, one bleaching at a lower temperature and the other at higher temperatures. Though the authors have suggested a tentative mechanism to interpret this result, further work is necessary to understand the nature of the two types of centres.

Models of *M*, *R* and *N* centres first given by Seitz[10] in 1946 were consistent with the available experimental data until 1957. However, some simple experiments by Van doorn[11] in 1957 showed that the equilibrium between *F* and *M* centres is controlled by the equation

$$\frac{C_M}{C_F^2} = K(T) \qquad \ldots(1)$$

where C_M and C_F are the concentrations of *M* and *F* centres. This indicates that the *M* centre is a hydrogen molecule like centre consisting of two *F* centres in the nearest neighbouring positions. Soon after this Pick[12] suggested that the *R* centre consists of three neighbouring *F* centres and the *N* centre consists of four neighbouring *F* centres. Schnatterly and Compton[13] have confirmed that these models of *R* and *N* centres are correct. For a detailed account of these centres, the reader is referred to an excellent review on the subject by Compton and Rabin[14]. We would like to indicate here briefly some of the important results of the recent work on *R*, *M* and *N* centres in KBr obtained at the National Physical Laboratory.

Jain[15] has studied the optical and thermal stability of *F* aggregate centres and has evaluated the oscillator strengths of these centres in KBr. The optical absorption as a function of time after bleaching by visible light for a known length of time is shown in Fig. 6. Since the total amount of excess alkali metal present in the crystal remains the same, the oscillator strength of the aggregate centres can be estimated[5] by measuring the relative changes in the optical density at the peak of *F*, *R*, *M* and *N* bands. If an additively coloured KBr crystal is bleached by visible light to generate a large number of *R* and *M* centres the relative number of centres changes in dark at room temperature slowly. The *N* centre concentration increases and the *M* centre concentration decreases. All these results can be used[5] to determine the oscillator strength of the *M*, *R* and *N* centres in terms of the oscillator strength of the *F* centres. The oscillator strength of *F* aggregate centres determined in this manner by Jain[15] is given in Table 1.

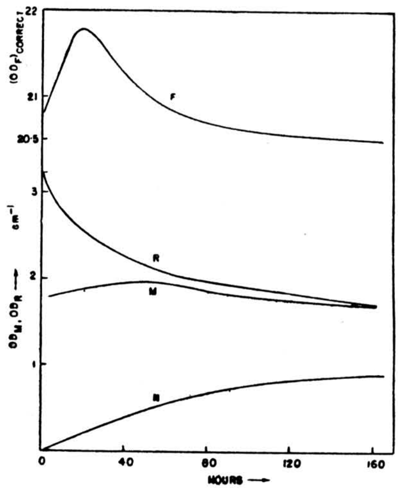

Fig. 6 — Variation of optical absorption under different bands as a function of time in dark at room temperature in KBr crystals [After V. K. Jain, *Optical and electrical properties of highly pure and doped KBr and NaCl crystals*, Ph.D. thesis, Delhi University, 1967]

TABLE 1 — OSCILLATOR STRENGTHS FOR *M*, *R* AND *N* CENTRES

(f_F = 0·48)

No.	f_R/f_M	f_M/f_F	f_M	f_R	f_N
1	3·82	0·221	0·106	0·41	0 366
2	4·18	0·213	0·102	0·45	0·337
3	3·64	0·235	0·112	0·39	0·386
Av.	3·9 ±0·3	0·22 ±0·01	0·107 ±0·005	0·42 0·03	0·36 ±0·03

Extensive work has been done on the electrical properties of electron excess centres[16,17] in this laboratory. All these centres act as donors in alkali halide crystals. The ionization energy is around one electron volt for *F* and *M* centres and a few tenths of an electron volt for the *R* and *N* centres. The fact that the excess conductivity due to these centres is electronic has been confirmed by simultaneous self-diffusion measurements in coloured crystals by Jain and Parashar[18]. However, if the crystal contains background divalent impurity, the large excess conductivity associated with the centres is not observed. In fact, conductivity is suppressed in this crystal by a large factor. This is due to the formation of relatively stable aggregates consisting of *F* centre cation vacancy and the impurity ion in the crystal.

Colloidal Centres

The optical, electrical and other studies of metallic particles in alkali halides make an interesting subject.

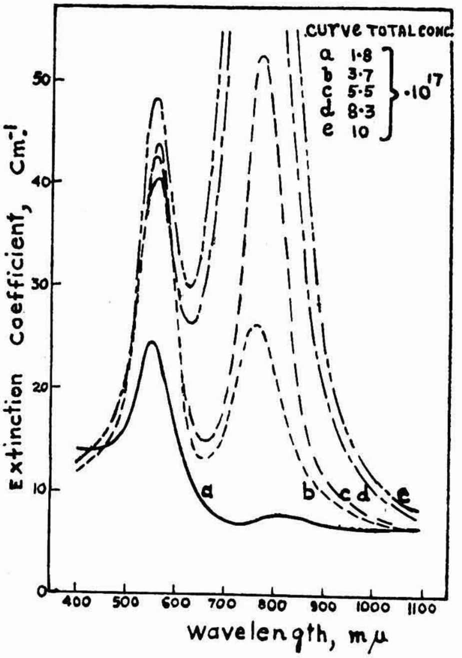

Fig. 7 — Absorption at room temperature for a series of KCl crystals with different concentrations of excess potassium after heat treatment at 400°C. for 15 min. and quenching to room temperature [After A. B. Scott & W. A. Smith, *Phys. Rev.*, **83** (1957), 982]

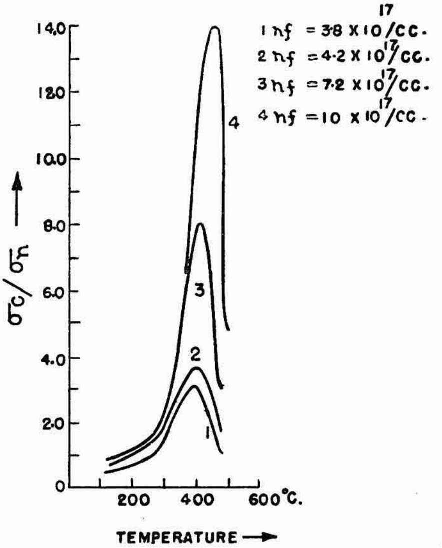

Fig. 8 — Plot of σ_c/σ_n versus temperature [n_F is concentration of *F* centres present at room temperature in quenched crystals. After S. C. Jain & G. D. Sootha, *Physics Chem. Solids*, **26** (1965), 267]

Fig. 7 shows the conversion of *F* band into colloid band[19] when the additively coloured crystals containing different concentrations of alkali metal are heated at a temperature between 300° and 400°C. It is seen from the figure that in crystals heated to 400°C., the *F* concentration is approximately constant and all the extra metal added to the crystal goes into colloidal centres. Based on these observations Scott and Smith[19] suggested that the equilibrium between the *F* centres and the colloidal particles is heterogeneous, the *F* centres forming the vapour phase and colloidal centres, the condensed phase. Subsequent optical work on these centres has been somewhat contradictory. Shatalov[20] has disputed the colloidal nature of these centres in KCl. His results do not support the idea that heterogeneous equilibrium between the *F* centres and the centres responsible for the other band exists. The controversy between the Russian and American workers has been resolved as a result of extensive work done by Sootha[21]. He has shown that exposure of crystals to visible light, even to a very small extent inadvertently, has a marked influence on the electrical and optical behaviour of the crystal on subsequent heating. The purity of the crystal is also important in determining the exact nature of the centres responsible for optical absorption peak formation near 7300 A. In zone refined and highly pure crystals, heated with great care to avoid exposure to light, a relatively pure colloidal band is formed and the heterogeneous equilibrium between the *F* centres and colloidal centres is confirmed by independent EPR and electrical measurements[21]. This work has revealed that Shatalov's failure to observe EPR absorption line due to the colloidal centres was due to the fact that his crystals containing background impurity had been exposed to light and the optical bands observed by him were different from the true colloidal band. In Fig. 8 the conductivity of the additively coloured crystal divided by the normal conductivity of the crystal is shown as a function of temperature for the four crystals containing different concentrations of excess alkali metal[17]. The conductivity increases in the temperature range where *F* centres are converted into metallic colloidal centres. The ratio of two conductivities obtained a peak value 14 in a heavily coloured crystal. At higher temperatures, the excess conductivities decrease because the colloidal centres are converted back into *F* centres. Careful examination of the curve shows that the peak position changes from 400° to 450°C. as the concentration of excess alkali metal increases from 10^{17} to 10^{18} cm.$^{-3}$. Excess conductivity is electronic due to the emission of thermal electrons into the conduction band of the crystal. The authors have shown that the shift in peak position in Fig. 8 provides independent evidence for the heterogeneous equilibrium between the *F* centres and metallic particles. From these measurements the authors were able to derive a value of 0·32 eV. electron affinity for KCl and a 0·9 eV. for the energy of sublimation of potassium metal which agrees with the known bulk value. It was mentioned earlier that the electronic nature of the conductivity was confirmed by Jain and Parashar[18] with the study of self-diffusion of potassium in potassium chloride. Their results, shown in

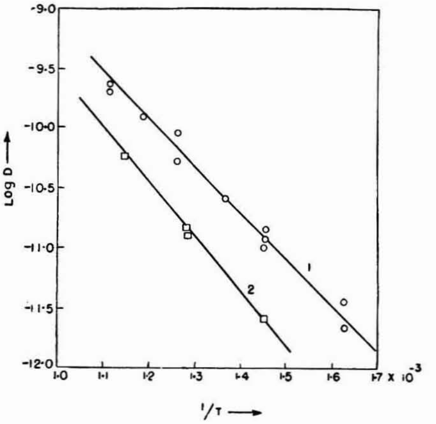

Fig. 9 — Plots of log of self-diffusion coefficient as a function of reciprocal of absolute temperature in uncoloured (curve 1) and additively coloured (curve 2) KCl crystals [After S. C. Jain & D. C. Parashar, *Physics Chem. Solids*, **24** (1964), 1269]

Fig. 9, indicate that the diffusion is considerably reduced in additively coloured crystals in the temperature range where Jain and Sootha observe an increase in conductivity. If the increased conductivity is ionic, it should be accompanied by a large increase in the diffusion coefficient. The excess conductivity, therefore, must be electronic.

We have discussed very briefly the recent work on some of the centres in alkali halides which give rise to optical absorption. Extensive work has been done on Z centres due to alkaline earth impurities in alkali halides. These centres are discussed in Part II of this review.

Summary

The electron excess centres, hole excess centres, vacant lattice points, impurities and other centres giving rise to absorption in the region 1700-10000 A. in alkali halides are enumerated. The electron excess centres and the colloidal centres are reviewed in greater detail. The absorption due to α and β centres, F centres and F aggregate centres, and the models of some of these centres are discussed. Recent work on F centres done in the National Physical Laboratory is reviewed. This work shows that in highly pure KCl crystals all F centres are identical optically, but thermal and thermoluminescence studies indicate that the centres can be divided at least in two classes, the 'soft centres' and the 'hard centres'. Some work on optical and thermal bleaching of the electron excess centres in KBr is discussed, and the oscillator strengths of the M, R and N centres are reported. The recent work on colloidal centres, which has cleared many obscure points, is also discussed. It is found that the optical absorption bands obtained between 700 and 800 mμ in KCl crystals belong to different species of centres. The pure colloidal band is obtained only if the crystals are highly pure and the work is done in absolute darkness. Some results on the electrical properties of the crystals containing electron excess centres and colloidal centres are also discussed.

References

1. SCHULMAN, J. H. & COMPTON, W. D., *Colour centres in solids* (Pergamon Press, Oxford), 1963.
2. DELBECQ, M., PRINGSHEIM, P. & YUSTER, P., *J. chem. Phys.*, **19** (1951), 574.
3. FUKUDA, A., *Sci. Lt, Tokyo*, **13** (1964), 64.
4. SEITZ, F., *Rev. mod. Phys.*, **26** (1954), 7.
5. SCHULMAN, J. H. & COMPTON, W. D., *Colour centres in solids* (Pergamon Press, Oxford), 1963.
6. MARKHAM, J. J., *The F centre in alkali halides* (Academic Press Inc., New York), 1965.
7. LUTY, F., *Z. Phys.*, **153** (1958), 247.
8. JAIN, S. C. & MAHENDRU, P. C., *Phys. Rev.*, **140** (1965), 957.
9. MITCHELL, P. V., WEIGAND, D. A. & SMOLUCHOWSKI, R., *Phys. Rev.*, **121** (1961), 484.
10. SEITZ, F., *Rev. mod. Phys.*, **18** (1946), 348.
11. VAN DOORN, *Philips Res. Rep.*, **12** (1957), 309.
12. PICK, H., *Z. Phys.*, **159** (1960), 69.
13. SCHNATTERLY, S. & COMPTON, W. D., *Phys. Rev.*, **135** (1964), A227.
14. COMPTON, W. D. & RABIN, *Advances in solid state physics*, Vol. 16 (Academic Press Inc., New York), 1964.
15. JAIN, V. K., *Optical and electrical properties of highly pure and doped KBr and NaCl crystals*, Ph.D. thesis, Delhi University, 1967.
16. JAIN, S. C. & SOOTHA, G. D., *Nature, Lond.*, **193** (1962), 566.
17. JAIN, S. C. & SOOTHA, G. D., *Physics Chem. Solids*, **26** (1965), 267.
18. JAIN, S. C. & PARASHAR, D. C., *Physics Chem. Solids*, **24** (1964), 1269.
19. SCOTT, A. B. & SMITH, W. A., *Phys. Rev.*, **83** (1957), 982.
20. SHATALOV, J., *Izv. Akad. Nauk. SSSR. Ser. Fiz.*, **22** (1958), 1324.
21. SOOTHA, G. D., *Optical, electrical and ESR investigations of colloids and other colour centres in pure and doped KCl and LiF crystals*, Ph.D. thesis, Delhi University, 1967.

Inhibition of Plant Pathogens by Higher Plant Substances*

P. N. THAPLIYAL & Y. L. NENE

Department of Plant Pathology, UP Agricultural University, Pantnagar, Naini Tal

THE presence of antimicrobial substances in higher plants is well known since ancient times. Egyptians probably used mixtures of certain vegetable oils for the preservation of mummies from protein decomposing bacteria. Greeks and Romans used the juice of green walnut shells against infectious fungal diseases of skin[1]. Clove oil is used even today to disinfect dental pulp cavities. The application of plant extracts for the control of a plant disease was attempted as early as 470 B.C. by Democritus[2]. However, it is only in recent years that intensive research is being made to discover antimicrobial substances from higher plants which could be used for the control of diseases caused by plant pathogens. The present article is a review of findings reported on the *in vivo* and *in vitro* inhibition of plant pathogens by substances from higher plants.

Antifungal and Antibacterial Substances

Inhibition in vivo

Diffusible substances — Exosmosis of materials from the external aerial surface of plants parallel to root exudates in soil is known to take place. The moisture film on plant surface carries both organic and inorganic substances in solution, released from the underlying plant tissue, and these may influence the germination of spores of surface microflora[3-5]. The principal antimicrobial substances biosynthesized by phanerogams are: alkaloids, glycosides, sulphur compounds, unsaturated lactones, fatty acids, phenols, quinones and their derivatives, and essential oils[6].

Phenolics — Phenolics comprise a vast class of compounds including anthocyanins, leucoanthocyanins, anthoxanthins, hydroxybenzoic acids, glycocides, sugar esters of phenolic acids, esters of hydroxycinnamic acids and coumarin derivates[7]. The possible general importance of naturally produced phenolic compounds in the disease resistance of plants has been suggested by Link and Walker[8], citing the common presence of phenolic compounds combined with pigments, tannins, glycosides, resins and gums as an additional evidence in the plant kingdom. The yellow pigments of flavone type were suggested to be the main phenolic compounds partly responsible for the resistance which some varieties of wheat show against stem rust fungus[9]. The presence of volatile and non-volatile antimicrobial substances in the fleshy pigmented onion scales is considered as a factor for the resistance of onions against *Colletotrichum circinans* (Berk.) Vogl. and more so because the removal of coloured scales renders these onions susceptible[10]. Protocatechuic acid, obtained in crystalline form from the water extracts of the pigmented scales, is highly active, whereas catechol, also identified in the extracts, accounts for some of the inhibitory activity[11,12]. Inhibitory substances obtained from the leaf surface can confer resistance when redeposited on otherwise susceptible leaves[5]. The extracted waxes from the leaf surface of apple varieties (Worcester-per-main and cox's orange pippin) resistant to *Podosphaera leucotricha* (Ell. & Everh.) Salm., when redeposited on the leaves in an aqueous solution together with a wetting agent, prevent the germination of the conidia on apple leaves. These waxes also protect *Vicia faba* L. leaves when inoculated with *Botrytis fabae* Sard. The main component separated by chromatography is a phenol with similar chromatographic and colour reactions to a fungitoxic substance which is found in water-washings of leaves of many trees and in the leaf and root exudates of *Vicia faba* L.[13].

Organic acids — Certain organic acids have been reported to impart resistance to some plants. Flax root excretions are supposed to be related to resistance to wilt caused by *Fusarium oxysporum* f. *lini* (Bolley) Snyder & Hansen[14,15]. Root excretions from these plants contain hydrocyanic acid in quantities sufficient to inhibit the growth in culture of *Fusarium oxysporum* Schl., susceptible varieties, on the other hand, release no detectable amount of cyanide[8]. Spore germination of *Verticillium albo-atrum* Reinke & Berth. is inhibited when incubated in closed vessel with uninjured apricot roots[16]. The reaction is explained as due to the presence of mandelonitrile in the mature apricot root bark, which is broken down into highly toxic hydrocyanic acid and mildly inhibitory benzaldehyde. It has been suggested that the absence of pathogen in the diseased apricot trees between January and June may be due to the excess release of hydrocyanic acid during this period. *Cicer arietinum* L. secretes malic acid from glandular hairs which inhibits spore germination of *Aschochyta rabie* (Pass.) Lab. The resistant varieties with more hairs secrete more malic acid in the later growth stages[4].

Unspecified compounds — Different wheat varieties have been reported to depress the germination of conidia of *Helminthosporium sorokinianum* Sacc. on their leaves. A similar depression of spore germination in the leaf secretions from these varieties has been observed by Van Velson[17]. However, there is insufficient understanding as to how these secretions act. Aren[3] suggested that epidermal excretions play an important part in establishing infection in case of *Plasmopara viticola* (Berk. & Curt. ex de Bary) Burl. & de Toni, because the surface active materials accumulating in the interphase between stomatal gas and infection drop govern the activity of the guard cell. The leaves of many plants, if simply washed with water for brief periods, yield aqueous extracts which inhibit

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the germination of many fungus spores. The low incidence of local lesions on the leaves of sugarbeet has been correlated with the presence of diffusible inhibitors. A rather small number of spores of *Cercospora beticola* Sacc. germinate in dew or water-washings collected from beet leaves. These washings are active even after considerable dilutions[18]. A positive correlation between resistance to a given race of *Fusarium oxysporum* f. *pisi* (Lindf.) Snyder & Hansen and toxicity of root diffusates from healthy plants of pea towards germination of the spores of the same race has been observed by Buxton[19]. The root exudates of two sorghum strains delay the spore germination of *Heliminthosporium turcicum* Pass. and of *Fusarium moniliforme* (Sheld) Snyder & Hansen. These two pathogens are unable to establish in the rhizosphere of these strains during the early period of growth[20].

Non-diffusible substances — Good evidence to show an intracellular compound playing role in the defence against disease is rather difficult to obtain. Phenols have been considered to play a role in rust resistance but how this happens is not clear[9,21]. Similarly, the fungitoxic alkaloid ' tomatin ' in tomato plants is present in insufficient concentrations to account for resistance[22]. Virtanen and coworkers[23,24] have characterized a number of fungistatic compounds found in plants. A knowledge of the distribution and changes during development of compounds such as chlorogenic, gallic and benzoic acids, and their derivatives would be most useful in determining the extent of part these substances play in disease resistance.

Phenols — The possible role of phenols in disease resistance has been suggested by various workers. Particularly, chlorogenic acid has been studied in detail from this point of view. The presence of more chlorogenic acid in the vascular system of young potato plants than is needed for *in vitro* inhibition of *Verticillium albo-atrum* Reinke & Berth. has been reported by McLean *et al.*[25]. Studies on the correlation between the distribution of chlorogenic acid in potato tubers and their resistance to potato scab [*Streptomyces scabies* (Thaxt.) Waksm. & Henrici] have supported the view that non-diffusible substances play a part in disease resistance *in vivo*[26-28]. The resistant varieties contain more chlorogenic acid and it is largely confined to the outermost tissue where the scab organism normally proliferates, and the tissue around the lenticels where infection occurs. Schaal and Johnson[27] tested *in vitro* the inhibitory effect of phenolic compounds on the growth of *Streptomyces scabies* (Thaxt.) Waksm. & Henrici and suggested that, in potato tubers, chlorogenic acid is enzymatically oxidized by tyrosinase to form quinones in tissues injured by the invading scab organism, and this might be the main mechanism involved in scab resistance. Higher concentration of chlorogenic acid is found in the roots of the resistant potato varieties than that in the susceptible ones[29]. Quinones are generally more inhibitory than the phenols to *Verticillium albo-atrum* Reinke & Berth.[30]. Patil *et al.*[31] investigated chlorogenic acid and free phenol content of potato roots at different stages of growth, and observed that their concentration decreases three weeks after presprouted, single eye seed pieces were transplanted. Decrease in free phenols also lowered the resistance of plants to *Verticillium albo-atrum* Reinke & Berth. Chlorogenic acid is not toxic to this organism up to 1000 p.p.m., but oxidation products inhibit the spore germination. Phenols are also associated with the resistance of sugarcane to red rot[32] and of red cedar heartwood to attack by wood decaying fungi[33]. Localized release of phenols, resulting from collapse of tonoplast due to the infection of white pine by *Cronartium ribicola* J. C. Fisher, in quantities toxic to the pathogen takes place. However, the localized release may not be sufficient to prevent the systemic development of blister rust of pines[34]. A rapid accumulation of phenols in resistant wheat varieties has been reported by Kiraly[35].

Sulphur compounds — A correlation between mustard oil content, antimicrobial activity, and resistance to *Xathomonas campestris* (Pammel) Dowson in cabbage has been reported by Beltykova and Gvozdyak[36]. Allyl and β-penethylisothiocyanates active components of mustard oil are effective against *Plasmodiophora brassicae* Woron[37]. The concentration of mustard oil in roots of crucifers is enough to inhibit the spore germination of *Plasmodiophora brassicae in vitro*. However, Link and coworkers were unable to find any difference in the mustard oil or glycoside content of resistant and susceptible crucifers, and concluded that mustard oils are not essential for club root resistance[38].

Alkaloids and glycosides — *Mahonia swaseyi* (Bukl.) Fedde and *M. trifoliolata* (Moric) Fedde plants flourish in cotton fields heavily infested with cotton root rot fungus [*Phymatotrichum omnivorum* (Shear) Duggar], probably due to the presence of berberine, an alkaloid in their roots[39,40]. A similar involvement of the alkaloid, ' solanine ', in protecting plants against *Cladosporium fulvum* Cooke, has been suggested by Schmidt and coworkers[41,42]. The presence of a number of inhibitors in the corn stalk as factors for resistance to *Diplodia zeae* (Schw.) Lev. infection has been reported by a number of workers[43-45]. A methoxy derivative of 2(3)-benzoxazolinone, MBOA, accounted for about half of the total resistance[44]. Recently, BeMiller and Pappelis[46] reported a relationship between the glycoside (MBOA) content and stalk rot resistance of corn stalks.

Unspecified compounds — A large number of plants contain compounds toxic to the plant pathogens, but the chemical nature of these compounds is not well understood. Barley seedlings contain an antifungal agent which protect them from *Helminthosporium sativum* Pamm., infection for few days[47]. The accumulation of antimicrobial substances in leaves and fruits of apple and pear varieties with different maturity times is known to take place[48]. The delay in the production of the mature lesions on banana leaves has been attributed to the production of some antifungal substance in response to the invading fungus (*Mycospherella musicola* Leach)[49]. The natural durability of *Eucalyptus* spp. seems chiefly due to the toxicity of methanol soluble constituents, highly effective against *Coniophora cerebella* [*C. puteana* (Schum. ex Fr.) Karst][50]. The immunity to *Phymatotrichum* *omnivorum* (Shear) Duggar is due to certain unidentified toxic material present in monocots but apparently absent in dicots[51]. However, the well-known resistance of monocots to crown-gall is not due to antibiotic[52].

Inhibition in vitro

Interest in the possibility of discovering important naturally occurring antimicrobial substances in plants has been increasing[53-57]. This is of particular interest to India, because in *Ayurveda*, the indigenous system of medicine, references are made to a large number of indigenous plants possessing medicinal properties. More attention is being given these days to obtain information on the uses of such plants with the help of modern techniques.

Osborn[58] carried out the first large-scale systematic search for the plants having antibacterial properties. She screened 2300 species of plants of which 63 were antimicrobial. The extracts of Ranunculaceae showed greater inhibitory effect than plants of other families studied. Extracts of certain Ranunculaceae are effective also against plant pathogens[59]. Peturshova[60] studied the fungicidal activity of 1281 species of plants from 184 families against a number of plant pathogens. Twenty-six species inhibited them all, whereas 1237 species were fungicidal to varying degree. Higher fungicidal activity was observed in species of Anacardiaceae, Compositae, Cruciferae, Labinatae, Liliaceae, Ranunculaceae, Rosaceae and Solanaceae. Abdullaeva[61] studied the antimicrobial properties of 400 species of plants from 70 different families against *Pseudomonas* (*X.*) *malvacearum* (Erw. Sm.) Dowson, *F. oxysporum* f. *vasinfectum* (Atk.) Snyder & Hansen, *Rhizoctonia* sp. and *Verticillium dahliae* Kleb. Exposure to the volatile fraction of the leaves of most of the plants inhibited the development of fungi and bacteria. Maximum activity was reported in the members of pine, cypress, aroid, lily and bean family. Activity is influenced by the environment; crucifers only from the mountainous regions are active; and leaves have more activity than stem. Maximum activity is observed in leaves during spring and during summer and autumn the activity sharply decreases. On the basis of the hypothesis that plants which remain apparently always disease-free may be doing so because they contain fungitoxic substances, Nene *et al.* (unpublished data) screened extracts from 77 plants out of which 13 showed antifungal properties and 8 of them inhibited the test fungus, *Colletotrichum papayae* (P. Henn.) P. Henn., completely.

Phenols — A substance quite active against various invaders has been noticed in the heartwood of *Abies balsamea* Mill[62]. Three compounds isolated from the balsam heartwood have been found to be selectively inhibitory to some fungi[63]. The compounds may be resins or balsam derivatives. The extracts from poison Sumae (*Rhus vernix* L.), garlic, and decoction of crocus bulbs are highly toxic to *Colletotrichum lauri*, causal organism of brown spot of *Laurus nobilis* L.[64]. Thujaplicin, from *Thuja plicata* Don, has three isomers varying quantitatively as well as qualitatively in their activity towards microorganisms, 'gamma-thujaplicin', a phenol, has been reported to be highly toxic to microorganisms[65]. The well-known resistance of conifers to destructive fungi is due to the presence of antimicrobial substances such as 'thujaplicin', possibly in conjugation with water-repellant oils in conifers[66]. Extracts of tannin containing plants, such as *Acacia arabica* Willd., *Emblica officinalis* Gaertn., *Terminalia arjuna* Bedd. and *T. bellerica* Roxb., are highly fungitoxic[67]. Polyphenols of low molecular weight and polymerized condensed tannins have been reported to be the main factors responsible for fungitoxicity in *Cassia fistula* L. and *Acacia catechu* Willd.[68]. Two compounds separated by chromatography from extracts of Russet and Netted Gem potato peel and pulp and which are fungistatic to *Helminthosporium carbonum* Ullst. and resemble in physical and chemical properties to chlorogenic and caffeic acids are presumed to be closely associated with natural immunity for *H. carbonum* Ullst. in potato[69,70].

Sulphur compounds — The bacteriostatic activity of volatile and non-volatile fractions of the extracts of *Allium sativum* L. and *A. cepa* L. has been studied by Abdullaeva[71]. Volatile fractions inhibit the growth of *Verticillium dahliae* Kleb., *Fusarium oxysporum* f. *vasinfectum* (Atk.) Snyder & Hansen, *Xanthomonas malvacearum* (E. F. Smith) Dows. and *Rhizoctonia* sp. Allicin, an antibacterial principle has been isolated from the *Allium sativum* L.[72]. Juices from garlic exhibit strong bactericidal and fungicidal activity, the volatile component being effective against plant pathogenic microorganism[73,74]. Expressed onion juice at 1: 1000 concentration has an inhibitory effect on the formation of colonies from mixed population of soil sample and it prevents the detachment of swarm spores of *Phytophthora infestans* (Mont.) de Bary. The conidia of *Aspergillus niger* Van-Teigh are killed *in vitro* by the volatile constituents of garlic and horse radish. Juices from garlic and onion are inhibitory to both *Corynebacterium rathayi* (E. F. Smith) Dows. and *Serratia marcescens* Bizio *in vitro*[1]. Raphanin, the active principle of the extracts of the seeds of radish (*Raphanus sativus* L.), has been extensively studied and it inhibits *in vitro* the growth of a wide range of organisms[75]. Radish seed extract is more active than cabbage and broccoli seed extracts when tested against *X. campestris* (Pamm.) Dows. The inhibitor is water soluble and dialysable, and contains protein, phenol and sulphur[76].

Alkaloids and glycosides — The observation that expressed juice from tomato varieties highly resistant to fusariosis exhibits fungistatic activity towards *Fusarium bulbigenum* f. *lycopersici* (Brushi) Wr. & Reinke[22] supports the earlier view that some varieties of tomato produce antimicrobial agents, capable of inhibiting the growth of fungus[77]. The active substance has been termed 'tomatin' (sny. lycopersicin), but its chemical composition is not yet completely known. The active compound from tomato plants with varying resistance has been shown to be a non-protein active against *Corynebacterium michiganense* (Erw. Smith) Jenson, *Erwinia aroideae* (Townsend) Holland, and *E. carotovora* (Jones) Holland. The sap from resistant tomato varieties (Meksikanskii and Vishnevidnyi) and resistant

Solanum nigrum L. are reported to be active against *C. michiganense* (Erw. Smith) Jenson; *Solanum nigrum* L. sap killed the test organism in 1 hr[78,79]. Constatin-4 derived from hemp has been found to be effective against a number of phytopathogenic bacteria, the reaction differed from organism to organism[80].

Anemonin, extracted from *Anemone* species, is one of the specific inhibitory substances recognized for a long time. Aqueous solution of anemonin in a concentration 1: 50,000 retards the growth of *Rhizopus nigricans* Ehrenb. *in vitro*[81]. Most of the members of family Ranunculaceae contain antifungal substances; maximum amount of the active principle is found in the buds of *Ranunculus polyanthemos* L., *R. lanuginosus* L. and *R. acer* L. and minimum in the fruits. In early autumn, the concentration of active principle is more in the roots of *R. acer* L. than in leaves[57]. Macerated leaves of *Ranunculus acer* L. completely inhibit the growth of *Fomes anosus* (Fr.) Cooke *in vitro*[59,82]. Virtanen and Hietala[83] isolated 2(3)-benzoxazolinone (BOA), an antifungal substance, from the pressed juice of young rye plants. A methoxy derivative of BOA, MBOA, was later isolated from crushed corn and wheat plants[45,84], and its structure was confirmed by synthesis[85]. Both the compounds (BOA and MBOA) are fungistatic to *Fusarium nivale* (Fries) Cesati up to a dilution of 0·4 mg./ml., beyond which they are fungicidal[86]. Two more factors have also been reported in the water extracts of corn tissue effective against *Diplodia zeae* (Schw.) Lev.[43]. The factors as well as the resistance for stalk rot decrease as the plant increases in height. Activity is noticed at all stages of growth and highest activity is found in leaves, followed by sheaths, upper portion of developing stem and tassels; lowest activity is found in the lower stem portions prior to flowering and all portions of fully developed stalk at flowering[44]. Extracts from young corn plants inhibit *F. monoliforme* Sheld. and *Giberella zeae* (Schw.) Petch. due to the presence of MBOA[45].

Essential oils — Essential oils extracted from *Mentha piperita* L., *Lavandula officinalis* Tourn. exl.[1] and from roots and flowers of radish[87,88] are antimicrobial. A group of antimicrobial acid substances is found in the roots of black radish which is effective against both phytopathogenic bacteria and fungi. The effective dilution varied from 1: 250 to 1: 10,00,000 depending upon the test organism used. Unlike other known compounds from *Raphanus* spp., this group is only mildly phytotoxic[87,88]. Antimicrobial activity of perfume oils[89,90], essential oils on wood-destroying fungi[91] and on phytopathogenic fungi[92-94] has been studied in detail. Oils from onion, garlic, *Cymbopogon citratus* (DC) Stapf. exhibit high activity. Pine oil is known to inhibit various species of fungi and has been used in fungicidal preparations[74,95]. The antimicrobial activity in the needles and berries of *Juniperus communis* L., due to the presence of juniper oil, varies with part of the plant, age and time of the year[96].

Miscellaneous compounds — A large number of plant extracts show antimicrobial activity. However, specific chemical substances responsible for the activity in these plants have not been worked out. In the absence of the information regarding the chemical nature of the active principles, they are being classified into (i) volatile and (ii) non-volatile substances.

Volatile substances — The antimicrobial compounds from the leaves of fruit-bearing apple trees show higher activity than those from apple seedlings. Apple leaves show higher activity during mid-July to mid-August and fruits at the time of technical maturity. A most active volatile fraction occurs in the leaves of pear tree and seedlings and the substances isolated from the volatile fraction kill fungi and bacteria[48]. The volatile substances from different parts of bird-cherry, oak, cherry, laurel, larch, etc., are bactericidal in varying degrees to *Pseudomonas citriputeale* (C. O. Smith) Stavens on citrus and other plants[74]. A more pronounced inhibition of spore germination than of mycelial development of *Venturia inaequalis* (Cooke) Wint. em Aderh is exhibited by the unstable volatile fraction from leaves of three apple varieties[97]. Nene and Krishna Kumar (unpublished data) have found aqueous extracts of *Erigeron linifolius* Willd. to be strongly antifungal when tested against a number of plant pathologenic fungi. The active principle appears to be at least partly volatile in nature. The authors of the present paper have noticed (unpublished data) strong antifungal activity in the garden nasturtium plant; the active principle is present in all parts of the plant which appears to be a volatile antifungal principle.

Non-volatile substances — Peyocactin, an antimicrobial substance, separated from ethanol extract of *Lophophora williamsii* (Lemaire) Coulter. inhibits a number of bacteria and fungi. Its inhibitory action against 10 strains of penicillin resistant *Staphylococcus aureus* Rosenbach is of particular interest to medical workers[98]. Expressed juice from a number of monocots inhibit the growth of *Phymatotrichum omnivorum* (Shear) Duggar, whereas juices from dicots are ineffective[51]. The bark extracts of different poplar varieties are fungistatic to *Dothichiza* (*Cyptodiaporthe*) *populea* Sacc. & Briard[99]. Masilungan *et al.*[100], at the National Institute of Science and Technology, Manila, Philippines, conducted mass screening of higher plants for antibacterial substances and for antitubercular antibiotics. These workers found that *Artocarpus rigida* Blume and *Brunfelsia americana* L. contain potent antifungal substances active against *Fusarium moniliforme* Sheldon. Nene and Thapliyal[101] reported antifungal properties of *Anagallis arvensis* L. Complete inhibition with 1:20 extracts was noticed with *Colletotrichum papayae* (P. Henn.) P. Henn., *Alternaria solani* (Ell. & Mart.) Jones & Grout, *Colletotrichum falcatum* Went., *Glomerella cingulata* (Stonem.) Spauld. & Schrenk., *Helminthosporium turcicum* Pass., *Pythium aphanidermatum* (Edson) Fritz. and *Rhizopus nigricans* Ehrenb., but not with *Aspergillus niger* V. Teigh. Root, stem and flower extracts are equally effective against the test fungus (*Colletotrichum papayae*). The leaf extract completely inhibits *C. papayae* at 1: 2,00,000 dilution; the active principle is heat resistant and is not destroyed by storing the leaves for one year at room temperature. Cacoa extract causes partial inhibition of zoospores germination and induces encystment in *Phytophthora palmivora* (Butler) Butler[102]. *Hevea brasillensis* Mull. Arg. leaves contain a toxic substance active against *Dothidella ulei* P. Henn. *in vitro*[103]. The extracts from epicarp and mesocarp of oranges, used alone or in combination, inhibit the growth of *Phomopsis citri* Fawcet[104]. The antimicrobial principle in the seeds of wheat and barley is extractable with water and methyl alcohol, and is not destroyed either by lypophilization, air-drying, or partial autoclaving[105]. Extracts from germinated barley seed are toxic to *Alternaria tenuis* Nees. but not those from ungerminated seeds[106].

Use of plant substances in disease control — A few of the plant extracts showing antimicrobial activity against phytopathogens have been tried for the control of the plant diseases. The experiments were of a preliminary nature and indicate only the possibility of using higher plants in actual disease control. No field scale experiments have been undertaken for this purpose. The available information is presented in Table 1.

Antiviral Substances

Bawden[108] has reviewed in detail the work done on inhibitors of viral infections including the inhibitors from the higher plants. Smith[109] has discussed the presence of virus inhibitors in plant saps and extracts, and their importance in the mechanical transmission of plant viruses. The information given in the following paragraphs is mainly to supplement the earlier reviews.

Activity in vivo — The first report of an inhibitor in the plant sap was made by Allard[110] in 1914. Serious investigations in this field started only after the development of local lesion technique[111] in 1929 because all experimenters before the development of this technique could note total inhibitory effect only. Since then a large number of plants have been tested and their reactions have been reported by various workers[112-115]. The findings of these workers have shown that the dilution of the test extract is an important consideration, while recording their reaction against a particular virus on a particular host plant. Bhargava[116] was able to transmit cucumber mosaic virus from beet to tobacco only by first diluting the sap ten times or more. The activity of coconut meat extract is sharply decreased on dilution. The undiluted extract which exhibits 99 per cent inhibition of tobacco mosaic virus (TMV) on *Nicotiana glutinosa* L. loses its activity completely when diluted 1/1000 times, but on further dilution to 1/10,000 the same extract increases the infectivity of the same virus by 14 per cent[117]. A similar increase in the infectivity of TMV on a number of hosts including tobacco and *N. glutinosa* L. has been observed when the otherwise inhibitory seed extract of *Capsicum* is diluted 450 times or more[118]. However, preparations from *Mesembryanthemum caprohetum* causes 99 per cent reduction in lesions produced by TMV on *N. glutinosa* L. even when the extract is diluted

TABLE 1 — USE OF SOME PLANT EXTRACTS IN PRACTICAL PLANT DISEASE CONTROL

Plant	Disease	Treatment and other details	Ref.
Allium cepa L.	Rose rust	Spraying with sap or water infusion	74
	Soft rot of carrots and storage and transit rot of apples	Water infusion of outer dry onion scales and of a slurry of healthy onion	74
	Fusarium lini infection of flax seed	Extract applied on infected soil	1
	Rhizoctonia solani infection of lettuce seed	do	1
	Pectobacterium carotovorum infection	Attack on potato slices	1
	Barley smut and seed-borne diseases of cotton	Extract used in seed treatment	74
	Loose smut of wheat	Soaking wheat in 3-4 per cent extract at 30°C. for 29 hr. Infection reduced to 1·4 and zero per cent respectively	107
A. sativum L.	Downy mildew of cucumber, cucumber scab, angular leaf spot of cucumber, downy mildew of radish, bean rust, bean anthracnose, bacterial blight of beans, early blight of tomato, and brown rot of stone fruits	1-20 per cent aqueous extract of garlic powder	73
	Downy mildew of cucumber and bean rust	Dust formulations of garlic powder	73
	Loose smut of wheat	Soaking wheat in 3-4 per cent extract at 30°C. for 29 hr	107
Anagallis arvensis L.	Brown rust of wheat and *Helminthosporium* leaf blight of maize	Preinoculation spray of shoot extract (1 : 10 and 1 : 100)	Nene, Y. L. & Thapliyal, P. N. (unpublished data)
Armoracia rusticana	*Xanthomonas malvacearum* infection of cotton seed; *Penicillium italicum* infection of oranges	Packed in a container having sufficient horse radish vapours	1, 74
Brassica sp.	*X. malvacearum* infection of cotton seed	—	74
Eucalyptus sp.	do	—	74
Mulgedium sp.	Rose rust	Spraying with plant sap	74
Triticum vulgare	Soft rot of lemon	Treating with the wheat grain extract	74

1/1250 times. Blaszczak *et al.*[114] recorded a marked reduction or total loss of the inhibitory activity of almost all plant extracts tested by them, when the extracts were diluted 10 times. Tests were made against the infectivity of potato virus X (PVX) on *Gomphrena globosa* L.

The antiviral substances present in the higher plants can be classified into the two following broad categories, viz. (i) substances acting on the host and thereby protecting it from subsequent viral infection and (ii) substances acting directly on the virus particle and thereby rendering them non-infective.

Substances having action on the host plant — It seems that the inhibition of infection by higher plant extracts depends on the host species inoculated and not on the identity of the virus. Gendron and Kassanis[119], by quantitative tests with several viruses on different species of host plants, established that those leaf extracts which inhibit viral infection of other species fail to do so with species from which the extracts come. Sugarbeet mosaic and cucumber mosaic virus (CMV) can be transmitted from beet to beet, but not from beet to tobacco at least when the undiluted sap is used as inoculum[116]. Other workers have also supported this finding[120-122]. The only exception to this behaviour is that the inhibitors present in lovage (*Ligusticum scoticum* L.) plant extract inhibit the infection of lovage plant by mosaic virus, though the virus is sap transmissible to tobacco and many other plants[123].

A large number of plants have been tested for their antiviral activity. The properties of some of the inhibitors present in the plants have been studied in detail. The information regarding the nature and properties of the extracts or of the inhibitor/inhibitors present in the extracts of the following plants is presented below.

Phytolacca decandra L. (pokeweed) — Allard[110,112] noticed that the CMV is mechanically transmitted from pokeweed to pokeweed but is not transmitted to tobacco. Duggar and Armstrong[124] observed that when pokeweed juice is added to sap containing TMV, it prevents infection of healthy tobacco plants. These workers also noticed a similar but weaker effect than that of pokeweed only in *Datura stramonium* L. from among a number of other plants investigated. This could be due to the lack of efficient testing techniques (local lesion technique) known till that time, Grant[113] showed that infectivity falls immediately after adding the juice to TMV and there is no further fall afterwards. The inhibitor is destroyed by boiling but is stable for long in stored juice[125]. According to Fulton[126] the virus is not permanently inactivated. The studies have revealed that the active principle is a glycoprotein, having 14-15 per cent nitrogen and 8-12 per cent carbohydrate[127]; the glycoprotein also occurs in the leaf extracts of *Phytolacca esculanta* Van Houtte. *Phytolacca acinosa* Roxb. also contains an inhibitor of cabbage black ring spot virus[128].

Cucumber — The cucumber plants seem to be insensitive to inhibitors, as the viral infection on cucumber is generally less affected by inhibitors, probably due to their presence in cucumber plant although in quite low concentration[119]. This may be the possible explanation for the successful transmission to this species of virus from rosaceous plants[129,130]. Sill[131] and Sill and Walker[132] found that all parts of cucumber plant except the corolla contain a stable inhibitor effective against CMV when inoculated on cowpea (*Vigna sinensis* Savi.). On the other hand, an unstable inhibitor has also been reported to be present in cucumber sap[133]. This inhibitor is effective in inhibiting the infection on cucumber plants also and is thus different from other inhibitors already reported from cucumber plants. Francki[134] noticed a reduction in the infectivity of partially purified CMV preparation when mixed with leaf extracts of healthy cucumber plant. Plant virus inhibitor is also found in the seed of cucumber[135].

Coconut — Milk and endosperm of coconut have been reported to contain inhibitors of viral infection[136,137]. More than 90 per cent reduction in the infection of TMV was obtained by the coconut meat extract when assayed on *N. glutinosa* L. The activity of coconut meat extract is reduced by 32 per cent when applied 12 hr after inoculation or when diluted 100 times[117]. Activity is unaffected by storage for 64 days; by heating the extract at 50°C. activity is lost but is regained on further heating.

Capsicum — *Capsicum* spp. contain inhibitors of a number of plant viruses[128, 138-141]. Seed extract of *Capsicum* strongly counteracts the infection when applied 24 hr or earlier prior to inoculation with TMV on tobacco, *N. glutinosa* L., *Datura stramonium* L., *Chenopodium amaranticolor* Coste & Reyn. and pinto beans (*Phaseolus vulgaris* L.), and also of pinto beans by southern mosaic virus[118]. The 10-fold dilution of juice has no adverse effect on its activity against potato virus X (PVX)[114]. On heating the juice at 60°C. for 10 min., activity is lost. Young seedlings also contain an inhibitor different from that in the seed and from that found by McKeen[139] in the juice of pepper leaves. The inhibitor is thermostable, and withstands *p*H variations, ageing *in vitro* and desiccation[118].

Oryza sativa L. (paddy) — Almost all parts of paddy plant contain an inhibitor effective against TMV when inoculated on pinto beans (*Phaseolus vulgaris* L.)[142, 143]. The inhibitor appears to be a high molecular weight protein[144].

Spinacia oleracea L. (spinach) — Spinach juice greatly reduces the number of local lesions produced by TMV on *N. glutinosa* L.[113]. Though the nature of the inhibitors in this juice is not fully understood, Kuntz and Walker[145] collected evidence that spinach juice contains two inhibitors one of which is ineffective against TMV infection on *N. glutinosa* L. but is effective against cabbage black ring spot viral infection. The latter seems to be a small stable particle, withstands boiling and exposure to concentrated ethanol, and diffuses through cellophane. The former may be a protein similar to the inhibitor from pokeweed. These substances appear to be responsible for the failure to transmit sugarbeet mosaic virus[146] and CMV[116] from sugarbeet or spinach to tobacco plants by sap inoculations, though aphids transmit them effectively.

Tetragonia expansa Murr. (*New Zealand spinach*) — The appearance of the primary virus symptoms on cowpea (*Vigna sinensis* Savi.) leaves is delayed when expressed sap of New Zealand spinach is mixed with tobacco ring spot virus. The sap contains two active fractions, one an inhibitor and the other an augmenter (a soluble oxalate salt) which increases the number of lesions[147].

Dianthus barbatus L. (*sweet william*) — The amount of inhibitor in sweet william plants varies from clone to clone. The tobacco ring spot virus is regularly transmissible from sweet william to sweet william but not from sweet william to tobacco, cucumber, *Datura stramonium* L., or *Antirrhinum majus* L. The inhibitor is destroyed by boiling at 80°C. or by ageing the sap for three days, withstands drying and does not diffuse through cellophane[122].

Tobacco — The variation in the infectivity of tobacco necrosis viruses prepared from tobacco saps by different methods has been explained as due to the presence of virus-inactivating system in tobacco leaves. The active ingredient[148] has also been isolated by centrifugation at 4000-8000 *g*. The antiviral activity of tobacco plants varies during growth and depends to a great extent on the environmental temperature. At 36°C. the inhibitory activity of resistant varieties is suppressed. The susceptibility of tobacco scion is reduced under the influence of metabolites of *N. glutinosa* L. stock[149]. The presence of antiviral fraction in the virus infected (by TMV or PVX) tobacco and other hosts has also been reported[150].

Miscellaneous plants — Blaszczak *et al.*[114] compared the efficacy of a number of plant extracts on the brown strain of potato virus X and also studied the effect of 10-fold dilution of juices on their effectivity, and of heating the extracts for 10 min. They observed that *Pelargonium hortorum* Bailey juice stands heating at 100°C. for 10 min. and is effective when sprayed 20 days before inoculation. The young top leaves show higher concentration of the inhibitor than older ones or stem. Simons *et al.*[115] observed 95-100 per cent reduction in TMV lesions on *N. glutinosa* L. by the leaf saps of 30 plant species; of these 20 were succulent, mostly belonging to Crassulaceae. Many of these were found to be active against potato virus Y. Coumarins, the active principles of some of the indigenous herbs and medicinal plants, have also been found to be antiviral[151, 152]. Raychaudhury[95] reported the inhibition of a number of plant viruses by plant extracts. Since information on the nature of the inhibitor(s) present in a large number of plants is meagre, names of such plants are listed in Table 2 along with their activity.

Substances acting on the virus particles — The rosaceous plants contain inhibitors of a different type than those occurring in pokeweed, sugarbeet and datura. The leaves, stems or roots of strawberry extracts contain tannin, which is enough to precipitate TMV and prevent it from infecting *N. glutinosa* L. even at 1 per cent level[150]. Van der Want[121] suggested that substances like tannins, which prevent infection of all plants, should be called ' absolute inhibitors ', to differentiate them from the ' relative inhibitors ', whose action depends on the species of plants used for inoculation. *Erigeron linifolius* Willd., which shows antifungal and nematostatic properties, inhibits infection of Scotia beans by TMV when mixed with the virus (Nene & Krishna Kumar, unpublished data). Since a related species, *E. canadensis* L., is also reported to contain tannic acid, which may be the main substance responsible for the antiviral activity of *E. linifolius*.

Nematocidal Substances

Activity in vivo through toxic secretions — The root system of an actively growing plant may secrete various chemical substances which may affect the nematodes in soil, either directly or through changes on other organisms of the rhizosphere[159]. Interplanting of *Asparagus* or marigold protects the host plants from getting infected, probably because of some toxic secretions from their roots[160, 161]. Rutabagas root secretions render burrowing nematodes unable to find the roots of corn[162].

Activity in vivo due to the presence of toxic compounds in tissue — In some cases the nematode population around the roots of resistant plants declines at a rate faster than that can be explained by starvation. It is supposed that the plant is actively toxic. *Asparagus*[161], marigold[160], *Poncirus trifoliata* Raf. and *Severinia buxifolia* Ten.[163] have been reported to be at least partially resistant because they contain compounds toxic to nematodes. The toxic juice expressed from the fibrous roots of *Asparagus* contained a glycoside with an aglycone component of low molecular weight[164].

Activity in vivo due to production of toxic compound as a result of infection — The general metabolic activity of the attacked cells may be diverted towards production of toxic compounds. The production of aromatic compounds may lead to the accumulation of phenolic compounds in the diseased tissue[165]. Wallace[166] showed that chrysanthemum varieties resistant to foliar nematodes browned quickly on infection and higher amounts of chlorogenic acid were found in the areas where nematodes had entered. Nematodes did not move out of this area and browning of the tissue in all resistant reactions may be due to the accumulation of ' phlobaphenes ' produced by oxidation of tannins to quinones and subsequent polymerization[167-169]. When lesion nematode feeds on peach roots, amygdalin is hydrolysed by nematode enzymes and hydrocyanic acid is released in amounts toxic to host as well as to the parasite[170]. Resistant peach root stocks are characterized by high concentrations of amygdalin.

Activity in vitro — Very little work has so far been done on the detection of nematocidal substances from higher plant extracts. The partially purified ether extracts of seeds of *Butea frondosa* Roxb. show nematocidal activity. When the worms are treated with purified extract (2 mg./litre), they are paralysed in 1-2 hr and then they die[171]. The extracts of *Erigeron linifolius* Willd. show nematostatic activity against *Anguina tritici* (Steinbuch) Filipjev. The motility of larvae is inhibited 6 hr after treatment, but regain motility in 24 hr when larvae are transferred to distil water (Nene & Kumar, unpublished data). Nene and Thapliyal[172] reported nematocidal properties of *Anagallis arvensis* L. Leaf extracts killed the larvae of *Anguina tritici* within 6 hr up to a

TABLE 2 — PLANTS SHOWING ANTIVIRAL ACTIVITY

Plant	Virus	Host	Antiviral activity	Ref.
Antirrhinum majus L.	TMV	*Nicotiana glutinosa* L.	—	113
Agropyron repens (Beau.) L.	do	do	—	117
Avena sativa L.	do	do	90-100 per cent reduction	153
Beta vulgaris L.	do	*N. glutinosa* L., French beans, *Datura tatula* L.	—	113, 119
	Crotalaria mosaic virus	—	Strong inhibition	141
B. vulgaris var. *cicla* L.	TMV	*N. glutinosa* L.	—	113
Cedrus deodara Loud (fruit extract)	CMV	*Chenopodium amaranticolor* Coste & Reyn.	—	140
C. deodara Loud	TMV	*N. glutinosa* L.	95-100 per cent inhibition	115
Chenopodium album L.	PVX	*Gomphrena globosa* L.	Complete inhibition	114
C. amaranticolor Coste & Reyn.	do	do	do	114
Citrus sp. (fruit extract)	—	—	—	125
Cyrtomium falcatum Presl.	TMV	*N. glutinosa* L.	95-100 per cent reduction	115
Cuscuta spp.	Tomato spotted wilt virus	do	—	154
	Lucerne mosaic virus	*Phaseolus vulgaris* L.	—	154
	Cabbage black ring spot virus	Tobacco and *Amaranthus retroflexus* L.	—	154
	Potato rattle virus	*N. glutinosa* L.	—	154
	CMV	*Vigna sinensis* Savi.	—	154
	Tomato bushy stunt virus	*N. glutinosa* L.	—	154
Datura stramonium L.	Crotalaria mosaic virus	—	—	141
D. stramonium L. (leaf juice)	PVX	*G. globosa* L.	—	114
D. stramonium L.	Cabbage black ring spot virus	—	—	128
D. metel L.	PVX	*G. globosa* L.	—	114
D. tatula L.	TMV	French beans, beets	—	119
Dianthus caryophyllus L.	Carnation mosaic virus	French beans, tobacco	—	121
	TMV	—	95-100 per cent reduction	153, 155
Eugenia peniculata Banks.	do	*N. glutinosa* L.	do	115
Euphorbia sp.	do	—	90-100 per cent reduction	153
Juniperus communis L.	do	*N. glutinosa* L.	95-100 per cent reduction	115
Lonicera caprifolium L.	do	do	do	115
Lycopersicum hirsutum	do	do	do	156
Lycopersicum sp. (fruit extract)	—	—	—	125
Mesembryanthemum spp.	TMV	*N. gutinosa* L.	99 per cent inhibition	115
	do	—	90-100 per cent inhibition	153
Nicotiana glutinosa L.	do	*N. glutinosa* L.	Very little effect	113
N. tabacum L.	do	do	do	113
Phaseolus vulgaris L.	do	do	do	113
Pelargonium hortorum Bailey	PVX	*G. globosa* L.	Complete inhibition	114
Pinus sp.	TMV	*N. glutinosa* L.	90-100 per cent inhibition	153
Raphanus sativus L.	Crotalaria mosaic virus	—	—	141
Schinus molle L.	TMV	*N. glutinosa* L.	95-100 per cent inhibition	115
S. terebinthifolius Raddi.	do	do	do	115
Solanum aviculare Forst.	do	do	—	157
S. capsicastrum L.	do	do	—	157
S. garsia	do	do	—	157
S. integrifolium Poir.	PVX	*G. globosa* L.	—	114, 157
S. tuberosum L.	do	do	—	114
Thuja orientalis L.	TMV	*N. glutinosa* L.	95-100 per cent inhibition	115
Trifolium pratense L.	PVX	*G. globosa* L.	—	114
Vicia faba L.	do	do	—	114
Zinnia elegans Jacq.	Dahlia mosaic virus	Dahlia	—	120
Members of Crassulaceae	TMV	*N. glutinosa* L.	95-100 per cent inhibition	115

dilution of 1:10. On further dilution, the activity declined significantly. While working with wheat nematode, the authors have noticed antinematode activity in the extracts of marigold, canna and paddy leaves. Strong nematocidal activity has been noticed in almost all parts of garden nasturtium (*Tropaeolum* sp.) when tested against *Anguina tritici*. The active principle is volatile in nature (Nene & Thapliyal, unpublished data).

Accumulation of chlorogenic acid is generally associated with the nematode resistant reaction of a number of plants. In *in vitro* tests, inhibition of the motility of foliar nematodes by chlorogenic acid has been noticed[166]. The *in vitro* nematocidal activity of the root sap of citrus root stock has been related to the resistance to the citrus nematode[173]. Since a lot of plant material is always buried in soil, it would be worth while to know more about nematocidal substances from such plants.

Conclusion

Considerable work on the screening of plant extracts for their activity against plant pathogens has been done. Such a screening can go on but the need now is towards attempts to develop materials that can be used on field scale for the control of plant diseases. To the best of our knowledge there is not a single material yet developed on the lines of pyrethrum as an insecticide. It is quite possible, as work progresses, that some plants will be found to yield antimicrobial substances useful in effective control of plant diseases. More work needs to be done to isolate and identify active ingredients, and synthesize the promising ones for use on a large scale.

Summary

A number of plants are now known to contain substances which are inhibitory to phytopathogenic fungi, bacteria, viruses as well as nematodes. Many such compounds which may possibly act as inhibitors in plants and others which can be used to cure various pathogen affected plants have been described. However, no compound obtained from plants has so far been used in the field control of any plant disease. This aspect needs more attention in future.

References

1. Kovacs, G., *K. vet. Hosk. Arsskr.*, (March 1964), 47.
2. Sharville, E. G., *The nature and uses of modern fungicides* (Burgess Publishing Co., Minnesota, USA), 1960, 3.
3. Aren, K., *J. wiss. Bot.*, **70** (1929), 93.
4. Hafiz, A., *Phytopathology*, **42** (1952), 422.
5. Martin, J. T., Batt, R. F. & Burchill, R. T., *Nature, Lond.*, **180** (1957), 796.
6. Pratt, R. & Dufrenoy, J., *Antibiotics*, 2nd ed. (J. B. Lippincott Co., London), 1953, 357.
7. Kuc, J., *Bull. Conn. agric. exp. Stn*, **663** (1963), 20.
8. Link, K. P. & Walker, J. C., *J. biol. Chem.*, **100** (1933), 379.
9. Newton, R. & Anderson, J. A., *Can. J. Res.*, **1** (1929), 86.
10. Walker, J. C. & Stahman, M. A., *A. Rev. Pl. Physiol.*, **6** (1955), 351.
11. Link, K. P., Dickson, A. D. & Walker, J. C., *J. biol. Chem.*, **84** (1929), 719.
12. Walker, J. C., Link, K. P. & Angell, H. R., *Proc. natn. Acad. Sci. U.S.A.*, **15** (1929), 845.
13. Topps, J. H. & Wain, R. L., *Nature, Lond.*, **179** (1957), 652.
14. Timonin, M. I., *Can. J. Res.*, **C 18** (1940), 444.
15. Timonin, M. I., *Soil Sci.*, **52** (1941), 395.
16. Flentje, N. T., Warcup, J. H. & Taylor, J. B., *Rep. Waite agric. Res. Inst.*, (1962), 71.
17. Sinha, S., *Indian phytopath.*, **18** (1965), 1.
18. Kovacs, A., *Phytopath. Z.*, **24** (1955), 283.
19. Buxton, E. W., *Nature, Lond.*, **181** (1958), 1222.
20. Rangaswami, G. & Balasubramanian, A., *Indian J. exp. Biol.*, **1** (1963), 215.
21. Newton, R., Lehmann, J. V. & Clarke, A. E., *Can. J. Res.*, **1** (1929), 5.
22. Irving (Jr), G. W., Fontaine, T. D. & Doolittle, S. P., *Science*, **102** (1945), 9.
23. Virtanen, A. I., *G. Microbiol.*, **2** (1956), 15.
24. Virtanen, A. I., Hietala, P. K. & Wahlroos, O., *Archs Biochem. Biophys.*, **69** (1957), 486.
25. McLean, J. G., Le Tournean, D. J. & Guthrie, J. W., *Phytopathology*, **51** (1961), 84.
26. Johnson, G. & Schaal, L. A., *Science*, **115** (1952), 627.
27. Schaal, L. A. & Johnson, G., *Phytopathology*, **45** (1955), 626.
28. Johnson, G. & Schaal, L. A., *Phytopathology*, **47** (1957), 253.
29. Lee Shufung & Le Tourneau, D. J., *Phytopathology*, **48** (1958), 268.
30. Le Tourneau, D. J., McLean, J. G. & Guthrie, J. W., *Phytopathology*, **47** (1957), 602.
31. Patil, S. S., Powelson, R. L. & Young, Roy A., *Phytopathology*, **54** (1964), 531.
32. Dufrenoy, J. & Edgerton, C. W., *Phytopathology*, **30** (1940), 5.
33. Southam, C. M. & Ehrlich, J., *Phytopathology*, **33** (1943), 517.
34. Boyer, M. G., *Can. J. Bot.*, **42** (1964), 979.
35. Kiraly, Z., *Phytopathology*, **52** (1962), 738.
36. Beltykova, K. I. & Gvozdyak, R. I., *Rev. appl. Mycol.*, **44** (1965), 3196.
37. Stahmann, M. A., Link, K. P. & Walker, J. C., *J. agric. Res.*, **67** (1943), 49.
38. Irving, G. W., in *Antibiotics*, edited by G. W. Irving & H. T. Herric (Chemical Publishing Co. Inc., New York), 1949, 187.
39. Greathouse, G. A., *Phytopathology*, **28** (1938), 592.
40. Greathouse, G. A. & Watkins, G. M., *Am. J. Bot.*, **25** (1938), 743.
41. Schmidt, M., *Planta*, **20** (1933), 407.
42. Agerberg, L. S., Schick, R., Schmidt, M. & Von Sengbusch, R., *Züchter*, **5** (1933), 272.
43. Beck, S. D. & Stauffer, J. F., *Ann. ent. Soc. Am.*, **50** (1957), 166.
44. Loomis, R. S., Beck, S. D. & Stauffer, J. F., *Pl. Physiol.*, **32** (1957), 379.
45. Whitney, N. J. & Mortimore, C. G., *Nature, Lond.*, **184** (1959), 1320.
46. BeMiller, J. N. & Pappelis, A. J., *Phytopathology*, **55** (1965), 1237.
47. Spencer, E. Y., Ludwig, R. A., De Mayo, P. & White, R. W., *Rev. appl. Mycol.*, **43** (1964), 893.
48. Nikitina, K. V., *Rev. appl. Mycol.*, **42** (1963), P662.
49. Calpouzos, L. (1963), *Rep. agric. hort. Res. Stn Univ. Bristol*, (1962), 111.
50. Rudman, P. & Da Costa, E. W. B., *Holzforschung*, **13** (1959), 112.
51. Ezekiel, W. N. & Fudge, J. F., *J. agric. Res.*, **56** (1938), 773.
52. Gal, I., *Rev. appl. Mycol.*, **43** (1964), 2199.
53. Fawcett, C. H., *Rev. appl. Mycol.*, **43** (1964), 893.
54. Hayes, L. E., *Bot. Gaz.*, **108** (1946), 408.
55. Little, J. E. & Gurbaugh, K. K., *J. Bact.*, **52** (1946), 587.
56. Nickell, L. G., *Econ. Bot.*, **13** (1959), 281.
57. PetursHova, N. I. & Meshchaninova, N. B., *Rev. appl. Mycol.*, **42** (1963), P365.
58. Osborn, E. M., *Br. J. exp. Path.*, **24** (1943), 227.
59. Vasilyauskas, A. P., *Rev. appl. Mycol.*, **44** (1965), 341.
60. Petursova, N. I., *Rev. appl. Mycol.*, **41** (1962), P502.
61. Abdullaeva, A., *Rev. appl. Mycol.*, **44** (1965), 966.
62. Etheridge, D. E., *Can. J. Bot.*, **40** (1962), 1459.
63. Hubbes, M. & Etheridge, D. E., *Proc. Can. Phytopath. Soc.*, **30** (1963), 10.
64. Mkervali, V. G., *Rev. appl. Mycol.*, **43** (1964), 3240.

65. ERDTMAN, H. & GRIPENBERG, J., *Nature, Lond.*, **161** (1948), 719.
66. RENNERFELT, E., *Friesia*, **5** (1956), 361.
67. JANARDHANAN, K. K., GANGULY, D., BARUAH, J. N. & RAO, P. P., *Curr. Sci.*, **32** (1963), 226.
68. BORDOLOI, D. N., BARUAH, J. N., GANGULY, D. & RAO, P. P., *Curr. Sci.*, **33** (1964), 408.
69. KUC, J., *J. Am. chem. Soc.*, **78** (1956), 2123.
70. CLARK, R. S., KUC, J., HENZE, R. E. & QUACKENBUSH, F. W., *Phytopathology*, **49** (1959), 594.
71. ABDULLAEVA, A., *Rev. appl. Mycol.*, **42** (1963), P241.
72. CAVALLITO, C. J. & BAILEY, J. H., *J. Am. chem. Soc.*, **66** (1944), 1950.
73. ARK, P. A. & THOMPSON, J. P., *Pl. Dis. Reptr.*, **43** (1959), 276.
74. TOKIN, B. P., *Rev. appl. Mycol.*, **41** (1962), P364.
75. IVANOVICS, G. & HORVATH, ST., *Nature, Lond.*, **160** (1947), 297.
76. MALEKZADEH, F., *Dis. Abstr.*, **23** (1963), 4493.
77. GOTTLIEB, D., *Phytopathology*, **33** (1943), 1111.
78. GALACHYAN, R. M., *Rev. appl. Mycol.*, **42** (1963), P235.
79. GALACHYAN, R. M., BUDAGYUN, E. G. & DAVTYAN, A. R., *Rev. appl. Mycol.*, **42** (1963), P235.
80. BELTYKOVA, K. I., *Microbiol. Zh.*, **24** (1962), 62.
81. BOAS, F., *Ber. dt. Bot. Ges.*, **52** (1934), 126.
82. SRIUBAITE, J., *Rev. appl. Mycol.*, **41** (1962), P575.
83. VIRTANEN, A. I. & HIETALA, P. K., *Acta chem. scand.*, **9** (1955), 1543.
84. VIRTANEN, A. I., HIETALA, P. K. & WAHLROOS, O., *Biol. Abstr.*, **31** (1957), 32704.
85. HIETALA, P. K. & WAHLROOS, O., *Acta chem. scand.*, **10** (1956), 1196.
86. WAHLROOS, O. & VIRTANEN, A. I., *Acta chem. scand.*, **12** (1958), 124.
87. NEHRASH, A. K., *Microbiol. Zh.*, **23** (No. 4) (1961), 32.
88. NEHRASH, A. K., *Microbiol. Zh.*, **23** (No. 5) (1961), 61.
89. MARUZZELLA, J. C. & HENRY, P. A., *J. Am. pharm. Ass. Sci.*, **47** (No. 7)) (1958), 471.
90. MARUZZELLA, J. C., BALTER, J. & KATZ, A., *Perfum. essent. Oil Rec.*, **50** (1959), 955.
91. MARUZZELLA, J. C., SCRANDIS, D. A., SCRANDIS, J. B. & GRABON, G., *Pl. Dis. Reptr*, **44** (1960), 789.
92. MARUZZELLA, J. C., *Pl. Dis. Reptr*, **47** (1963), 756.
93. MARUZZELLA, J. C., REINE, S., SOLAT, H. & ZEITLIN, A., *Pl. Dis. Reptr*, **47** (1963), 23.
94. MARUZZELLA, J. C. & BALTER, J., *Pl. Dis. Reptr*, **43** (1959), 1143.
95. RAYCHAUDHURY, S. P., *Bull. natn. Inst. Sci. India*, **24** (1962), 143.
96. SLAVENAS, J. & RAZINSKAITE, D., *Rev. appl. Mycol.*, **42** (1963), P365.
97. ISHCHENKO, L. A., *Rev. appl. Mycol.*, **42** (1963), P267.
98. MCCLEARY, J. A., SYPHERD, P. A. & WALKINGTON, D. L., *Econ. Bot.*, **14** (1960), 247.
99. LOESCHKE, V. & BUTIN, H., *Rev. appl. Mycol.*, **42** (1963), P157.
100. MASILUNGAN, V. A., KALAW, C. V., DELIS, F. & MASILUNGAN, C., *Philipp. J. Sci.*, **92** (1963), 421.
101. NENE, Y. L. & THAPLIYAL, P. N., *Naturwissenschaften*, **52** (1965), 89.
102. TURNER, P. D., *Phytopathology*, **53** (1963), 1337.
103. FIGARI, A. & ECHANDI, E., *Phytopathology*, **55** (1965), 125.
104. EL-TOBSHY, Z. & SINCLAIR, J. B., *Pl. Dis. Reptr*, **48** (1964), 925.
105. ARK, P. A. & THOMPSON, J. P., *Pl. Dis. Reptr*, **42** (1958), 959.
106. ZEMANEK, J. & BARTOS, P., *Rev. appl. Mycol.*, **41** (1962), P450.
107. GERA, S. D., MUNJAL, R. L. & CHANAN SINGH, *Indian Phytopath.*, **16** (1963), 105.
108. BAWDEN, F. C., in *Advances in virus research*, Vol. 2, edited by K. M. Smith & M. A. Lauffer (Academic Press Inc., New York), 1954, 31.
109. SMITH, K. M., in *Plant viruses* — Methuen's monographs on biological subjects (Methuen & Co. Ltd, London, and John Wiley & Sons Inc., New York), 1960, 107.
110. ALLARD, H. A., *Bull. U.S. Dept. Agric.*, (No. 40), (1914).
111. HOLMES, F. O., *Bot. Gaz.*, **87** (1929), 39.
112. ALLARD, H. A., *Phytopathology*, **8** (1918), 51.
113. GRANT, T. J., *Phytopathology*, **24** (1934), 331.
114. BLASZCZAK, W., FRANK ROSS, A. & LARSON, R. H., *Phytopathology*, **49** (1959), 784.
115. SIMONS, J. N., SWIDLER, R. & MOSS, L. M., *Phytopathology*, **53** (1963), 677.
116. BHARGAVA, K. S., *Ann. appl. Biol.*, **38** (1951), 377.
117. WEERARATNE, V. & RICH, A. E., *Phytopathology*, **51** (1961), 579.
118. FELDMAN, J. M., *Annls épiphyties*, **14** (1963), 377.
119. GENDRON, Y. & KASSANIS, B., *Ann. appl. Biol.*, **41** (1954), 183.
120. BRIERLEY, P. & SMITH, F. F., *Pl. Dis. Reptr*, **34** (1950), 363.
121. VAN DER WANT, J. P. H., *Tijdschr. PlZiekt.*, **57** (1951), 72.
122. WEINTRAUB, M. & GILPATRICK, J. D., *Can. J. Bot.*, **30** (1952), 549.
123. SMITH, K. M. & MARKHAM, R., *Phytopathology*, **34** (1944), 335.
124. DUGGAR, B. M. & ARMSTRONG, J. K., *Ann. Missouri Bot. Garden*, **12** (1925), 359.
125. JOHNSON, J., *Phytopathology*, **31** (1941), 679.
126. FULTON, R. W., *Phytopathology*, **33** (1943), 647.
127. KASSANIS, B. & KLECZKOWSKI, A., *J. gen. Microbiol.*, **2** (1948), 143.
128. JOSHI, R. D., *Agra Univ. J. Res.*, **11** (No. 2) (1962), 103.
129. MOORE, J. D., BOYLE, J. S. & KEITT, G. W., *Science*, **108** (1948), 623.
130. FULTON, R. W., *Phytopathology*, **42** (1952), 413.
131. SILL, W. H., *Phytopathology*, **41** (1951), 32.
132. SILL, W. H. & WALKER, J. C., *Phytopathology*, **42** (1952), 349.
133. WEINTRAUB, M. & WILLISON, R. S., *Phytopathology*, **43** (1953), 328.
134. FRANCKI, R. I. B., *Virology*, **24** (1964), 193.
135. CROWLEY, N. C., *Aust. J. biol. Sci.*, **8** (1955), 56.
136. GENDRON, Y., *C.r. hebd. Séanc. Acad. Sci. Paris*, **230** (1950), 1974.
137. LUCARDIE, M., *Tijdschr. PlZiekt.*, **57** (1951), 172.
138. HIRAI, T., *Science (Japan)*, **19** (1949), 223.
139. MCKEEN, C. D., *Can. J. Bot.*, **34** (1956), 891.
140. RAYCHAUDHURY, S. P. & CHADHA, K. C., *Indian Phytopathology*, **18** (1965), 96A.
141. VASUDEVA, R. S., *Sci. Rep. agric. Res. Inst., New Delhi*, 1961 (1963), 87.
142. ALLEN, T. C. & KAHN, R. P., *Phytopathology*, **47** (1957), 515.
143. KAHN, R. P., ALLEN, T. C. & ZAUMEYER, W. J., *Phytopathology*, **50** (1960), 847.
144. JONES, W. A., JACOBSON, M. & KAHN, R. P., *Nature, Lond.*, **184** (1959), 1146.
145. KUNTZ, J. E. & WALKER, J. C., *Phytopathology*, **37** (1947), 561.
146. HOGGAN, I. A., *Phytopathology*, **23** (1933), 446.
147. BENDA, G. T. A., *Virology*, **2** (1956), 438.
148. BAWDEN, F. C. & PIRIE, N. W., *J. gen. Microbiol.*, **16** (1957), 696.
149. MOLDOVAN, M. YA, *Biol. agric. Sci.*, **2** (1964), 85.
150. SELA, I. & APPLEBAUM, S. W., *Virology*, **17** (1962), 543.
151. KNYPLE, J. S. & GUBANSKI, C., *Naturwissenschaften*, **47** (1960), 308.
152. CHAKRAVARTY, D. P., SEN, M. & BOSE, P. K., *Trans. Bose Res. Inst.*, **24** (1961), 31.
153. WEERARATNE, V., *Dis. Abstr.*, **22** (1961), 1373.
154. SCHMELZER, K., *Rev. appl. Mycol.*, **36** (1957), P173.
155. KAMMEN, A. V., NOORDAM, D. & THUNG, T. H., *Virology*, **14** (1961), 100.
156. GOLDIN, M. I. & BUDAGYAN, E. G., *Rev. appl. Mycol.*, **43** (1964), 963.
157. HOOKER, W. J. & KIM, W. S., *Phytopathology*, **52** (1962), 688.
158. BAWDEN, F. C. & KLEEZKOWSKI, A., *J. gen. Microbiol.*, **2** (1948), 173.
159. RHODE, R. A., *Phytopathology*, **55** (1965), 1159.
160. OOSTENBRINK, M., KUIPER, K. & S'JACOB, J. J., *Nematologica Suppl.*, **2** (1957), 424S.
161. RHODE, R. A. & JENKINS, W. R., *Bull. Md agric. exp. Stn*, **A-97** (1958), 19P.
162. CHRISTIE, J. R., *Plant nematodes, their bionomics and control* (Florida Agricultural Experimental Station, Florida, USA), 1959, 34.
163. VAN GUNDY, S. D. & KIRKPATRICK, J. D., *Phytopathology*, **54** (1964), 419.

164. Steele, A. E. & Price, C., *J. Am. Soc. Sug. beet Technol.*, **12** (No. 4) (1963), 299.
165. Frankas, G. L. & Kiraly, Z., *Phytopathol. Z.*, **44** (1962), 105.
166. Wallace, H. R., *Nematologica*, **6** (1961), 49.
167. Barker, K. R. & Sasser, J. N., *Phytopathology*, **49** (1959), 664.
168. Christie, J. R., *Proc. helminth. Soc. Wash.*, **16** (1949), 104.
169. Dropkin, V. H. & Nelson, P. E., *Phytopathology*, **50** (1960), 442.
170. Mountain, W. B. & Patrick, Z. A., *Can. J. Bot.*, **37** (1959), 459.
171. Koleysaj, R. & Kurup, P. A., *Curr. Sci.*, **32** (1963), 456.
172. Nene, Y. L. & Thapliyal, P. N., *Indian Phytopath.*, **19** (1966), 26.
173. Kirkpatrick, J. D., Van Gundy, S. D. & Bitters, W. P., *Phytopathology*, **52** (1962), 738.

A New Approach to Carcinogenesis: A Molecular Model for the Regulation of Normal Growth, Differentiation & Carcinogenesis*

M. B. SAHASRABUDHE
Indian Cancer Research Centre, Parel, Bomay 12

ATTEMPTS at chemotherapy of cancer have in the past been directed almost entirely at interfering the nucleic acid synthesis. Unfortunately, however, the realization that rapid nucleic acid synthesis and rapid cellular proliferation are only the symptoms of the disease and not the cause of malignancy is becoming obvious only now. Treating the symptoms, therefore, is not likely to have any lasting consequences. It is, probably, for this reason that complete cures from cancer have very rarely, if at all, been achieved in the clinics. The nature of the primary change, which appears so very insignificant in the early stages as to elude observation, but which has an important role in the transformation of a normal cell into malignant type, has not so far been discovered.

The main characteristics of malignancy, as distinct from normal regeneration, is the irreversible and sustained de-repression of DNA synthesis. The rate of DNA synthesis, however, varies from tumour to tumour. In embryonic cells the DNA synthesis is not repressed. It is only after the differentiation process has set in that repression of DNA synthesis becomes evident. Thus unrepressed DNA synthesis is an inherent property of the cell and its repression is an acquired characteristic which appears later in the evolutionary process of cellular differentiation. The process of de-differentiation, therefore, must involve, as a first step, the de-repression of DNA synthesis. The process nearest to de-differentiation in a normal cell, and which has been fairly well studied, is the regeneration seen after partial hepatectomy. The time course of events, which precede de-repression, can be studied by following the events which lead to *de novo* synthesis of DNA polymerase in liver regeneration.

Normally, DNA polymerase synthesis starts 16 hr after hepatectomy and continues till about 20th hour or so (Fig. 1). The reasons for the time lag of 16 hr between hepatectomy and initiation of DNA polymerase synthesis are not properly understood. But one fact, which apparently seems to have been ignored in the past, is that the synthesis of a specific protein in the early stages is essential for initiating the DNA polymerase synthesis. For example, administration of puromycin, a drug which interferes with the translation of codes from messenger RNA to protein synthesis, between 0 and 8 hr, inhibits and delays DNA polymerase synthesis[1].

Similar events are known to occur in chemical carcinogenesis also and these are shown in Fig. 2. Here the DNA polymerase activity increases to about double the value in 6 days of carcinogen feeding and it goes on increasing to three times the control value in about 3 weeks[2]. Administration of actinomycin D, a substance which interferes with the transcription process, in the early hours of carcinogen administration, not only delays the incidence of malignancy but reduces the yield of tumours also[3]. This would support the contention that initiation of DNA polymerase synthesis is dependent on synthesis of a particular protein. If by some means this protein is not synthesized, de-repression of DNA synthesis

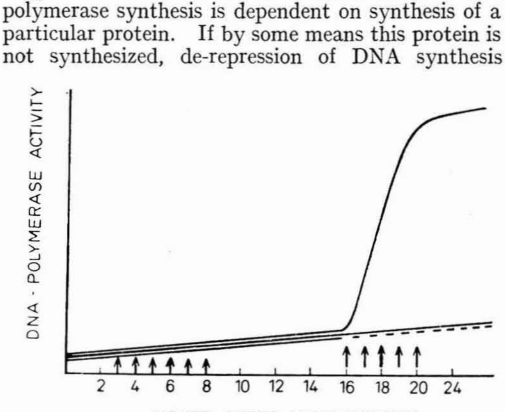

Fig. 1 — DNA polymerase activity after hepatectomy [Rise in biosynthesis of DNA polymerase takes place between 16 and 20 hr after hepatectomy. No rise in DNA polymerase seen when puromycin is administered either between 3 and 8 hr or 16 and 20 hr. Arrows indicate period of puromycin administration]

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*Based on a series of invited talks given by the author at the Indian Institute of Science, Bangalore 12.

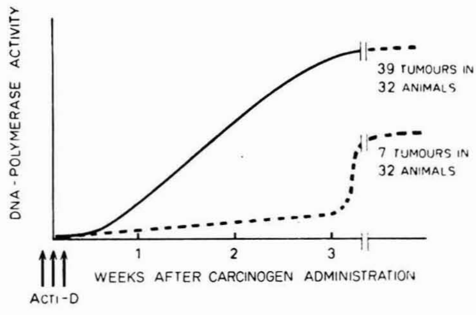


Fig. 2 — DNA polymerase activity after carcinogen administration [Schematic representation of DNA polymerase levels and incidence of tumours after carcinogen treatment. Arrows indicate actinomycin D administration, — carcinogen treated and - - - actinomycin D injected carcinogen treated animals. After Gelboin & Klein[3]]

does not take place, and as a consequence of this, regeneration or carcinogenesis also is delayed.

What is the nature of this protein? How it initiates DNA polymerase synthesis is not yet clear. There is, however, one fact which may have relevance here and that is the synthesis of NAD is lowered immediately after carcinogen administration or after hepatectomy. Further NAD synthesis is invariably reduced whenever there is DNA synthesis[4]. Synthesis of DNA and the operation of HMP enzymes, on the other hand, appear to be coupled[5]. The data on the levels of NAD synthesizing enzymes *in vivo* are given in Table 1. Here a lowering of about 30 per cent is seen in all the cases of carcinogen administration, whereas a 75 per cent lowering is seen immediately after hepatectomy. But in the same tissues, *in vitro* tests, however, showed that the levels of the NAD synthesizing enzymes were intact. This means that the enzyme moiety is intact and the apparent reduction in *in vivo* activity may be due to the masking of the active sites of the enzyme, thus making these unavailable for binding with the precursors NMN and/or ATP.

In order to verify whether the state of the enzyme molecule *vis-à-vis* its reactants, namely ATP and NMN, has anything to do with the repression or de-repression of DNA synthesis, the following experiments were carried out. Hepatectomized rats were divided into three groups. One group was kept as control without any further treatment, while the other two groups received nicotinamide or ATP immediately after the operation and also at 6 hourly intervals. The animals were killed at 48, 72, 96 and 120 hr after hepatectomy. Mitotic index and incorporation of tritiated thymidine in the livers were studied. Administration of nicotinamide or ATP reduced both the mitotic index and the incorporation of tritiated thymidine (Table 2). This suggests that the protein, which acted as a de-repressor of DNA synthesis, loses this activity and becomes a repressor when complexed with either NMN or ATP. This switching on of a de-repressor to repressor activity when complexed with a metabolite is not an altogether new idea. Jacob and Monod[6] have successfully applied this concept to explain many biological phenomena.

TABLE 1 — LEVELS OF NAD SYNTHESIZING ENZYMES IMMEDIATELY AFTER HEPATECTOMY OR CARCINOGEN ADMINISTRATION

	Dose	Interval	Fall in *in vivo* enzyme activity % of control*
Control liver			100
Regenerating liver			75
DAB	10 mg.	72 hr	28
20 MC	50 mg.	8 days	40
Isoniazide	100 mg.	3 days	37
Nicotine	750 μg.	6 hr	27

*No fall of activity in *in vitro* assay of enzyme.

TABLE 2 — EFFECT OF ADMINISTRATION OF NICOTINAMIDE OR ATP ON INCORPORATION OF TRITIATED THYMIDINE AFTER HEPATECTOMY

Interval after hepatectomy hr	Normal	Cells showing incorporation	
		Nicotinamide treated	ATP treated
48	10-12	—	5-6
72	8-9	3-4	5-6
96	7-9	3-4	6-7
120	7-8	6-7	6-7

In hepatectomy the de-repression of DNA synthesis is temporary and is probably caused by a humoral agent masking the active sites of the NAD synthesizing enzyme and thus preventing the combination of NMN and/or ATP with the enzyme molecule (Fig. 3). The humoral agent has been shown to be competitively displaced either with larger quantities of NMN and ATP as shown in Table 2 or with replacement of blood from hepatectomized animals with that from non-hepatectomized intact animals[7]. In malignancy, however, the de-repression is sustained and irreversible. This will be possible if the sites on the enzyme molecule, where the complexing takes place, are permanently deleted. It is a well-established fact that NAD synthesizing activity is permanently lowered in all the tumours[8]. Direct data on the nature of the binding sites of the enzyme molecule and whether these are deleted in malignancy are not available at present. There is, however, circumstantial evidence to suggest that the active sites where ATP combines may be the free carboxy group either from glutamic acid or aspartic acid. Further, our data on the amino acid composition of nuclear proteins, shown in Table 3, indicate that aspartic acid is partially deleted in malignancy and that the proportions of valine increase[9]. This observation, coupled with the fact that NAD synthesizing enzymes are exclusively located in the nucleus[10], may mean that either the profile of nuclear proteins is altered in malignancy such that aspartic acid containing proteins decrease while those containing valine increase, or that aspartic acid is deleted from some peptide fragment and that its place is taken by valine. Experiments are underway in our laboratory

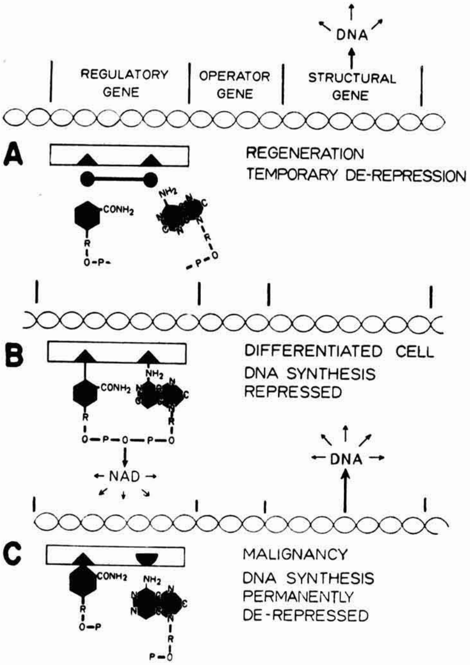


Fig. 3 — Schematic representation of de-repression of DNA in carcinogenesis and after hepatectomy [(A) Transitory de-repression of DNA synthesis following hepatectomy. Active sites (▲—▲) on the protein are masked by humoral agent (●—●) resulting in decreased NAD synthesis and de-repression of DNA synthesis. (B) Masking agent disappears or is competitively removed, thus facilitating complex formation of protein with NMN and/or ATP. DNA synthesis is repressed and NAD synthesis is facilitated. (C) Postulated mutated portion at the active side (◡) of protein. Metabolite-protein complex formation inhibited resulting in sustained and irreversible de-repression of DNA synthesis and decreased NAD synthesis]

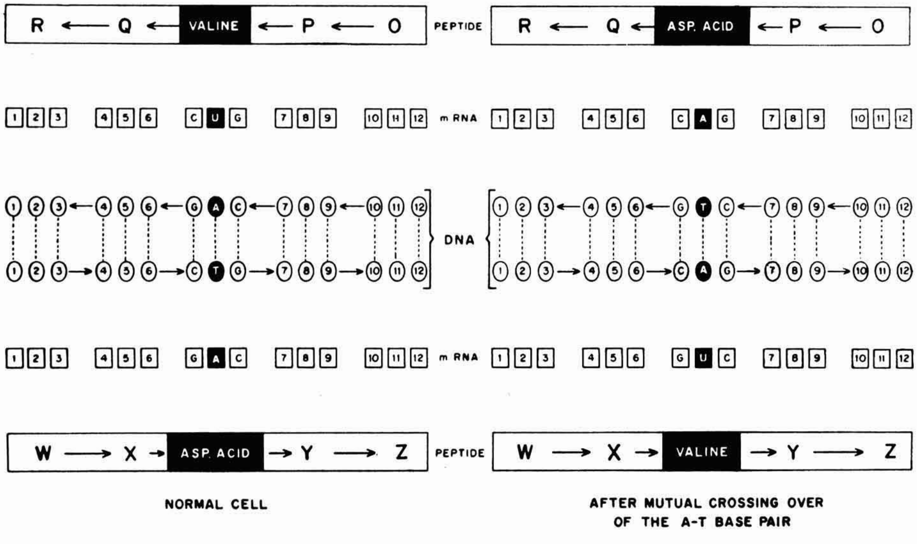
TABLE 3 — AMINO ACID COMPOSITION OF DNA PROTEINS OF LIVERS OF NORMAL, NEW BORN (EMBRYONIC) AND BUTTER YELLOW FED ANIMALS

	Amino acid content (μg./g. of amino nitrogen)		
	Control	Embryonic	Butter yellow fed
Aspartic acid	1105	1129	541
Glutamic acid	1155	1154	1130
Glycine	396	668	383
Threonine	770	833	713
Alanine	330	286	304
Tyrosine	656	961	728
Valine	165	146	328
Histidine	656	522	664
Lysine	528	344	459
Methione	260	250	248
Arginine	2272	2420	2489
Phenylalanine Leucine Isoleucine	528	428	455

to investigate this aspect and these will be reported elsewhere.

In the absence of these data, it may not be out of place to examine theoretically the biological feasibility of replacement of aspartic acid with valine in a protein moiety. The code for aspartic acid is GAC and that for valine is GUC[11]. Thus mutation at only one point on the DNA molecule would be necessary. The postulated changes in the DNA molecule would be as shown in Fig. 4. Here thymine is replaced with adenine in one of the DNA strands. In effect this turns out to be a mutual crossing over of one A-T base pair at one position between the two strands of

Fig. 4 — Molecular model showing (on the right) the postulated mutual crossing over of A-T base pair in DNA in malignancy and its consequences in changing the code in m-RNA from GAC (aspartic acid) to GUC (valine)



DNA. In a model which visualizes such a change, the base composition of the DNA would remain unaltered. This seems to be in accord with well-established observations. No one has yet detected any changes in the gross base composition of DNAs from normal and malignant sources.

In summary, therefore, the following working hypothesis may be postulated, pending definitive data, to aid further work to explain the mechanism of transformation of a normal cell to malignant type. A mutual crossing over of one A-T base pair between the two strands of the regulatory gene, which regulates DNA synthesis, is suggested. This change results in alteration in the sequence of the amino acids in the appropriate proteins, aspartic acid being replaced with valine at one place. In the absence of aspartic acid at appropriate sites, the attachment of ATP or NMN with the protein molecule is impaired, resulting in the loss of enzyme activity and accumulation of that form protein moiety which causes de-repression of DNA synthesis. Since this is a permanent change, caused by a mutation at the regulatory gene site, it leads to a sustained and irreversible cellular proliferation, which is so very characteristic of malignancy.

Summary

A working hypothesis to explain the mechanism of transformation of a normal cell to malignant type has been put forth. It envisages a mutual crossing over of adenine and thymine between the two strands of DNA at a site on the regulatory gene responsible for DNA synthesis. This results in alteration in the genetic code causing replacement of aspartic acid with valine at one point in the appropriate protein. The loss of aspartic acid probably transforms the protein which normally represses DNA synthesis into an altered type which acquires the property of causing de-repression of DNA synthesis. Since the elaboration of altered protein continues as a result of a permanent change caused by mutation at the regulatory gene site, it leads to a sustained and irreversible cellular proliferation and malignancy.

References

1. GIUDICE, G., KENNEY, F. T. & NOVELLI, G. D., *Biochim. biophys. Acta*, **87** (1964), 171.
2. FURLONG, N. B. & THIMANN, A. J., *Proc. Soc. exp. Biol. Med.*, **115** (1964), 541.
3. GELBOIN, H. V. & KLEIN, M., *Science, N.Y.*, **145** (1964), 1321.
4. SAHASRABUDHE, M. B., *Nature, Lond.*, **182** (1958), 163.
5. BEACONSFIELD, P., GINSBURG, J. & KOSINSKI, Z., *Nature, Lond.*, **205** (1965), 50.
6. JACOB, F. & MONOD, J., *J. molec. Biol.*, **3** (1961), 318.
7. GRISHAM, J. W., LEONG, G. F., ALBRIGHT, M. L. & EMERSON, J. D., *Cancer Res.*, **26** (1966), 1476.
8. MORTON, R. K., *Nature, Lond.*, **181** (1958), 540.
9. SAHASRABUDHE, M. B., APTE, B. K., ABOOKAKER, V. S. & JAYARAMAN, R., *Biochem. Biophys. Res. Commun.*, **7** (1962), 173.
10. SIEBERT, G., *Expl. Cell. Res. Suppl.*, **9** (1963), 389.
11. NIRENBERG, K., LEDER, P., BERNFIELD, M., BRIMACOMBE, R., TRUPIN, J., ROTHMAN & O'NEAL, C., *Proc. natn. Acad. Sci. U.S.A.*, **53** (1965), 1161.

Seminar on Biological Aspects of Leather Manufacture

A seminar on "Biological Aspects of Leather Manufacture" will be held at the Central Leather Research Institute, Madras, commencing from 31 January 1968. Among the biological problems to be discussed at the seminar are: (i) animal health problems related to leather manufacture, parasitic, bacterial and viral diseases in living animals affecting the quality of hide/skin; effective control of the diseases and improvement of hide quality; (ii) influence of animal breed, living conditions, death of the animal, delay in cure, vein mark, etc., on the qualities of hide/skin and finished leather; (iii) use of modern insecticides in the prevention of insect damage to stored hides and skins; standardization of insecticides; (iv) effect of red heat, salt stain, salt stippen, etc., on finished leather; improvement over the existing methods of curing by using modern antiseptics along with curing salt; newer approaches to curing; evaluation of raw hides and skins; standardization of flaying, trimming and quality of cured hides and skins in Indian trade — criteria of standardization; (v) coloured stains on chrome blue and other leathers; organisms and the pigments responsible for staining; prevention of stains; (vi) microbial activity in tan liquors; mould growth on pickled pelts; leathers and leather goods; prevention of mould growth; evaluation of fungicides; and (vii) histological and electron microscopical studies of skin/hide and wool fibres; application of histological techniques in leather research.

The biochemical problems to be discussed will include: (i) enzymatic dewooling and unhairing of skins and hides; fellmongering of skins; mechanism of enzyme unhairing; (ii) mechanism of bating; production of different enzyme bates; evaluation of bates; (iii) biosynthesis and biological degradation of skin protein; chemical and physical properties of different skin proteins; (iv) non-fibrous proteins and non-protein constituents of hides and skins; and (v) biological treatment of tannery effluents; utilization of tannery wastes and byproducts.

The last date for the submission of abstracts is 15 August and that for full papers 15 October 1967. Further details can be had from Sarvashri R. Bhaskaran and S. C. Nandy, Central Leather Research Institute, Adyar, Madras 20.

REVIEWS

DYNAMICAL THEORY OF GROUPS AND FIELDS by Bryce S. DeWitt (Gordon & Breach Science Publishers, New York), 1965. Pp. v+248. Price $ 5.95 (cloth); $ 2.95 (paper)

The book is based on a series of lectures the author gave at a summer school in 1963. It covers a wide variety of topics selected judiciously from the vast literature on advanced quantum theory and elementary particle physics. Several chapters are devoted to purely group theoretical matters. Their purpose is to provide the background necessary for understanding field theory and some of the latest developments in the theory of elementary particles. The basic ideas and results are presented without making much use of the machinery of sophisticated group theory. Representations, generators, structure constants are first defined and the Lie-Cartan commutation rules are stated in a way which leads to the important concepts of ' roots ' and ' weights '. In Chapter 13, a rather unfamiliar topic is taken up for discussion — the group of general coordinate transformations in a Riemannian space. The matrix representations of this group are provided by tensors or tensor densities obeying suitable transformation laws.

The first three chapters of the book are also purely mathematical. Contact with quantum theory is established through the theory of measurement and the laws of propagation of small disturbances. In Chapter 6, Green's functions for the various fields and their integral representations are discussed in the traditional manner and the concept of the Feynman propagator is introduced. This prepares the ground for discussing quantum field theory with which the book is mainly concerned. The basic ideas of field quantization are given in outline in Chapter 10 and more advanced questions are considered in the last eight chapters which are by no means easy to assimilate. The standard theory of the S-matrix, as formulated by Tomonaga, Schwinger, Dyson and Feynman, is given in Chapter 21 and used in the succeeding chapters for calculating the self-energy, radiative corrections, and cross-sections for scattering, pair production and pair annihilation. The unitarity of the S-matrix is proved in Chapter 21 and again under more general conditions in Chapter 23. The important question of renormalization is considered in Chapter 24, the divergences of the S-matrix are analysed, and the nature of the counter terms needed to yield finite results is examined.

In this short review it is impossible to give anything but a vague idea of the contents and the scope of the book. There is no doubt that it will serve as a source from which the student interested in advanced quantum theory can draw a good deal of material needed for his research work. The numerous problems distributed liberally through the text go far toward fulfilling the aims of the book.

S. DATTA MAJUMDAR

TOPOLOGICAL GROUPS by L. S. Pontryagin (Gordon & Breach Science Publishers, New York), Second Edition, 1966. Pp. xv+543. Price $ 32.50 (reference edition); $ 17.50 (professional edition)

The book under review is the English translation of the Russian original. In this translation only small changes are made in notation and also in substance from the original text. The subject of topological groups is a very fascinating one, combining in itself the study of two mathematical structures, namely a group and a topological space. This branch of mathematics has become popular since the publication of the first edition of this book in 1952. Anyone with a keen mathematical outlook and possessing a knowledge of topics usually covered in graduate courses can study this subject with much interest. The first edition of this book was widely used and appreciated. Various additions have been made in this edition. A classification of the Lie groups based on their Lie algebras is the most important addition. A new chapter dealing with topological division rings and fields is introduced. The theory of integral equations on a topological group is included. The treatment of covering spaces is enlarged.

The book contains 11 chapters. The first three chapters form the basis for the remaining chapters. Chapter 1 deals with the theory of groups which involves only the algebraic form of multiplication. Chapter 2 deals with topological spaces where the operation of passage to a limit is the main consideration. In Chapter 3, the basic ideas of topological groups are given where both the algebraic and topological operations are combined. The material contained in Chapter 4 devoted to topological division rings and fields, though important and interesting, could have been pushed to the end of the book to maintain continuity or could have been altogether omitted to give space to include more detailed presentation of the topics dealt with in Chapter 11. The theory of linear representations of compact topological groups is given in Chapter 5. A detailed study of the structure of commutative groups is given in Chapter 6. Chapter 7 is devoted to the concepts of differentiable and analytic manifolds and their relation to a Lie group. In Chapter 8, the structure of finite dimensional compact groups and the structure of compact transformation groups acting on finite dimensional spaces are discussed. Chapter 9 is concerned with the study of the universal covering of a group where the relation between the local and global properties of topological groups is investigated. Chapter 10 deals with the basic theory of Lie groups and Lie algebras and Chapter 11 is devoted to the investigation of compact Lie groups and their classification.

The book is written in a beautiful style. Interesting examples are given at the end of almost every paragraph of the book. Discussions and proofs of various related topics of importance are found in every chapter. Terms which are to be defined are underlined in the section on notation; this could have been followed up in the main text also. There are a few printer's mistakes, but none of them is of a serious nature. The book contains a useful bibliography and a fairly good index of the subject matter. It is hoped that the representation theory of Lie groups, which is of current interest, will be included in a future edition of the book. A study of this book will be very rewarding to everyone interested in mathematics and mathematical physics.

T. VENKATARAYUDU

ADVANCES IN THEORETICAL PHYSICS: Vol. 1, by Keith A. Brueckner (Academic Press Inc., New York), 1965. Pp. x+323. Price $12.00

This book is a collection of review articles on unconnected topics like the Padé approximant method, nuclear theory, hydromagnetics, ion transfer reaction, and elastic scattering of electrons by atoms, written by specialists in the respective fields. The object in publishing this series of articles is to give the theoretical physicist ready access to important advances in other fields.

The first article contains a discussion of the 'Padé approximant method' developed towards the end of the last century. It is used for obtaining quantitative information about functions that are known only from their power series and qualitative behaviour.

The next article is concerned with the theory of the 'giant dipole resonance' which shows itself up as a peak in the cross-section for photon absorption by nuclei at an energy of about 20 MeV. This indicates the existence of a collective dipole vibration common to all nuclei. The position and the width of the resonance is calculated with the help of an interaction Hamiltonian which contains products of electromagnetic potentials of the photon and the charge-current density of the nucleons.

The third article is on the 'optical model' in which the interaction of a given particle with a composite system of particles is approximately described by replacing the latter by an effective potential. The potential can be derived from the many-body Schrödinger equation or by using field theoretic techniques.

The fourth article contains a discussion of certain problems in hydromagnetics. The work reviewed here was motivated by research into the possibilities of controlled thermonuclear reaction but can be used for studying the behaviour of a plasma or any conducting fluid in the presence of a magnetic field. The electromagnetic equations for the quasistatic case together with the equations of hydrodynamics form the set of fundamental equations of the subject. The plasma is described as a single fluid of density ρ, velocity V, and pressure P. Gravitational and electrostatic effects are neglected and terms leading to dissipation are dropped.

In the last article the problem of elastic scattering of electrons by atoms is considered. The many-body problem is reduced to a one-body problem with an equivalent potential. The idea is old, but the author has given an account of the more recent researches some of which are highly interesting. It has also been shown how the Pauli principle can be incorporated in the formalism.

S. DATTA MAJUMDAR

CLASSICAL MECHANICS by T. W. B. Kibble (McGraw-Hill Book Co., London), 1966. Pp. xv+296. Price 42*s*.

This book offers a lucid and coherent exposition of the principles of higher mechanics and is pre-eminently suited for the Honours and M.Sc. students of Indian universities. The author starts from first principles assuming little detailed knowledge beyond that of differential and integral calculus. The basic concepts of space, time, mass and force are discussed in the introduction in the light of the ideas of the relativity theory. The next four chapters are devoted exclusively to the mechanics of a single particle. Throughout the book the tendency is to lay stress on those aspects of the subject which are of importance in other branches of physics. Certain topics are, therefore, included which are usually not discussed in text-books on mechanics. Lagrange's equations are introduced at an early stage in a way which is likely to present no serious difficulty to a beginner. The question is taken up again in Chapter 11 and the equations are rederived from a more general standpoint. Chapters 8, 9 and 10 deal with the mechanics of a system of particles and rigid bodies. The tensor character of the moment of inertia is established, Lagrange's and Euler's equations of motion are set up and solved in simple cases. However, as the book is meant for beginners only mathematical complications have been kept to a minimum. In fact, the only motion that is studied in any detail is that of a symmetrical top with one point on its symmetry axis fixed. Topics like the free motion of an unsymmetrical top have been considered to be beyond the scope of the book.

In Chapter 6, the potential theory is discussed in bare outline. The dipole and quadrupole moments of a charge distribution are derived. But, for the reasons stated above, no mention is made of the boundary value problem or Green's function.

The last chapter is devoted to the Hamiltonian formulation which has played a central role in the development of quantum mechanics. In the concluding portions of this chapter the author brings out the relationship between symmetries and conservation laws, a topic directly related to some aspects of elementary particle physics.

The problems given at the end of each chapter have been carefully framed so as to enable the reader to obtain a clearer understanding of the theoretical principles. The reviewer has no doubt that the book will serve as a good introduction to the study of higher physics.

S. DATTA MAJUMDAR

VIBRATIONS, WAVES AND DIFFRACTION by H. J. J. Braddick (McGraw-Hill Book Co. Inc., New York), 1966. Pp. x+217. Price 36*s*.

This book has arisen out of the course of lectures that the author gave to the first-year students at the Manchester University. It does not presume much prior mathematical knowledge on the part of the reader; the mathematics that is used is largely explained. Our own first-year B.Sc. students should be able to follow the book easily. However, this does not imply that mathematics is avoided; all that it means is that techniques like dispersion relations, Fourier transforms, convolutions, delta function and Kirchoff's theorem are not simply used but developed in the text. There are eight chapters: on harmonic oscillators, forced oscillations, waves, Fourier analysis, dispersive media and group velocity, stationary wave patterns, reflection, and Huygens' principle and diffraction.

This is an excellent book and the reviewer thoroughly enjoyed reading it. The author explains the mathematical steps adequately, but does not get so engrossed in this task as to lose sight of the physical picture. The interplay of mathematics and physics is beautiful. The physical illustrations are from sound, optics, electric circuits and electromagnetic theory.

There are some minor improvements that can be made in the next edition. In many figures the quantities that are plotted along the coordinate axes are not stated. There are some slips: thus, the phase difference of two harmonic motions in the last line of page 18 should be δ not θ; the term $m = n$ should be excluded from summation in Eq. (1.17); the last term in the upper line of Eq. (3.25) should be $\frac{1}{C}\frac{\partial^2 I}{\partial^2 x^2}$ not $\frac{1}{C}\frac{\partial^2 I}{\partial t^2}$; the signs in the line after Eq. (2.22) are incorrect, etc. The index at the end of the book is unsatisfactory; for example, the reviewer looked for Helmholtz resonator, transfer impedance and heterodyne principle in the index, but did not find them.

The book can be recommended for study to our B.Sc. students.

Vachaspati

Selected Papers on the Transfer of Radiation edited by Donald H. Menzel (Dover Publications Inc., New York), 1966. Pp. iv+269. Price \$ 3.00

Theories of transfer of radiation have numerous applications in physics, astrophysics and engineering. It is refreshing to find in print some of the important papers (six in all) on the subject, which are difficult to find. The collection includes the famous paper by Arthur Schuster 'On radiation through a foggy atmosphere' in which he brought out the importance of scattering in such studies. In the two papers, 'On the equilibrium of the sun's atmosphere' and 'Diffusion and absorption in the sun's atmosphere' (both translated from German), K. Schwarzschild applied the theory to the distribution of temperature in solar atmosphere, while A. S. Eddington in his paper, 'On the radiative equilibrium of the stars', applied the theory to stellar interiors. In the note 'On the absorption of radiation within a star' S. Rosseland showed that the reciprocal of opacity (and not opacity) should be averaged in order to get the mean opacity coefficient. The main objective of the book is to make available to the reader the important and basic study by E. A. Milne on the 'Thermodynamics of stars'. This has been reprinted from *Handbuch der Astrophysik*. In this study Milne obtained the equations of radiation transfer and their application to sun's chromosphere and studied other problems regarding the stellar interiors.

F. C. Auluck

Infrared Instrumentation and Techniques by A. E. Martin (Elsevier Publishing Co., Amsterdam), 1966. Pp. x+180. Price 65*s*.

Infrared methods play an important role in the elucidation of molecular structure and are being used extensively in industry for process control and rapid analysis. With the availability of a wide variety of commercial spectrometers of various degrees of sophistication, it has become necessary for any practising spectroscopist to be familiar with the current developments in the instrumentation in this field. Dr A. E. Martin who has been in this field for over thirty years and is a director of one of the world's leading manufacturers of infrared equipment has in the present book given a lucid account of the fundamental principles of the instrumental side of infrared spectroscopy, covering at the same time some of the recent developments, such as the interferometric spectrometer and the attenuated total reflection.

The book has been divided into six chapters. After giving a very short account of the historical background in Chapter 1, the author proceeds to deal with the sources, detectors and dispersion devices in Chapter 2. The condensing systems for use with detectors have been described well with the help of neat sketches and in fact the liberal use of diagrams to illustrate the optical principles is an attractive feature of this book. The Golay cell, germanium bolometer for use at low temperature, germanium immersion, and light pipes have been explained in some detail. In discussing the performance of prism and grating as dispersing devices the author has dealt with the effects of curvature of spectral image, the relative merits of wavelength and wavenumber presentation, stray radiation effects, precautions to be taken during calibration, effects of unequal slits and similar topics of great practical importance. Although limitation of space has been given as the reason for summarizing the features of only British instruments and some of the better known US models, it would have been nice if the author had included some comments on spectrometers of German origin. The properties of various window materials including IRTRAN have been summarized in the form of a useful table.

In Chapter 3, dealing with miscellaneous instruments, a description of spectrosorter, infrared gas analyser, optical pyrometers and milk analyser has been given. Chapter 4 contains a detailed account of the theoretical considerations of interferometric spectrometers and it is a pity that the author did not consider it worth while to discuss any practical instrument other than the Grubb-Parsons spectrometers. In view of the extensive contributions of the Japanese and the German workers to this recent development some description could have been given of their interferometers. Chapters 5 and 6 deal with the accessories and the experimental methods and techniques of IR spectroscopy. The effects of antireflection coatings (blooming) and the principles of attenuated total reflection are among the important topics discussed in these two chapters. A list of 100 important references has been included at the end of the book.

This book will be found extremely useful not only by those who are about to commence work in this field but also by senior workers, since a lot of material which has not been previously published has been included in it.

P. S. NARAYANAN

ZONE MELTING by Hermann Schlidknecht (Verlag Chemie, Weinheim, and Academic Press Inc., New York), 1966. Pp. xii+222

The book is of great value to solid state physicists interested in preparing single crystals of high purity and to chemists interested in the production of pure fractions by crystallizing mixtures of various substances. Zone melting is a very useful economic method of obtaining high melting materials in an extremely pure state. It is based on the fact that at the freezing interface the solute concentration in the solid phase generally differs from that in the liquid phase. The author has dealt with the problem of solid-liquid phase equilibrium of binary, ternary and higher order systems with remarkable clarity. Zone melting can be profitably utilized in eutectic systems. The author has given a lucid exposition of how zone melting can be utilized for a variety of purposes. Isolation of pure compounds from mixtures of isomers and homologues, and ice zone melting which is of particular importance in biochemistry have been discussed in detail. A considerable portion of the book has been devoted to details of equipment. This knowledge would be highly useful to workers engaged in similar problems. A separate chapter is devoted to the zone melting of elements and inorganic substances. It gives the methods employed by different workers in the field for producing substances in the pure state. These informations are valuable to those who intend to specialize in this field. The book would be useful to a large group of laboratory workers.

K. D. CHAUDHURI

COMPUTERS IN BIOMEDICAL RESEARCH: Vol. 2, edited by Ralph W. Stacy & Brouce Waxman (Academic Press Inc., New York), 1965. Pp. xix +363. Price 112*s*.

The authors of the book had already made a mark by their earlier writings in the electro-biological field as well as through Vol. 1 of this book. The book like Vol. 1 is useful both for the engineer to whom it gives an insight of computer technology and vision to look into the needs of biomedical scientists, and for the biomedical man for whom it presents a coherent picture of technical details as well as the applicability of this modern approach and technique of computing and automatic data processing. Starting from the discussion of analogue to digital conversion system it gives a description of the LINC and special purpose digital computers finding use in biological research. After bringing out some theoretical points relating to the applicability of these devices to biomedical problems, specific research programmes and possible future developments have been considered very aptly. The chapters on simulation on ecological system, atrial fibrillation, the computer techniques for the study on circulation, and respiratory parameters are of as much interest to research workers as to clinicians or the basic biologists. The discussion on hospital automation through computer time sharing brings into focus some aspects which may be beneficial to the administrator as well as for normal hospital activities. The usability of computers in psychology and psychiatry points to the possible application of this information in mental sciences. In fact the book has given quite a few leads for future thought to scientists, whether they are clinicians, medical scientists, biologists, neurophysiologists or specialists in computer sciences, and deserves a prominent place on the bookshelf of every good library and of scientists.

B. K. ANAND

THE MEASUREMENT OF AIR FLOW by E. Ower & R. C. Pankhurst (Pergamon Press Ltd, London), Fourth Edition, 1966. Pp. viii+367. Price 65*s*.

This is the fourth edition of a book originally published in 1937, dealing with the techniques of measurement of velocity in fluid flow. Its evident success is not surprising in view of the few reference books available on this highly practical subject, which is of concern to engineers and research workers in industry and laboratory alike.

The treatment is straightforward and well presented. The standard method of velocity determination by the measurement of fluid pressures, and the pressure probe characteristics are described in terms of the basic theory and practical considerations. The application of this technique for velocity and mass-flow measurement in ducts is discussed. The use of standard orifice and nozzle type flowmeters is also described. A comprehensive chapter is devoted to the theory and practice of the vane anemometer. Another chapter deals with the characteristics of liquid manometers. A brief description of the hot-wire technique is also given. A useful new chapter on the measurement of pulsating flows has been included.

The significant addition to this new edition appears to be the material on compressible flow measurement contributed by the second author. Indeed, the considerable progress and refinement in the technique of low velocity determination using pressure probes achieved in wind tunnel establishments are reflected in the relevant chapters of this book, and no doubt represent the contribution of Dr Pankhurst who is a well-known authority on wind tunnels. This reviewer feels particularly gratified for the way the considerable experience in this field at the disposal of the wind tunnel engineers has become more widely available through this book.

Since the information presented in this work will be of maximum use to engineers concerned with flow measurements in industrial duct systems, it was perhaps a good idea to include a chapter describing the basic features of flow in a circular pipe. However, the scope and organization of this chapter leave something to be desired. Nearly 10 pages (out of 37) in this chapter deal with the resistance of bends and effects of turning vanes, which do not appear relevant to the main purpose of this chapter. This reviewer would have liked to see a somewhat more expanded treatment of the physical nature of flow in ducts, including non-circular cross-sections as are often encountered in industrial systems. The important topic of diffusers gets a very brief mention (sudden expansions, although mentioned in the subtitles p. 110, are not touched in the text at all), and even then most of the discussion is concerned with means of flow stabilization in diffusers, which again are not relevant to the problem of flow measurement.

The use of pitot-rakes in duct flow measurements is common practice, and the reviewer is surprised that no mention of this method has been made here. A brief description of flow-visualization techniques (standard practice in wind tunnels) for a preliminary, qualitative observation of the flow field where possible, so that a better approach to the problem of flow measurement in a given situation can be decided, should enhance the utility of this book.

Apart from these minor criticisms, this book is recommended to practising engineers and laboratory workers. It is to be hoped that a cheaper edition of this book will be forthcoming so that it can be owned by students who should also find this a useful reference.

D. M. Rao

Introduction to the Chemical Process Industries by Richard M. Stephenson (Reinhold Publishing Corp., New York), 1966. Pp. v+474. Price $ 14.75

The technology of sulphuric acid has required a few volumes for an exhaustive treatment. It is so for ammonia and sugar also, and the task of including a larger number of industries in a single volume of reasonable size is a difficult one. The problem would be what to exclude and how to limit the scope. The decision and choice are entirely the author's and the present volume covers more than a hundred products, nearly half of them being organic chemicals and a quarter of them polymers; inorganic chemicals comprise the rest.

The book starts with a brief review of thermodynamics and kinetics followed by six chapters dealing with inorganic chemicals. The next ten chapters cover selected organic products. The last chapter comprising nearly a fifth of the book is devoted to high polymers. The field covers natural salts, manufactured soda ash, caustic soda, chlorine, sulphuric acid, fixed nitrogen, inorganic phosphorus and fluorine compounds, coal and petroleum, olefines and their products, acetylene and its derivatives, halogenated paraffins, products from carbon monoxide and hydrogen, oxidation products of hydrocarbons, cyclic intermediates, surface active agents, and natural and synthetic elastomers and polymers, including some recent ones.

In most cases the treatment starts with an outline of the uses and economics confined to USA followed by a discussion of the basic chemical processes involved. Equilibrium data are presented in the form of graphs in a few cases and values of ΔH°_{298} and ΔF°_{298} have been given for many of the reactions. Simplified flow sheets of the manufacturing processes have been presented for one-third of the products. Many items receive a very brief treatment, some of them being even cursory. This is inevitable when the technology of more than hundred products is compressed in a book of less than 500 pages. A large number of references to original sources, many of them published after 1955, has been provided, some of these being as recent as 1964 in a book published in 1966.

The book " includes only those processes which any chemical engineer or chemist might reasonably be expected to be familiar with " and is recommended as an introduction to the process industries at the undergraduate level.

B. Narayan Das

Principles of Steelmaking by A. K. Biswas (Asia Publishing House, Bombay), 1966. Pp. x +412. Price Rs 25.00

This book is a welcome addition to the relatively small number of text-books on iron and steelmaking presently available to undergraduate metallurgy students and technical personnel in steelworks. It is also welcome as the first such effort by an Indian author.

Going through the book, one cannot but be impressed by the wealth of information collected by the author from the original sources, viz. the research publications from the industry and research establishments. In this regard, the author's acquaintance with German technical literature has been of special value.

As the author is associated with the Indian Iron & Steel Co. Ltd, Burnpur, he has been able to include much useful information in the book from actual steelmaking practice. There are 13 chapters in all. Chapter 3 constitutes a novel and interesting attempt to systematize information on the numerous multicomponent systems of interest to steelmakers.

Unfortunately, the kinetics of steelmaking reactions and the electrochemical concepts underlying slag-metal reactions have not been given their due importance by the author.

The book is well printed and produced, but the cost seems to be relatively high for an undergraduate text-book published in India.

T. R. Anantharaman

Principles of Industrial Microbiology by Alan Rhodes & Derek L. Fletcher (Pergamon Press Ltd, Oxford) 1966. Pp. xviii+320. Price 35*s*.

Industrial microbiology has taken rapid strides during the past quarter of a century; still information relating to some of the recent processes, or improvements effected in the older ones, is not easily accessible for one reason or the other. The authors of this volume have tried to place before its readers the underlying principles of biochemistry, microbiology and chemical engineering which contribute in achieving success in microbiological industries.

The structure of the book is logical. It is divided into twenty-one chapters: Introduction; Design of a fermentation unit; Industrial applications of genetics of microorganisms; Culture collection laboratory; Principles of sterilization, sterility and asepsis; Nutrition of microorganisms and media for industrial fermentations; Agitation and aeration of microbial fermentations; Food microbiology; Fermentation products related to sugars; Fermentation products formed from pyruvate by facultative anaerobes; Fermentation products formed by the anaerobic activities of butyric acid bacteria; Fermentation products related to intermediates of the citrate cycle; Production of penicillin antibiotics; Biosynthesis from acetate in relation to production of griseofulvin and the tetracycline antibiotics; Vitamin B_{12} structure, biosynthesis and production; Oxidative disposal of sewage, industrial wastes and aromatic compounds by microorganisms; Industrial uses for microorganisms in single step enzymic processes; Some screening methods employed in the search for new antibiotics; Continuous culture of microorganisms; Industrial methods for production of vaccines; and Present trends and possible future developments in industrial microbiology. The treatment is throughout clear and informative. The authors have taken great care to cite recent literature and give equations and diagrams to explain the mechanisms. A good index is given at the end.

The book would prove invaluable to biochemists, engineers, microbiologists and industrialists.

J. V. BHAT

CHEMICAL EQUILIBRIUM by A. J. Bard (Harper & Row Publishers, New York), 1966. Pp. xi+202. Price Rs 22.88

The title of this book is misleading. It neither deals with the principles of chemical thermodynamics nor with the methods for determining equilibrium constants. Actually, it is a recipe book for calculating the concentrations (activities) of the various species from the known values of equilibrium constants for different type of processes (e.g. acid-base dissociation, complex ion formation, redox reaction, etc.). Most of the material covered in this book, except Chapters 8 (graphical methods) and 10 (numerical and computer methods), can be found in any standard undergraduate text on physical or analytical chemistry. Thus, the book (as it is meant to be) loses much of its value as a complementary text. Nevertheless, it is a well-written and well-illustrated book. The author has given carefully chosen references for further reading and problems for practice at the end of each chapter.

On page 10 (Table 1.1) dimensions for K of the general reaction have been left out. Cu^{2+} and Zn^{2+} are shown to be in zero oxidation state on page 83. Except for a few minor typographical errors (p. 29 Eq. 3.24 and third line from bottom) the book is well produced.

The book can be useful for students of B.Sc. (Pass and Hons.) in this country.

D.J.

PUBLICATIONS RECEIVED

CARBOCYCLIC NON-BENZENOID AROMATIC COMPOUNDS by Douglas M. G. Lloyd (Elsevier Publishing Co., Barking, Essex), 1966. Pp. x+220. Price 70s.

THE NEUROCHEMISTRY OF ARTHROPODS by J. E. Treherne (Cambridge University Press, London), 1966. Pp. viii+156. Price 30s.; $ 6.00

THEORY OF SPECTROCHEMICAL EXCITATION by P. W. J. M. Boumans (Hilger & Watts Ltd, London), 1966. Pp. xi+383. Price £ 5

RECENT DEVELOPMENTS IN PARTICLE PHYSICS edited by M. J. Moravcsik (Gordon & Breach Science Publishers Inc., New York), 1966. Pp. 263. Price $ 15.00

LOCAL ATOMIC ARRANGEMENTS STUDIED BY X-RAY DIFFRACTIONS edited by J. B. Cohen & J. E. Hilliord (Gordon & Breach Science Publishers Inc., New York), 1966. Pp. 381. Price $ 22.00

FASCINATING PROBLEMS IN ORGANIC REACTION MECHANISMS by Subramania Ranganathan (Holden-Day Inc., San Francisco), 1967. Pp. 88. Price $ 5.00

GERMANIUM by V. I. Davydov, including RADIOACTIVE ISOTOPES OF GERMANIUM by P. Rudenko & L. V. Kovtun; translated from the Russian (Gordon & Breach Science Publishers Inc., New York), 1967. Pp. 417. Price $ 18.00

THE CYTOLOGY OF THE PROTEIN SYNTHESIS IN AN ANIMAL CELL by B. V. Kedrovskii; translated from the Russian (Gordon & Breach Science Publishers Inc., New York), 1967. Pp. xi+467. Price $ 14.50 (paper); $ 29.50 (cloth)

NOTES & NEWS

Measurement of vacancy concentrations in metals at the melting point

A new technique for measuring vacancy concentrations (C_v) in metals, which overcomes the difficulties experienced till now in such measurements, has been reported [*J. appl. Phys.*, **37** (1966), 4717]. The only satisfactory method available developed for measuring absolute vacancy concentrations involves the measurement of the difference between the macroscopic linear expansion (Δl) and the lattice parameter expansion (Δa), relative to the values of length l_0 and parameter a_0 at some reference temperature (T) at which the vacancy concentration is negligible. The value C_v in equilibrium at T is then given by

$$C_v = 3[(\Delta l/l_0)-(\Delta a/a_0)]$$

However, the extension of this method for measurement of C_v in alloys is beset with several difficulties such as the production of alloy specimens to the required degree of homogeneity and the maintenance of temperature uniformity. Because of these difficulties, the advantages of simultaneous measurements tend to become more apparent than real. The basic principles of the new technique suggested are: (i) to use small specimens which will facilitate eventual study of alloys and (ii) separate measurements of length change and lattice parameter change. Measurements of Δl are made on samples 1 cm. long by an interferometric dilatometer and that of Δa by a powder diffractometer technique using a sample taken from the dilatometer specimen. Macroscopic thermal expansion measurements are made at several temperatures between the room temperature and the melting point using an automatically recording Fiezeau type interferometric dilatometer. The measurement of specimen temperature is carried out by Pt-Pt-13 per cent Rh thermocouples suitably positioned. A high temperature attachment for use with a Philips vertical circle X-ray diffractometer is employed for the measurement of $(\Delta a/a_0)$ and the value at melting point is extrapolated from low temperature data. Experimental determination of C_v for aluminium gave a value closely agreeing with the value reported in literature. The accuracy of measurements of $\Delta l/l_0$ is 1 in 10^5 and the interferometric technique has the advantage of using only small specimens thus simplifying the problems of chemical uniformity in alloys. The new technique has shown that it is possible to estimate C_v using separate measurements of length and lattice parameter and that the new technique is capable of distinguishing between vacancy type and interstitial type defects in a crystal.

Quantum-counting spectroscopy

The versatility of the quantum-counter as a tool for solid state spectroscopy, especially in the extreme regions of 1 and 500 μ, has been recently pointed out and new techniques have been described for using quantum-counting cycles to extract spectroscopic information about the active media [*J. appl. Phys.*, **37** (1966), 4806]. Since this method furnishes information only for the levels participating in the quantum-counting, it cannot replace the conventional spectroscopic studies but will be of great value in supplementing the information normally available. At present the effectiveness of the active elements as spectroscopic tools for the analysis of their constituent materials is recognized and the gas laser is used for the investigation of the infrared transitions in the noble gases. But it is pointed out that the quantum-counter is even more versatile than the laser as an element for self-spectroscopy, because it does not have a critical threshold for operation. As a spectroscopic tool the quantum-counter can be used with particular advantage to measure three parameters: the transition frequencies, the lifetimes of both fluorescent and nonfluorescent levels and the line widths at transitions among the levels. The spectrometer used for frequency determination in the far infrared region is based on the Fabry-Perot interferometer and in operation the output from a photodetector is monitored, as the resonator length is varied at a slow fixed rate. In the spectrometer specially designed for studies in the near infrared region the crystal is clamped to the cold finger of a metal Dewar. The cryostat is fitted with three windows around the perimeter to allow optical access to the crystal. One window is used for the fluorescent output while the other two allow radiations at ν_1 and ν_2 to be pumped in separately. The fluorescent output is detected by an EMI 9558QB photomultiplier and after phase-sensitive detection, displayed on a recorder. The line width for the infrared lines can be determined from the change in cavity length between the half-response points of the fluorescent output. The methods for measuring the lifetimes of different levels involve chopping either both or one of the output beams and then monitoring, respectively, the relative phases of the two choppers when the fluorescence is maximized or the phase of the single chopped beam relative to the phase of the fluorescent output. The relative phase may be measured directly using the phase control on a synchronous demodulator.

The method is extremely flexible because of the extremely wide span of frequencies used to excite quantum-counting cycles, from 14 cm.$^{-1}$ to more than 14000 cm.$^{-1}$. The quantum-counting advantage is evidenced by the fact that throughout the work photomultipliers can be used, even for the 14 cm.$^{-1}$ spectroscopy; and in the far infrared enough sensitivity is available as to use thermal radiations as source. The new method will be of great value in high resolution measurements where conventional spectroscopy is severely hampered by energy limitations.

Proteins from alkanes and microorganisms

In the drive for finding new sources of proteins, a new continuous fermentation process has been developed jointly by Esso Research & Engineering Corp., USA, and Switzerland's Nestlé Alimentana [*Chem. Engng News*, **45** (No. 2) (1967), 46]. In the new process, simple cell proteins, which may become the new source of protein in the next decade, are grown from yeast or bacteria nourished by a C_{13}-C_{19} high purity normal alkane substrate. The economics of the process depends on the choice of suitable hydrocarbon substrate and organisms capable of using the substrate and process conditions. Of the different hydrocarbons studied, hydrocarbons below C_{13} have been found to exhibit much lower growth rates and cell yields, while hydrocarbons above C_{20} have been found to partially solidify under the desired process conditions. The substrate selected, which eliminates the formation of undesired products, was a mixture of normal C_{13}-C_{19} alkanes. The pharmaceutically pure substrate is separated from petroleum distillate by molecular sieves and containing 99 per cent normal C_{13}-C_{19} alkanes and the remaining of isoparaffins and naphthenes.

The growth, cell yield and amino acid composition of the product are the determining factors in the selection of suitable microorganisms and out of the various species screened, bacteria and yeast, each with its own advantages have been selected. Yeasts, besides being larger than bacteria, thus simplifying recovery, offer other advantages in high lysine content and capacity for growing at lower *p*H, where contamination is less likely to occur. On the other hand, the evaluated bacteria have a higher protein content, greater growth rate and require simple medium than the yeasts. Besides, the amino acid content of bacteria can be controlled by changing the process conditions, thus tailoring the end product to complement the proteins in the remainder of the diet.

In the process envisaged, aerobic fermentation with residence times ranging from 1 to 4 hr takes place under aseptic conditions in an aqueous solution containing phosphate salts. Nitrogen is supplied by ammonia, which also helps in maintaining the *p*H. After fermentation the cells are separated by centrifuge; washed to remove adhering growth medium and reduce the salt content. Finally the cells are dried to yield the product after undergoing a heat treatment to destroy viable organisms.

The final product is a blond, white powder rich in vitamins with a neutral flavour and which is 'basically non-toxic and nutritionally adequate'. A small-scale pilot plant has been successfully operated.

Isolation of deoxyribonucleic acid from microorganisms

A new isolation procedure for DNA, involving multistep liquid-liquid extraction with an aqueous polymer two-phase system has been developed at the Department of Biochemistry, University of Umea, Sweden. The superiority of the new method over the commonly used method of Marmur [*J. molec. Biol.*, **3** (1961), 208] lies in its simplicity, rapidity and reproducibility. The method is comparatively mild and avoids extensive use of organic solvents and precipitation of DNA which may otherwise lead to changes in the structure of DNA.

A crude lysate prepared by treating the cell suspension (approx. 3-4 g. cells/25 ml. of 0·15*M* NaCl, 0·015*M* sodium citrate) with 2 ml. Duponal for 20 min. at room temperature is shaken with an equal volume of a mixture of chloroform-isoamyl alcohol (24:1, vol./vol.) for 20 min. and centrifuged at 7000 r.p.m. for 20 min. The upper layer containing the high molecular weight nucleic acid is pipetted off. The lysate is then clarified by centrifugation at 15000 r.p.m. for 20 min. The bacterial extract is then partitioned in a system of 4*M* NaCl, DNA remaining in the lower phase while most proteins move to the upper phase. Extraction with a new upper phase of the system (D_5-polyethyleneglycol$_4$, 0·005*M* NaH_2PO_4, 0·005*M* Na_2HPO_4, 0·001*M* sodium citrate) decreases NaCl concentration to about one-third of the original, thereby altering the weight composition of the phase system. DNA is thus transferred to the upper phase while high molecular weight RNA in the lower phase. DNA is recovered in about 90 per cent yield in 15 additional extractions.

If desired, RNA can be transferred to the upper phase by changing the ionic composition to (D_5-polyethyleneglycol$_4$), 0·005*M* Na_2HPO_4, 0·005*M* Na_3PO_4 [*Biochem. biophys. Acta*, **134** (1967), 37].

A new procedure for analysing brain lipids

A new microanalytical technique capable of effecting complete analysis of 24 classes of brain lipids on as little as 150 mg. of brain tissue has been reported [*Biochemistry*, **5** (1966), 3405]. The methods used so far could determine only 11-14 classes of lipids of ox brain. The new technique, besides enabling the analysis of all the known brain lipids, has added three more phospholipids (choline plasmalogen, inositol plasmalogen and phosphatidylglycerol) to the list of hitherto known brain lipids. However, the new method has its limitations also; (i) it does not give any information on the fatty acid composition of the phospholipids except sphingomyelin, and (ii) it is unable to distinguish lyso compounds from their parent lipids.

Individual phospholipid determination in the new procedure involves selective mild alkaline and acid hydrolyses of the brain tissue followed by fractionation of the water-soluble phosphates (diacylphosphoglycerides and plasmalogens) on anion-exchange columns and of the alkali-acid stable products (sphingomyelin, glycerophosphoethanolamine) on silica acid columns. The determination of brain lipids other than the phospholipids is facilitated by an initial fractionation of the neutral and glycolipids on a Florisil column which allows the cholesterol assays to be made without interference from phospholipids.

Gas chromatographic separation of serum thyroid hormones

So far, paper, column or thin layer chromatography combined with the arsenite colour reaction was generally employed for determining thyroid hormones in serum. However, this method though sensitive is non-specific and there is interference by both organic and inorganic substances during preliminary separations. This difficulty has been overcome by the development of a gas chromatographic method affording higher resolution and easier separation. Iodinated tyrosines and thyronines, because of their low vapour pressure, are converted into their derivatives before being gas chromatographed. Experiments with NO-bistrifluoroacetyl methyl esters have shown it to be the most suitable derivative for this method.

An aliquot (1-3 μl.) of a suitable derivative of the composite mixture of iodine compounds is chromatographed using an F & F model 402 equipped with a flame ionization detector and Moseley I-mV. recorder. A 4 ft glass column packed with 3-8 per cent SE 30 on 80/100 mesh Diatoport S(F & M) is used with helium carrier at 750 ml./min. flow. Operating temperatures are: injector, 270°C.; column, 250°C.; and detector, 250°C. The peaks obtained thus correspond fairly well to the retention times of the individual components [*Analyt. Chem.*, **38** (1966), 1751].

Increasing the protein content of plants

The possibility of increasing the protein content of several food and forage crops by as much as 80 per cent by treating them with trace amounts of simazine [2-chloro-4,6-bis(ethylamino)-*s*-triazine], a herbicide used to control weeds around fruit trees, has been reported from the Michigan University, USA.

Simazine increases the ability of the plant to synthesize protein from its carbohydrate content by increasing the activity of the enzyme nitrate reductase, which reduces nitrate to nitrite, a form of nitrogen readily synthesized into amino acids and hence into protein. Most of the experiments with simazine were conducted on plants in controlled environment chambers. Simazine is used at 0·01-0·09 p.p.m. level in nutrient culture.

At 72°F. in the day and 62°F. at night, 0·04 p.p.m. simazine increases protein content of rye by 50 per cent over untreated plants. At lower temperature (62°F. in the day and 52°F. at night), the increase of protein content is 80 per cent. With peas, at 72°F. in the day and 62°F. at night, 0·08 p.p.m. simazine increases the protein content of both foliage and seed by 50 per cent. Increases of 25-40 per cent are obtained with corn, lettuce, cucumber and squash.

The action of simazine allows a plant to produce protein more efficiently and also enables a plant to thrive on lower amount of nitrogen. Similar effects of simazine were obtained with crops in the field by applying simazine at the time of planting [*Chem. Engng News*, **45** (No. 8) (1967), 23].

Fungus resistant resins

The synthesis of chlorinated alkyd resins, resistant to fungal attack and suited for use in the tropics, has been reported. The alkyd resins were chlorinated under such conditions that the unsaturated fatty acid portion would be chlorinated, in preference to the aromatic ring. This has been achieved by bubbling chlorine through a solution of the resin in carbon tetrachloride till the reaction mixture becomes pale yellow. Two such resins containing 28 and 38 per cent chlorine respectively have been prepared, pigmented solely with titanium dioxide and tested for resistance to fungal attack under conditions of a tropical secondary rain forest. Their performance has been compared with that of titanium dioxide pigmented paints based on linseed oil. The latter was covered in 3 months with *Pullalaria pullulans*, *Morilia siliphila*, *Cladosporium herbarum* and *Trichoderoma virida*, whereas even after 9 months the newly developed resins showed little fungal growth [*Nature, Lond.*, **212** (1966), 1039].

CSIRO Ore Dressing Laboratory, Melbourne

The annual report of the Ore Dressing Laboratory (CSIRO, Melbourne) for the year 1965-66 records the progress made in the several research projects and specific industrial problems that were under investigation during the year. Two important aspects of mineral processing — ore breakage and flotation concentration — have received much attention. Grindability characteristics of several Australian ores, chemistry of flotation pulps, flotation characteristics and behaviour of McArthur river Zn-Pb ores are among the problems studied.

In a study of the chemistry of flotation pulps, it was shown that plant sampling and measurement of *p*H, oxygen content and redox potential of the pulp under plant conditions offer no difficulty. It was also found that the use of lime instead of soda ash makes it easy to collect large samples of clear solution of pulp for chemical investigation.

An attempt was made to separate chalcopyrite from pyrite by selective flotation. A chemical condition had to be created in the pulp, which would result in pyrite depression without interfering with chalcopyrite flotation. This was attempted by the addition of calcium ions (lime) to the pulp; the relevant factors are Ca^{2+} concentration, *p*H and oxygen content, control of the last factor being the most difficult.

An unsuccessful attempt was made for the quantitative determination of tungsten in ores by cathode ray oscillography. Though peaks were readily obtained, the peak heights could not be directly correlated with any amount of tungsten, because the sample could contain a series of polytungstates.

A process for the recovery of bronze from mint sweepings has been developed. Recovery of copper from low grade waste dumps derived from open cut mining of a sulphide ore is under study. An effort is being made to tap the lead-zinc ores of the McArthur river.

During the year grindability tests were carried out in several mines as also rod mill impulse tests with different size ranges of galena. A gravity concentration study of the movement of solid spheres in water along a vertical tube was made and a correlation between terminal velocity and d/D values developed.

National Institute of Communicable Diseases, Delhi

The annual report of the institute for the year 1964 records the progress made in the various fields of study — routine as well as original. A variety of strains of malarial parasite and insect colonies of mosquitoes, house-fly, bedbug, fleas, fish as well as microorganisms were maintained for use in special studies on malaria transmission and insect susceptibility. An *Aedes* survey in connection with dengue-like fevers in different parts of India was conducted. Eighteen drugs (Mis. 552 to Mis. 569) were screened for antimalarial activity on *P. gallinaceum* in chicks. Investigations were conducted on the epidemiology of (i) plague in South India, (ii) diarrhoea, dysentery and gastro-enteritis in New Delhi, (iii) peripheral neuritis in a village in Baroda district, (iv) infectious hepatitis in Delhi, and (v) febrile illness in Visakhapatnam.

Twenty-nine derivatives of 2-methyl-3-aryl-6-methyl/chloro/bromo-8-bromo-4-(3)-quinazolones have been synthesized as potential antimalarials, amoebicides and anticonvulsants. Disubstitution has been introduced in the 3(3)-quinazolone nucleus at 6 and 8-position, to study its effect on the biological activity of 3-aryl-4(3)-quinazolone derivatives. 4:(8′-chloro-4′-quinaldyl) amino-*x*-disubstituted amino-*ortho*-cresols have been synthesized as potential antimalarials and amoebicides.

For the *in vitro* estimation of hetrazon (diethyl carbamazine) used in the treatment of filariasis, bromophenol blue has been found to be a better chromogenic agent than the previously known agents. It gives satisfactory results at low *p*H. Laboratory colonization of mosquitoes, *Anopheles culicifacies* Giles, was attempted by induced mating technique. It was observed that the glucose-fed females are easier to inseminate than the blood-fed females; with blood feed the ovary develops causing a curvature of the sternites, thus making it difficult for the claspers of males to get a firm grip on to the female genitalia.

Attempts were made to establish laboratory colonies of *Armigeres subalbatus*, an efficient laboratory vector for filariasis; of *Aedes (Stegomyia) vittatus* and of fowl-tick (*Argas persicus*). Investigations on standardization of rearing of *C. p. fatigans* in the laboratory were undertaken. Bromophos has been found to be an effective insecticide against *C. fatigans*, *Ae. aegypti*, *A. subpictus*, *X. cheopis* and *M.d. vicinanebulo*. Studies on the joint action of ethyl alcohol and insecticides, e.g. DDT, γ-BHC and methoxychlor, against *Culex p. fatigans* have shown the enhancement of the toxic effect of chlorinated hydrocarbon insecticides by the addition of alcohol.

The susceptibilities of sand-flies (*P. argentipes*) to DDT and dieldrin, *Pendiculus humansis capitis* and *P. h. corporis* to chlorinated hydrocarbon insecticides, house-flies to tugon, rat-flies (*X. cheopis*) to organo-phosphorus compounds, gamma BHC, malathion and baytex, bedbugs (*Cimex hemipterus*) to vegetable oils and dog-fleas (*C. canis*) to DDT and dieldrin have been determined.

FORTHCOMING INTERNATIONAL SCIENTIFIC CONFERENCES, 1967

Date	*Conference*	*Place*
14-19 August	Seventh International Conference on Medical and Biological Engineering	Stockholm
21-25 August	Fourteenth International Symposium on Microscopy	Cambridge, England
28 Aug. to 1 Sept.	International Symposium on Reactions of Oxygen with Organic Compounds	San Francisco
28 Aug. to 1 Sept.	International Theoretical Physics Conference on Particles and Fields	Rochester, NY
28 Aug. to 2 Sept.	Third International Symposium on Organometallic Chemistry	Munich
3-9 Sept.	Eighth International Conference on Ionization Phenomena in Gases	Vienna
3-9 Sept.	International Embryological Conference	Bern
4-7 Sept.	International Congress on the Application of Shell Structures in Architecture	Mexico
4-8 Sept.	International Conference on the Strength of Metals and Alloys	Tokyo
4-10 Sept.	Twenty-first International Congress of Pure and Applied Chemistry	Prague
5-9 Sept.	Tenth International Congress of Microbiological Standardization	Budapest
5-9 Sept.	Twenty-seventh International Congress of the Pharmaceutical Sciences	Montpellier, France
6-8 Sept.	International Hydrology Symposium	Fort Collins
7-13 Sept.	International Conference on Nuclear Structure	Tokyo
11-15 Sept.	Sixth International Conference on High Energy Accelerators	Cambridge, Mass.
11-15 Sept.	Fifth International Congress on Cybernetics	Namur, Belgium
11-15 Sept.	International Symposium on Information Theory	Athens
11-16 Sept.	International Congress on Magnetism	Boston
12-16 Sept.	Tenth International Conference on Coordination Chemistry	Tokyo
13-14 Sept.	International Symposium on High Voltage Insulation Vacuum	London
15-19 Sept.	Sixth International Aerosol Congress	Berlin
18-22 Sept.	Fifth International Symposium on Erythrocytes	Berlin
20-22 Sept.	International Symposium on Surface Phenomena of Metals	London
25-29 Sept.	International Mass Spectrometry Conference	Berlin
September	Second International Congress of Parasitology	Washington, DC
1-6 Oct.	Thirty-fourth International Foundry Congress	Paris
3-5 Oct.	International Conference on Hydraulic Research	Brno, Czech.
10-13 Oct.	Fourth International Conference on Methods of Immediate Separation and Chromatography	Heidelberg
24-26 Oct.	Fourth International Congress on Steel Utilization	Luxembourg
October	Fourth Conference on the Exploding Wire Phenomenon	Boston

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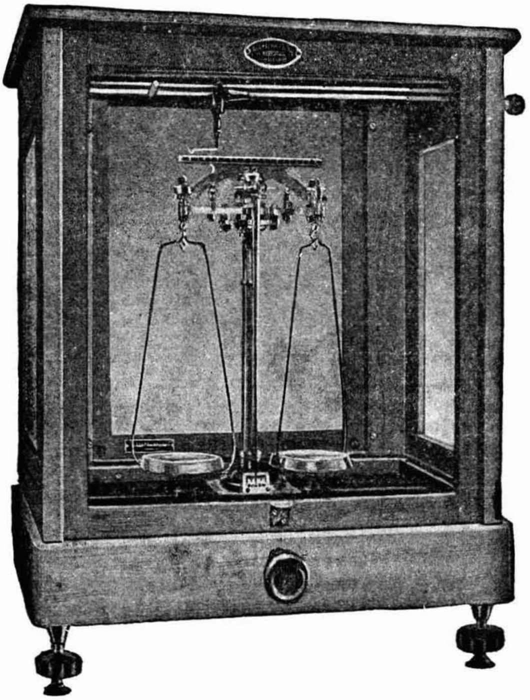

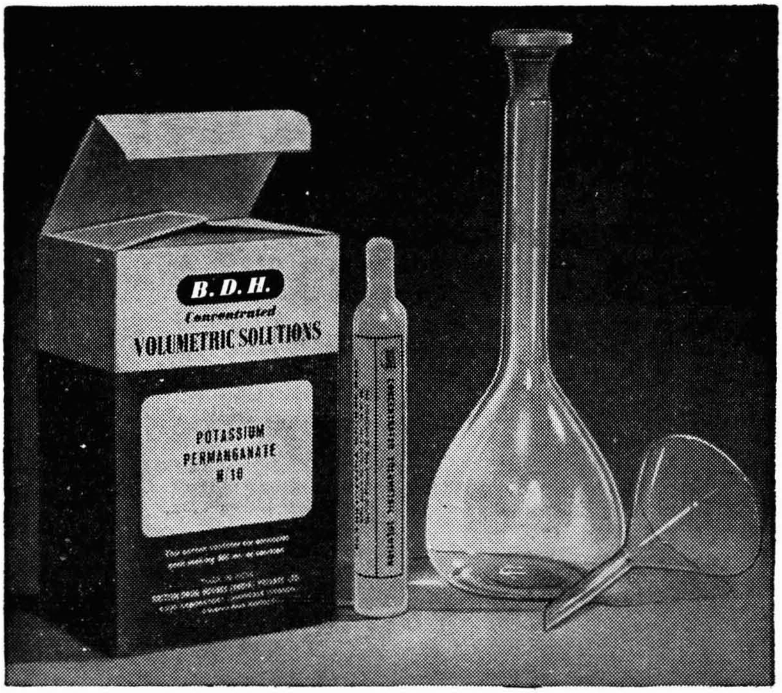
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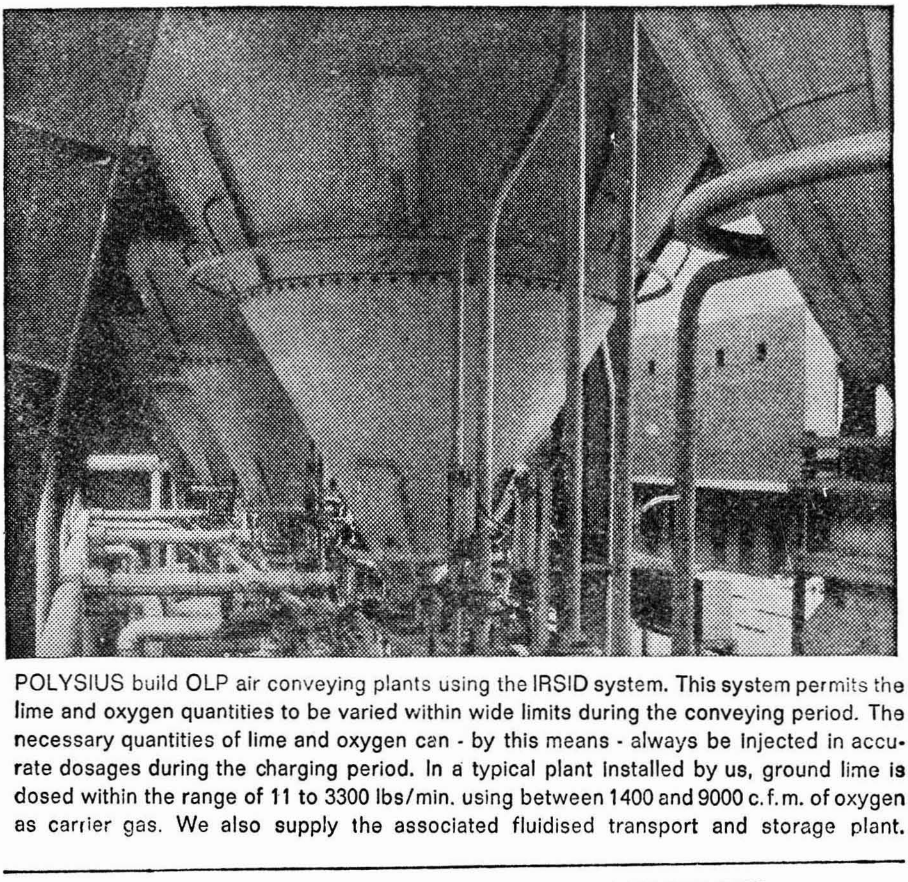

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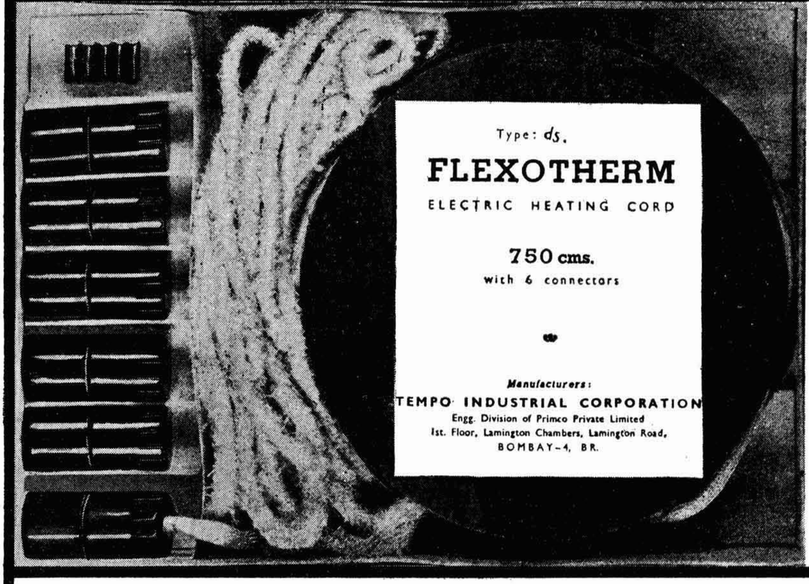

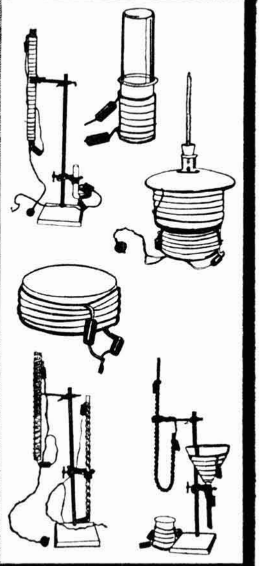

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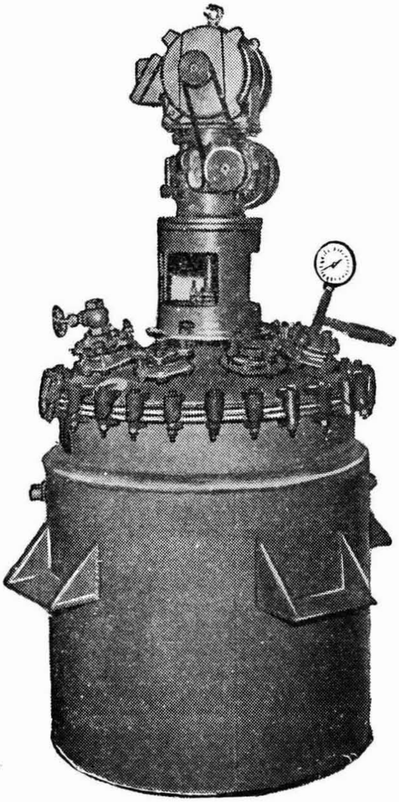

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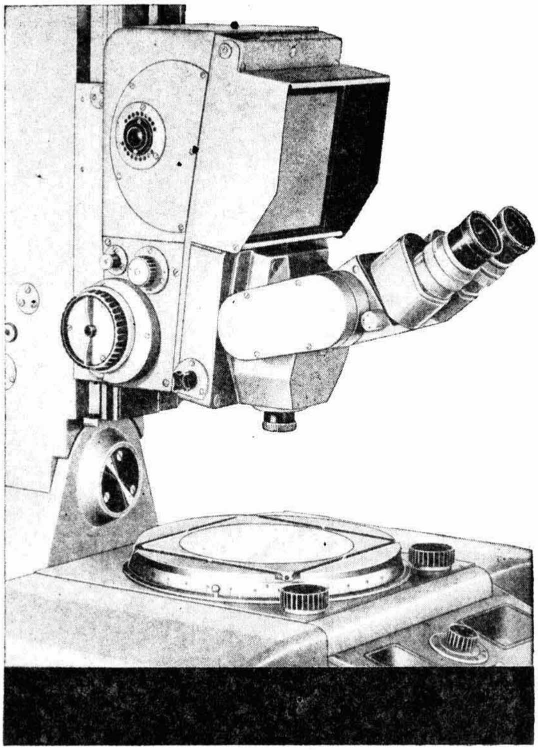

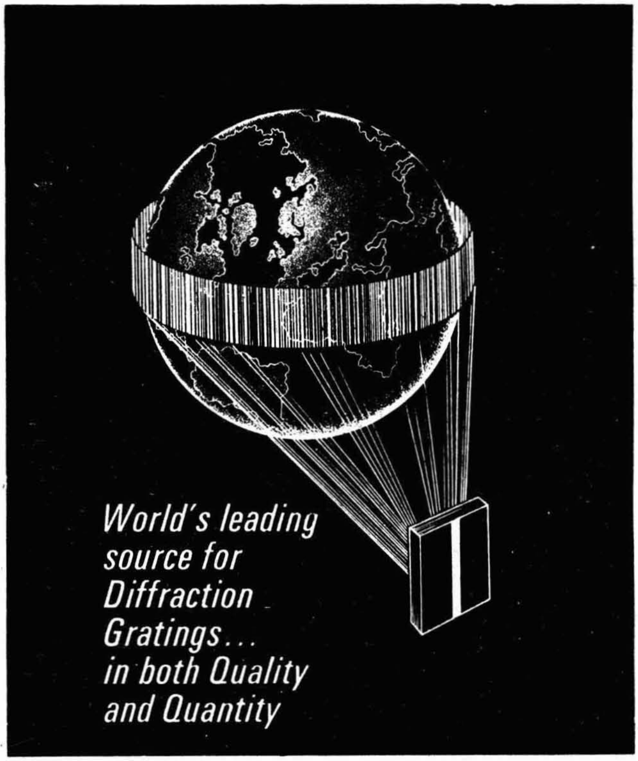

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