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ERRATUM

Article entitled "Symposium on the Chemistry of Natural Products", 24 (No. 7) (1965), pp. 348-52: Page 349, correct structures of the compounds (IV) and (VI) are given below.





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Food Technology & Food Deficit

TARGETS for the production of all types of foodgrains, pulses and oilseeds to be achieved by the end of the Third Plan (1965-66) have been estimated at 95,693,000, 16,586,000 and 7,672,000 tons per annum respectively. The corresponding estimates for these crops by the end of the Fourth Plan (1971-72) are 139,401,000, 20,180,000 and 10,438,000 tons respectively. Whether these targets will be achieved remains to be seen but one must be prepared for shortages. During 1964-65, 7,000,000 tons of foodgrains were imported, and there is no guarantee that we will be able to produce enough to overcome the shortages which are bound to go on increasing with the steady growth of population and a consequent demand for more food.

Concerted efforts are being made continuously to increase agricultural production to meet the targets set by such measures as bringing more land under cultivation, providing better irrigation facilities, introduction of improved agricultural practices, use of more fertilizers, soil conservation, plant protection, etc. Efforts are also being made. though not vigorously and intensively, to prevent loss of foodgrains, oilseeds, etc., due to rodent, insect and mold damage. However, the technological aspects of processing and preparing the agricultural produce for the consumer, and the utilization of byproducts of food industries which could help in stretching our food resources have not received the attention they deserve. The potentialities of unconventional, and hitherto unexploited and not fully utilized sources of food, in not only increasing our food resources quantitatively but also from the point of view of improving the quality and nutritive value of the predominantly cerealrich and protein-deficient Indian diet, have not been fully appreciated.

The processing of rice and pulses from the point they are harvested and finally reach the consumer. and the utilization of oilseed cakes for edible flour are typical examples of what modern food technology and research can achieve to augment our food resources both quantitatively and qualitatively. In 1963-64, the paddy harvest was estimated at 52,000,000 tons and the yield of head rice 36,489,000 The average yield of head rice from paddy tons. in India is 62-68 per cent as compared to 70-72 per cent in USA and Japan. A loss of 5-10 per cent is reported to occur while milling and polishing rice. Polishing of rice in Indian mills is carried too far, to the extent of removing 10-12 of the rice as bran as against 5-6 per cent prescribed by law. If the latter two operations alone are carried out efficiently and on modern lines by extending rice milling industry and modernizing it, it is possible to

have another 10 per cent more rice. Theoretically, a total saving of 11,000,000 tons of rice is possible by modernizing our rice industry and by preventing losses due to other causes. This could more than offset the imports of foodgrains. Similarly, supplies of pulses, which form the chief protein component of our diet, could be augmented by 10-15 per cent by adopting more efficient and modern methods of dehusking.

At present about 35 per cent of rice produced is milled in the organized sector yielding about 1,500,000 tons of bran from which 225,000 tons of good quality edible oil could be had to supplement our oil and fat resources of 4 million tons.

Indian diet is deficient in protein, both quantitatively and qualitatively. As against an average minimum requirement of 65 g. of protein per head per day, the amount available is barely 50 g., which is largely made up of vegetable protein, the animal protein complement being 5 g. Oilseed meals and flours could provide 4,000,000 tons of food material as well as the much needed protein. At present groundnut alone could provide 1,000,000 tons of high quality protein; other oilseed meals, particularly cottonseed meal, have not yet been processed on any large scale. Thus by the use of oilseed proteins, it is possible to meet the non-cereal vegetable protein requirement of diet by 80 per cent and provide an additional 12 g. of protein per head

The above examples are just to illustrate the immense possibilities and potentialities of modern food technology. The Central Food Technological Research Institute (CFTRI), Mysore, have either completed or have taken up many useful projects not only on the problems discussed above but also in respect of fish and fish products, poultry, meat, fruits and vegetables, etc., with a view to developing suitable preservation and processing methods and minimizing losses of these food products at various stages. However, it is not enough to work out processes; they have to be widely applied on a large scale to achieve tangible results. For example, the plant set up at Madras for the manufacture of edible flour from groundnut cake is yet to work at its full capacity of 10 tons per day. Early steps should also be taken to modernize the chief engineering processes of the food industry, such as milling, dehydrating, freezing, evaporating, canning, etc., and adapt and improvise them to indigenous needs. A technological base should be gradually established such that the cycle of producing raw materials, food manufacture and distribution is well coordinated. Measures should also be taken to train personnel, produce equipment, supply raw materials with predetermined specifications and provide necessary

transport and storage facilities needed for a modern food industry.

Our food production will steadily increase during the successive plans, but the losses of food materials will also proportionately go up if we continue to employ outmoded methods of conservation, protection and processing of food products. In all these fields the CFTRI has done much pioneering and useful work, and in any programme for modernizing the food industry in the country, the talent and expertise of CFTRI, and also the processes developed by it should be fully utilized.

Publication of Research Communications by Indian Authors in Foreign Periodicals

THE results of a sample survey* carried out by the Indian National Documentation Centre provides interesting information about the number of research papers by Indian authors published in some of the well-known scientific periodicals abroad. The survey covers 750 foreign periodicals published during 1964 and deals with 23 subject fields. The data provided may be taken as a fair estimate of the situation as it obtains today.

According to the survey, the total number of papers published in the various periodicals during 1964 was 1406. The subject fields accounting for the majority of papers published are: chemistry including biochemistry, 354; physics, 323; medicine, 138; mathematics including mechanics, astronomy, astrophysics and statistics, 110; technology and useful arts, 97; and engineering, 83. In general, the number of papers published is more in pure sciences than in applied sciences; the least number of papers (3) were published in the field of statistics. In chemistry, out of the total number of papers (354), organic chemistry, biochemistry, physical chemistry and analytical chemistry account for 109, 99, 84 and 54 papers respectively; inorganic chemistry papers numbered only 18. In physics, out of 323 papers, nuclear physics alone accounted for 184 papers.

A rough estimate of the total number of research papers published by Indian workers both in Indian and foreign periodicals during 1964 is about 7500. It would not be correct to speculate why a sizeable proportion of the research papers, representing perhaps the best ones, are published in foreign periodicals, before carrying out a fact-finding survey to find out the exact reasons for this situation from the research workers themselves. Such a survey could also provide answers to scientific publication problems, such as adequacy or otherwise of the existing periodicals published in the country, their standard, usefulness, etc. The present survey indicates the scope and need for specialized journals in some specialized areas. For example, the number of papers published in nuclear physics could sustain a new journal devoted to the subject. Similarly, there appears to be a case for a separate journal for organic chemistry.

Divergent views are expressed about the practice of Indian research workers publishing their work abroad. However, a weighty argument against this practice is that every country should have scientific periodicals of high standard which reflect the progress of scientific research and this practice retards the proper development of scientific periodicals in the country. It is, therefore, for the research workers themselves to build up quality journals by publishing at least a part of their best work in periodicals published in India. They should also shoulder the responsibility of initiating proposals for new periodicals in specialized fields where the need is felt. For example, the Society of Biological Chemists, India, suggested to the Council of Scientific & Industrial Research the need for a separate journal for biochemistry, and the present survey justifies its establishment. It would be useful if the subject of publication of scientific periodicals in the country is under constant review by a committee made up of members drawn from research councils, scientific societies, universities and research institutions, so that scientific periodicals published maintain a high standard and cater effectively to the needs of the scientific community.

^{*}Guha, B., Gupta, A. K., Joseph, A. & Kachroo, M. L., Ann. Lib. Sci. Doc., 12 (1965), 76-86.

International Conference on Internal Conversion Process: A Report

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A N International Conference on the Internal Conversion Process was held at Vanderbilt University, Nashville, Tennessee (USA), from 10 to 13 May 1965. The conference was attended by over one hundred delegates representing various countries, including Yugoslavia, Sweden, Hungary and India; Sweden providing half a dozen delegates reflecting the contribution that country has made to the understanding of internal conversion. It was indeed a busy conference with sessions continuing till late in the evening. The conference was devoted to both theory and experiment, the latter predominating. Curiously enough, internal conversion represents a unique situation with experiment ahead of theory.

Regarding improvements in experimental techniques, Hultberg (Sweden) reported on the refinement in the internal-external (IEC) method with an improved calculation of the photoelectric crosssection, correction for photoelectron scattering and for finite dimensions of the spectrometer aperture. Hollander (USA) described the use of semiconductor detectors for internal conversion coefficients. Lewin (Holland) pointed to the doubtfulness of the peak to beta spectrum (PBS) method with reference to the 412 keV. transition in Hg-198. Thosar (India) summarized the situation regarding agreement between theory and experiment. There was general agreement as regards $2^+ - 0^+ E2$ conversion coefficients, the previously reported anomalies being traced to improper accounting of the various corrections. Other E2 transitions needed to be carefully reinvestigated to prove or disprove the large deviations pointed out by Ramaswamy (India). Such deviations would be disturbing to the theorists !

An elegant technique to determine the particle parameters was described by Stone (USA), and consists of measuring the angular distribution of gamma rays and conversion electrons from oriented nuclei. Such an experiment on ¹³⁷Ce revealed excellent agreement between the 'point nucleus' values and experiment for an M4 transition. Further, validity of the 'point nucleus ' approximation was established by Deutch (Denmark) from an analysis of e-Y correlations and extracting b_2 values for pure transitions.

Hamilton (USA) referred to the agreement between theory and experiment as regards L_2/L_3 ratios and deviations for L_1/L_2 and L_1/L_3 ratios for E2 transitions. An interesting report came from Geiger (Canada), in which appreciable deviations in the sub-shell ratios were reported for a high multipolarity (E5) transition. Rose (USA) pointed out that theoretical M-shell coefficients were not meant to be accurate. An important contribution was made by Gerholm (Sweden) in confirming the presence of E0 in direct competition with M1 and E2 in $2^1 \rightarrow 2$ transitions in vibrational nuclei as predicted by Church and Weneser.

Rose (USA) drew attention to the anomalies in the calculated values of the American group as represented by himself and the Russian group. Sliv and Band. He emphasized the need for undertaking an independent calculation suggesting that a calculation of M-shell would provide for other shells with comparative ease. There are already attempts in this direction as represented by the contributions at the conference by O'Connel (USA) and Bhalla (USA). It was reassuring to hear from Kisslinger (USA) that the pairing correlations had little effect on the conversion coefficients.

Considering the deliberations of the conference, one would agree that this was the most opportune time to take stock of things.

Chemical & Non-chemical Interactions: A Symposium

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A SYMPOSIUM on Chemical and Non-chemical Interactions, the first of its kind organized at the University of Gorakhpur, was held from 13 to 15 February 1965. It was supported by the University Grants Commission and convened by Prof. R. P. Rastogi, Head of the Chemistry Department, University of Gorakhpur, Gorakhpur.

Basically all interactions are electrostatic in character. However, very often quantum mechanical principles modify this character particularly in the case of van der Waals' interactions. From energy considerations, this kind of interaction is perhaps the weakest, the chemical interaction leading to covalent bonding being the strongest. Our knowledge about these two extremes though meagre is considerably advanced as compared to intermediate cases like the hydrogen bond formation and charge-transfer interaction. The symposium covered very nearly the whole spectrum from van der Waals' interaction to chemical interaction. In fact this was the novel feature of the symposium. In Indian universities the theoretical aspects of the subject are seldom given due emphasis in the postgraduate and research studies. Thus the holding of the symposium was a long-felt necessity. It provided an opportunity for scientists in the field from a number of universities and research institutes to meet and discuss the problems and see if the wide gaps in our knowledge in the field could be filled. Such fruitful discussions, it was hoped, would go a long way in stimulating greater and planned research activity in the area.

Several scientists from abroad were approached and it was unfortunate that they could not attend the symposium because of various difficulties. Of these, Dr Barker of Australia, Prof. Guggenheim of Reading University, UK, Prof. McGlashan of Exeter, UK, and Dr Williamson of New Zealand contributed papers for presentation at the symposium.

The response of the Indian scientists was spontaneous and encouraging and as many as 40 of them, drawn from various universities and research institutions, participated in the symposium. Prof. A. C. Chatterji, then Vice-Chancellor of Gorakhpur University, himself an eminent physical chemist, welcomed the delegates and Dr M. L. Dhar, Director, Central Drug Research Institute, Lucknow, delivered the inaugural address. In his address Dr Dhar emphasized the importance of the topic as its undertaking was absolutely necessary to interpret innumerable complicated life processes.

The programme of the symposium was divided into the following sessions: (1) General and van der Waals' interactions, (2) Coulombic and ionic interactions, (3) Dipolar interactions, (4) Charge-transfer interactions, (5) Surface interactions, (6) Interactions with high energy particles, and (7) Chemical and miscellaneous interactons. Every paper presented evoked keen interest as it was invariably followed by stimulating discussions. As many as 37 papers were presented at the symposium.

General and van der Waals' Interactions

The proceedings of the symposium opened with the presentation of a paper of Dr J. A. Barker (Division of Physical Chemistry, CSIRO, Melbourne, Australia) entitled 'Forces between inert gas atoms' by Prof. R. P. Rastogi. Information on the forces between pairs of atoms, according to Dr Barker, could be derived from gas properties, molecular beam scattering and some theoretical calculations. Computer methods could be used for evaluating virial coefficients in the equation of state. Experimental data on gas transport properties were examined and some preliminary results on the question of additivity of potential energy in crystalline argon derived.

Dr Kartar Singh (Defence Science Organization, New Delhi) presented a paper on 'Intermolecular potentials'. In investigating detonation phenomenon, it is essential to have an accurate knowledge of intermolecular potential. Under high pressure prevailing in detonation front, the distance of approach of molecules towards each other is low. A realistic intermolecular potential, determined by quantum mechanical methods, was discussed. It described the properties at short distances in a satisfactory way. Doubts about the correctness of Amdur's data on scattering in molecular beam experiments was expressed. The paper provoked a stimulating discussion in which Dr S. C. Saxena, Prof. R. P. Rastogi and Prof. C. N. R. Rao took a prominent part.

The next paper entitled 'Molecular interactions and their determination' presented by Dr S. C. Saxena (Rajasthan University, Jaipur) was also followed by a very lively discussion initiated by Prof. C. N. R. Rao and Dr Kartar Singh. In his paper Dr Saxena discussed various types of interactions between non-polar molecules. Polar interactions were also considered. In the case of gases various equilibrium and non-equilibrium properties were considered, while in the case of solids cohesive energy, compressibility and thermal expansion were discussed.

A paper entitled 'Molecular interaction in hydrocarbons' was presented by Shri Jagannath. It described work done in collaboration with Shri J. Misra, Dr H. L. Girdhar and Prof. R. P. Rastogi. In this paper molecular interaction in saturated and unsaturated hydrocarbons was examined. A comprehensive study of the principles in the case of linear and branched chain hydrocarbons was made. Corner's model seemed to provide a fairly good approximation. Analysis showed that hydrocarbons having similar number of $-CH_a$ groups in side chain and branched chain have similar form of intermolecular potential.

The last paper was contributed by Prof. E. A. Guggenheim (Reading) and Prof. M. L. McGlashan (Exeter). It described a revised and correct version of their earlier contribution on repulsive energy in sodium chloride and potassium chloride crystals. The calculation of Coulombic interaction, dipoledipole interaction and quadripole-dipole interaction term was described. The first and second order derivatives of repulsive energy with respect to separation were also estimated.

Coulombic and Ionic Interactions

The proceedings of the second session presided by Dr Kartar Singh started with a paper by Shri G. P. Johari entitled 'Ion-solvent interaction: Conductimetric behaviour of MgSO₄ and LaFe(CN)₆ in dioxane-formamide mixtures' describing his work done in collaboration with Dr P. H. Tewari (Gorakhpur University). The conductance data for 2:2 salt in the aforesaid solvents were analysed by Fuoss-Onsager equation and reasonable \wedge° , K_a and a_j parameters were obtained. The data for the 3:3 salt could be predicted by the theory. In contrast to Fuoss-Bjerrum theory, log K_a as a function of D^{-1} was found to be non-linear at lower D values.

Dr Vishnu (Gorakhpur University) described his work on ion association in unsymmetrical electrolytes done in collaboration with Shri Madan Srivastava. Existence of an ion pair of the type PbCl⁺ in solution of Pb ion in KCl (maintained at constant ionic strength by the addition of potassium perchlorate) exclusively at low KCl conc. (0.05-0.1M) was established with the help of polarographic technique. A mechanism for the electrode reaction was also proposed.

Dr Amar Nath presented the paper on the 'Effect of irradiation on electrical conductivities of some cobalt chelates 'done at the Atomic Energy Establishment, Trombay, with Drs S. Khorana, V. Ramshesh and J. Shanker. The electrical conductivities of some cobalt chelates before and after irradiation and in the presence and absence of oxygen were measured. Both the presence of oxygen as well as irradiation altered the conductivity. An attempt was made to correlate the electrical properties with the thermal annealing behaviour of reactor-irradiated cobalt chelates.

Dipolar Interactions

Dr Balakrishna (Allahabad University) presented a paper on 'Dipole-dipole interaction and dielectric polarization in polar liquids and solutions'. In the interaction of permanent dipoles the interaction energy could be considered as made up of the sum of three terms: (a) the electrostatic interaction energy, (b) the Debye-Falkenhagen energy of interaction and (c) the London dispersion energy between two induced-charged distributions. The paper attempted to critically examine these various contributions and see how far they had been explicitly or implicitly incorporated in the theories of Onsager, Van Vleck, Frohlich and Kirkwood. The results obtained by the author in his experiments on dielectric polarization in the polar media were discussed in detail and supported the hypothesis of hydrogen bond formation.

The next two papers were by Dr A. K. Barua (Indian Association for the Cultivation of Science, Calcutta). The paper entitled 'Interaction between bound double polar molecules' was presented by Dr A. Das Gupta. Due to long-range attractive forces, polar gases associate significantly even at moderately high pressures. The interactions between dimers and monomers in polar gases were investigated and the results checked by calculating the viscosity of steam and ammonia at high pressures.

Another paper discussing 'Formation of dimers in polar gases' by A. K. Barua, P. K. Chakrabarti and Anil Saran was presented by Shri Anil Saran. In order to calculate the percentage of dimers in a polar gas at a particular pressure and temperature, the contribution of bound double molecules to the second virial coefficient was calculated by assuming the dipoles to be in the head to tail position and this contribution was found to be related to the equilibrium constant for dimerization.

The paper presented by Dr S. N. Bhattacharya (Indian Association for the Cultivation of Science), entitled 'On solution of globular molecules with dipolar interactions', sought to combine non-polar central forces and non-central forces of both weak dipolar and of structural origin into a single potential. Neglecting higher order terms the excess thermodynamic functions of mixture of non-polar globular molecules with weakly polar globular molecules were found to consist of three terms: pure non-polar, pure dipolar, and structural. Agreement between predicted and experimental value was found to be satisfactory for 3 systems for which experimental data were available.

Charge-Transfer Interactions

The first paper presented in this session with Prof. D. Sharma as Chairman dealt with 'Some aspects of charge-transfer interactions in non-electrolytes mixtures'. This contribution by Dr A. J. Williamson and Mr I. D. Watson (Otago University, New Zealand) was read by Prof. Rastogi. Particular attention was paid by the authors on the need to consider such interactions in mixtures of tetrahalide molecules with molecules containing groups with electron donor properties such as aromatics, ethers and amines. Evidence for interaction was obtained by a study of phase diagrams, spectrophotometric measurements and thermodynamic properties like heats of mixing.

The paper by Dr Williamson was followed by a stimulating talk on 'Charge-transfer complexes' by Prof. C. N. R. Rao (Department of Chemistry, Indian Institute of Technology, Kanpur). In his hour-long talk he reviewed the thermodynamics and spectroscopy of charge-transfer and hydrogenbonded complexes.

Shri P. P. Singh (M.L.K. Degree College, Balrampur) presented a paper on 'Donor acceptor interaction' describing preparation and infrared spectra of the complexes of stannic chloride with certain amides and substituted ureas. In his paper on 'Polarization of the chargetransfer band', Dr Mihir Chowdhury (Indian Association for the Cultivation of Science) described his work carried out at the Pennysylvania State University, USA, with Dr Lionel Goodman. The polarization of the charge-transfer band was determined in glassy solution by photoselection technique. The degree of polarization thus determined threw light on the asymmetry of the structure of some of the complexes studied.

The paper entitled 'Molecular interaction in liquid mixtures' presented by Shri Jagannath described his work done with Prof. R. P. Rastogi. Volume of mixing and heat of mixing for mixtures of cyclohexane and carbon tetrachloride and of benzene and carbon tetrachloride were measured at various temperatures. Spectrophotometric measurements were also made for mixtures of benzene and carbon tetrachloride in cyclohexane. Dielectric polarizations for the mixtures of benzene and carbon tetrachloride were also measured. The results confirmed prominent interaction between unlike molecules. The possibility of existence of contact pair was also discussed.

Lastly, Dr Gobinda Basu (Indian Association for the Cultivation of Science) described the temperature dependence study of the charge-transfer band of $Li_2[Cu_2Cl_6]2H_2O$. The brown-red compound showed a magnetic phase transition at low temperature (4.2°K.). The magnetic phase transition is due to the spin interaction between the neighbouring copper ions through the chlorine ion. This phenomenon is known as superexchange interaction and in order to study its effect on the metal ligand bond, the charge-transfer band of the single crystal as a function of the temperature was investigated. The spectral results were interpreted in terms of the ligand-field theory.

Surface Interactions

The first two papers presented in this session with Prof. Satya Parkash as Chairman described the work done by Dr Wahidul Malik and his associates at Roorkee University. Shri Surendra P. Verma read the paper entitled 'Physico-chemical studies on the binding of dyes with surface active agents: Part I — Spectrophotometry of malachite green and rhodamine 6G in presence of alkyl-aryl sulphonic acids'. Besides routine spectrophotometric measurements, Klotz method, used for determining the binding of the dye with a protein, was also tested in this case. Evidence for micelle formation by the association of 20-70 molecules could be obtained. The CMC values lay in the concentration range between 8.0×10^{-5} and $12.0 \times 10^{-5}M$.

The second paper presented by Shri Shamin Anwar described permeability of electrolytes through parchment supported iron oxide membranes. The permeability values for the untreated ferric oxide membrane as determined by constant flow method of Hartung and Willis were of the order: KCl, KBr, KNO₃, KCNS and K_2SO_4 in millimoles per hour. Treatment of the membrane with an anionic soap rendered the membrane more permeable. The results were discussed in the light of the recent theories on membrane permeability. Shri V. N. Singh (Banaras Hindu University) presented a paper entitled 'Diffusion studies of alkali metal ions in agar-agar gel' describing the work done by him with Dr B. M. Shukla.

The next two papers described the work done by Dr B. B. Prasad and his associates at the Banaras Hindu University. The first of these presented by Shri A. N. Gupta described adsorption of iodide ions from aqueous solutions by strongly ignited copper, cerium and zirconium oxides, and the other paper presented by Shri P. S. M. Tripathi discussed the results obtained in a study of desorption of iodide ions adsorbed on nickel oxide.

Dr S. N. Srivastava (Agra College, Agra) presented a paper on 'The interaction of colloidal particles with special reference to the role of macromolecules in van der Waals' interactions'. He reviewed the theory of Derjaguin, Verwey and Overbeek (DVO theory) regarding total interaction between two colloidal particles and applied it to the stability of an emulsion of aliphatic hydrocarbon in water. An attempt was also made to study the influence of adsorption of a protein on the van der Waals' interaction assuming the quantitative validity of the DVO theory.

In his paper, Prof. M. C. Rastogi (Regional Engineering College, Jamshedpur) made an attempt to give a theoretical treatment of the ion-exchange phenomenon occurring in the colloidal systems on the basis of the Stern model of the double layer. Because of model consideration, it was found to be more suitable to explain the changes that would occur in the electrical double layer in the presence of surface active agents.

Dr (Miss) K. K. Rohatgi (Chemistry Department, Jadavapur University, Jadavapur, Calcutta) presented her paper on 'Nature of bonding in dye aggregates in aqueous solutions'. The work was done in collaboration with Dr G. S. Singhal. The aggregation characteristics of dyes, Na-fluorescein and rhodamine was studied in aqueous solutions. The two dyes differed in their absorption and fluorescence spectra. In the case of rhodamine, aggregation is an entropy directed process and is probably brought about by hydrophobic bonding, whereas for fluorescein it is an enthalpy directed processes involving hydrogen-bonded system.

Interactions with High Energy Particles

In the absence of the group of workers from the Atomic Energy Establishment, Bombay, and Dr S. R. Mohanty (Banaras Hindu University) only two papers were presented in this session. The one by Dr B. M. Shukla and Shri S. P. Misra (Banaras Hindu University) described the studies on 'Isotope effect of recoil Br-80 and Br-82 atoms under (n, r) process'. The results were discussed in the light of 'ion-molecular reaction' and 'auger-electron reaction' ideas. A scheme was also suggested regarding the stabilization of recoil Br-80 and Br-82 atoms.

The other paper presented by Dr R. S. Rai (Rajasthan University, Jaipur) described some fundamental processes in radiation chemistry. Chemical effects of high energy radiation on some organic systems in the liquid state were presented in some details to elucidate the mechanism of energy transfer processes in radiation chemistry.

Chemical and Miscellaneous Interactions

In the last session Prof. A. C. Chatterji presented his paper on 'Oxidation of some simple organic molecules by chromic acid'. In most of the cases the temperature coefficients, relative entropies, heats and free energies of activation and frequency factors were calculated and the effect of substitution, catalysts, etc., were observed.

The paper by O. N. Perti and H. D. Pathak (Department of Chemistry, D.S.B Government College, Naini Tal) on the 'Action of ultraviolet radiation on a mixture of methane, ammonia, carbon dioxide and hydrogen in presence of water' was presented by Dr H. D. Pathak.

The next two papers by Prof. Satya Prakash and his collaborators at Allahabad University dealt with the action of ultrasonic waves. Whereas the first one entitled 'Ultrasonics and chemical reactions' described experimental work to study the effect of ultrasonic waves (1 Mc/s.) on the aqueous solutions of some dyes and organic halides, the next one on 'Ultrasonically produced cavitation' was a review.

The paper by Prof. R. C. Kapoor (Jodhpur University) dealt with a polarographic study of 'The interaction between Hg (II) and cysteine'.

Dr R. D. Srivastava (Lucknow University) presented a paper describing 'A solubility method for the study of specific interaction'. The experimental work dealt with the specific interaction of *m*-dinitrobenzene with naphthalene, phenanthrene and anthracene molecules in carbon tetrachloride.

The paper on 'Chemical interaction in solid state' by R. P. Rastogi, Y. N. Chaturvedi, B. L. Dubey and P. S. Bassi dealt with solid state reaction between mercurous chloride and iodine to form mercuric chloride and mercurous iodide. A quantum mechanical explanation of the proposed mechanisms was given.

Shri Kehar Singh (Gorakhpur University) presented paper on 'Reaction rates and affinities' describing his work done in collaboration with Dr R. C. Srivastava (Department of Chemistry, Regional College of Education, Ajmer). Phenomenological relations for chemical reactions were critically examined and it was shown that in general the rate of a reaction can be expressed as a power series in affinity. The conditions under which second and higher order symmetry would be obeyed were also determined. Experimental data on isomerization of pentenoic acids was examined.

The last paper of the symposium presented by Dr S. C. Tripathi (Gorakhpur University) discussed 'Reaction mechanism of hydroformylation reaction using cobalt carbonyl as a catalyst'. The work was done at the University of Manchester.

In his concluding remarks, Prof. Mata Prasad, Chairman of the last session, expressed appreciation for the lively and stimulating discussions during the symposium. In view of the intense academic activity and the tight programme during the three days he felt that the symposium was a great success.

Symposium on CNS Drugs

A Symposium on CNS Drugs will be held during 24-30 January 1966 at the Regional Research Laboratory, Hyderabad. The symposium is expected to be attended by about 45 invited participants from India and abroad. The proceedings of the symposium will be published by the

middle of 1966 by the Council of Scientific & Industrial Research, New Delhi, and distributed outside India by the Pergamon Press, London. Further details about the symposium may be obtained from Dr P. B. Sattur, Regional Research Laboratory, Hyderabad 9.

Effective Mass of Electrons & Holes in Semiconductors from Magneto-optical Laser Emission Studies

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THE effective mass of electrons and holes in semiconductors is an important parameter for determining the band structure and the scattering mechanism. The most widely used direct method of measurement of effective mass seems to be that provided by the cyclotron resonance experiments. However, this method has been successfully applied to only a limited number of semiconductors. The use of lasers has been suggested for cyclotron resonance experiments in the infrared region. Studies of the shift of peak emission in magneto-optical lasers also provide a direct method of measuring the scalar effective mass. This is illustrated with the data obtained from magneto-optical studies in InAs and InSb diode lasers. It is felt that the effective mass values derived from such studies will be more accurate than those found by other available methods, since in a laser the emission is coherent and of high spectral purity and the probabilities of most of the indirect transitions are minimized, leading to accurate measurement of the change of band gap in a magnetic field. The effective mass can also be determined from the shift of peak incoherent emission in semiconductors in a magnetic field, but the accuracy will be smaller due to large line widths of the spontaneous emission. It is expected that direct determination of effective mass in GaAs, GaSb, InP, GaAs_x P_{1-x} and InAs_x P_{1-x} , for which cyclotron resonance data have not been reported, could be done by this method because these semiconductors have shown laser emissions over a wide range of temperatures. The orientation of the magnetic field and the extent of doping bring significant changes in the emission intensity and linearity of the magnetic shift which are discussed in a later section. These changes for different orientations of the magnetic field are expected to give some insight to the tensor properties of the effective mass.

Determination of Effective Mass in Semiconductors

The important available methods of determining effective mass in semiconductors make use of the measurements of cyclotron resonance, oscillatory magneto-absorption, Hall effect, magneto-resistance, Faraday rotation and thermoelectric power.

In the cyclotron resonance method¹, the current carriers in a semiconductor crystal are accelerated in spiral orbits about the axis of a static magnetic field H. The angular rotation frequency ω_c of the carriers of effective mass m^* is given by the usual cyclotron equation

$$\omega_o = \pm \frac{cH}{m^*c} \qquad \dots (1)$$

By studying the resonant absorption of energy from an r.f. electric field perpendicular to the static magnetic field, ω_c is found out and thus m^* can be calculated.

Cyclotron resonance experiments for large band gap semiconductors in the microwave range require operation at low temperatures (1.2-4.2 K.) and optical excitation by visible or infrared light. Such experiments with these semiconductors can, however, be done at comparatively higher temperatures for increased thermal ionization of impurities. The use of smaller values of τ , the mean time between collisions, at higher temperatures can be made possible at the expense of a larger magnetic field by increasing the frequency of the electric field to near infrared wavelengths. Magnetic fields of the order of 1000 kilogauss will be required and hence pulsed operation is essential. Here the use of gas discharge and semiconductor lasers as infrared generators may be suggested which give extremely monochromatic infrared, visible and ultraviolet radiations. The use of lasers will help correctly locate the absorption peaks because of the high spectral purity and stability of laser emissions.

A second direct method of measurement of effective mass is provided by the oscillatory magneto-absorption effect². The underlying phenomenon involves, as in cyclotron resonance, the quantization of energy levels of the carriers in a magnetic field. The quantized energy levels of the conduction band in a magnetic field of induction density B are spaced by an amount hcB/m^* and so the spacing between the absorption maxima gives a direct measure of m^* (h represents $h/2\pi$). The effective masses in a given semiconductor as determined separately by the cyclotron resonance and the oscillatory magneto-absorption experiments should be in close agreement. This is due to the common feature of the origin of the two absorption phenomena. Thus the method of oscillatory magneto-absorption measurement is also a very accurate way of determining the effective mass but has unfortunately been reported for only a few semiconductors.

Measurements of Hall effect and conductivity³ may also be combined to provide values of the effective masses of electrons and holes. This is only an approximate method.

Data for computing m^* can again be obtained from measurements of magneto-resistance⁴. The change of resistivity with magnetic field gives the Maxwellian average of the relaxation time of charge carriers, $\langle \tau \rangle$, which may be combined with the values of mobilities of electrons and holes at high magnetic fields, obtained from Hall effect measurements, to give the effective masses. Other methods include measurements of Faraday rotation⁵ and thermoelectric power⁶. The Faraday effect is a potentially accurate way of determining effective mass because the product of refractive index and rotation is inversely proportional to the square of the effective mass. The method of thermoelectric power measurement will give incorrect results for non-spherical energy bands, since many approximations for spherical energy surfaces are involved in the formulae used for calculations.

The results obtained by various methods are often found to be divergent. The inconsistency of the values of effective mass found out by various methods possibly arises due to two reasons: (i) the formulae used for effective mass calculations have limited range of validity; and (ii) the implications of the factors which affect the effective mass in a semiconductor are not clearly understood. For example, the equation $\mu_c/\mu_h = (m_h/m_c)^{3/2}$, μ_c and y_h being the mobilities and m_e and m_h the masses of electrons and holes respectively, used in the determination of effective mass by Hall effect and conductivity measurements is frequently mentioned in the literature without any indication of its limitations. In the measurement of magnetoresistance, the use of soldered side contacts introduces a contribution to the observed change in resistance in the magnetic field caused by a shorting out of the Hall voltage in the vicinity of the contacts. In the thermo-electric power measurement, the relaxation time due to lattice scattering is represented by a simple power law of the form $\tau = aE^{-s}$. This means that the relaxation time does not include the effects of impurity scattering, scattering by dislocations, and scattering by the optical modes of lattice vibrations. Again, the values of S, a constant, are usually assumed to be either 1/2 or zero, which is not always true.

Effective Mass from Observed Magnetic Shift of Peak Emission in Laser Diodes

It is known that the peak emission from laser diodes occurs at a frequency very nearly equal to that of band gap. Recent studies^{7,8} show that the application of a magnetic field of moderate strength results in a measurable shift of the frequency of peak emission. This shift has been found to vary linearly with the intensity of the magnetic field over a considerable range. It seems that the effective mass can be more correctly estimated from this observed shift by making use of the fact that this shift is inversely proportional to the effective mass.

The energy momentum relation for two simple parabolic bands in a semiconductor is given by

$$E_1 = E_{10} - h^2 K^2 / 2m_c \qquad \dots (2)$$

$$E_2 = E_{20} + \hbar^2 K^2 / 2m_h \qquad \dots (3)$$

where E_{10} and E_{20} are the energies at the edges of the valence and conduction bands, K is the crystal momentum vector and m_k and m_c are the effective masses of the hole and the electron respectively. For an applied magnetic field in the Z direction, we can write an effective mass Schroedinger equation for the carriers in each of these two simple parabolic bands. The solution of this type of equation has been obtained by Landau and gives rise to discrete magnetic levels⁹ in both the conduction and valence bands of the form

$$E_n = \pm (n + \frac{1}{2}) \hbar \omega_c \pm \hbar^2 K_s^2 / 2m^* \qquad \dots (4)$$

where $\omega_e = eH/m^*c$ is the cyclotron frequency for the carrier in a magnetic field H, and the energy levels are referred to the bottom of the conduction and top of the valence bands. For the shift in the optical energy gap with H, we may write

$$E_{g}(H) = E_{g}(H = 0) + (he/2m^{*}c).H$$
 ...(5)

In diode lasers, m^* is actually the reduced mass since both electron and hole take part in radiative recombination. But taking the valence band shift to be very small due to the larger mass of holes, m^* becomes very nearly equal to the effective electron mass. Thus measuring the magnitude of the shift of peak emission, the effective mass can be found out from Eq. (5). This will be shown by determining the effective mass from the reported values of the magnetic shift of peak emission in InAs and InSb laser diodes.

It has been reported⁷ that the peak emission of InAs diode laser operating at 4·2°K. is at 31,168 A. in a magnetic field of 4·1 kilogauss and shifts to a wavelength shorter by 13 A. by increasing the magnetic field to 9·1 kilogauss. The change of band gap is by 0·001 eV. for a change of magnetic field by 5 kilogauss. Substituting these values in Eq. (5), we get the reduced mass, as mentioned in the previous paragraph, can be taken to be very nearly equal to the effective electron mass and agrees remarkably well with Zwerdling's value of $m_r = 0.03 m$. in InAs.

The change of peak emission energy with magnetic field has also been studied⁸ for InSb diode laser. It is found that the frequency of the peak emission in InSb laser diode operating at 1-7°K. shifts from 0-239 to 0-243 eV, for an increase of magnetic field from 21 to 30 kilogauss. From Eq. (5), these values give a reduced mass of 0-013 *m*, which also can be taken to be very nearly equal to the effective electron mass in InSb and is the same as the most likely value of the effective electron mass ($m_c = 0.013 \text{ m}$) obtained by other measurements.

It has been suggested^{10,11} from theoretical considerations of the experimentally observed effects of uniaxial strain on laser diode emission that the optical transitions involved in a laser take place mostly between the conduction band and the acceptor states. The effective mass for the acceptor states when substituted in the reduced mass measured by the laser method will thus give the most accurate value of the effective electron mass. The effective mass for the acceptor states is defined by the relation $E_A = E_H.(m^*/m).K^{-2}$, where E_A , E_H are the ionization energies of the acceptor state and of hydrogen respectively, and K is the dielectric constant.

However, under the high degeneracy used in a laser diode, the acceptor band can be considered to be merged with the valence band edge leading approximately to band-to-band laser transitions. The probability of interband optical transitions is highest for electrons and holes near the band edges, thus the effective mass determined by the laser method refers to the near band edge minimum mass.

Effects of Magnetic Field and Doping on Laser Diode Emission

It is quite natural to expect significant changes of both the coherent and incoherent diode emissions by the application of a magnetic field, since the rates of spontaneous and stimulated emissions depend on the density of states and the transition probability which in turn are affected by the magnetic field.

It has been actually observed^{7,8,12} that the application of a magnetic field, either transverse or parallel to the current flow, lowers the threshold current density in a laser diode. But the effect is greater for magnetic fields transverse to the current and saturates for increasing fields. The lowering of the threshold and increased intensity with magnetic field suggest an increase in transition probability with H. Since the initial states are the exciton or the free electron states rather than the donor levels, the application of a magnetic field results in the enhancement of the density of states and consequently increasing the laser transition probability.

In a magnetic field, the quantization of the energy levels takes place in a plane perpendicular to the magnetic field. For carrier motion perpendicular to the magnetic field, as in transverse fields, the quantization of energy will be effective to a greater extent giving greater enhancement of the density of states. Also an additional amount of lowering of the threshold occurs in a transverse magnetic field due to the deviation of the current by the magnetic field. The current now being restricted to smaller regions acquires larger density values, thus providing the stimulated emission with a further lowering of the threshold.

The orientation of the magnetic field has also a characteristic effect on the incoherent diode emission. The incoherent emission should increase with the enhancement of the densities-of-states for all values of magnetic fields, either transverse or longitudinal. But it was actually observed⁸ that the incoherent emission increases linearly with magnetic field parallel to the current flow, whereas for transverse magnetic field the incoherent emission increases for low values of fields but decreases at high fields. The reason for the decrease of incoherent diode emission at high transverse magnetic field is not clearly understood.

However, the incoherent emission is undesirable and for accurate measurement of the magnetic shift, the application of high magnetic field in the transverse direction is preferred for increase of coherent emission and decrease of incoherent emission.

The conditions of doping necessary for obtaining laser action and large linear diamagnetic shift of peak laser diode emission are mutually exclusive and an optimum doping should be used as a compromise between the two.

Population inversion required for initiating laser action can only be obtained in forward biased, highly doped (very degenerate) diodes, and the doping to be used should satisfy the inequality condition¹³ given by

$$F_c - F_h > h\nu \qquad \dots (6)$$

 F_c and F_h being the quasi-Fermi levels and $E_g = hv$.

But for very high dopings, the donor levels will merge into the conduction band, the bottom of which will be scriously distorted resulting in nonlinear variation of the shift of peak emission with magnetic field. This was actually observed¹⁴ in heavily doped GaAs laser diode in which the peak emission varied quadratically with the magnetic field. The quadratic shift was found to be approximately equal to the shift for the ground state of a hydrogenic donor and possibly the initial states under this condition are the bound hydrogenic states.

However, for correctly determining the effective mass, linear diamagnetic shift of the emission line to higher energy should be obtained and this can only be expected if the initial state of the transition is in the conduction band of pure material. This underlines the need for using optimum doping for which the above condition is satisfied. For heavy dopings, the magnitude of the magnetic shift obtained will also be small.

Direct Determination of Effective Mass in Semiconductors and in Mixed Semiconducting Solid Solutions

Cyclotron resonance, as mentioned earlier, can be tried for directly determining the effective mass in GaAs, GaSb and InP at comparatively higher temperatures in large magnetic fields, by increasing the frequency of the electric field to near infrared wavelengths where the use of lasers as infrared generators will give more accurate results.

However, these semiconductors have shown laser emission over a wide range of temperatures (1·2-300°K.) and the effective mass can be determined from the observation of the magnetic shift of peak laser emission. Operation at lower temperature, however, is essential to observe the magnetic shift effect. The shift of peak laser emission will be small in these cases due to the larger effective electron mass. To effect an observable shift, large magnetic fields will be required. These are calculated using Eq. (5) and known values of effective masses found from indirect measurements (Table 1).

The values of effective mass in mixed semiconducting solid solutions like $GaAs_xP_{1-x}$, $InAs_xP_{1-x}$, etc., have not been reported in the literature. But laser emission has already been reported in these semiconductors over a wide range of temperatures and, consequently, the study of the magnetic shift enable one to determine the effective mass in these compounds. The effective mass, determined by the band gap, will vary in these semiconductors with the percentage composition of phosphorus, since addition of phosphorus increases the band gap. Incidentally, these alloy crystals can contain up to 50 per cent phosphorus and still have the direct-gap band structure characteristics.

Semi- conducting group 111-V compounds	Approx. values of effective mass from indirect measurements		Reduced mass	Approx. peak emission energy*, eV.		Approx. magnetic field
	m _c ¹ m	mh/m	n:rint	1.7°K.	4·2°K.	a shift of peak laser emission by 10 ⁻³ eV. kilogauss
GaAs GaSb InP	0-06 0-047 0-073	0.50 0.39 0.724	0·53 0·042 0·066	1·4999 0·774 1·390	1·498 0·7736 1·389	9·1 7·224 11·35

TABLE 1 -- CALCULATED VALUES OF MAGNETIC FIELD REQUIRED FOR AN OBSERVABLE LASER EMISSION SHIFT IN SOME GROUP III-V COMPOUNDS

*The approximate peak emission energy at these low temperatures has been calculated from the known room temperature values of the band gap.

Conclusion

Accurate values of effective mass in semiconductors can only be obtained from direct measurements. The most widely used direct method of measurement utilizes cyclotron resonance absorption whereas the method of laser emission shift is a regenerative resonant radiation process. The laser emission line is very sharp as regenerative narrowing of the spectral width takes place with increasing current densities above threshold which is not the case with absorption experiments. This gives more accuracy in the measurement of the exact change of band gap in a magnetic field. For many of the intermetallic semiconducting compounds and for usual values of the magnetic field, the frequency of the cyclotron resonance absorption falls in the infrared and for some of the compounds, the effect is not at all noticeable. To obtain pronounced and more accurate results in these cases, one may either utilize lasers in cyclotron resonance absorption experiments as infrared generators which are capable of delivering large outputs of high spectral purity, or observe the shift of peak laser diode emission in a magnetic field. Transverse magnetic fields are preferred for greater increase of emission intensity and an optimum doping should be used. It is felt that the tensor properties of the effective mass can also be determined by observing the magnitude and linearity of the magnetic shift in laser diodes for different orientations of the magnetic field. The method of laser emission shift is, however, applicable only to direct band gap semiconductors, for indirect band gap semiconductors are incapable of supporting laser action. If laser emission could at all be obtained in indirect band gap semiconductors by using very heavy dopings where the K-selection rule does not hold, still then this method will not be fruitful because of the extremely small expected magnetic shift.

Summary

The methods of measurement of effective mass of electrons and holes in semiconductors are briefly reviewed. The use of lasers is suggested for

cyclotron resonance absorption experiments in large band gap semiconductors. It is also shown that studies of the shift of peak coherent emission in high magnetic field in laser diodes provides a direct method of measuring the scalar effective mass and this is exemplified with InAs and InSb. The effects of magnetic field and doping on the laser diode emission are discussed. The possibility of directly determining the effective mass in GaAs, GaSb and InP, and also in semiconducting mixed solid solutions is mentioned. This method is expected to give better results, though applicable only to direct band gap semiconductors.

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Luminescence Behaviour & Laser Action in Rare Earth Chelates

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VITH the recent observation of laser action in europium benzoyl acetonate1,2, interest has been revived in the study of luminescence properties of organic metal complexes, specially those of the rare earth ions. The rare earth ions have the advantage of well-protected inner 4f shell from which line luminescence can be obtained. The special feature of this system is that the emitting ion is excited by an energy transfer process rather than by direct absorption of pump radiation. The chief attraction of this system as compared with inorganic hosts for the metal ion (e.g. ruby) lies in the strong absorption associated with the ligand. Since the quantum yield of this material is high³ (0.85), one may expect very efficient use of pump energy. Rare earth chelates have sharper emission lines than most other larger molecules and this circumstance in conjunction with their broad ultraviolet absorption and fairly high quantum yield (QE) has drawn attention to the possibility of designing lasers using such che-lates⁴⁻⁶. The absorption is at about 3000 A. and emission is around 6000 A. region.

Luminescence Behaviour of Chelates of Rare Earth Ions

Intramolecular energy transfer in complexes of rare earth ions was first observed by Weissman³ and later confirmed by Sevchenko and Trofimov7. Weissman reported results of a preliminary study of the lifetime and fluorescence efficiency of a large number of complexes of Eu. From the effect of temperature, solvent and the nature of the ligand, it was concluded that: (1) the light absorbed by the organic ligand is emitted as the line spectrum of the central metal ion; direct excitation of the metal ion was not responsible for the line emission; (2) the decay time for a given complex depends very little on temperature but the OE changes enormously with temperature suggesting that the major part of the loss of excitational energy occurs prior to the excitation of the rare earth ion. However, deactivation appears to take place by non-radiative processes of those rare earth ions which do receive excitation energy; (3) the efficiency of energy transfer depends on the type of ligand attached to the rare earth ion. There is steady decrease in the efficiency of energy transfer from the covalent, benzene-soluble benzoyl acetonates to the ionic crystals of platinocyanide. The conclusions of Weissman for Eu chelates were corroborated by Crosby and Kasha⁸ for Yb chelates.

A systematic study of such intramolecular energy transfer in rare earth chelates has been conducted by Crosby and coworkers⁹⁻¹³. They have shown that the photoluminescence of lanthanide chelates can be roughly divided into three classes. The following classification was obtained for benzovl acetonate and dibenzoyl methide chelates of rare earth:

(i) Gd, La and Lu — well-defined luminescence spectra, high yield, $\phi_p/\phi_F > 100$ for Gd B₃, no line emission.

(ii) Pr, Nd, Ho, Er, Tm and Yb — low total luminescence yield, significant decrease in ϕ_P/ϕ_F , weak line emission of central ion.

(iii) Sm, Eu, Tb and Dy — weak molecular phosphorescence for Sm and Dy; bright line emission characteristic of the ion for Eu and Tb.

In the first class are those compounds such as lanthanum and gadolinum chelates whose luminescent properties are similar to the organic component of the molecule. In the second class, although the organic luminescence is decreased, there is very little or no rare earth fluorescence. In the third class there is predominance of ion fluorescence.

The luminescence of the first class then consists of organic fluorescence and phosphorescence characteristic of the chelating agent itself. This suggests that the luminescence process in these chelates is the same as in the organic compounds alone, i.e. excitation to the singlet state by absorption of radiation, followed by intersystem crossing to a triplet level. The increased yield of long-lived phosphorescence relative to fluorescence in this class of chelates suggests increased perturbation by the metal ion, facilitating intersystem crossing to the triplet state. Phosphorescence emission from the triplet state then becomes competitive with deactivation by fluorescence emission. Since no line emission is observed, energy transfer to the energy level of the metal ion is very inefficient.

Crosby et al.⁹⁻¹³ have further demonstrated that the difference in emission behaviour of different complexes of rare earth ions can be correlated by comparison of the triplet state energy of the ligand in the complex and the resonance energy level of the lanthanide ions. The requirement for line emission from a given chelate is that the lowest triplet state energy level of the complex must be nearly equal to or must lie above the resonance energy level of the rare earth ion. In the hydrated crystals, Gd^{3+} is the brightest emitter of all the rare earths¹⁴, but the chelates show only intense well-defined molecular luminescence because the resonance line is much higher than any of the triplet states of the ligand.

Since Eu and Tb exhibit high luminescence yield it may be suggested that energy transfer from triplet state to the resonance level of the ions is efficient. The compounds are chemically similar and relatively stable; therefore, it is expected that a uniformly strong coupling between the ligand and the other central metal ions for all chelates of the same series should exist. Energy transfer in other ions should also be as efficient. The difference in emission intensity then seems to be due to non-radiative dissipation within the energy levels of the ions.

The next point of interest, then, is to consider what factor will eventually decide the probability of emission within the ion, once the excitational energy has reached the emitting level. For efficient emitters large energy gaps exist between the re-sonance levels and the lower levels of the ions; consequently, the radiative process competes favourably with non-radiative ones. There is a rough correlation between the number of 4f levels present to which transfer can occur and the efficiency of Therefore, the conditions for quenching process. high quantum yield for line emissions is that the spacing of the 4f levels should be large. Those ions which possess numerous closely packed 4f levels offer many paths for energy transfer. As a result triplet state is very efficiently depleted and the non-radiative degradation is more competitive.

From the absorption and fluorescence spectra of Eu^{3+} in alcohol solutions, Joos and Hellwege¹⁵ and Sayre *et al.*¹⁶ have been able to identify the levels involved in the emission of the rare earth fluorescence as ${}^{5}D_{0}$ and ${}^{5}D_{1}$ states. In the latter work the splitting of the ${}^{7}F_{1}$ and ${}^{7}F_{2}$ states into 3 and 5 levels respectively has been observed. The symmetry of the chelate in the solid and in solution may be tetragonal or lower¹⁷. Principal emission is due to ${}^{5}D_{0}{}^{-7}F_{2}$ transition and this set contains the frequency that can be made to exhibit stimulated emission.

The radiative lifetime for ${}^5D_{0}{}^{-7}F_2$ transition can be calculated from the oscillator strength obtained from the absorption data. When this is compared with the fluorescence decay time at 300°K., it is found that at this temperature only 10 per cent of the energy reaching the Eu³⁺ appears as fluorescence. The efficiency increases at lower temperature^{18,19}.

Path of Energy Transfer from Ligand to Metal Ion

The precise path of this energy transfer process is not very clear yet. But it appears that it is via the triplet state and not directly from the singlet fluorescent state of the ligand. Either 4f levels of the ion do not couple with singlet states or other competitive processes such as fluorescence, internal conversion or intersystem crossing are more efficient. Once the complex reaches the triplet level, radiative decay is spin forbidden and the non-radiative process of energy transfer is then competitive.

In general, it appears that in the case of efficient emitters such as Eu chelates, the transfer does not occur from the ground state of the triplet. This is concluded from the observation that the decay time of metal ion fluorescence is considerably shorter than that of phosphorescence whenever both are observed in the same compound. The transfer coald occur from an excited vibrational level of the triplet level or from a second triplet slightly higher in energy than the first. The second possibility seems to be more likely since in the first, the transfer process will have to compete with vibra-



Fig. 1 - Energy level diagram of Eu chelate

tional deactivation (lifetime, $\tau = 10^{-12}$ sec.). No transfer process as fast as this seems probable. The energy level scheme²⁰ describing all these processes is given in Fig. 1.

Conditions for Laser Action

The mathematical treatment of the kinetics is much simplified by assuming the existence of a steady state. Equations are set up in terms of the following transition probabilities:

 W_{14} , the transition probability for the singlet absorption which depends on the molar extinction coefficient and the intensity of exciting radiation; A_{41} , A_{T_41} , the spontaneous transition probabilities for the organic fluorescence and phosphorescence; A_{4T} , A_{TT_6} and A_{T3} , the transition probabilities for the radiationless processes indicated; A_{32} , the spontaneous transition probability for the ion fluorescence; A_{31} includes the probabilities for all the other transitions originating from level 3, so that A_3 $= A_{32} + A_{31}$, the probability of de-excitation of level 3 by any process, radiative or non-radiative; and W_{21} , W_{12} , the transition probabilities between 1 and 2 (probably thermal). The steady state equation for the population of each state is then given by

$$\begin{aligned} \frac{dN_2}{dt} &= W_{12}N_1 - W_{21}N_2 + A_{32}N_3 = 0\\ \frac{dN_3}{dt} &= A_{T3}N_T - A_3N_3 = 0\\ \frac{dN_4}{dt} &= W_{14}N_1 - (A_{4T} + A_{41})N_4 = 0\\ \frac{dN_T}{dt} &= A_{4T}N_4 - (A_{TT_*} + A_{T3})N_T = 0\\ \frac{dN_{T_*}}{dt} &= A_{TT_*}N_T - A_{T_*1}N_{T_*} = 0\\ N_0 &= N_1 + N_2 + N_3 + N_4 + N_{T_*} + N_T \end{aligned}$$

where N_i is the population of the *i*th level and N_0 is the total concentration of the chelate in molecules per cm.³.

To a good approximation, neglecting W_{12} compared with W_{21} from the steady state solution, the expressions for N_1, N_2, \ldots , etc., can be obtained.
An efficient chelate laser material would be one in which the excitation energy reaches the rare earth ion with minimum loss. This requires that the quantities A_{TT_o}/A_{T3} and A_{41}/A_{4T} must be very small. In a number of Eu chelates such as triand hexafluoroacetyl acetonates, organic luminescence concurrent with ion fluorescence is readily observed. In these compounds there is marked increase in these ratios which makes it more difficult to establish a large population in level 3. Since the lasing condition is $N_3 \gg N_2$,

$$\frac{N_3 - N_2}{N_0} \approx N_3 / N_0 = -\frac{W_{14}}{bW_{14} + c.4_3} \quad ...(10)$$

where

$$c = 1 + \frac{A_{TT_q}}{A_{m}}$$

 $b = 1 + \frac{A_3 \cdot A_{TT_0}}{A_3 \cdot A_{TT_0}}$

Further with two other conditions, $A_3/A_{T3} \ll 1$ and $A_{32}/W_{21} \ll 1$, it should be possible to maintain the necessary populations in level 3.

To obtain a numerical estimate of W_{14} , i.e. the pump power requirement, one has to know the values of the ratios A_3/A_{T_01} and A_{TT_0}/A_{T3} . The value of the first ratio can be obtained from the decay constants of ion emission and organic phosphorescence. No experimental determinations of A_{TT_0} and A_{T3} are available. However, those compounds which show strong organic phosphorescence, A_{TT_0}/A_{13} must be larger than those which do not. This merely has the effect of increasing the pump power requirements whenever phosphorescence occurs. But if the lifetime of the phosphorescent state is also large then this may act as a trap by effectively preventing many molecules from participating in the laser action. This cannot be compensated by increased pump power. Whenever such a possibility arises the spectroscopic properties of the ion emission alone are not sufficient to determine whether or not a compound will act as a laser. This restricts the class of chelates in which laser action can be attained.

In a highly interesting and detailed study, Filipescu *et al.*²¹ have investigated the effect of substituents on the ligand chromophore on intramolecular energy transfer in Eu and Tb diketone chelates. The effect of the substituent has been assessed for each step involved between initial absorption of pump energy to final emission by the metal ion in a dilute solution of the chelate in EPA solvent. The effect of substituent may manifest in three ways: (1) by affecting the nature of the absorbing chromophore, (2) by changing the degree of overlap between metal-oxygen bond, and (3) by introducing asymmetry in the environment of the emitting ion.

Preparation of Rare Earth Chelates with Improved Luminescence

These considerations suggest certain guiding rules for the preparation of chelates of rare earth with improved emitting characteristics. In general, two approaches appear to be feasible: (1) using a suitable ligand which will transfer its energy more efficiently to the emitting ion and (2) enhancing the absorption and fluorescence probabilities by suitable changes in the environment of the emitting ion such that the Laporte forbidden ${}^{5}D_{0}{}^{-7}F_{2}$ transition becomes more allowed.

The first approach is based on the fact that the efficiency of rare earth ion emission will increase with the efficiency of intramolecular energy transfer which, in turn, will be due to better coupling between the acceptor and the donor moiety. In order to minimize internal conversion it is desirable to protect the electronic energy rich moiety (potential donor) from external perturbations. This can be done by enclosing it in a sheath which itself is a poor acceptor and thereby insulates the donor (by acting as a buffer) from better energy acceptor in its environment. The theoretical aspect of the problem has been discussed by a number of workers²²⁻²⁴. A simple experimental approach for developing this 'insulating sheath' for lanthanide chelate systems has been discussed by Halverson et al. 25-27.

In the case of β -diketone chelates of rare earth metal ions, the general formula can be written as ML_3 where M represents the metal ion and L the ligand ion which is β -diketone in these cases. The ligand is directly attached to the central metal ion via the oxygen atoms. The same ligand ion is also the chromophore. Since the chromophore is directly involved in the chelate bond, it can be referred to as a 'chelating chromophore' and may be represented as



The light absorbing power can be enhanced by attaching unsaturated substituents to the C-skeleton so as to extend the conjugated grouping. In general, the energy levels of the chelating chromophore will be the same as those of the β -diketone enolate ion.

The energy rich portion of an excited lanthanide chelate consists of the chelating chromophore and the chelated lanthanide ion. This is the moiety which is to be wrapped in an insulating sheath. Since the stored quanta are in the visible or ultraviolet region, the available energy levels in the insulating sheath should be far removed from this range. The sheath should be bulky to prevent the close approach of like systems, quenching impurities and undesirable solvent components to the energy rich moiety. Groupings which satisfy the energy requirements placed on the insulating sheath include saturated hydrocarbons, fluorinated and or chlorinated hydrocarbons, etc. Since the exterior of the sheaths will determine solvent compatibility, the solute and the solvent system cannot be chosen independent of each other.

Two ways in which this bulky insulating sheath can be attached to the chelating chromophorelanthanide system are: (1) substitution on the chelating chromophore and (2) the use of appropriate 'synergic agents'.



Fig. 2 = Structure of (a) Eu (acetyl acetonate)₃ $|\phi, very low;$ τ . 226 μ sec.] and (b) Eu (dipivaloylmethide)₃ $|\phi, low but 20$ per cent higher than in (a); τ , 310 μ sec.]

Substitution on the chelating chromophore ---The simplest chelating chromophore will be H.CO.CH-CO.H, but this will be unstable. On replacement of its terminal H by CH_3 we get acetyl acetonate ion (Fig. 2a). This can represent the start of an insulating sheath. But the methyl groups are not very bulky and, therefore, not very effective. A considerable increase in the bulk can be obtained by introducing tert-butyl group forming dipivaloylmethide ion (Fig. 2b). When the tris-chelate is formed, these tertiary butyl groups appear on the periphery of a rather compact ball like structure with the lanthanide ion at the centre. From the molecular models, it can be visualized that there may be still some space for the penetration by small molecules. Water may give rise to hydrates. Instead of using rigid tertiary butyl groups, long floppy alkyl chains can be substituted. Even better insulation can be expected from fluorinated hydrocarbons grouping such as trifluoromethyl and pentafluoroethyl. These may also change the energy levels of the chromophore by inductive effect.

Use of synergic agents in the insulating sheath --The neutral chelate contains three units of uninegative ligand ion to tripositive metal ion. When these three ligands are diketones, there are six oxygen atoms available for coordination to the rare earth ions. There is considerable evidence that the lanthanide ions prefer seven or eight or even nine oxygen atoms in their coordination sphere²⁸⁻³⁰. In many cases this preference may be satisfied by water molecules which pass undetected. This behaviour furnishes a means for completing the insulating sheath by using appropriate synergic agents ^{31,32}. These are neutral molecules such as trioctyl phosphine oxide (TOPO) which have good lone oxygen atoms for coordination to the metal ion. Combined with bulky saturated hydrocarbon tail directed away from the metal ion, they form a very good insulating sheath. These can be 'hooked' on to the metal ion. In case of the Eu ion, the stable coordination number appears to be about eight. Thus the neutral compound EuL_a can attach two synergic agent groups to give $\operatorname{EuL}_3^3S_2$ complex. For example, $\operatorname{Eu}(\operatorname{TFAC})_3(\operatorname{TOPO})_2$, La(TTA)₃(TBP)₂, Tb(HFAC)₃(TOPO)₂, Eu(HFAC)₃-(DHSO)₂, where TFAC is trifluoroacetyl acetonate: HFAC, hexafluoroacetyl acetonate; TTA, theonyl trifluoroacetonate; TBP, tributyl phosphate; DHSO, dihexyl sulphoxide; and TOPO, trioctyl phosphine oxide. Synergic agents of interest are trialkyl group V oxide, alkyl dialkyl phosphinates, dialkyl alkyl phosphonates, trialkyl phosphates and dialkyl sulphoxides.

It is believed that the presence of water molecules coordinated to the metal ion is deleterious³² specially in hydrogen-bonded solvents. The bond is relatively strong, the number of vibrational quanta involved for water to be an acceptor is only 5 or 6, and the H-bonded solvent is a good energy sink. Replacement of H₂O by R₃P = O, where R is an alkyl group, gives a weaker bond, the energy per P-O vibrational quanta is a third as large, and energy transfer to the rest of the molecule is not so good. Hence this is a good synergic agent for an insulating sheath.

The synergic agent may also contain a chromophore provided it is protected in the same fashion as the chelating chromophore. Thus sulphoxide grouping in BHSO provides a chromophore absorbing in the region 3000 A. This may also transfer energy to the metal ion.

Two general techniques are employed for the preparation of synergic agent complex: (1) Lanthanide tris-chelate is mixed with dilute hydrocarbon solution of the synergic agent, the ratio of ligand to synergic agent being 2-4:1; since the chelate is insoluble in this solvent, reaction proceeds very slowly at room temperature and it is difficult to obtain synergic agent-free complex. (2) An aqueous solution of Eu³⁺ as nitrate is equilibrated with an ether solution of chelating agent as free ligand or NH4 salt, plus synergic agent. Mole ratio of L to S is fixed at 3:2 and volume is adjusted to give 1:3:2 ratio for Eu3+: L:S. The complex EuL3S2 is formed in quantitative yield and collects in ether phase (amber oil, m.p. 0°C.). [Emission in the region, 6100-6225 A. (5D0-7F2); excitation, 2800-3800 A.; and solvent, 3:1 ethanol + methanol, 1:1 methylcyclohexane-3-methylpentane.

The use of a synergic agent complex increases the quantum efficiency by 3-10 and the lifetimes by 1·5-2·5 times at room temperature, in a low viscosity medium such as alcohol or hydrocarbon. This indicates considerable improvement as a laser material (Table 1).

These synergic agents may be considered as a special type of Lewis bases34. Enhancement of fluorescence yield has been observed by Kropp and Windsor³³, on substitution of deuterium for H in the chelating ligand. Same purpose is accomplished by Lewis bases³⁴. The nature of the atom of the base having unshared electron pair is not the determining factor. Tri-ethyl amine, trisn-butyl phosphate or tri-n-butyl phosphorothioate in which donor atoms are N, O and S respectively are equally effective. Enhancement of fluorescence is observed in liquid, plastic and glassy solutions of Tb, Eu and Sm chelates. Therefore, this effect of Lewis bases has been explained as due to decreased quenching loss at the ligand and the ion sites as a result of microscopic order and rigidity introduced by these electron donors.

Compound	Solvent	$\begin{array}{c} Molar\\ conc.\\ \times 10^3 \end{array}$	°C.	τ µsec.	ø
Eu(AC) ₃	3:1 ethanol- methanol	ŀ	25	226	
Eu(DPM)	do		25	310	
Eu(TFAC) ₃	do		25 80	435	0.044 0.15
Eu(HFAC).	do		25	430	0.16
			80	460	0.24
· · · ·			-135	477	0.24
Eu(HFAC) ₃ (DHSO) ₂	1:1 methyl- cyclohexane 3-methyl- pentane	0·5 +	25	641	0.39
Eu(HFAC) _a (TOPO) _a	do		25	791	0.79
Eu(TFAC) (DASO).	do		25	463	0.13
Eu(TFAC),(TBP),	do	0.5	25	741	0.18
Eu(TFAC), (TOPO),	do		25	742	0.43
EuCl., 6H.O40			20	120	
3, 512			-196	120	

TABLE 1 — LUMINESCENT LIFETIME (τ) and Quantum Efficiency (ϕ) of Some Eu Chelates (after Halverson et al. 25)

Further evidence for enhancement caused by eightfold coordination as in the case of synergic agent complexes has been obtained from the observation that Eu-benzoyl acetonate and Eudibenzoylmethide lase better, when prepared from pyridine solutions³⁵⁻³⁸. The molecular formula has been found to be Eu(BA) PvH+ where the four benzoyl acetonate ligand is coordinated to Eu³⁺. The emission spectra for ${}^{5}D_{0}-{}^{7}F_{2}$ transition is consistent with the selection rules derived from a distorted dodecahedral arrangement of eight oxygens around the central Eu ion.

The second approach to the problem of preparing better laser materials has been explored by Gallagher³⁹ by using ligands such as perchlorate, chloride. nitrate, EDTA, DTPA (diethylene triamine penta acetate) to form unique asymmetric environment surrounding the rare earth ions. These ligands do not absorb in the region of pumping radiation. Besides, they form primarily ionic bonds and, therefore, energy transfer from ligand to metal is not possible. In these complexes intensification of the spectra, shift to longer wavelengths and incrystal field splitting are observed. creased Hundredfold increase in fluorescence is observed without the benefit of energy transfer. The emission of ${}^{5}D_{0}{}^{-7}F_{2}$ increases 40-fold with DTPA and nearly 100-fold with EDTA. With nitrates it is less. Crystal field splitting of many new laser chelates have been observed by Nugent *et al.*⁴⁰. An interesting effect of inorganic ions on the

spectroscopy of the chelates has recently been shown by a number of workers^{41,42}. Samelson et al.⁴² observed a shift in the emission line of Eu-benzovl acetonate at 6131 A. when sodium acetate was added to the system. At still higher concentrations of Na⁺, a new line appeared at 6114 A. Laser action can be observed simultaneously in both the wavelengths. The salt effect thus enables for the first time a tuning of the laser emission by chemical means. Other ions such as Li⁺, K⁺, NH⁺ are equally effective.

Concluding Remarks

Fluorescence decay times (τ) and quantum efficiency (QE) of rare earth chelates are also being measured by improved techniques to obtain accurate data for evaluation of laser threshold parameters⁴³⁻⁴⁶. It is generally observed that τ and QE differ markedly on chelation⁴⁷ as compared to unchelated salts of Eu and Tb. Lanthanide ions generally have long lifetimes due to the forbidden transition during emission process which involves ΔJ much greater than one⁴⁸, though selection rule permits $\Delta J = \pm 1$ only.

Till now only Eu and Tb have been found to give useful laser materials. Gd, although a very bright emitter, has not proved useful due to its high resonance energy level to which efficient energy transfer from the ligand is not possible. Sm and Dy also emit line spectra in their chelated form but the intensity and lifetime are not enough for laser action. Two independent features contribute to the presence of fluorescence in the middle of the rare earth group⁴⁹: (1) the presence of wide gaps in the energy level diagram and (2) the absence of close coupling of the excited ion to the crystal lattice. It has been observed that N-coordinated compounds may give improved emission characteristics as compared with O-coordinated compounds. The latest observation is that in contrast to intramolecular energy transfer discussed so far, intermolecular transfer can also take place^{50,51}. 4-4'-dimethoxy benzophenone initiates laser action in Eu3+ in presence of Tb^{3+} only. No emission is observed in the absence of Tb^{3+} . The latter serves as an intermediate for the two-step transfer.

Although the feasibility of using rare earth chelates has been established beyond doubt, it can be exploited only when high quantum yield chelates, which can work effectively at higher temperatures, can be obtained. The main advantage of liquid lasers in continuous wave mode is that it can be used at a higher power level where usual solid laser ceases to operate due to heat dissipation. The problem is simplified in liquid laser where recirculation is possible. Till now useful laser action has been observed only in highly viscous media at low temperatures. The object of modern lines of research is to extend the useful range to higher temperatures, that is, to obtain chelating system which will have very few 'loose bolts' so that many quenching processes are prevented.

Summary

With the observation of laser action in Eubenzoyl acetonate, the interest in the study of rare earth chelates has been greatly stimulated. Recent work on the preparation of chelates with improved luminescence behaviour and conditions for their laser action are discussed.

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Relaxation Phenomenon & Chemical Kinetics in Chemically Reactive Media

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T is observed that acoustic absorption in fluids is, in general, in excess of the value predicted by the classical Stoke-Kirchhoff theory¹⁻³. Jeans⁴ in 1916 suggested that this excess absorption can be explained by assuming an energy transfer from the external to the internal degrees of freedom (thermal relaxation). Einstein⁵ in 1920 gave a theoretical treatment explaining the excess acoustic absorption in nitrogen peroxide assuming an energy transfer between the two reversible molecular states of nitrogen peroxide (chemical relaxation). The idea has since been further developed⁶⁻²⁹.

Relaxation Phenomenon

The passage of a sound wave involves a momentary compression of the fluid which, in addition to increasing the density, also produces an increase in pressure because of an increase in the mean kinetic energy of translation of the molecules. However, as compared to the increase in density, the increase in pressure does not occur instantaneously because some of the extra energy of translation responsible for the increase in pressure is always transferred to the internal molecular states which require a finite time to release the energy. After the density has begun to decrease, the pressure goes on increasing as the energy is transferred back from the internal to the translational state. Thus, excess pressure and excess density get out of phase, resulting in an effective transformation of acoustic energy into heat corresponding to a dissipation of the sound energy. For acoustic waves of a period far removed from the relaxation time (which is a measure of the time lag), the contribution to absorption due to this cause is not very large, but for waves with a period comparable to the relaxation time, this phenomenon is fully effective and results in a large acoustic absorption.

The mechanism of relaxation is generally considered to be of three types: (i) thermal, (ii) structural, and (iii) chemical. Thermal relaxation has been used to explain the observed excess absorption in gases and in some liquids, structural relaxation to explain the excess absorption in water and chemical relaxation to account for the observed absorption in certain chemically reactive media. It is seen, however, that in most of the liquids, no one single process is able to explain the observed excess absorption; it is assumed to be the combined effect of the various processes.

Chemical Relaxation and Kinetics of Reactions

A chemically reactive medium consists of various constituents which are in equilibrium with each other. If this equilibrium has significant sensitivity to pressure or temperature, it is perturbed when a sound wave is propagated through the medium. In most cases of disturbance of equilibrium, pressure variation is the predominant factor responsible for the perturbation in the medium. However, instantaneous equilibrium will not be realized during the propagation of the sound waves because of the finite time required for the equilibrium to be re-established after the system has been perturbed. As a result the density variations within the medium will be out of phase with the pressure variations resulting in relaxational absorption.

As an application of this phenomenon, the rate of reaction, the activation energy, the equilibrium constant, the reaction heat and the volume change resulting from the chemical reaction can be calculated by measuring the velocity and absorption of sound in the dynamic equilibrium system. The determination of rate constants of fast processes, lying in the region of relaxation times $10^{-5}\text{-}10^{-9}\,\text{sec.}$, by ultrasonic relaxation technique is particularly noteworthy because the kinetics of these fast processes cannot be investigated by the usual experimental methods like measurements of density, index of refraction, conductivity, adiabatic pressure changes, temperature changes or rotation of the plane of polarized light. In the investigation of reactions with half time less than 10⁻⁴ sec. special techniques are required to follow the reaction directly after mixing the components.

The application of ultrasonic relaxation technique to measure fast reaction rates is, however, limited to cases in which the frequencies of absorption maxima are experimentally accessible and the equilibrium constant is neither too large nor too small, i.e. in which significant amounts of all the components are present at equilibrium and the ultrasonic absorption due to other causes such as viscosity and thermal conduction is not so large as to mask the relaxation absorption.

Another limitation of the ultrasonic relaxation technique which is common to all types of relaxation measurements relates to the interpretation of ultrasonic relaxation effects in systems where several processes occur simultaneously having relaxation times differing by less than a factor of ten. Under such circumstances it is difficult to assign a particular relaxation frequency or time to a given process because of coupling effects.

Theoretical Treatment

Theories regarding ultrasonic relaxational absorption in relation to kinetics of reactions have been put forward by a number of workers¹⁷⁻²⁹. In all these treatments equations are derived relating the sound absorption to the relaxation time, physico-chemical constants and thermodynamic constants of the chemical reaction the relaxation time in turn being a function of composition, temperature and rate of the forward and the reverse reactions.

Freedman's treatment - This treatment¹⁷ does not take into consideration the volume change accompanying the chemical reaction. In this case, a general equation for a chemical reaction at equilibrium is assumed to be of the type

$$\sum_{i=1}^{n} a_i A_i = 0$$

where A_i represents the components of the reaction and a_i their stoichiometric coefficient, a_i being greater than zero if the components are produced by the reaction and less than zero if the components are consumed in the reaction. Damköhler's method¹³ as used in the case of gases is employed in this general equation to derive the equation for the excess acoustic absorption.

The equation so derived for the excess acoustic absorption per wavelength $(\alpha\lambda)_r$ due to the chemical reaction is

$$(\mathbf{z}\boldsymbol{\lambda})_{r} = \pi \widetilde{\gamma}_{0} \left(\frac{v}{v_{0}} \right)^{2} \frac{(C_{P}^{0} - C_{P}^{0})C_{P}^{*} U^{*}}{(C_{P}^{0})^{2} + (C_{P}^{\infty})^{2} \left(\frac{\omega D}{U} \right)^{2}}$$

where $C_{P_r}^0, C_{\Gamma}^0$ are the equilibrium values of the heat capacities; γ_0 , the ratio of the two heat capacities at equilibrium; v_0 and v_i the sound velocities at very low and experimental frequencies respectively; ω , the angular frequency of the sound waves; U, the gross reaction rate of the reaction; D a factor defined as

$$D = \left[\sum_{n_t}^{a_t^2} - \frac{(\sum a_t)^2}{n_t} \right]^{-1}$$

where n_i is the number of moles of the component A_{ii} , n_i is the total number of moles of the solution including the solvent, C_P^p the contribution of the chemical reaction to the total heat capacity given as

$$C_p^r = DR \left(\frac{\Delta H}{RT} \right)^2$$

where R is the universal gas constant; T, the absolute temperature of the medium; ΔH , the heat of reaction; and $C_{p}^{\boldsymbol{\omega}}$, the contribution of the individual components to the heat capacity given as

$$C_P^0 = C_P^\infty + C_P^r$$

In the above equation for $(\alpha \lambda)_r$ the term D/U has the dimensions of time and is called the relaxation time τ . In terms of the measured relaxation frequency and the heat capacities, it is given as

$$\tau = \frac{D}{U} = \frac{C_P^0}{2\pi \nu_m (C_P^0 - \bar{C}_P^r)}$$

where y_m is the relaxation frequency pertaining to maximum acoustic absorption.

Manes treatment — Manes¹⁸ has considered a general equilibrium equation

$$aA+bB+\ldots \rightleftharpoons_{k_{-1}}^{k_1} qQ+rR+\ldots$$

where a, b, \ldots are the stoichiometric coefficients and A, B, \ldots the components of the reaction. The relaxation time in terms of this equilibrium equation is defined as

$$\frac{1}{\tau} = x \cdot \frac{d(-\Delta F)}{d\xi} = -\frac{d \log (-\Delta F)}{dt}$$

where ΔF is the free energy difference per mole of the products and the reactants, $d\xi/dt$ represents the net reaction rate U, ξ representing the degree of advancement of the reaction, and x a proportionality factor characteristic of the system.

Using this value of relaxation time in Hall's treatment¹⁴, the equation for acoustic absorption per wavelength is given as

$$(\mathrm{x}\lambda)_r = rac{2\pi(eta_0-eta_{\mathbf{w}}\omega au)}{eta_0+eta_{\mathbf{w}}\omega^2 au^2+(1+\omega^2 au^2)^{1/2}(eta_0^2+eta_{\mathbf{w}}^2\,\omega^2 au^2)^{1/2}}$$

where β_0 and β_∞ are the equilibrium and instantaneous values of the adiabatic compressibility defined in terms of the general equilibrium equation. Applying this treatment to the restricted case of a chemical reaction involving no volume change, the equation for absorption per wavelength reduces to the same form as obtained by Freedman.

Tabuchi's treatment — Tabuchi²⁶ has presented a more general treatment than Freedman or Manes. He has considered not only the change in the internal energy of the solution but also a change in its volume while deriving an equation for the relaxation absorption of an acoustic wave passing through a chemically reactive medium.

The relationships for the relaxation time, sound velocity and absorption per wavelength according to this treatment for the general equilibrium equation are

$$\begin{split} \frac{1}{\tau} &= 2\pi \mathbf{v}_m (C_P^{\,\omega} C_V^{\,\omega} / C_P^0 C_V^0)^{1/2} \\ &= U_f V \left(\sum_A \frac{q^2}{n_A} + \Psi_A \right) + U_b V \left(\sum_Q \frac{q^2}{n_Q} + \Psi_Q \right) \\ v^2 &= \frac{1}{\wp_Q^0} \cdot \frac{C_P^0 C_V^0 + C_P^{\,\omega} C_V^{\,\omega} \wp^2 \tau^2}{(C_V^0)^2 + (C_V^{\,\omega})^2 \omega^2 \tau^2} \end{split}$$

and

and

$$\left(\alpha\lambda\right)_{r} = \frac{\pi\omega\tau\left(C_{V}^{0}C_{P}^{\infty}-C_{P}^{0}C_{V}^{\infty}\right)}{C_{P}^{0}C_{V}^{0}+C_{P}^{\infty}C_{V}^{\infty}\omega^{2}\tau^{2}}$$

where C_{P}^{0} , C_{V}^{0} are the equilibrium values of the heat capacities, C_{P}^{∞} , C_{V}^{∞} are the contributions due to the individual components to the heat capacity, V is the volume of the solution, ρ is the density of the solution, Ψ_{A} , Ψ_{Q} are defined as:

 $\Psi_A = \left(\frac{1}{V}\right) \sum_{A \ L} \sum_{a \ L} al \ f_{AL} |f_A|$

$$\Psi_{Q} = \left(\frac{1}{V}\right) \sum_{Q \ L} \sum_{L} q l f_{QL} |f_{Q}|$$

l is the thermal expansion coefficient; f_A , the activity coefficient of a component A; \sum_A , \sum_Q , \sum_L signify summations for the components on the left-hand side, right-hand side and on both sides of the general equilibrium equation respectively; U_f , U_b

are the gross reaction rates for the forward and backward processes respectively and are defined in terms of the general equilibrium equation as

$$U_f = k_1 . a_A^a . a_B^{b_i} . \ldots = k_1 \pi_A . a_A^a$$

and

$$U_b = k_{-1}.a_Q^q.a_R^r \ldots = k_{-1}\pi_Q.a_Q^q$$

 k_1 , k_{-1} are the forward and backward reaction rate constants respectively, a_A is the activity of a component A given as (n_A/V) and π is the activity product of the ionic system.

Eigen-Tamm treatment — Eigen and Tamm²¹⁻²⁴ starting from the usual expressions of chemical kinetics have considered the influence of relaxation of stepwise electrolytic dissociation on the propagation of sound waves, deriving relationships for relaxation time and absorption per wavelength.

For a dissociation reaction (single step system) of the type

$$A + B \underset{k_{*}}{\overset{k_{-2}}{\rightleftharpoons}} AB$$

the derived relationships for relaxation time and absorption per wavelength are given as

and

$$\frac{1}{\tau} = k_2 (1 - n_{AB}) + k_{-2}(n_A + n_B)$$
$$(\alpha \lambda)_r = \frac{\pi (\Delta V^0)^2}{\beta_0 RT} \cdot \frac{n_0 \delta(1 - \delta)}{1000 (2 - \delta)} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2}$$

where n_0 is the molar concentration of the reactant; n_A , n_B and n_{AB} , the mole fractions of the entities indicated by the corresponding subscripts; k_2 and k_{-2} , the dissociation and association rate constants respectively; δ , the degree of dissociation; ΔV^0 , the partial molal volume change for the reaction; and β_0 , the isothermal compressibility of the solution.

partial molal volume change for the solution, Δv , the β_0 , the isothermal compressibility of the solution. The applicability of the above expressions is restricted to reactions in very dilute solutions. For higher concentrations it is necessary to consider the activity coefficients; the expression for relaxation time in such a case is modified to the form

$$\begin{split} \frac{1}{\tau} &= k_2 + k_{-2}^0.\pi_f.\delta.n_0 \left(2 + \frac{\partial \log \pi'}{\partial \log \delta} \right) \\ &= k_2 + k_{-2}' \end{split}$$

where k_{-2}^0 is defined in terms of k_{-2} as $k_{-2} = k_{-2}^0 . \pi^f$ and π^f is the activity quotient.

For a multistep relaxation process,

$$A + B \stackrel{k_{-1}}{\rightleftharpoons} AB_1 \stackrel{k_{-2}}{\rightleftharpoons} AB_2 \stackrel{k_{-3}}{\rightleftharpoons} AB_3 \stackrel{k_{-4}}{\rightleftharpoons} \dots AB_n$$

having relaxation times $\tau_1, \tau_2, \tau_3, \ldots$ for the subsequent steps such that each part of the reaction proceeds very quickly compared to the next one, that is, where the different relaxation times represent a discrete sequence of the type $\tau_1 \ll \tau_2 \ll \ldots \tau_n$; in terms of reaction rates this sequence can be written as

$$k_1$$
, $k_{-1} \gg k_2$, $k_{-2} \gg k_3$, $k_{-3} \gg \ldots k_n$, k_{-n}

The expressions for relaxation time are

$$\begin{split} &\frac{1}{\tau_1} = k_1 + k'_{-1} \\ &\frac{1}{\tau_2} = k_2 + \frac{k'_{-1}}{k'_{-1} + k_1} \cdot k_{-2} = k_2 + k'_{-2} \\ &\frac{1}{\tau_3} = k_3 + \frac{k'_{-2}}{k'_{-2} + k_2} \cdot k_{-3} = k_3 + k'_{-3} \end{split}$$

with k'_{-1} , k'_{-2} , k'_{-3} ... in the form

$$\begin{split} k_{-1}^{\prime} &= k_{-1}^{0} \pi^{f} \bigg[n_{A}^{0} \bigg(1 + \frac{\partial \log \pi^{f}}{\partial \log n_{B}^{0}} \bigg)_{n_{A}} + n_{B}^{0} \bigg(1 + \frac{\partial \log \pi^{f}}{\partial \log n_{A}^{0}} \bigg)_{n_{B}} \bigg] \\ &= k_{-1}^{0} \cdot \delta \cdot n_{0} \pi^{f} \bigg[2 + \bigg(\frac{\partial \log \pi^{f}}{\partial \log \delta} \bigg)_{n} \bigg] \end{split}$$

where n_i^0 represent the equilibrium concentrations. The corresponding expression for absorption per wavelength is obtained as

$$(\alpha\lambda)_r = \sum_{j=1}^n A_j \frac{\omega\tau_j}{1+\omega^2 \tau_j^2}$$

where

$$A_{j} = \left[\frac{\pi \left(\Delta V^{0}\right)^{2}}{\beta_{0}RT} \cdot \frac{n_{0}\delta \left(1-\delta\right)}{1000(2-\delta)}\right]_{j}$$

These expressions are applicable only to relatively weak electrolytes in which the ionic cloud effect can be neglected in the collision process of the ions or to strong electrolytes of high concentrations where the subsequent steps in the reaction system are slow, i.e. where $\tau_1 \ll \tau_2 \ll \tau_3 \ldots$ etc. *Valleau's treatment* — Valleau²⁹ has developed a

Valleau's treatment — Valleau²⁹ has developed a theory of sound absorption for the general case of any two interacting equilibria in solutions having arbitrary rate constants unlike Eigen and Tamm who have assumed the rate constants to be progressively decreasing with every step of the reaction system. A relaxation viscosity in addition to shear viscosity and bulk viscosity has been considered to cause sound absorption in systems in equilibrium.

The derived expression for absorption coefficient is of the form

$$\frac{\alpha}{\omega^{2}} - \frac{\alpha_{b}}{\omega^{2}} + \frac{\tau_{y}A_{yz} + \tau_{z}A_{zy} + [\omega\tau_{y}/(1 - YZ)]^{2}\tau_{z}B_{z}}{1 + \{\omega\tau_{z}/(1 - YZ)\}^{2}\tau_{y}B_{y}} + \frac{[\omega\tau_{z}/(1 - YZ)]^{2}\tau_{y}B_{y}}{1 + \{\omega^{2}[\tau_{y}^{2} + 2YZ\tau_{y}\tau_{z} + \tau_{z}^{2}] + \omega^{4}\tau_{y}^{2}\tau_{z}^{2}\}/(1 - ZY)^{2}}$$

where $\omega = 2\pi v$ and α_b is the absorption due to viscosity and other background effects. The quantities y, z are the parameters like the concentration of substances taking part in the chemical reaction or the populations of certain vibrational levels of a particular molecular species and the quantities A_{yz} , A_{zy} , B_y , B_z , Y and Z are given in terms of the parameters y, z as

$$\begin{split} A_{yz} &= \frac{\rho^2 v (-\hat{c}y/\hat{c} \log y Q)_z (\delta_y + Z.\delta_z)^2}{2RT(1 - YZ)^2 [1 + (\hat{c}y/\hat{c} \log Q_y)_z (\hat{c} \log F_y/\hat{c}y)_{p,T,z}]} \\ B_z &= \frac{\rho^2 v (\hat{c}z/\hat{c} \log Q_z)_y \, \delta_z^2}{2RT[1 + (\hat{c}x/\hat{c} \log Q_z)_y (\hat{c} \log F_z/\hat{c}z)_{p,T,y}]} \\ Y &= \frac{(\hat{c}y/\hat{c} \log Q_y)_z [1 + (\hat{c}z/\hat{c} \log Q_y)_y (\hat{c} \log F_y/\hat{c}z)_{p,T,y}]}{(\hat{c}z/\hat{c} \log Q_y)_y [1 + (\hat{c}y/\hat{c} \log Q_y)_z (\hat{c} \log F_y/\hat{c}z)_{p,T,z}]} \end{split}$$

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where

$$\begin{split} \delta_{y} &= \Delta V_{y} - \left[\frac{\partial V}{\partial T}\right]_{p} \cdot \frac{\Delta H_{y}}{C_{p}} \\ \delta_{z} &= \Delta V_{z} - \left[\frac{\partial V}{\partial T}\right]_{p} \cdot \frac{\Delta H_{z}}{C_{p}} \end{split}$$

In these equations ρ and V are the specific gravity and volume of the solution; v, the sound velocity (cm./sec.); C_{p} , the specific heat of the solution (cal./g. deg.); Q_y , Q_z , the stoichiometric quotients for the reactions (litres/mole) given in terms of the ratio of the thermodynamic constant K and the quotient F of the activity coefficients; and ΔV_y , ΔH_y , the volume and enthalpy changes in the y-reaction. The relaxation times τ_y , τ_z are given by the relation

$$\frac{1}{\tau_y} = mk_{-y}^{\mathbf{0}} P^{\mathbf{0}} . N_y^{\mathbf{m}} \left[\left(\frac{\partial \log Q_y}{\partial y} \right)_z + \left(\frac{\partial \log F_y}{\partial y} \right)_{z, \mathrm{T}, P} \right]$$

where *m* is any power; k_{-y}^0 , the equilibrium value of the association rate constant; P^0 , an arbitrary positive function of concentration at equilibrium; and N_y is the numerator of the quotient Q_y at equilibrium.

For a reaction system where $\tau_z \ll \tau_y$, the B_y term can be discarded and the denominator can be well approximated at all frequencies to $[1+\omega^2\tau_y^2](1-YZ)^2](1+\omega^2\tau_z^2)$, giving the relaxation absorption as the sum of two single relaxations

$$\frac{\alpha_r}{\omega^2} \approx \frac{\tau_y A_{yz} + \tau_z (A_{zy} - B_z)}{1 + \omega^2 \tau_y^2 / (1 - YZ)^2} + \frac{\tau_z B_z}{1 + \omega^2 \tau_z^2}$$

For a system where A_{zy} and B_z are approximately equal, this expression can be further approximated to

$$\frac{\alpha_r}{\omega^2} \approx \frac{\tau_y A_{yz}}{1 + \omega^2 \tau_y^2 / (1 + YZ)^2} + \frac{\tau_z B_z}{1 + \omega^2 \tau_z^2}$$

A comparison of the above expression with Eigen-Tamm expression

$$\frac{\alpha_r}{\omega^2} \approx \frac{B_y \tau_y}{1 + \omega^2 \tau_y^2} + \frac{B_z \tau_z}{1 + \omega^2 \tau_z^2}$$

shows that the characteristic time of the low frequency relaxation according to Valleau is $\tau_y/(1-YZ)$

rather than τ_{y} . Due to this change in the relaxation times in the two theories, not only the magnitude of the predicted absorption peak at low frequencies but also the position of the low frequency relaxation region differ. However, the absorption values at higher frequencies by the two expressions agree fairly well.

Study of Chemical Kinetics by Relaxation Method

The relaxation absorption as investigated by Bazulin³⁰ and Lamb and Pinkerton³¹ in case of acetic acid and by Lamb and Huddart³² in case of propionic acid and attributed to a monomer-dimer reaction of the type $2A \rightleftharpoons A_2$ has been studied by Freedman¹⁷ to determine the mole fraction equilibrium constant, heat of reaction and reaction rates at equilibrium. It has been considered that when the system at equilibrium is perturbed by the passage of acoustic waves, only temperature changes³³. The calculated values are shown in Table 1.

To compare the values of the heat of reaction with other data, Freedman, by using a formula of Moelwyn-Hughes³⁴, according to which

$$\Delta H_{\text{liq}} / \Delta H_{\text{vapour}} = \frac{\epsilon + 2}{3\epsilon}$$

where ϵ is the dielectric constant of the liquid, has calculated the heats of reaction as -6.5 kcal./mole and -8.2 kcal./mole for acetic acid and propionic acid respectively which are fairly in good agreement with those shown in Table 1. On experimental basis Davies *et al.*³⁵ have found a value of -6.0 kcal./mole for the heat of reaction of the monomer-dimer reaction of acetic acid, which is also in agreement with that obtained by Freedman.

Kurtze and Tamm³⁶ have discussed various models of relaxation processes to explain the observed results in a number of aqueous electrolytic solutions and estimated the activation energy in cases of hydrated bi-bivalent electrolytes undergoing dissociation by using Eyring's equation^{37,38}.

$$k_j = \frac{KT}{h}$$
. exp $(-\Delta F_j/RT)$

Liquid	Temp. °K.	Mole fraction equil. constant	Gross reaction rate mole litre ⁻¹ sec. ⁻¹	Sp. rate constant for dissociation sec. ⁻¹	Heat of reaction (ΔH) kcal. mole ⁻¹
Acetic acid	293 303 313 323 333	61-97 43-58 31-34 23-04 17-21	$\begin{array}{c} 0.97 \times 10^{5} \\ 1.87 \times 10^{5} \\ 3.53 \times 10^{5} \\ 6.56 \times 10^{5} \\ 11.70 \times 10^{5} \end{array}$	$\begin{array}{c}1\cdot10\times10^{5}\\2\cdot18\times10^{5}\\4\cdot22\times10^{5}\\8\cdot08\times10^{5}\\14\cdot90\times10^{5}\end{array}$	-6.21
Propionic acid	281·2 294·2 304·2 314·2 324·2	$\begin{array}{c} 30{\cdot}40 \times 10^2 \\ 14{\cdot}54 \times 10^2 \\ 8{\cdot}68 \times 10^2 \\ 5{\cdot}26 \times 10^2 \\ 3{\cdot}32 \times 10^2 \end{array}$	$\begin{array}{c} 3 \cdot 03 \times 10^4 \\ 8 \cdot 67 \times 10^4 \\ 18 \cdot 10 \times 10^4 \\ 34 \cdot 80 \times 10^4 \\ 67 \cdot 20 \times 10^4 \end{array}$	$\begin{array}{c} 3 \cdot 08 \times 10^{4} \\ 8 \cdot 90 \times 10^{4} \\ 18 \cdot 70 \times 10^{4} \\ 36 \cdot 40 \times 10^{4} \\ 71 \cdot 00 \times 10^{4} \end{array}$	-9-33

TABLE 1 -- DATA FOR THE MONOMER-DIMER REACTION IN CASE OF ACETIC ACID AND PROPIONIC ACID (AFTER FREEDMAN¹⁷)

Temp. ℃.	Equil.	Specific re	action rates	Gross reaction rate	Heat of reaction	Activation
		Forward direction $k_1 \times 10^{-5}$ sec ⁻¹	Backward direction $k_{-1} imes 10^{-6} \text{ sec.}^{-1}$	$\frac{U \times 10^{-6}}{\text{mole litre}^{-1}}$	(ΔH) kcal. mole ⁻¹	forward direction kcal. mole ⁻¹
10	0.06312	0.99	1.57	1.16]		
15	0.06813	1.17	1.72	1.36		
20	0.07346	1.41	1.92	1.61		
25	0.07895	1.69	2.15	1.92 5	2.5	5.88
30	0.08467	1.92	2.31	2.18		
35	0.09051	2.31	2.55	2.63		
40	0.09663	2.69	2.79	2.93		

TABLE 2 - DATA FOR ETHYL FORMATE (AFTER TABUCHI⁴¹)

where K is the Boltzmann constant; h, the Planck's constant; ΔF_j , the activation energy; and k_j , the specific rate constant. The experimental activation energies are: nickel sulphate, 8.6; cobalt sulphate, 6.0; and magnesium sulphate, 6.5 kcal./mole. However, in the case of magnesium sulphate, Wilson³⁹ obtains a somewhat higher experimental value for the activation energy.

Eigen⁴⁰ has discussed the mechanism of high speed ion reactions on the basis of measurements of absorption of ultrasonic waves in solutions involving bimolecular reactions. The rate constant of the order 10^{10} - 10^{11} litre mole⁻¹ sec.⁻¹ expected for reactions involving H⁺ and (OH)⁻ ions has been observed experimentally in the case of aqueous solutions of ammonia and sulphuric acid indicating that these systems undergoing hydrolysis involve highly penetrating H⁺ and (OH)⁻ ions. The reaction equations

and

$$\mathrm{NH}_3 + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{NH}_4 + (\mathrm{OH})^-$$

$$\begin{split} \mathrm{H}_2\mathrm{SO}_4 - \mathrm{H}_2\mathrm{O} &\Rightarrow \mathrm{HSC}_4 + \mathrm{H}_3\mathrm{C} \\ \mathrm{HSO}_4^* \rightleftharpoons \mathrm{H}^+ + \mathrm{SC}_4^{2+} \end{split}$$

have been assumed for these systems on the basis of this argument.

Tabuchi⁴¹, considering Karpovich's⁴² rotational isomerism model about the C-O bond for liquid ethyl formate, has calculated the heat of reaction, the activation energy, the equilibrium constant and the rates of isomerization of ethyl formate from the measurements of dispersion of acoustic velocity. The calculated values are shown in Table 2.

Krishnamurthy and Surayanarayana⁴³⁻⁴⁵ have studied the reaction rates in aqueous solutions of magnesium acetate, calcium acetate, strontium acetate, sulphur dioxide and nitrogen peroxide undergoing hydrolysis and dissociation reactions using Tabuchi's theory. For acetates of calcium, magnesium and strontium a dissociation reaction of the type

$$M\Lambda_2 \rightarrow M\Lambda^+ + \Lambda^-$$

 $M\Lambda^+ \rightleftharpoons M^{2+} + \Lambda^-$

has been considered while in case of sulphur dioxide and nitrogen peroxide, hydrolysis processes

$$\begin{split} &\mathrm{SO}_2 + \mathrm{H}_2 \mathrm{O} \Rightarrow \mathrm{H}_2 \mathrm{SO}_3 \\ &\mathrm{H}_2 \mathrm{SO}_3 \rightleftharpoons \mathrm{H}^+ + \mathrm{H} \mathrm{SO}_3^- \end{split}$$

and

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

 $HNO_2 \Rightarrow H^+ + NC_3$

have been assumed. The calculated values of the specific rate constants and the partial molar volume change for these reactions in solutions of various concentrations are given in Table 3. It is seen from the results that Brönsted's relationship^{46,47}

$$\log_{10} k_{-1} \propto \mu^{1/2}$$

(where μ is the ionic strength of the solution) for the ionic reactions in solutions is observable in these cases indicating that the reaction is between two ions of opposite sign.

In the case of sulphur dioxide, however, Eigen $ct \ al.^{48}$ have considered a one-step hydrolysis reaction

$$SO_2 + H_2O_3 + H^+ + HSO_n$$

in which the total equilibrium adjustment of the reaction occurs within less than 10⁻⁶ sec. depending on H⁺ and HSO₃ concentrations. The specific rate constants on this basis are calculated to be $3\cdot4 \times 10^6$ sec.⁻¹ and 2×10^8 litre mole⁻¹ sec.⁻¹ in the forward and backward directions respectively at 20°C. for an ionic strength of 0·1 mole per litre – values close to those of Krishnamurthy and Suryanarayana.

Stucher *et al.*⁴⁹, attributing the relaxation absorption in the case of potassium cyanide solutions to a hydrolysis reaction of the type

$$KCN \rightarrow K^{+} \oplus CN^{-}$$

 $CN^{-} \oplus H_{*}O \rightleftharpoons HCN \oplus OH^{-}$

have calculated the partial molar volume change, specific rate constants and the energy of activation for the process using Eigen's theory. The values so obtained are given in Table 4.

We have studied⁵⁰⁻⁵² the free energy of activation, the equilibrium constant, the heat of reaction and the reaction rates for hydrolysis and dissociation reactions taking place in aqueous solutions of calcium acetate, lead acetate, zinc acetate, zinc sulphate and acetic acid using Freedman and Tabuchi theories. The reaction involved in zinc acetate solution is suggested to be the formation of an activated complex of the type

$(CH_3COO)_2Zn + H_2O \rightleftharpoons Zn(CH_3COO)_2.H_2O$

This complex dissociates with a rate constant k in the form

 $Zn(CH_3COO)_2$, $H_2O \rightarrow Zn^{2+} + 2(CH_3COO)^- + H^+ + OL^-$

Compound	Temp.	Conc.	Ionic	Sp. rate	Partial	
	ι.	litre-1	u mole litre-۱	Forward direction sec. ⁻¹	Backward direction litre mole ⁻¹ sec. ⁻¹	volume change cm. ³ mole ⁻¹
Magnesium acetate	29	0·30 0·25 0·20 0·15	0.53 0.46 0.38 0.30	$\begin{array}{c} 1 \cdot 20 \times 10^7 \\ 1 \cdot 36 \times 10^7 \\ 1 \cdot 52 \times 10^7 \\ 1 \cdot 73 \times 10^7 \end{array}$	$\begin{array}{c} 2{\cdot}04\times10^8\\ 2{\cdot}30\times10^8\\ 2{\cdot}58\times10^8\\ 2{\cdot}95\times10^8\\ \end{array}$	-1.6 -1.6 -1.7 -1.8
Calcium acetate	29	0·30 0·25 0·20 0·15	0.52 0.45 0.38 0.30	$\begin{array}{c} 0.90 \times 10^7 \\ 0.99 \times 10^7 \\ 1.11 \times 10^7 \\ 1.27 \times 10^7 \end{array}$	$\begin{array}{c} 1\!\cdot\!61\!\times\!10^8 \\ 1\!\cdot\!77\!\times\!10^8 \\ 2\!\cdot\!98\!\times\!10^8 \\ 2\!\cdot\!27\!\times\!10^8 \end{array}$	6·6 6·5 6·3 6·8
Strontium acetate	29	0-30 0-25 0-20 0-15	0.55 0.48 0.40 0.31	$\begin{array}{c} 0.96 \times 10^7 \\ 1.06 \times 10^7 \\ 1.18 \times 10^7 \\ 1.35 \times 10^7 \end{array}$	$\begin{array}{c} 1\!\cdot\!41\!\times\!10^8 \\ 1\!\cdot\!55\!\times\!10^8 \\ 1\!\cdot\!74\!\times\!10^8 \\ 1\!\cdot\!99\!\times\!10^8 \end{array}$	5·4 5·7 5·5 6·5
Sulphorous acid	28	0·100 0·050 0·025 0·0125	0·38 0·024 0·015 0·009	$\begin{array}{c} 8{\cdot}31\times10^6\\ 10{\cdot}56\times10^6\\ 11{\cdot}35\times10^6\\ 11{\cdot}47\times16^6\end{array}$	$\begin{array}{c} 5{\cdot}10\times10^8 \\ 6{\cdot}48\times10^8 \\ 6{\cdot}97\times10^8 \\ 7{\cdot}04\times10^8 \end{array}$	76 60 60 65
Nitrous acid	28	0·05 0·03 0·01 0·0025	0.056 0.034 0.012 0.004	$\begin{array}{c} 9{\cdot}55\times10^5 \\ 12{\cdot}00\times10^5 \\ 19{\cdot}00\times10^5 \\ 25{\cdot}60\times10^5 \end{array}$	$\begin{array}{c}1{\cdot}91\times10^9\\2{\cdot}40\times10^9\\3{\cdot}79\times10^9\\5{\cdot}02\times10^9\end{array}$	39 (mean value)

TABLE 3 DATA FOR AQUEOUS SOLUTIONS OF MAGNESIUM ACETATE, CALCIUM ACETATE, STRONTIUM ACETATE, SULPHUR DIOXIDE AND NITROGEN PEROXIDE AT VARIOUS CONCENTRATIONS (AFTER KRISHNAMURTHY AND SURVANARAYANA⁴³⁻⁴⁵)

TABLE 4 — DATA FOR THE HYDROLYSIS REACTION OF POTASSIUM CVANIDE AT 25°C. (AFTER STUEHER $ct~al.^{49}$)

Conc.	Partial	Activation	Sp. rate constants			
mole litre ⁻¹	molar volume change cm. ³ mole ⁻¹	the process HCN \pm OH ⁺ \rightarrow H ₂ O \pm CN \pm kcal. mole ⁻¹	Forward direction sec. ⁻¹	Backward direction litre mole ⁻¹ sec. ⁻¹		
$\left. \begin{smallmatrix} 0\cdot01\\ 0\cdot05 \end{smallmatrix} \right\}$	12.4	6 + 2	$\begin{cases} 5\cdot3 \times 10^4 \\ 5\cdot0 \times 10^4 \end{cases}$	$\begin{array}{c} 3{\cdot}8\times16^9\\ 3{\cdot}6\times10^9\end{array}$		

TABLE 5 DATA FOR THE ACTIVATION REACTIONS IN AQUEOUS SOLUTIONS OF ZINC ACETATE AND ACETIC ACID (AFTER PANCHOLY AND SINGAL^{50–52})

Electrolyte	Temp. K.	Conc. mole litre ¹	Free activation energy keal. mole ⁻¹	Rate constant in the forward direction $k_1 \times 10^{-7}$ sec. ⁻¹
Zine acetate	293 298 303 308 318	0.1	4-4	$\begin{cases} 3.48 \\ 3.76 \\ 4.40 \\ 5.12 \\ 6.61 \end{cases}$
Acetic acid	293 298 303 } 308 318	5.25	5.2	$\begin{cases} 2 \cdot 26 \\ 2 \cdot 63 \\ 3 \cdot 05 \\ 3 \cdot 52 \\ 4 \cdot 81 \end{cases}$

For acetic acid the view that a monomer-dimer reaction

$2(CH_{3}COOH) \rightleftharpoons (CH_{3}COOH)_{2}$

is responsible for relaxational absorption is supported. For zinc sulphate a one-step dissociation reaction

$ZnSO_4 \rightleftharpoons Zn^{2+} + SO_4^{2-}$

is considered and for aqueous solutions of calcium acetate and lead acetate a reaction scheme of the type

$$M\Lambda_2 \rightarrow M\Lambda^+ + \Lambda^- M\Lambda^+ \rightleftharpoons M^{2+} + \Lambda^-$$

is assumed to cause the excess acoustic absorption. The calculated values of the physico-chemical constants and the reaction rates are given in Tables 5 and 6. It is seen that the values of these constants as obtained from other sources agree reasonably with the present values.

Valleau and Turner⁵³ have studied volume changes, stoichiometric quotients, activation energy and rate constants of the chloride complexes of cadmium by taking measurements of ultrasonic absorption and velocity between 13 and 143 mc/s. at 16°, 25° and 35°C. of 0-25*M* aqueous solutions of cadmium ions containing various amounts of hydrochloric acid, using Valleau's extension²⁹ of Eigen-Tamm theory.

In the cadmium-chloride system there occur the following four association reactions:

$Cd^{2+}+Cl^{-} \rightleftharpoons CdCl^{+}$	(w)
$CdCl^+ + Cl^- \rightleftharpoons CdCl_2$	(x)
$CdCl_2 + Cl^- \rightleftharpoons CdCl_3^-$	(y)
$CdCl_{3}^{*}$: $Cl_{2}^{*} \Rightarrow CdCl_{4}^{2^{*}}$	(.:)

Electrolyte	Conc.	Temp.	Activation energy		Heat of	Disso-		Rate constants			
	litre ⁻¹	tre ⁻¹	Forward	Reverse	(ΔH)	constant	Freedman theory		Tabuchi theory		
			kcal. mole ⁻¹	kcal. mole ⁻¹	KCal, mole		Gross reaction rate $U \times 10^{-7}$ litre mole ⁻¹ sec. ⁻¹	Forward reaction rate $k_1 \times 10^{-8}$ sec. ⁻¹	Forward reaction rate $k_1 \times 10^{-7}$ sec. ⁻¹	Back- ward reaction rate $k_{-1} \times 10^{-8}$ litre mole ⁻¹ sec. ⁻¹	
Calcium acetate	1.0		-2.0	4.9	-6.9	$ \begin{cases} 0.217 \\ 0.123 \\ 0.073 \end{cases} $	0·83 0·65 0·48	5·69 4·11 2·86	1·92 1·66 1·41	0·89 1·35 1·94	
Lead acetate	1.0	$20 \\ 35 \\ 50 \end{bmatrix}$	-2.3	3.8	-6.1	$ \begin{cases} 0.215 \\ 0.129 \\ 0.081 \end{cases} $	0·97 0·72 0·54	6·60 4·70 3·30	2·40 2·00 1·67	1·11 1·54 2·05	
Zinc sulphate	1.0	$20\\35\\50$	-3·2	8.4	-11.6	$\begin{cases} 0.005 \\ 0.002 \\ 0.001 \end{cases}$	0·24 0·17 0·11	1·43 0·97 0·66	0·47 0·38 0·28	9·19 19·66 35·32	

Table 6 — Data for Dissociation Reaction in Aqueous Solutions of Calcium Acetate, Lead Acetate and Zinc Sulphate (after Pancholy and Singal⁵⁰⁻⁵²)

TABLE 7 — DERIVED VALUES OF THE RATE CONSTANTS FOR THE CADMIUM CHLORIDE REACTION y AT SELECTED LIGAND CONCENTRATIONS OF THE CHLORIDE ION (AFTER VALLEAU AND TURKER⁵⁰)

Molar conc. g. mol. litre ⁻¹	Dissoc rat litre	te $(k_y \times 10^{\circ})$ te mole ⁻¹ s	action ⁻⁸) ec. ⁻¹	Recom rat	bination the $(k_{-y} \times 1)$ sec. ⁻¹	reaction 0 ⁻⁸)
	15·9°C.	24.7°€.	35·1°C.	15•9°C.	24.7°C.	35·1°C.
1.59	0.87	1.1	1.4	1.6	2.0	2.1
1.98	0.96	1.2	1.5	1.5	1.8	1.9
2.34	1.0	1.3	1.5	1.3	1.5	1.6
2.69	1.1	1.3	1.6	1.1	1.2	1.4
3.03	1.1	1.3	1.6	0.92	1.0	1.2
3.35	1.1	1.3	1.7	0.78	0.83	1.0

The observed relaxation has been interpreted in terms of the interacting association reactions y and z. The derived values of the rate constants, stoichiometric quotients and volume changes for the association reactions y and z are given in Tables 7 and 8. The uncertainty of accuracy is estimated to be 15 per cent in the case of k_y or k_{-x} ; 50 per cent in the case of k_z or k_{-z} ; 40 per cent in the case of stoichiometric quotients and 5 per cent in the case of the temperature variations in the derived values of the ΔV 's, k_z and k_{-x} are not significant.

The activation energy for the dissociation reaction y determined from Arrhenius' plot is found to be $2\cdot3\pm0.5$ kcal. per mole and the activation energy of the association reaction y from here is obtained as $4\cdot5$ kcal./mole.

Conclusions and Future Trends

The above review of the chemical kinetics by ultrasonic techniques suggests that Freedman's theory, though approximate as it assumes negligible volume change for the reversible equilibrium TABLE 8 — DERIVED VALUES OF THE RATE CONSTANTS AND STOICHIOMETRIC QUOTIENTS FOR THE CADMIUM CHLORIDE REACTION (z) AND OF THE VOLUME CHANGES FOR THE REACTIONS y AND z (AFTER VALLEAU AND TURNER⁸³)

Temp °C. v	b. Disso- ciation reaction rate $(k_z \times 10^{-9})$ litre mole ⁻¹ sec. ⁻¹	Recombi- nation reaction rate $(k-z \times 10^{-9})$ sec. ⁻¹	Stoichio- metric quotient (Qz) litre mole ⁻¹	Volume change for the y-reaction (ΔV_y) ml. mole ⁻¹	Volume change for the z-reaction (ΔV_z) ml. mole ⁻¹
15.9	5.0	10.0	0.5	3.8	-38
24.7	4.0	8.0	0.55	2.8	-35
35.1	6.0	10.0	0.6	5.8	-42
			Mea	n = 4.1	-38

process, is useful inasmuch as it does not require prior knowledge of the physico-chemical constants of the reaction. It can be used to derive the values of certain physico-chemical constants under the limited conditions. Tabuchi's theory, on the other hand, is very thorough and involves functions which can be used to examine the actual physical conditions of the reversible process. In the case of Eigen-Tamm theory it is seen that it is an approach altogether different in outlook from Freedman and Tabuchi, and involves easily measurable physical properties of the liquid or the solution and at the same time is very thorough. Valleau's theory is a further extension of Eigen-Tamm theory.

A preliminary study has also been made to explore the possibility of extending the ultrasonic relaxation technique to measurement of reaction rates in cases where half period of the reaction is more than 10^{-4} sec. This study is particularly difficult because in the low frequency range the acoustic absorption is generally far too low to permit adequate accuracy in laboratory measurements. The method suggested for this study is the pressure step function technique⁵⁴⁻⁵⁶. According to this technique the system under investigation is exposed to a pressure step and a property of the system like electrical conductivity is measured. This method may bridge the gap between the conventional techniques for the measurement of chemical kinetics data and ultrasonic relaxation technique used for fast reactions. It is also of interest to recall in this context that explosive reactions⁵⁷ occurring in gasoline engines have been analysed by ultrasonic pulses propagated through the combustion chamber.

Summary

The various developments relating to the concept of relaxation phenomenon as applicable to the observed excess absorption of acoustic waves in fluids in general and chemically reactive media in particular have been reviewed. The use of ultrasonic relaxation technique to study reaction kinetics in the case of chemically reactive media is discussed.

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Occurrence of Acetylene Compounds in Medicinal Plants*

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TP to about twenty years ago acetylene compounds were considered to be accessible by synthesis only, except tariric acid, an isomer of stearolic acid, which had been found to occur in nature in 1892 by Arnaud¹. This acid remained for a long time a single observation. Then, in 1933, carlina oxide which at the beginning of this century had been isolated from the silver thistle by Semmler² was recognized as acetylene derivative³. Another substance occurring in nature and containing an acetylene bond was discovered in 1935 by Russian scientists⁴ in the essential oil of the composite plant, Lachnophyllum gossypinum. This finding, quite unusual at that time, remained unconfirmed, until in 1941 Sörensen and Stene⁵ found also in the essential oil of the odourless camomile (Matricaria inodora) the methyl ester of an alkyne carboxylic acid. The results of plant chemistry of the following years, particularly since 1950, led to the surprising realization that acetylene compounds occur in plants more frequently. In the meantime more than 150 acetylene compounds have been isolated^{6,7} and undoubtedly the number of these compounds will increase. Up to now only a fraction of higher and lower plant families has been searched for from this viewpoint. The reason that the discovery of natural acetylenes took place so late may be attributed to the fact that these compounds are frequently present in plants in small concentrations only. For their isolation lengthy work-up procedures are necessary which become even more difficult in so far as frequently several chemically similar compounds occur simultaneously. Separation of all these compounds becomes possible only through careful chromatography or counter-current distribution.

Furthermore, purification is rendered more difficult by the partially poor ability of the acetylene compounds to crystallize and their great tendency to polymerize. The latter is catalysed by light and takes place faster in the solid state than in solution.

Ultraviolet spectra of these compounds are very characteristic and are of importance for proof and elucidation of structure. The spectra of polyynes and en-polyynes are marked by several sharp maxima and may be differentiated from the absorption curves of polyenes by the determination of band distances. The wavenumber difference of polyenes amounts to about 1500 cm.⁻¹, while that of the polyynes and en-polyynes is approximately 2000 cm.⁻¹. The evaluation of the ultraviolet spectra generally permits to recognize the chromophoric system of polyynes so that often an oxidative degradation of the substance can be avoided. The infrared spectra permit identification of functional groups, allene and vinyl structures as well as *cis*- and *trans*-configurations of the ethylene bond. Studies of nuclear magnetic resonance spectra may be envisaged as an important tool for the elucidation of the structure of acetylene compounds.

Partial or complete hydrogenation and identification by gas chromatography of the products obtained have also been used with advantage. However, the final proof of the structure can only be provided by synthesis.

Of the acetylene compounds found so far, more than one half were found in higher plants (Angiospermae). They belong largely to the family Compositae. Other plant families in which acetylene compounds have been found are given in Table 1.

A minor group of acetylene compounds also occurs in the seed-fat of some tropical trees. They are some C_{18} acids which are esterified with glycerol and occur in amounts up to 80 per cent in the oils. Some of these acids are given in Table 2.

A third group of natural acetylene compounds was found in culture fluids of lower plants. Their discovery was made during the systematic search for antibiotically active substances.

In the present report not all the acetylene compounds found in nature are discussed but only such cases are included which are of pharmaceutical interest (Table 3).

A drug previously often employed in European medical practice is *Rhizoma graminis*. The drug contains approximately 0.05-0.06 per cent of an essential oil of a characteristical somewhat sweet odour. From this oil Treibs¹⁷ was able to isolate a strongly unsaturated compound which he described as agropyrene. This compound was at first assigned the structure of a 1-phenyl-2-hexene-4-yne. However, the synthetic compound possesses different properties than the natural substance. Finally, in

 TABLE 1
 PLANT FAMILIES IN WHICH ACETYLENE

 COMPOUNDS HAVE BEEN FOUND TO OCCUR

Family	Approx. No. of species containing alkynes	Family	Approx. No. of species containing alkynes
Compositae	500	Euphorbiaceae	1
Valerianaceae	1	Simarubaceae	3
Labiatae	No. un-	Papilionaceae	1
	known	Lauraceae	1
Verbenaceae	No. un-	Loranthaceae	No. un-
	known		known
mbelliferae	20	Santalaceae	3
Araliaceae	1	Olacaceae	3
Diniaceae	i	Gramineae	2

^{*}Paper presented at the 15th Congress of the Indian Pharmaceutical Society held at Pilani, December 1963.

I ABLE 2	ACETYLENE (ARBOXYLIC	ACIDS	ISOLATED	FROM	THE	SEED-FAT	OF !	SOME	ROPICAL	TREES	

Compound	Structure	Investigators
Tariric acid	$H_{3}C - (CH_{2})_{10} = C = (CH_{2})_{4} - COOH$	A. Arnaud ¹
Nimenynic acid (santalbic acid)	$H_3C - (CH_2)_5 - CH - CH - C - (CH_2)_7 - COOH$	S. P. Ligthelm and H. M. Schwartz ⁸
8-Hydroxyximenynic acid	$\Pi_3 C - (C\Pi_2)_5 CH - CH C = C - CH - (CH_2)_7 - COOH$	S. P. Ligthelm ⁹
	OH	
Isanic acid (erythrogenic acid)	$H_2C - CH - (CH_2)_4 - C - C - C - (CH_2)_7 - COOH$	A. Steger and J. van Loon ¹⁰ A. Castille ¹¹
Isanolic acid	$H_3C - (CH_2)_2$ $CH = CH - C$ $C - C$ $C - CH_2 - CH - (CH_2)_6 - COOH$ OH	H. P. Kaufmann <i>et al.</i> ¹² A. Seher ¹³
Bolecic acid	$H_{a}C = CH + (CH_{a})_{a} - CH = CH - (C + C)_{a} - (CH_{a})_{a} - COOH$	E M. Meade ¹⁴
Dihydrobolecic acid	$H_3C - (CH_2)_3 - CH = CH - (C = C)_2 - (CH_2)_2 - COOH$	H. H. Hatt et al.15
Goric acid	$H_2^{-}C = CH - (CH_2)_2 - CH = CH - (C - C)_2 - CH - (CH_2)_6 - COOH$	H. P. Kaufmann <i>et al.</i> ¹²
Octadeca-trans-11, trans-13-dien-9-ynoic acid	$H_3C - (CH_2)_3 - CH - CH - CH - CH - Cc = C - (CH_2)_7 - COOH$	H. H. Hatt et al. ¹⁶

TABLE 3	Naturally Occurring Acetyl of Pharmaceutical Valui	ene Compounds
Compound	Structure	Investigators
1-Phenyl- 2-hexene- 4-yne	C ₆ H ₅ .CH ₂ .CH: CH.C ; C.CH ₃	W. Treibs ¹⁷
Agropyrene (capillen)	$C_6H_5.CH_2.C \stackrel{\circ}{\underset{\circ}{\leftarrow}} C - C \stackrel{\circ}{\underset{\circ}{\leftarrow}} C.CH_3$	J. Cymerman- Craig et al. ¹⁸ R. Harada ¹⁹
Capillin	C ₆ H ₅ .C.C∃C C∃C.CH ₃ ∥ O	K. Imai ²⁰

1959, in a joint investigation by Cymerman-Craig et al.¹⁸ the structure of a 1-phenyl-2,4-hexadiyne was established by synthesis as that of agropyrene. This hydrocarbon was found to be identical with 'capillen' isolated from Artemisia capillaris by Arima and Okamoto²¹ in 1930. The structure of 'capillen' has been established in 1954 by Harada¹⁹. In the presence of atmospheric oxygen, capillen is converted by autoxidation and light to 1-phenyl-2,4-hexadiyne-1-one, the latter being also isolated from Artemisia capillaris and called capillin by Imai²⁰. Capillin is marked by an intense fungicidal action but it is too toxic to find a therapeutical application.

Phenylhexenyne has been found by Russian scientists in *Artemisia scoparia*. 1-Phenyl-2,4-hexadiyne-1-ol was discovered as acetate (I) in *Chrysanthemum frutescens* by Bohlmann and Kleine²² in 1962.

Phenylpentadiyne (II) could be identified as a constituent occurring along with capillen. Also, the corresponding ketone (III) occurs in a Chrysanthemum species. Furthermore, Japanese²³ discovered capillarin (IV), an alkynyl derivative of coumarin, in *Artemisia capillaris*.

Homologues of agropyrene were found by Sörensen and Sörensen²⁴ in Coreopsis species, for instance, a 1-phenylheptadiyne and a 1-phenylheptatriyne aside from aliphatic C_{13} -yne hydrocarbons.





For carlina oxide isolated from the essential oil of carline thistle (Eberwurz) (*Carlina acaulis*) by Semmler² 70 years ago, an allene structure (V) was first of all postulated. This, however, could not be proved by synthesis. Only later investigations by Gilman *et al.*³ led to the correct structure of 1-phenyl-3-furyl-2-propyne (VI). The synthesis of the latter was carried out via various ways by Pfau *et al.*²⁵ in 1935 as well as by Paul²⁶ in 1936.

In another Carlina species (*Carlina vulgaris*) occurring in Norway, Sörensen and Sörensen²⁷ discovered a C₁₃-en-triynediene alcohol as acetate.

Shatteböl and Sörensen²⁸ succeeded in cyclysing in vitro the terminal dienyne structure to a phenyl ring. The question remains open whether this conversion of an unsaturated aliphatic compound into an aromatic one takes place in the cell as well. This conversion is discussed in the biochemistry for shikimic and prephenic acids.

Jones *et al.*²⁹ could prepare an isocarlina oxide from phenylendiynol. One should expect that carlina oxide should be accessible from isocarlina oxide via an intermediate having allene structure.



Chart 1 --- Schemes for the synthesis of carlina oxide: (A) synthesis due to Pfau et al.25; and (B) Paul's synthesis

It is also an open problem whether the synthesis of the furan ring proceeds in a manner indicated above.

Other furyl alkynes have been isolated too, e.g. 1-(2'-furyl)-1,7-nonadiene-3,5-diyne³⁰ (VII) and 1-dihydrofuryl-1-nonene-3,5,7-triyne³¹ (VIII).

Schmidt-Thomé³² was able to show that the root extract of Eberwurz possesses a vigorous bacteriostatic action on gram-positive bacteria and that carlina oxide alone is associated with the antibiotic properties. In the animal experiments, however, carlina oxide proved to be too toxic, a property which it has in common with many of the alkyne compounds found.

Thus, the toxic principles of *Cicuta virosa*, *Oenanthe* crocata and *Aethusa cynapium* were recognized, their structures clarified (Table 4) and the synthesis carried out by Lythgoe and coworkers^{33,36} as well as by Bohlmann and Viehe³⁷.

VII

Atractylodin

$$CH = CH - (C \equiv C)_3 - CH_3$$

In Scandinavian countries Matricaria inodora is used in popular medicine in a manner similar to Matricaria chamomilla in Middle Europe. Sörensen and Stene⁵ who investigated in 1941 this plant for its contents of matricaria camphor found the matricaria ester (Table 5). As mentioned earlier, Russian chemists⁴ previously had discovered the lachnophyllum ester in the essential oil of Lachnophyllum gossypinum. Both the structure of matricaria ester as well as that of lachnophyllum ester have been firmly established by synthesis; most of the time they occur jointly in Compositae. This is also true of stereoisomers, like cis-trans matricaria ester and cis-trans lachnophyllum ester. The latter was also found in roots of Bellis perennis by Holme and Sörensen⁵³. Their occurrence in 40 other species of Compositae which are perhaps of less pharmaceutical interest has been proved.

Also cis-dehydromatricaria ester was found in Artemisia vulgaris³⁹, and trans-dehydromatricaria ester in the root of Matricaria inodora⁴². Both substances occur also in Achillea millefolium⁵⁴. Cis-dihydromatricaria ester was isolated, among several plants, from Solidago sempervirens⁴⁰, and dehydromatricaria acid isobutylamide from Achillea plarmica⁵⁴ (Table 5).

Closely related to the C_{10} esters is the C_{10} alcohol, matriciarianol, which has been isolated from some Compositae in which it is present as ester.

A primary C_{10} alcohol containing 3 acetylene and 1 ethylene bonds and corresponding to dehydromatricaria ester occurs in various Matricaria species like *Matricaria chamomilla*, according to Christensen¹⁶.

TABLE 4 — TOXIC PRINCIPLES ISOLATED FROM Cicuta virosa, Ocnanthe crocata^{26,27} AND Acthusa cynapium

 $\begin{array}{ccc} Compound & Structure \\ \hline Cicutoxin† & HOCH_2 - [CH_2)_2 - [C = C)_2 - (CH = CH)_3 - *CH(OH) - C_3H_7 \\ \hline Cicutol† & HOCH_2 - (CH_2)_2 - (C : C)_2 - (CH = CH)_3 - C_4H_8 \\ \hline Oenanthotoxin† & HOCH_2 - CH = CH - (C = C)_2 - (CH = CH)_2 - (CH_2)_2 - *CH(OH) - C_3H_7 \\ \hline Oenanthotoxin† & HOCH_2 - CH = CH - (C = C)_2 - (CH = CH)_2 - (CH_2)_2 - *CH(OH) - C_3H_7 \\ \hline Oenanthoton† & HOCH_2 - CH = CH - (C = C)_2 - (CH = CH)_2 - (CH_2)_2 - CO - C_3H_7 \\ \hline Oenanthoton† & HOCH_2 - CH = CH - (C = C)_2 - (CH = CH)_2 - CO - C_3H_7 \\ \hline Aethusint † & H_3C - CH = CH - (C = C)_2 - (CH = CH)_2 - C_3H_8 \\ \hline Aethusanol A‡ & H_3C - CH = CH - (C = C)_2 - (CH = CH) - C_3H_7 \\ \hline Aethusin epoxide‡ & HOCH_2 - CH = CH - (C = C)_2 - CH = CH - CH - CH - C_3H_5 \\ \hline O \\ \hline Aethusanol B epoxide‡ & HOCH_2 - CH = CH - (C = C)_2 - CH = CH - CH - CH - C_2H_5 \\ \hline O \\ \hline O \\ \hline \end{array}$

*Asymmetric carbon atom. ⁺B. Lythgoe et al.^{33,34}. ⁺F. Bohlmann et al.³⁵.

Compound	Structure	Investigators
Matricaria ester	$CH_3 - CH = CH - C = C - C = C - CH = CH - COOCH_3$	N. A. Sörensen and J. Stene ⁵
Lachnophyllum ester cis-Dehydromatricaria	$\begin{array}{c} CH_{3}-CH_{2}^{e.e.}CH_{2}-C \cong C-C \cong C-CH \cong CH = CH-COOCH_{3}\\ CH_{3}-(C \cong C)_{3}-CH = CH-COOCH_{3}\\ eis\end{array}$	W. W. Wiljams et al. ⁴ N. A. Sörensen et al. ^{38,39}
cis-Dihydromatricaria	$CH_3 - CH = CH - (C \equiv C)_2 - CH_2 - CH_2 - COOCH_3$	N. A. Sörensen et al.40
Dehydromatricaria acid isobutylamide	$CH_{a} - (C = C)_{a} - CH = CH - C - NH - CH_{2} - CH(CH_{a})_{2}$	F. Bohlmann and H. Jastrow ⁴¹
Matricarianol	$H_3C-CH=CH-(C=C)_2-CH=CH-CH_2OH$	N. A. Sörensen et al.27,42-45
cis-Dehydromatricarianol	$H_3C - (C \equiv C)_3 - CH = CH - CH_2OH$	P. K. Christensen ⁴⁶
Chamomilla ester	$H_{3}C - (C = C)_{2} - (CH = CH)_{3} - CH_{2} - CH_{2} - O - C - CH_{3}$ <i>trans</i>	F. Bohlmann et al.47
Artemisia ketone	$H_{3}C - (C \equiv C)_{3} - CH = CH - CH_{2} - CH_{2} - C-C_{2}H_{5}$	K. Stavholt & N. A. Sörensen ³⁹ F. Bohlmann <i>et al</i> ^{48,49}
Falcarinone	$n - C_{7}H_{15} - CH = CH - CH_{2} - (C = C)_{2} - C - CH = CH_{2}$	F. Bohlmann et al. ⁵⁰
Dehydrofalcarinone	$CH_2 = CH - (CH_2)_5 - CH = CH - CH_2 - (C \equiv C)_2 - C - CH = CH_2$	F. Bohlmann et al. ⁵¹
Falcarinolone	$n - C_{7}H_{15} - CH = CH - CH - (C = C)_{2} - C - CH = CH_{2}$	F. Bohlmann et al. ⁵⁰
Falcarindione	$n - C_7 H_{15} - C H = C H - C - (C = C)_2 - C - C H = C H_2$	F. Bohlmann et al. ⁵⁰
Pontica epoxide	$CH_3 - (C = C)_3 - CH = CH - CH - CH - CH = CH_2$	F. Bohlmann et al.52
Cota epoxide	$CH_3 - (C \equiv C)_3 - CH - CH - CH = CH - CH = CH_2$	F. Bohlmann et al. ⁵¹
· ·	\sim	

TABLE 5 — SOME ACETYLENIC COMPOUNDS ISOLATED FROM MATRICARIA, LACHNOPHYLLUM AND SOME OTHER SPECIES

In 1960 Bohlmann *et al.*⁴⁷ were able to isolate the acetic acid ester of tridecatrienediynol in small amounts from *Matricaria chamomilla*. For the new compound they proposed the name chamomilla ester. The ethylene bonds are present as *trans*-configuration, while the alcohol isolated by Christen-sen⁴⁶ contains a *cis*-ethylene bond. The constitution was proved by synthesis.

Aside from *cis*-dehydromatricaria ester, a C_{14} entriyne-ketone, artemisia ketone (Table 5), was found in *Artemisia vulgaris*³⁹. Also in some other Umbelliferae, ketones of this type occur, for instance, falcarinolone and falcarindione in the root of *Carum carvi*³¹.

There were also found epoxides as, for example, pontica epoxide, a C_{13} -dientriyne epoxide, in Artemisia pontica⁵². Another C_{13} -epoxide, cota epoxide, occurs in the roots of Anthemis cota; it has the epoxide ring on C_{5-6} . Just recently, Bohlmann et al.⁵² discovered enolether polypnes (IX-XI) consisting of five and six rings in the common camomile (Matricaria chamomilla) and Tanacetum vulgare as well as in various other Chrysanthemum and Artemisia species.

During the search for antibiotic substances present in culture fluids of microorganisms and lower plants compounds of acetylene structure were also encountered. Of the more than 50 isolated substances, a few examples are given in Table 6.



Suzuki et al.⁶¹ isolated acetylenedicarboxylic acid amide from the culture fluid of *Streptomyces chibeansis* and called it cellocidin. The substance retards effectively the growth of *Mycobacterium tuberculosis*. Noteworthy with this substance is its cytostatic effect on NF-mice sarcoma *in vitro* at a concentration of 5 mg. per cent.

tion of 5 mg. per cent. Mycomycin^{55,62}, a C_{13} acid containing 2 acetylene and 4 ethylene bonds of which 2 are accumulated, is unstable at room temperature and decomposes explosively at 75°. Upon treatment with alkali it undergoes rearrangement to isomycomycin which contains 3 acetylene and 2 ethylene bonds in conjugation. This means that allene-acetylene rearrangement has taken place which is accompanied by a simultaneous decrease of antibiotic activity toward *Mycobacterium tuberculosis*.

From culture fluids of various Basidiomycetes a mixture containing acetylenes having antibiotic activity was isolated which could be characterized by Bu'Lock *et al.*⁵⁶ (Table 6). The mixture consists of an unsaturated C_{11} acid, nemotinic acid, the corresponding lactone nemotin, and the unsaturated C_{12} acid, odyssic acid and its corresponding lactone odyssin. These 4 substances contain likewise the allene bond aside from acetylene and ethylene bonds. Like mycomycin they are unstable and optically active. According to Bu'Lock and Gregory⁶³, nemotinic acid is present as glycoside.

From culture fluids of fungus *Polyporus anthraco-philus* seventeen C_{10} acetylene compounds were isolated by Bu'Lock *et al.*⁵⁷. Of these compounds 13 were structurally elucidated. They are partially identical or similar in structure with compounds isolated from Compositae.

The antibiotics isolated from the culture fluid of Agrocybe dura are derived from a C_8 acid. Bu'Lock and coworkers⁵⁸ proved for agrocybin the structure of an amide of 8-hydroxy-2,4,6-octatriynoic acid which was also synthesized. Anchel⁶⁰ isolated from culture fluids of *Clitocybe diatreta* two acetylene compounds, namely diatretyne I and diatretyne II.

Diatretyne I is the semiamide of a dicarboxylic acid. Diatretyne II bears a nitrile group instead of an amide group. Both substances were synthesized. Only Diatretyne II possesses antibiotic activity.

These examples may suffice to show the multiplicity of polyacetylenes occurring in nature. Not only hydrocarbons of different degree of saturation have been found but also those with aromatic or heterocyclic substituents, like polyacetylenes carrying various functional groups.

For some time we have been investigating medicinal plants whose constituents being responsible for the pharmacological action are still unknown. To these plants belongs *Arnica montana*, a classical medicinal plant, which frequently has been the subject of investigations.

Through pharmacological investigations by Forst and Naunyn-Schmiedebergs⁶⁴ a strong effect on heart and circulation in rabbits and cats was found upon parenteral application of aqueous and alcoholic extracts of the flowers of *A. montana*. This effect cannot solely be caused by choline which occurs in dry flowers to the extent of about 0.1 per cent. According to Forst, the drug must still contain two more unknown substances which influence the circulation. One of them has a toxic effect on the heart and can be extracted with petroleum ether. The other compound is very unstable and exercises a marked blood pressure increasing action.

TABLE 6 A	NTIBIOTIC SUBSTANCES ISOLATED FROM THE CULTURE FLUIDS OF MICH	ROORGANISMS
Compound isolated	Structure	Investigators
	FROM CULTURE FLUIDS OF Streptomyces chibeansis	
Mycomycin Isomycomycin	$\begin{array}{llllllllllllllllllllllllllllllllllll$	W. D. Celmer and I. A. Solomons ⁵⁵
F	ROM CULTURE FLUIDS OF VARIOUS VARIETIES OF BASIDIOMYCETES	
Nemotinic acid Nemotin	$\begin{array}{c} HC C-C C-CH = C = CH - CH(OH) - CH_2 - CH_2 - COOH \\ HC C-C = C - CH = C = CH - CH - CH_2 - CH_2 \\ \end{array}$	J. D. Bu'Lock <i>et al.</i> ⁵⁶
Odyssic acid Odyssin	$\begin{array}{c} (\dot{O} \dot{C} = O \\ H_{3}C - (C - C)_{2} - CH = C = CH - CH(OH) - CH_{2} - CH_{2} \\ H_{3}C - (C - C)_{2} - CH = C = CH - CH - CH_{2} - CH_{2} \\ \dot{C} \dot{C}O \end{array} $ COOH	
	FROM CULTURE FLUIDS OF Polyporus anthracophilus	
	$\begin{array}{l} HOOC-CH=CH-C C-CC-CH=CH-COOH\\ trans\\ H_3C-CH=CH-CC-C-C-C-CH=CH-COOH\\ H_3C-CH=CH-CC-C-C-CH=CH-CH_2OH\\ H_3C-CH=CH-CC-C-C-CH=CH-CH_2OH\\ HOOC-CH=CH-CC-C-C-CH=CH_2-COH\\ HOOCH_2-CH_2-CH_2-CC-C-C-C-CH=CH-COOH\\ \end{array}$	J. D. Bu'Lock <i>et al.</i> ⁵⁷
	FROM CULTURE FLUIDS OF Agrocybe dura	
Agrocybin	$HOCH_2 - C = C - C - C - C - CONH_2$	J. D. Bu'Lock <i>et al.</i> 58
	FROM CULTURE FLUIDS OF Clitocybe diatreta	
Diatretyne I Diatretyne II	$HOOC-CH=CH-C-C-C-C-CONH_{2}$ $HOOC-CH=CH-C-C-C-C-N$	M. Anchel ⁵⁹ M. Anchel ⁶⁰

Nothing is known about the chemical properties of these substances, except for the presumption supported by different observers that they seem to be very unstable.

We have investigated this drug once more and focused our attention at first on the root^{65–67}. By extraction of air-dry Arnica roots with petroleum ether or pentane (excluding light and oxygen as far as possible), an extract has been obtained which on chromatography yields a mixture of polyacetylenes in an amount of 0-2 per cent of the petroleum ether extract. Kepetition of the chromatographic procedure using pentane-benzene mixtures on alumina six different polyacetylenes have been separated; probably two more are present. Maintaining an atmosphere of nitrogen and a careful application of the chromatographic procedure are prerequisites for success.

For comparison, fresh roots of *Arnica foliosa* and *Arnica longifolia* were treated in the same manner. However, only a few plants of this material were at our disposal. As can be seen from Table 7, the polyynes found in the three Arnica species are not the same in every case.

The structure of the 4100-compound which represents the larger part of the mixture could be elucidated relatively fast (Fig. 1A). The compound is a C_{13} hydrocarbon, tri-1-decen-3,5,7,9,11-pentayne.

ADDE 7	- POLVACETVLENES	AND CHROMOPHORES	OCCURRING IN	Arnica montana,	.1. foliosa AND .	1. longifolia
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λmax.	Compound	0	ccurrence in,	0,7 70
AE		.1. montana	.4. foliosa	.1. longifolia
4100	$CH_a - (C C)_5 - CH - CH_2$	3.6	-	+
3905	$CH_2 - CH = CH - (C - C)_1 - CH = CH_2$.<0.3	- [-]	+
4020	$CH_{2} - (C - C)_{5} - CO - CH_{3}$	0.3		+-
3985	$-(\mathbf{C} - \mathbf{C})_4 - \mathbf{C}\mathbf{O} - \mathbf{O}\mathbf{r}$	<0.3	-+	÷
3760	$-CH = CH - (C - C)_4 - CH = CH - CH = CH - CH = CH - (C - C)_4 - CH = CH - (C - C)_4 - CH = CH - CH - CH - CH - CH - CH - CH$	- :0.3		
3830	3830-compound (unknown)		1.	+
3630	3630-compound (unknown)	. :0.3		
3540	3540-compound (unknown)		-1-	+
	*Chromopho	re.		



λ, mμ

.

Fig. 1 - Ultraviolet absorption curves of the compounds isolated from Arnica montana (Λ-E) and A. foliosa (F) Λ, 4100-compound in pertoleum ether; B, 4020-compound in pentane; C, 3905-compound in pentane; D, 3985-compound in pentane; E, 3760-compound in pentane containing 1 per cent benzene; and F, 3830-compound in petroleum ether;

The substance is extremely unstable. The weakly yellow crystals decompose within a few minutes making the determination of the melting point impossible. In solution the compound is relatively stable. The proportion in dry roots amounts to about 4-20 mg. per cent.

The polyyne was also detected in Arnica flowers. The compound was isolated by Sörensen *et al.*⁶⁸ from species of the tribe Inuleae and Heliantheae and was synthesized by Jones *et al.*⁶⁹. The hydro-carbon occurs in small amounts also in various other plants.

By comparison of the ultraviolet and infrared spectra as well as by perhydrogenation and gas chromatography of the hydrocarbon, the identity of the isolated compound with the substance found previously was ascertained.

Partial hydrogenation with Lindlar⁷⁰ catalysts leads to tridecahexaene. This alkyne might be responsible for the toxic action of Arnica preparations described in the literature. Mention has already been made of the occurrence of toxic acetylenes in *Cicuta virosa* and *Oenanteae crocata*. The effective toxicity of this compound in oral applications of mice LD_{50} has been found to be 15 mg./kg.

Also, the 3905-compound (Fig. 1C) is a C_{13} acetylene hydrocarbon, namely trideca-1,11-diene-3,5,7,9tetrayne. The compound occurs in dry roots of *A. montana* to the extent of 0.03 per cent. Its constitution could also be elucidated easily. Perhydrogenation leads to tridecane which could be identified by gas chromatography.

The fine-structured ultraviolet spectrum of the 4020-compound (Fig. 1B) indicates the presence of a pentayne chromophore which has not yet been described in literature.

Furthermore, the infrared spectrum indicates the presence of a terminal CH_3 group; terminal vinyl or ethynyl groups are missing. The substance is also very unstable, and its preparation in the pure state in larger amounts is laborious due to the small content in the drug (0.4 mg. per cent). Perhydrogenation leads to tri-2-decanone. Therefore, the substance is assigned the structure of tri-decapentayne-2-one.

The structure of the 3985-compound is still unknown. The fine-structured ultraviolet spectrum (Fig. 1D) points to an enyne chromophore. The band distances are about 2000 cm.⁻¹. The drug contains this compound in an amount of about 0.4 mg. per cent.

Through the band distances of about 2000 cm.⁻¹ the ultraviolet spectrum of the 3760-compound (Fig. 1E) indicates the presence of an entetraync chromophore. Perhydrogenation leads to a C_{13} hydrocarbon. The amount of this compound in the drug is so small that so far no more data could be ascertained.

The 3830-compound found only in Arnica foliosa and Arnica longifolia exhibits an ultraviolet spectrum as given in Fig. 1F. The spectrum shows band distances of about 2000 cm.⁻¹. This fact also points to the presence of an enyne chromophore.

Along with the polyynes, the hydroxythymol dimethylether is also extracted from roots as was found earlier by Sigel⁷¹. In addition, 8,9-dehydro4-hydroxythymol dimethylether occurs in Arnica roots.



Tridecenpentayne isolated from dry Arnica roots is like the proven phenolethers associated with fungicidal and bactericidal $action^{72}$. Table 8 shows the concentration of these compounds necessary to cause total inhibition of growth of fungi and bacteria. The fungicidal action of the isolated enpentayne is by a factor of about ten larger than that of capillin. The latter was used as standard substance. The polyacetylene from *A. montana* exhibited the same bacteriostatic activity as capillin toward *Staphylococcus aureus*.

Thus it exceeded the activity of phenol ethers by a factor of more than twenty. The effective toxicity of enpentayne is half as much as that of capillin. Nevertheless, this polyacetylene cannot be disregarded as a partial cause of the poisoning effect, that has been observed in several cases with Arnica preparations.

Previously, *Pulicaria dysenterica* has frequently been used in place of *Arnica montana*. In fresh roots of *P. dysenterica* which nowadays finds only little use we have found 10 polyacetylenes⁷³; of these, 5 alkynes occur in Arnica roots also (Table 9).

 TABLE 8 — FUNGICIDAL AND BACTERICIDAL ACTIVITIES OF

 CAPILLIN AND THE COMPOUNDS ISOLATED FROM Arnica montana

(Complete inhibition of growth at conc., %)

Strain	Capillin*	•	From A	. montan	a
		Enepent- ayne*	4-Hy- droxy- TDE ⁺	Thymol methyl- ether	Δ ^{4,5} Dehy- dro-4-
		Υ.		ounce	hydroxy TDE†
St. aureus	0.01	0.01	0.2	0.2	0.2
Ps. aeruginosa		0.1	0.2	0.2	0.2
Esch. coli	0.02	0.005	0.2	0.2	0.2
Tr. mentagro- bhites	0.005	0.01	0.1	0.05	0.01
M. gypseum	0.002	0.01	0.1	0.1	0.05
C. albicans		0.1	0.2	0.2	0.2
A. niger		0.1	0.2	0.2	0.2
Tr. schönleini	0.002	0.01	0.05	0.1	0.05
Ep. floccosum	0.001	0.01	0.05	0.1	0.01
Tr. rubrum		0.01	0.05	0.01	0.1

*Effective toxicity LD (mg./kg.) against mouse in the case of capillin is 7 (i.p.) and in case of enepentayne it is 15-5 (oral).

[†]TDE, thymol dimethylether.

TABLE 9	- Po	LYACE	TYLENES	ISOLATE	D FROM	PULICARIA
SPEC1	ES AN	о Тні	EIR ULT	RAVIOLET	SPECTRAL	DATA
		[K.	E. Schu	LTE et al.	73	

(Ultraviolet maximum was recorded in the long wave region)

λ_{\max}	Pulicaria							
	dysen- terica	vulgaris	odora	uligin.	sicul.			
3905	*	-1-	-	+				
4015	+ *	-		+				
4100	+*	-+-	-+-	+	-+-			
3985	+*	_	-	-				
3825	÷	-+-	-1-	-				
2665	-+-	-	-		-			
3755	+*		-					
3545	+	+	-	-+	_			
2635	-+-	-	-	_	-			
3890	÷		-	-	-			

*Also isolated from Arnica montana.



Fig. 2 – Ultraviolet absorption spectra of (A) 3125- and 3110-compounds isolated from *Grindelia robusta*; and (B) 3480-compound and isomycomycein isolated from *Tagetes* evercta

This result that looks first surprising becomes understandable, if we realize that both plants stand in two neighbouring tribes of the Compositae family.

The structures and chromophores of the isolated compounds are summarized in Table 10.

Also, the thymol 3-methylether, hydroxythymol dimethylether and the dehydro derivative are associated with acetylenes in this plant.

We were able to isolate so far 2 polyacetylenes from the root of another member of Compositae, *Grindelia robusta*⁷⁴, which has also been used therapeutically. The ultraviolet spectrum (Fig. 2) of the 3123-compound corresponds to the matricarianol acetate. This ester was identified in several species of Compositae by Holme and Sörensen⁷⁷. One has reason to assume that the second polyacetylene (3110 A.), according to its optical properties and behaviour on the alumina column, is the free alcohol, the matricarianol, which occurs in *Matricaria chamomilla* and *M. inodora*.

From the resin which is separated on top of the flower shortly before blooming, two polyacetylenes could be isolated. Both of them possess an endiynene chromophore and are probably identical with matricarianol or matricarianol acetate respectively.

It is of interest to note that in the root of Valeriana officinalis also a polyacetylene, 4100-compound (hydrocarbon) has been found by us⁷⁴. The same hydrocarbon occurs also in the root of *Ricinus communis*⁷⁵. The overground parts of this plant, however, contain the *trans*-dehydromatricaria ester (Table 10).

Surprising was it for us⁷⁶ to find also in green sprouts of wheat, polyacetylenes, namely the 3950compound, in a later investigation the 3910-compound, and in smaller amounts a 3830-compound, while the underground parts again contained the 4100-hydrocarbon.

While the alkynes described so far were extracted from the plant material with petroleum ether, we⁷⁸ were able to isolate from *Tagetes erecta* a polyacetylene soluble in water-methanol, which could be separated from its accompanying byproducts through counter-current distribution. The substance has a dienetriyne chromophore which is very similar to that of isomycomycin, the latter being formed from mycomycin by alkali treatment.

Isomycomycin is a 3,5-tridecadiene-7,9,11-triynoic acid. The substance isolated by us has almost the same ultraviolet maxima; the carbonyl band in the infrared spectrum is missing. On the other hand, the 'Molisch' reaction is positive. Furthermore, the infrared spectrum shows strong bands (at 1260 and 1070 cm.⁻¹) for secondary OH groups.

Moreover, the compound is optically active. These findings along with the solubility properties of the substance make it probable that here an alkyne is bonded to a glycoside. The first alkyne

TABLE 10 -- COMPOUNDS ISOLATED FROM Pulicaria dysenterica, Valeriana officinalis, Ricinus communis AND Triticum sativum AND THEIR ULTRAVIOLET SPECTRAL DATA

(Ultraviolet spectra were taken in the long wave region)

Compound	Structure
Amax.	ISOLATED FROM P. dysenterica
4100† 4020† 3905† 3985† 3890† 3825† 3750† 3545† 2665† 2635†	$\begin{array}{c} H_{3}C-(C_{-}C)_{3}-CH=CH_{2}\\ H_{3}C-(C_{-}C)_{3}-CO-CH_{3}\\ H_{3}C-CH=CH=CH-(C_{-}C)_{4}-CH=CH_{2}\\ -C=C-C=C-CC_{-}(C_{-}C)_{4}-C=C^{-*}\\ -C=C-(C_{-}C)_{4}-C=C^{-*}\\ -C=C-(C_{-}C)_{4}-*\\ -C=C-(C_{-}C)_{3}-C=C^{-*}\\ -C=C-(C_{-}C)_{2}-*\\ -C=C-(C_{-}C)_{2}-*\\ \end{array}$
	ISOLATED FROM V officinalis
4100‡	$CH_3 - (C - C)_5 - CH = CH_2$
	ISOLATED FROM R. communis
4100§	$\begin{array}{c} \mathrm{CH}_3-(\mathrm{C=C})_5-\mathrm{CH=CH}_2\\ \mathrm{CH}_3-\mathrm{CH=CH}-(\mathrm{C=C})_3-\mathrm{COOCH}_3\\ trans\\ trans-\mathrm{dehydromatricaria\ ester}\end{array}.$
	ISOLATED FROM T. sativum
4100¶ 3910¶ 3950¶ 3830¶	$\begin{array}{c} CH_2 = CH - (C - C)_5 - CH_3 \\ CH_3 - CH = CH - (C - C)_4 - CH = CH_2 \\ - CH = CH - (C - C)_4 - CH = CH \end{array}$

*Chromophore. †K. E. Schulte et al.⁷³. ‡P. Busch⁷⁴. §H. Bornfleth⁷⁵. ¶J. Rheinbay⁷⁶.



bonded to a glycoside was described in 1960 by Bu'Lock and Gregory⁶³. They found that nemotinic acid isolated from Basidiomycetes is partially glycosidically bonded.

From Tagetes erecta, Zechmeister and Sease⁷⁹ in 1945 isolated α -terthienyl (XIX), Uhlenbrock and Bijloo⁸⁰ isolated from African modifications of *T. erecta*, 3-butenynyl-2,2'-bithienyl (XX) besides α -terthienyl; these thiophenes are the active principles against nematodes.

F. Bohlmann and P. Herbst (unpublished work) found yet another bithienyl derivative (XXI).

The co-occurrence of thiophene and polyacetylene in the same plant is of special interest from the point of view of biosynthesis, as in other plants, too, thiophenes and polyacetylenes containing the same or a similar number of carbon atoms have been found. The thiophene derivatives (XII-XXI) and acetylenes occurring in the same plant are given in Table 11.

Junipal was isolated in 1955 by Birkinshaw and Chaplen⁸¹ from the steam-distilled components of metabolic products of *Daedalea juniperia* Murr., a fungus which causes the decaying of wood of *Juniperus virginia*. The corresponding alkyne having the same number of carbon atoms has not yet been found; it might be that it is 2,4,6-octatriyn-1-ol.

Alkynes having the same number of carbon atoms as 2-phenyl-5-propinyl-thiophene have been isolated from *Corcopsis grandiflora* by Sörensen and Sörensen⁸² in 1958, and those having the same number of carbon atoms as 5-propinyl-(2-thienyl)acrylic acid methylester found in *Chrysanthemum vulgare* by Guddal and Sörensen⁸³ in 1959 have been isolated from the same plants.

Of the three thiophene derivatives found by Sörensen⁸⁴ in *Matricaria inodora*, two corresponding alkynes have been isolated from the same plant. The thienyl-yne-ene-ester has been found⁸⁵ in *Anthemis nobilis* in addition to dehydromatricaria ester and artemisia ketone. Sörensen and Sörensen⁸⁶ discussed a hypothesis according to which the formation of thiophene compounds in plants is supposed to proceed in such a manner



Chart 2 - Formation of thiophenes by the *in vitro* addition of H₂S to polyacetylenes

TABLE	11	- THIOPHENE	DERIVATIVES	AND	ALKYNES	OCCURRING	IN	THE	SAME	PLANT
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Plant	Alkyne	Thiophene	Investigators
Daedalea juniperia	$[CH_{\bullet} - (C = C)_{\bullet} - CH_{\bullet}OH]$	XII	[. H. Birkinshaw and P. Chaplen ⁸¹
Coreopsis grandiflora	$CH_3 - (C = C)_3 - C_8H_5$	XIII	J. S. Sörensen and
Change and how and a second		VIV	N. A. Sörensen ⁸²
Chrysaninemum vuigarc	$CH_3 - (C C)_3 - CH = CH - COOCH_3$	XIV	E. Guddar and N. A. Sorensen
Matricaria inoaora	$CH_3 - (C C)_3 - CH = CH - (CH_2)_2 - CO - C_2H_5$	AV	N. A. Sorensen"
Matricaria inodora	$CH_3 - (C - C)_3 - (CH = CH)_3 - H$	XVI	N. A. Sörensen ⁸⁴
Anthemis nobilis	$CH_3 - (C \equiv C)_3 - CH = CH - COOCH_3$	XVII	F. Bohlmann et al. ⁸⁵
Bidens leucanthus	$CH_3 - CH = CH - (C C)_4 - CH = CH_2$	XVIII	F. Bohlmann et al. ⁸⁵
Tagetes erecta	$[-(C = C)_{2} - (CH = CH)_{2} -]^{*}$	XIX	L. Zechmeister and J. W. Sease ⁷⁹
	(Schulte et al., unpublished work)	XX	J. H. Uhlenbrock and - L. D. Biiloo ⁸⁰
×.		XXI	F. Bohlmann (unpublished work)



Chart 3 - Syntheses of 2-phenyl-5-(phenylethinyl)-thiophene and 2-phenyl-5-(phenylbutadiynyl)-thiophene

that H_2S adds to a diyne forming thereby the thiophene ring. Therefore, it was of interest to test *in vitro* the feasibility of H_2S addition to polyacetylene expecting formation of the corresponding thiophene derivative (Chart 2).

We started our experiments^{87,88} using simple 1,4-disubstituted butadiynes which are relatively easily accessible through coupling of 1-alkynes. They may be converted into the corresponding thiophenes upon warming in ethanol-water or acctone-water in weakly alkaline medium. As can be seen from Chart 2, it is possible in this way to cause H₂S to react with both diacetylene, despite its two terminal triple bonds, and methyldiacetylene, containing one terminal triple bond.

Even alkynes containing 3 and 4 acetylene bonds undergo these reactions. Diphenylhexatriyne and diphenyl-octatetrayne have been found to react with H₂S under the conditions selected by us.

2-Phenyl-5-(phenylethinyl)-thiophene was formed from diphenylhexatriyne and 2-phenyl-5-(phenylbutadiynyl)-thiophene from the appropriate octaterrayne in good yields (Chart 3). Acetylene bonds not taking part in the reaction could be proved by hydrogenation, infrared and ultraviolet spectra and oxidative degradation. If the solution is saturated with H_2S and heated up to about 90°, diphenyldithenyl is formed.

Our experiments^{87,88} were then extended to cover the synthesis by the same method, namely H_2S addition to the appropriate alkynes, of thiophene derivatives found in nature.

First, we reacted hydrogen sulphide with phenyl-1,3,5-heptatriyne (XXIV); the latter was obtained in good yield from methyldiacetylene (XXIII) and phenylacetylene bromide (XXII) according to a



method of Chodkiewicz⁸⁹. The expected 2-propynyl-5-phenylthiophene was not obtained instead two substances identified as 2-methyl-5-(phenyl-2-mercaptoethenyl)-thiophene (XXVI) and 2-methyl-5-(phenylethinyl)-thiophene (XXV) were isolated. This means that the ring had not been closed between C_1 and C_4 but between C_3 and C_6 . More-over, partially for a second time H_2S had added to the remaining acetylene bond. However, the attempt to convert compound (XXV) into compound (XXVI) by prolonged introduction of H2S was unsuccessful. If, however, the experimental conditions were altered such as not to apply to the alkyne an excess but equimolar amounts of hydrogen sulphide (generated from sodium sulphide and hydrochloric acid in solution) only compound (XXV) could be isolated using an excess of Na2S, the pH value was maintained at 9-10 during the reaction. In the meantime we have been able to synthesize this thiophene via a different route.

CH3-C≡C-C≡CH + BrC ≡ C - CH2OH



Chart 4 - Synthesis of junipal (L. Hörner⁸⁷)



Chart 5 - Synthesis of junipal (G. Bohn⁹⁰)

To prepare junipal^{87,88} we coupled methyldiacetylene (XXVII) with bromopropargyl alcohol (XXVIII) according to the method of Chodkiewicz⁸⁹ already mentioned and obtained in good yield 2,4,6-octatriyne-1-ol (XXIX). This was reacted with Na₂S (Chart 4). For the 5-propynyl-(2-hydroxymethyl)-thiophene (XXX) a characteristic ultraviolet spectrum was observed although the compound could not be isolated immediately. Therefore, the raw material was directly oxidized with activated manganese dioxide in methylenechloride to obtain the expected aldehyde, junipal (XII), in 34 per cent yield related to octatriynol. Melting point, ultraviolet and infrared spectra as well as degradation products obtained oxidatively agreed both with those obtained via a different way

Chart 6 — Synthesis of the methyl ester of cis-β-(5-propynyl-2-thienyl)-acrylic acid

(Chart 5) used in my laboratory, and with those stated by Birkinshaw and Chaplen⁸¹.

The methylester (XIV) of $cis-\beta$ -(5-propynyl-2-thienyl)-acrylic acid was found by Guddal and Sörensen⁸³ in *Chrysanthemum vulgaris*. This compound had the same number of carbon atoms as dehydromatricaria acid, a 2-decaene-4,6-triyn-1-oic acid, and could also be obtained through the reaction between this alkynoic acid and H₂S according to the method described in Chart 6.

Dehydromatricaria acid is accessible through reductive coupling of methyldiacetylene bromide and 4-pentyn-2-en-1-ol according to Chodkiewicz⁸⁹ followed by oxidation. From the reaction of the acid with H₂S a mixture of *cis-trans*-5-(propynyl-2-thicnyl)-acrylic acid was obtained. After esterification with diazomethane the *cis-* and *trans*-esters could be separated by chromatography on alumina.

The same products were obtained by preparing separately the *cis*- and *trans*-forms of dehydromatricaria ester followed by reaction with H_2S . Here, however, yields were not as good since partial saponification took place during the reaction of the ester in alkaline medium. In this case also the data obtained by us agreed with those stated by Sörensen.

Also, the synthesis of an z-terthienyl is according to our method in considerably better yield possible by reacting 1,4-dithienyldiacetylene with hydrogen sulphide. Starting with thiophene aldehyde and causing this to react with malonic acid, Bohn and coworkers^{40,91} obtained thiophene aerylic acid (XXXI). Through bromination, decarboxylation and elimination of HBr he obtained thiophenacetylene (XXXII). This could be converted into dithienyldiacetylene (XXXIII) by oxidative coupling. After reaction with H₂S he obtained terthienyl (XXXIV) in good yield; 60 per cent compared to about 10 per cent obtained by the method of Zechmeister and Sease⁷⁹; melting point, ultraviolet and infrared spectra agreed with those recorded in literature.



The sulphur-containing amino carboxylic acids cysteine and homocysteine as well as oligopeptides like glutathione may function as, respectively, H_2S and SH donors in the cell. The substances mentioned may split off hydrogen sulphide in alkaline medium. In the plant this splitting is probably



IXXXX

effected by desulphhydrase. Its maximum of activity lies around pH 7·4-7·6, that is, in a region in which according to our findings thiophene formation from polyacetylene and H₂S is possible.

2,5-Bis-(1'-hydroxyisopropyl)-thiophene (XXXVI) is formed *in vitro* from 2,7-dimethyl-3,5-octadiyne-2,7-diol (XXXV) by warming at 60-70° for 15 hr with cysteine in 0·1N KOH^{91,92}.

On the other hand, only traces of the corresponding thiophene are formed in the reaction of 7-phenyl-2-heptene-4,6-diyne-1-ol with cysteine in 0·1*N* KOH and ethanol. Chiefly an amphoteric ether insoluble product having an ultraviolet absorption maximum at 293 ma is formed which is identical with the substance obtained by boiling 2-phenyl-5-(3'-hydroxy-I'-propen-1'-yl)-thiophene with cysteine in alkaline solution. It could be that we here are dealing with a thioether aminocarboxylic acid formed by cysteine addition to the double bond of the side chain.

Better results were obtained with glutathione that splits off H_2S in alkaline medium more easily. In the presence of this tripeptide the natural substances *trans*-7-phenyl-2-heptene-4,6-diyn-1-ol (XXXVII), *trans*-lachnophyllum acid (XXXVII) and *trans*-dehydromatricaria acid (XXXIX) are readily converted in good yield into the corresponding thiophenes, in 0.1N KOH and at room temperature.

It is still an open problem whether the ring formation in this reaction proceeds via the stage of addition of the SH group of the glutathione to



the triple bond followed by elimination of the remaining moiety of glutathione under proton addition and formation of the thiophene ring. The alternative would be the reaction of the triple bond with SH ions generated in the nascent state by the action of alkali.

In this connection it might be of interest to point out that Bohlmann *et al.*⁵² isolated a new group of sulphur-containing polyacetylenes (XL) and (XLI) which possess an S-methyl group. The compounds isolated from *Chrysanthemum segetum* may formally be derived from benzyldiacetylene or benzoyldiacetylene respectively by addition of methyl-mercaptan found in the same plant.

Probably another mechanism of formation is responsible for thiophene compounds bearing, respectively, a —OH or —OCH₃ group in 3-position of the thiophene rings (XLII) and (XLIII) and isolated from *Artemisia vulgaris*. Bohlmann⁹³ used the hypothesis of thiophene formation from β -dicarbonyl compounds as drawn up by Sörensen and Sörensen⁸⁶ to discuss it in connection with series of thiophene derivatives.

Schulte and Mitarb (unpublished work) have investigated the formation of the polyacetylene and of the propynyl-thienyl-acrylic acid ester in the root of *Chrysanthemum vulgare* during one vegetation period (Fig. 3). The dehydromatricaria ester is formed first and 5 weeks later the thiophene is





Fig. 3 — Formation of polyacetylene and propynyl-thienylacrylic acid ester in Chrysanthemum vulgare roots

formed; the latter is at the time of blooming present in considerably larger amounts than the sulphurfree compound. The amount of alkyne acetate changes in a similar manner during the course of one vegetation period.

We hope to be able to shed more light on the correlation between polyacetylenes and thiophenes by employing radioactively marked substances. Thus, we have at first fed cysteine hydrochloride with the nutrient medium to young growing plants of Chrysanthemum vulgare (Schulte, K. E. & Mitarb, unpublished work). After a short period of time, S-35 could be detected in thiophene. However, this does not prove that sulphur transfers directly from cysteine into the thiophene ring. It is more likely that still unknown intermediates are passed.

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Marine Fouling in Indian Waters

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THE settlement and growth of animals and plants on submerged surfaces in a marine environment is commonly known as 'marine fouling'. The growth of these biota on the different surfaces poses serious problems of considerable economic interest. Fouling affects propulsion and thereby the economical operation of boats and ships¹. It reduces the efficiency of underwater acoustic devices and the normal service life of many marine structures. Pipes and conduits under marine use get clogged by the profuse growth of these organisms often resulting in the breakdown of such systems. The problem of marine fouling has, therefore, attracted the attention of biologists, chemists and engineers alike and a great volume of literature on marine fouling and its prevention has accumulated. However, in spite of many contributions and suggestions, boat owners and harbour authorities all over the world are still being plagued by this problem. Heavy financial investments have been made and are being made with the hope of tackling marine fouling and its prevention more successfully.

The monograph on marine fouling and its prevention by the Woods Hole Oceanographic Institution, USA, is of particular interest². This work, apart from providing a comprehensive review of the problems involved, biology of the organisms and the prevention of fouling, includes an extensive bibliography covering up to the year 1949. While an impressive body of information has been compiled on the biology of

fouling organisms of England³, the Continent⁴, Pacific Islands⁵, Australia⁶ and Canada⁷, our information on this problem along the extensive coasts of India with its numerous ports is comparatively inadequate. Erlanson⁸ made a preliminary survey of the marine boring organisms in Cochin harbour in the year 1936 and her report also contains brief references to fouling organisms recorded. Paul^{9,10} studied the growth, sexual maturity and breeding of certain sedentary organisms in the Madras harbour. At Krusadi Island in the Gulf of Mannar, Kurivan¹¹ conducted observations on the fouling organisms of pearl oyster cages and the attachment of marine sedentary organisms on different surfaces12. Kuriyan and Mahadevan¹³ further studied the effect of light and colour of the substratum on the settlement of barnacles. Investigations by Daniel were directed towards the systematics14, development15, settlement¹⁶ and gregarious attractions¹⁷ of certain marine fouling organisms. Several aspects of the settlement such as the primary film18, illumination19, colour of the substratum²⁰ and the seasonal variations in the succession of the fouling communities²¹ in the Madras harbour were also studied and recorded by him. Ganapathy et al.22 studied the biology of fouling in the Visakhapatnam harbour. Further observations in the Madras harbour were made by Antony Raja^{23,24} on the distribution, succession and growth of sedentary organisms. Recently, Balasubramanyan and Menon²⁵ studied the characteristics of some of the fouling organisms in Cochin harbour, while investigating into the causes of timber destruction due to marine organisms.

These researches are bound up with systematic and detailed fundamental studies on the biological, anatomical and physiological characteristics of the marine fouling organisms. The Committee for the Protection of Timber against Marine Borer Attack, constituted by the Forest Research Institute, Dehra Dun, in 1955 also included detailed studies on the marine fouling organisms at different localities along both the coasts of India. Today studies and investigations pertaining to marine fouling organisms and their prevention are being supported by many universities, harbour authorities, navy and defence organization, fisheries departments and various other private agencies. Becker in his report26 to the Government of India on the protection of wood against marine borers has offered useful suggestions for a similar study on marine foulers in Indian waters.

The Fouling Community

The organisms that constitute the fouling community comprise a large assemblage of more than 2000 species of both animals and plants². They include microscopic forms such as bacteria, fungi, diatoms, protozoans and rotifers and macroscopic forms like sponges, coelenterates, flat worms, bryozoans, tubeworms, amphipods, barnacles, molluscs, etc. The animals that foul are principally the sedentary or sessile forms occurring in the shallow waters along the coast. Different kinds of algae also contribute to the fouling community. The barnacles, tubeworms, bryozoans and mussels are by far the most important forms from the point of view of surface coverage, volume and weight. Many free living animals are also found amidst the sedentary organisms that form the fouling community and they must be considered as an inseparable part of this group. The chief among them are the planarians, nemertines, polychaetes, isopods, decapods, gastropods and also pisces.

Both qualitative and quantitative differences have been recorded on the characteristics of the fouling assemblages on structures of different substrata such as ships' bottom, buoys, concrete, rock, fibres, wood, metal and glass. Further, in the different seasons these substrata may hold various types of fouling flora and fauna depending on their location in different regions along the coast under varying ecological conditions and also at different sites within the same harbour²⁷. The fouling complex that occur on temporary substrata somewhat differ from that of the natural population accumulated on permanent objects under immersion the former containing a large number of species.

In India, the different members of the fouling community have been identified and studied in some detail at Visakhapatnam²², Madras^{9,10,21}, Krusadi¹¹ and Bombay²⁸. A total of nearly 54 different species of fouling organisms have been recorded from Visakhapatnam harbour, 60 species from Madras harbour, 57 species from Krusadi and about 50 from Bombay and neighbouring areas.

A newly exposed surface under immersion gets rapidly coated with microscopic organisms referred to as primary film or slime film, which comprise bacteria, diatoms, algal spores, mixed with organic and inorganic detritus, mud, sand and other particulate materials suspended in sea water. It has been found that the composition of the primary film is different in different areas. Zobell²⁹ found that the primary film consists mainly of bacteria on the eastern coast of the United States. In the sub-tropical waters of Australia, $Wood^{30}$ found that the film is composed of diatoms and algal spores. Daniel¹⁸ observed at Madras that the film is composed of 38 species of diatoms and 14 species of algae and a smaller proportion of bacteria. Balasubramanyan and Menon²⁵ have recorded bacteria, diatoms and protozoans as foremost of all settling organisms on the test panels in the port of Cochin. American workers like Weiss³¹, Phelps Austin (as cited by Weiss), and Australian workers like Wood³⁰, Scheer³² support the view that bacterial slime forms the primary settlement. Different stages in the development of the primary film has been noticed by various workers. According to Harris³³ there are three stages in the development of the primary film, namely bacterial slime, diatom flora and the attachment of higher animals. But Kuriyan's observations³¹ of ten-day blocks have not shown any separate stages. He adds that although a certain amount of primary film is formed consisting probably of bacteria and diatoms, the other organisms either settle simultaneously or follow immediately. It seems reasonable to assume that while some fouling organisms need this primary film, others are capable of attaching to even clean or newly submerged surfaces. Probably in some species larvae settle more readily on filmed surfaces. According to Daniel¹⁸ the primary film is an essential prerequisite for the attachment of barnacles and serpulids. However, the exact role of the 'primary film' in the fouling sequence requires further elucidation.

The primary film is followed by waves of other fouling organisms which settle and grow. The presence of certain species is essential for facilitating the subsequent attachment of other forms, which lead a sort of interspecific dependence. This biological succession involves definite relations between organisms and is occasioned by factors of the environment. The earlier forms play a role for the . subsequent establishment of forms that arrive later. In some cases the earlier forms are displaced or smothered as a result of successive settlement. The result of these is the establishment of a climax community comprising forms, which are slow growing and long living.

The only studies regarding this biotic succession in India are those of Daniel²¹ and Antony Raja²³ in Madras and Ganapathy *et al.*²² at Visakhapatnam. According to Daniel²¹ the primary film is followed by barnacles, tubicolous polychaetes, polyzoans, molluscs, ascidians and once again the barnacles, which finally occupy the whole area crowding out all other forms. Daniel further observed that the same sequence of events, taking place, irrespective of the season during which it is exposed²¹.

In the observations on the succession of fouling community at Visakhapatnam harbour²², the first arrivals have been reported to be bacteria, diatoms, protozoans and hydroids followed by serpulids, hydroids and polyzoans, and which again are followed by simple ascidians, sea anemones, barna-cles and oysters. However, Antony Raja²³ during his studies has found no clear-cut succession as has been reported from California⁵⁵, New Port³² and Australia³⁶, where a true ecological succession with a well-defined community dominating at every stage, leading to a climax recognized by a single community, has been recorded. Based on his observations Antony Raja²³ suggested that the ecological succession, if any, is not true, regular and definite, but is considerably modified under the prevailing ecological conditions. There was no clear seasonal succession in the Madras harbour as there were no sharp and well-marked seasons as is usually seen in all temperate countries.

Physical Factors

The qualitative and quantitative structure of the marine fouling community, their settlement, rate of growth, the breeding intensity and survival rate have a great bearing on the very many essential physical factors prevalent in the living media, the important of which are temperature, salinity, pollution, turbidity, water movements, 'nature, texture and colour of the substratum and the incidence of light falling on them.

Temperature - It is believed that no other environmental factor is as important as temperature. It greatly determines the geographical distribution of the different fouling organisms. American workers³⁷ have divided the oceans of the world into a series of ten zones, representing varying grades of fouling intensity. Zones 1 and 2 comprise a world-wide belt running roughly 30 degree north and 30 degree south of the equator, represent the zone of greatest fouling intensity (India comes under this zone), whereas zones 9 and 10 (the Antarctic and Arctic seas) are the zones with the lowest fouling intensity. The paramount importance of the temperature factor in controlling the breeding intensity of the marine animals has been discussed by Orton³⁸. It is known⁹ that in the tropics, where the temperature does not show considerable fluctuations between the maxima and the minima, there is apparently no distinct periodicity in the breeding of marine animals particularly among the marine fouling organisms under reference. The constant settling down of generations of organisms, production of several offsprings in a year, their rapid growth and attainment of sexual maturity at a surprisingly early stage are all brought about as a result of the constant prevalence of high temperature throughout the year. These contribute to a high, well pronounced and continuous fouling in the Indian tropical waters. The noted absence of seasonal succession²¹ in tropical waters is due to the temperature factor which does not fluctuate so markedly as in the case of higher latitudes. Probably higher temperature can stimulate sexual activity, accelerate the development of the gonad, hasten maturity and shorten the free

swimming larval period. Based on these factors, the fouling organisms can be classified as those with continuous attachment throughout the year, those with continuous attachment but with increased frequency during definite periods, those with limited attachment during some definite period of the year and a fourth type attaching at two separate periods of a year.

Since temperature cycle is a mere reflection of the annual fluctuation in solar radiation, it has further influence on the marine fouling animals in other ways such as affecting the rate of photosynthesis of microscopic plants, which form a part of the complicated food web of the sea. Temperature also influences precipitation thereby controlling the salinity of the medium through excessive run-off.

Salinity - Salinity of the water has been recognized as an important factor controlling the occurrences of these fouling organisms. Salinity factor is relatively important in a country like India where the two prevailing monsoons cause considerable amount of rainfall over the region. Accordingly the salinity shows considerable variation along the coasts of India. While salinity and specific gravity ranges are insignificant in the open ocean, in estuaries and harbour areas salinity fluctuations are very much marked due to land drainage. Many of the marine organisms in these special habitats, through years of acclimatization and physiological adjustments have shown considerable tolerance for a wide variation in salinity. Experiments relating to this aspect have been very few in India. The marine borers *Martesia striata³⁹*, *Sphaeroma* sp.⁴⁰ have been found to live in waters of very low salinity. Many of the barnacles and other fouling organisms are killed and sloughed off during periods of very low salinity and on the onset of normal conditions, the areas left bare are recolonized by the fresh planktonic larvae brought in by the tidal currents and other movements of the medium. This is also what has been observed by the present author while conducting observations on the biology of fouling in the Cochin harbour.

Salinity also affects the breeding of marine animals⁴¹ and retards their growth rate⁸, thereby reducing the intensity of fouling in areas where low salinity prevails. Observations at Cochin²⁵ have shown that fouling has been the least in quantity and quality during the monsoon period, which extends from the middle of May to the end of November (south-west and north-east inclusive), and the cause is reasonably attributed to the fall in the salinity of the water during that period. The hydrographic conditions are further complicated by the nature of the basin and the tidal influences.

The horizontal and vertical distribution of fouling organisms are also controlled to a considerable extent by the distribution of salinity in the area. A gradation can be seen in the occurrence of some of the fouling organisms in estuaries or in the lower reaches of river mouths. They also exhibit a characteristic zonation in distribution, correlated with the distribution of salinity. The toleranee of different species shows variation and a few survive even nearly in fresh water. Certain strains of barnacles and some species of bryozoans and shipworms belong to this category. There are also certain fouling elements which are characteristic of estuarine areas and are unable to survive in marine situations. The extent of fouling by marine species in estuaries depends on the degree to which the salinity varies with the tide.

Pollution - Pollution is yet another physical factor of importance in the biology of fouling, particularly within the enclosed waters of the harbours. Pollution is the outcome of sewage, industrial waste, oil, etc., finding their exit into the natural waters and changing both their physical and chemical nature. The substances that pollute may be harmful by possessing toxic effects or may lead to a serious depletion of oxygen of the medium resulting from oxidation of organic matter. Such waters are mostly free from any normal life. On the other hand, certain substances may act as nutrients thereby enriching the medium. In such situations detritus feeders, mud tube dwelling polychaetes and amphipods42 show luxurious growth and characteristic indicator species can be recognized43. It may also be mentioned that the two factors, salinity and pollution, can, to a large extent, be the limiting factors of the environment causing a natural check over the fouling community.

Turbidity — The enclosed waters of the harbour and other bodies of coastal waters contain silt, detritus and other particulate matter in fine suspension. These particles of suspended matter affect the organisms in many ways. It can smother sessile forms and may form a mat-like cover over the substrata thereby preventing the settlement of certain species. Large quantities of suspended matter can clog the respiratory organs and can disable normal functioning of the ciliary feeders. Thick silt and resulting turbidity reduces the penetration of light preventing the growth of green plants. Those forms, which need plants as a substratum for settlement, are, therefore, unable to settle in such a medium. Studies on fouling intensity in relation to turbidity of the environment require detailed investigations.

Waves, tides and currents - Movements of the medium (water) because of waves, tides and currents also can affect the dispersal, settlement and growth of sessile organisms. Water movement facilitates the existence of sessile animals, since food particles are brought to them and their waste products in turn are carried away. These movements also help the distribution of the larvae and thus prevent overcrowding in any particular substrata. These movements of water mass are sometimes harmful when the larvae of these littoral forms are swept far away to the open sea where settlement is impossible or to places where conditions are unfavourable for settlement. The velocity of water currents on the surface of the substratum is important since larvae of foulers select suitable sites for settlement in relation to the velocity gradient of currents44. The attachment and survival of barnacles are mostly influenced by water currents. Crisp and Stubbings45 have found that current has very little influence on the cyprids at the time of fixation. Regarding the effect of the

stage of tide on the settlement of barnacle cyprids conflicting views are expressed by various workers^{16,46-49}.

Light, colour, nature and texture of substratum — Many of the larvae of foulers are negatively phototropic and they prefer darker surfaces, while a few are positively phototropic. There seems to be no agreement among various workers as regards the probable effect of light on the settlement of barnacle cyprids. Visscher and Luce⁴⁷ observed that the barnacle cyprids "react negatively to light at the time of attachment", while Weiss⁴⁶ and McDougall⁵⁰ are of the view that they are positively phototropic at the time of attachment. Pyefinch⁴⁸ was not able to arrive at any definite conclusions regarding the effect of light on the settlement of barnacle cyprids. Investigations of Kuriyan and Mahadevan¹³ at Krusadi Island have revealed that barnacles attach mainly on surfaces deeply submerged and that those on a block near the surface are confined to its under side away from abundant light. Sunlight, according to them, has an effect on the settlement of barnacles.

Colour of the substratum exposed also exerts a profound influence on the settlement of sedentary organisms^{13,20,42,50,51}. It has been found that red, black and white attracted large numbers, blue, green and grey had fewer, and grey panels attracted the poorest number. These findings have still to be confirmed by repeated laboratory and service tests. This information is of great importance since this would help in incorporating the required colour pigments in the formulation of antifouling compositions for commercial exploitation.

The nature and texture of the substratum have marked effect on the settlement of marine sedentary forms48,51-54. This is particularly true in the case of barnacles probably due to the walking movement of barnacle cyprids prior to final settlement as reported by Visscher⁵². He states that the cyprid larvae make exploratory movements covering appreciable distances before attachment. Barnes and Powel⁵⁴ found that the projecting bristles of staple cloths by their number and stiff character may prove a source of irritation or may mechanically restrict the movements of the cyprids. Thus the quantity and quality of fouling organisms seem to show variations with reference to nature and texture of the substratum on which they settle such as rock, concrete, asbestos, earthern tiles, glass, metallic surfaces and fibrous structures.

Abrasion — Abrasion or 'molar action' over fouled surfaces caused by water-borne stone particles and sands through action of wave and currents is important for fouling organisms as they may interfere with their normal growth rate. Marine boring organisms weaken the solid structures by riddling through the substrata. Protective devices such as hard shells, anchoring structures like byssus threads, and colonization are probably adaptations to withstand the abrasive action of the medium.

Chemical Factors

The availability of dissolved gases like oxygen and carbon dioxide and nutrient salts like phosphates and nitrates in the aquatic environment

in which the fouling organisms have to complete their life has a profound influence on the whole community both directly and indirectly. Their abundance in the environment is of direct critical concern to the life of organisms in respective habitats. Oxygen may act as a limiting factor in certain estuaries and harbour areas with sewage influence. The decay of organic material may also deplete the oxygen content which in turn may restrict or reduce the organisms present in an area. In certain harbours of India with heavy pollution the oxygen content is always low and the production of hydrogen sulphide is noted⁵⁵. Under such lethal conditions, oysters, mussels and other fouling organisms remain closed within their shells and cease feeding. This leads to a temporary cessation or inadequacy in feeding resulting in their poor growth or they ultimately perish when such conditions continue to persist for too long. The presence of phosphates and nitrates affect phytoplankton production, which in turn influences zooplankton comprising the free swimming larvae of many of the fouling organisms and thus these inorganic salts can indirectly affect the settlement and growth of fouling organisms in any locality.

The existence of a mutual relationship between marine fouling and boring organisms has been noted by various workers^{42,56}. Many of the fouling organisms, particularly those with special calcareous protective structures, offer a physical barrier to the subsequent borer settlement in the same substratum or perhaps may be the fouling organisms prey upon the larvae of the borers. It is also often questioned whether there is any evidence of a casual relation between the onset of fouling and the initiation of corrosion, or vice versa. Authentic information on this subject of fundamental studies on the mechanism by which marine organisms directly or indirectly affect corrosion and the role of fouling organisms in preventing corrosion in tropical waters is still wanting.

The conventional method of preventing fouling is by the application of traditional antifouling paints on submerged surfaces. Such paints contain toxic materials like copper or mercury or arsenic poisons. The problem that is being faced in the use of these paint compositions are that the poisonous components leaches out at varying rates in the course of time and as such a standard and regulated leaching rate for these toxic substances under prolonged immersion have to be worked out. The firm attachment of certain major fouling forms like barnacles, oysters and tubeworms to the surface also favours their persistence on ship's bottom in active use. Susceptibility of the various fouling organisms to the different poisons has to be studied in greater details. Suitable metallic sheathing is also adopted for protecting the hulls of wooden boats. Copper and copper-based alloys have been able to resist marine fouling to a great extent under normal conditions of exposure in the port of Cochin (Central Institute of Fisheries Technology, unpublished records). The use of mechanical devices such as ultrasonic vibrations has also been tried with encouraging results to keep the hulls of ships clear of fouling organisms⁵⁷. Reinforced plastics with a surface inhibiting settlement are being tried at present as a new material for boats hull, but it is too early to arrive at any positive conclusions regarding its efficacy against marine fouling.

Conclusion

The problem of marine fouling and its successful prevention thus appears to be an evasive subject that requires a careful handling. It might be possible to tackle this important problem with ease in the coming years provided adequate research investigations are taken up to fill up the broad gaps in the existing knowledge on the subject. Though the historical background of this subject dates back to the early nineteenth century, to the days of Sir Humphry Davy, still the intricacies of the problem are not well understood particularly as regards to their prevention to a level of perfect satisfaction. A thorough study on the different marine fouling organisms, their mode of attachment, complete life cycle, their reaction to environmental conditions and other characteristics seems to be very important without which no further progress could be made.

The environmental influences that control the settlement and growth of the organisms must be given due emphasis in studies on fouling. The physico-chemical variables of the sea water, the effects on the time of exposure, the nature of the substratum and its location in relation to tidal changes and depth, the mechanical effects of currents and conditions of illumination are few important factors that affect a natural population. Intraspecific and interspecific competitions and the presence or absence of predators and parasites also have an abiding influence. The intensity of fouling in an area is, therefore, dependent upon very many factors as stated above that are either directly or indirectly concerned.

Effective methods for the prevention of fouling can be devised only after a correct appreciation and assessment of the above-mentioned factors. The problem very much varies with the quality and quantity of fouling in any given locality. The results obtained from investigations have, therefore, only local application. This makes the problem of eradication all the more complicated, expensive and time consuming. The reactions of closely allied forms are different⁵⁸ and, therefore, a precise and accurate determination of the species occurring in a locality becomes an essential prerequisite. This must be the foundation of all further enquiries in an approach to the biological aspect of the marine fouling problem. It is unfortunate that there is a tendency to subordinate the importance of taxonomic enquiries. Even the most important members of the fouling community that occur in the major harbours of India have yet to be correctly identified. Perhaps this is one of the reasons for the delayed progress in enforcing suitable antifouling measures.

Realizing the economic importance of the problem in Indian waters, the Craft Materials Section of the Central Institute of Fisheries Technology (Craft & Gear Wing) at Cochin has taken up detailed research investigations on several aspects of marine fouling with a view to developing and employing effective principles of their control particularly on the hulls of fishing boats whose numbers are constantly on the increase.

Summary

The problem of marine fouling and its prevention is a subject of very great economical importance to all maritime nations of the world. A brief review of the work on marine fouling in India and elsewhere is presented in this paper. The findings relating to the composition of the fouling community, their quantitative and qualitative differences, the different members that constitute the fouling community, the role of the primary film and its significance, the seasonal and ecological succession of biotic communities are discussed. Outstanding contributions relating to such environmental factors as temperature, salinity, pollution, turbidity, waves, tides and currents, light, colour, nature and texture of the substratum and abrasion have been reviewed and discussed with particular reference to the conditions prevailing in India. The problem of marine fouling in Indian waters and suggestions for future work mainly based on the work hitherto done have been dealt with. Fifty-eight contributions relating to various aspects of marine fouling carried out till 1964 have been considered.

Acknowledgement

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CHEMISTRY OF LAC by P. K. Bose, Y. Sankaranarayanan & S. C. Sen Gupta (Indian Lac Research Institute, Namkum, Ranchi, Bihar), 1963. Pp. 225. Price Rs 26.60

In the preface it is stated that "The preparation of the present volume was motivated by the idea that an up-to-date review covering previous records and scattered observations on the chemical aspects of lac might be of value in understanding its nature and in stimulating further researches in this field". It is further stated that the compilation of this volume was completed in 1953-54, but owing to various reasons, its publication was considerably delayed.

In the meantime the Indian Lac Research Institute has published a comprehensive monograph on *Lac* (1962), but the book under review is restricted essentially to the chemistry of lac resin.

Chapter I gives a short historical review of the subject, some relevant information about lac cultivation and the different types of lac and their uses. Physical properties and chemical constants are given in Chapter II; composition of various lacs and methods of isolation of individual components are dealt with in Chapter III. Constituents of lac resin are treated in the next chapter, which is perhaps the most important part of this book. The next two chapters deal with the structure of the two major component acids. The remaining chapters deal with 'Structure of lac molecule', 'Minor constituents', ' Partial synthesis and polymerization of shellac', 'Miscellaneous treatments', and 'Identification of shellac'. There is an addendum in which relevant information, available up to 1962, is given. Author and subject indices and a two-page errata complete the book.

The authors have done a great service in bringing together in one volume all the relevant information about lac which should lead to a greater interest in this unique material.

Further research on the composition and constitution of lac acids is essential, if this versatile resin is to meet the increasing competition from the various synthetic resins.

The book is particularly recommended to all organic chemists who are working in the field of natural products.

N. R. KAMATH

MAMMALIAN PROTEIN METABOLISM: Vol. 1, edited by H. N. Munro & J. B. Allison (Academic Press Inc., New York), 1964. Pp. xv+566. Price \$18.50

Current awakening of interest on the importance of proteins in nutrition and insight into the mechanism of protein synthesis have each resulted in a spate of specialized literature on protein metabolism as a whole and the present treatise, in two volumes, provides an up-to-date account of the various biochemical, nutritional and pathological aspects of protein metabolism. The volume under review, confined to biochemical mechanisms, portrays a wealth of information in eleven chapters written by 12 leading investigators in the field from, with one exception, Britain and the United States.

A historical introduction detailing the origin and growth of current concepts of protein metabolism is followed by accounts dealing with digestion and absorption of proteins in the non-ruminant and ruminant mammal, transport mechanisms of free amino acids in various tissues, metabolic transformations and degradations of amino acids, defined steps in protein biosynthesis, tissue and plasma protein turnover and homeostatic mechanisms, proteinhormone interrelationships, general aspects of their regulatory mechanisms and, finally, nitrogen elimination from the body.

The course of protein metabolism is determined by a mosaic of interactions between various agencies, among them dietary supply of amino acids, carbohydrates, fats and other essential nutrients as well as by the secretory activities of the endocrine glands. The various aspects of this complex picture have been ably examined and evaluated by the different contributors, although it is perhaps inevitable that, in a compilation of this kind, there should be some omissions. For example, the reviewer would have liked a reference, in discussing the lability of tissue proteins, to the effects of dietary proteins on tissue enzyme activities. Again, when considering RNA metabolism in relation to turnover, one would have expected a reference to the rapidly accumulating knowledge on tissue RNA profiles determining protein synthesis. Likewise, the discussion on nitrogen excretion products is incomplete without a reference to the current recognition of various, hitherto unknown, nitrogenous bases in the urine.

Nevertheless, in its comprehensive approach, the book maintains a general continuity of reading from chapter to chapter and the uniformly critical presentation of the subject matter together with, oftentimes, the delineation of new and unknown areas of research as well as the selected bibliography appended to each chapter, marks the volume as a source book, not only for the graduate student who requires an advanced survey of the whole subject, but also to the specialist in nutrition, biochemistry, clinical chemistry, medicine and, indeed, all aspects of biology, who needs an authoritative account of selected areas of protein metabolism.

A. SREENIVASAN

BIOLOGICAL EFFECTS OF MAGNETIC FIELD edited by Madeleine F. Barnothy (Plenum Press Inc., New

York), 1964. Pp. ix+324. Price \$ 16.00 As early as 1818 Amici suggested the possibility of electric currents being present in living cells. Later, Bacquerel and Faraday thought it possible to produce biological effects with magnetic fields. In spite of these early observations, sufficient qualitative and quantitative work on the biological effects of magnetic fields has only been done in the last decades and it is, therefore, very fascinating for students of biophysics, to have this excellent volume edited by Prof. M. F. Barnothy. Even though it is a small budget of contributions from the leading figures in this new and exciting field of study, it makes one realize the immense possibilities of magnetic field as a powerful analytical and therapeutic tool in medicine.

The text in the present volume has been divided into the following parts: theoretical considerations; effects of strong magnetic fields in vitro; effects of very weak magnetic fields; and an up-to-date bibliography. Each part is further subdivided into several chapters, written by well-known workers in their respective fields. At many places it would appear that a significant beginning has been made in different directions and the experiments described stimulate one to think deeply on the subject. The effect of magnetic fields on genetic code has been elegantly explained by Prof. Barnothy on the basis that very similar to Zeeman effect, magnetic field may bring about a split of the energy levels of nucleotide bases and may thus excercise influence upon the stability of genetic code. A few experiments have been described to support this view, but it is clearly stated that a definite connection of magnetic field with genetic code is yet to be experimentally established." Magnetic fields have also been applied to the phenomena of growth and development and evidence has been presented to support the general assumption that magnetic field causes mitotic retardation. In one of the chapters tumours have been shown to be rejected in cases of homotransplants due to stress caused by magnetic fields. The lengthening of life span of mice with isotransplants in magnetic fields has also been seen to occur. The experiments reported on the effect of magnetic field on spontaneous mammary gland carcinoma may on further study lead to a solution of cancer therapy.

In one part of the book experiments have been described to illustrate the interference by magnetic fields in the production of large molecules such as proteins, RNA and DNA. Fibroblast proliferation in wound healing has been observed to be clearly delayed by magnetic field suggesting that the enzymatic production of large protein molecules and other biological polymers is inhibited by magnetic fields. The observations, although of a preliminary nature, are interesting and certainly call for further study.

Studies on inhibition of bacterial growth in magnetic field have also been described in this book. One of the chapters is also devoted to the reactivation of trypsin by magnetic fields after partial loss of its activity. Magnetic fields have been shown to probably reorganize the enzyme at or near the active site.

The exhaustive bibliography provided at the end of the book should prove useful to those interested in this new field of research. We live encompassed by physical forces and it is worth while to take up physical forces separately and investigate their biological effects. This book shows how a beginning has been made in this direction by investigating biological effect of magnetic fields.

S. C. Agarwala

Caraka Samhitā — A SCIENTIFIC SYNOPSIS by Priyadaranjan Ray & Hirendra Nath Gupta (National Institute of Sciences of India, New Delhi), 1965. Pp. viii + 120. Price Rs 15.00 or 20s.

The monograph is a synoptic survey of the Caraka samhitā, a well-known medical treatise of ancient India. The distinguishing feature of this monograph lies in its presentation. Concepts about man, matter and universe, origin of diseases, discussions on health and longevity, classification, diagnosis and treatment of diseases, medical education, physicians' role in society and many other topics of biological interest which occur in the original treatise in a scattered manner have been coordinated and systematized from a scientific point of view. Most of the materials have been arranged in tabular forms for ready reference and rapid survey. The English and Latin equivalents of all Sanskrit names are given to avoid ambiguity in their identification and the synoptic survey is well documented.

A brief résumé of the contents of the monograph is presented below:

The identification of the authorship and exact date of composition of *Caraka samhitā* offers considerable difficulty. The available evidence indicates the treatise to be a record of the deliberations of a congress of medical experts in ancient India.

The approximate date of the composition of the text by *Caraka samhitā* which formed the basis of Drdhabala's redaction is estimated to be about A.D. 100.

Caraka samhitā is primarily an exposition of *Ayurveda*, the science of life. Besides classification of diseases, the treatise presents ethical, metaphysical and philosophical ideas prevalent in India during those times.

The eight branches of *Ayurreda*, the ten scientific topics of coverage and the division to eight sections for discussion proposed are catalogued under the 'Scope and subdivisions' of the treatise.

'The concepts and theories' in *Caiaka samhitā* deal with the following:

(a) Man and matter: Following the philosophical doctrine of Sāmkhya and Vedānta, Caraka holds that the individual man and the external world are the manifestations of one and the same eternal spirit (Brahman) and a sound mind and a sound body are prerequisites for the beautific experience of the Divine or Brahman in man.

The elemental composition of man and the visible world, the understanding of truth, the aims and objectives of life, descriptive analysis of matter, animate and inanimate, the role of *Purusa* or transient self in the life of the person and many other metaphysical concepts dealing with mind, body and matter are some other facets of *Caraka saṃhilā*'s presentation.

(b) Modes of origin of living beings: The process of fertilization, the interrelationship of mind, body and soul and the concept that life is indestructible and that birth is nothing new but a transition of an already existing spirit and that spirit is the eternal self, are some of the philosophical teachings featured in *Caraka sanhitā*.

(c) Caraka also attempts to explain the factors involved in the origin of the male or female focus,

the growth and development of the embryo, and inheritance of congenital defects. The importance of nutrition of the parents on the progeny is emphasized.

The *Karma* of the individual is given a prominent role in the mental make-up and the general well-being of the person.

Humoral theory of diseases postulates the wellknown Tridosha theory for explaining the origin of diseases and considers all pathological conditions of the mind and the body, and even their degrees of severity, to be direct results of morbid and aggravated humours.

Factors influencing memory, classification and the interpretations of dreams form some interesting features discussed in *Caraka samhitā*.

Since philosophy, religious practices and healthy living are interwoven, the ethics in *Caraka samhitā* constitute an important feature of healthy living. Caraka recognizes the three primary desires: desire for self-preservation (*Pranaisana*), desire for wealth (*Dhanaisana*), and a desire for a happy future (*Paralokaisana*) to be the springboards for all action.

The laws of *Karma* are not considered immutable by Caraka. He mentions that fruits of certain actions can be averted by proper conduct and medication. Great importance is hence attached to right conduct (*Sadvratta*) for preservation of physical and mental health and in securing sense control (*Indriyavijaya*).

' Physiological processes' are presented under the divisions of ' Digestion and metabolism ' and ' Movements of fluids through the human body and tastes'.

Great significance is attached to the production of heat which is said to be the basis of life processes. The processes of digestion, absorption, metabolism of food and incorporation into body constituents and excretion of waste products discussed give a glimpse of biochemical and physiological knowledge of the times.

The description of innumerable *strotamsi* or fluid currents, their anatomical configuration and the source of individual *srotas* presents the circulatory system as conceived in the days of Caraka.

'Taste' is given an important role in the therapentics of Caraka. Taste and after-taste, the nature of basic and complex tastes, inherent properties of tastes, their derangement in pathological conditions and the beneficial physiological actions of the sub-tances belonging to the basic taste groups are described in detail.

Health and longevity: Personal hygiene ranks topmost amongst the measures for maintenance of health and vigour. Caraka enjoins a disciplined life involving personal cleanliness, regulated physical exercise and avoidance of excesses of any kind.

Caraka recognizes the influence of environment on health and physique of the individuals.

Dietetics forms an important and integral part of the *Caraka samhitā*. Stress is laid upon the significant role of diet in health and sickness. No distinction is made between food and drug since both exert specific actions on the body. The text mentions in detail the digestibility, nutritive value and medicinal actions of several hundreds of different edible and potable substances of various classes.

Rejuvenation therapy is a prominent feature of the *Caraka samhitā*. It is suggested that even in old age it is possible to regain youth and remain youthful for a very long period.

The need for public health measures to prevent the spread of disease was well recognized by Caraka. Public sanitation and pure water supply are dealt with in the text.

Physicians in *Caraka samhitā*: Selection of candidates for the study of medicine, the training programme, the duties and responsibilities of the physician, the code of conduct in dealing with the patients are exhaustively treated by Caraka. Friend-ship towards all, compassion for the ailing, devotion to professional duties and a philosophical attitude to cases with fatal endings have been defined as the four cornerstones of medical practice.

Caraka samhitā gives directions for the diagnosis of a large number of diseases from a consideration of their etiology, symptoms and prognosis.

Different types of treatment have been described by Caraka. These include oral medication, eye drops, gargles, medicinal smoking, unguents, suppositories, enema, douches, sweating, bleeding, surgical excision, bandaging and psychiatric methods for curing mental conditions.

Poisons: The types of poisons, toxic effects, the mode of action and specific antidotes are discussed in detail. It was realized that even deadly poisons can be converted into excellent medicines by the right method of application and medicinal values of many venoms and vegetable poisons have been mentioned.

Weights, measures and techniques used for the compounding of medicines and the chemical processes adopted in the preparation of drugs present some interesting facets of the chemical knowledge available during Caraka's times.

Vibhagavaidva or the theory of classification is a feature of Caraka samhilā.

The days of *Somvaisara* (solar year), the nature of the habitable land, the types of living creatures, plants and vegetation, the physiological actions of the plants, the medicinal uses of *dravya* (material substance), diseases, poisons and *krmis* have all been subjected to analysis and classified.

The twenty tables covering nearly three-fourths the space are the special features of this monograph. The information widely dispersed in the original text is systematically documented and scientifically presented.

M. SIRSI

How TO WRITE EFFECTIVE REPORTS, programmed by Federal Electric Corporation (Addison-Wesley Publishing Co. Inc., Reading, Mass.), 1965. Pp. ix+310. Price \$ 6.95

This book differs from other books on technical writing in that it is based on a new learning technique called 'programmed instruction'. The learner works himself with it, takes active part in it and learns a small amount of material at a time. When mistakes are made, he is taught what the mistake is and how to proceed further in the study.

Technical writing is a neglected art in India. Mere accumulation of knowledge without effective presentation in the form of the written word will not serve the desired purpose of wide circulation and subsequent utilization of the knowledge. The need for organizing regular courses for technical writing at the college level to train scientists, engineers, lawyers and other professionals to express ideas clearly, accurately and briefly has been underlined in the reviewer's earlier review [this journal, 23 (1964), 114]. Cur experience, as also elsewhere, is that the problems of writing do not merely relate to spelling, grammar, syntax or semantics. The organization of ideas in the proper sequence in a manner suited to meet the requirements of the particular audience to whom they are directed, the style and format, choice and arrangement of contents, graphic and tabular presentation, etc., are some parts of the mechanics of report writing. To scientists and engineers, writing for the manager, the specialist, the semi-technical man or the layman, the writing exercise is of paramount importance.

This book will be a useful adjunct to numerous books which have appeared on technical writing and editing and style manuals. It is an effective programmed instruction course which will enable students to write successfully in their profession. It trains the student how to collect ideas, present ideas to a particular audience, determine the type of report and its parts, choose the style and words appropriately, recognizing loaded words and slanted presentations, and represent his data. The book, being a selfinstructor, can be used by any student. A 17-page instructor's guide is also supplied with the book.

K. RAJAGOPALAN

THEORY OF CRYSTAL DISLOCATIONS by A. H. Cottrell (Gordon & Breach Science Publishers, New York), 1964. Pp. ix+91. Price \$ 2.50 (paper bound); \$ 4.50 (cloth bound)

This book is based on a course of lectures given at Les Houches by Prof. Cottrell in 1956 and deals with the basic theory of dislocations in crystals. It comprises nine chapters. The chapter headings given below indicate the field covered: (1) Dislocations and slip; (2) Geometrical properties of dislocations; (3) Geometry of dislocated crystals; (4) The elastic field of a dislocation; (5) Dynamics of moving dislocations; (6) Forces on dislocations; (7) Structure of the centre of a dislocation; (8) Imperfect dislocations; and (9) Dislocations and the properties of crystals.

The exposition of the subject is systematic and lucid as is characteristic of Prof. Cottrell. The book has been meant to be a theoretical one and the reader unacquainted with the subject will find it profitable to read a book like *Dislocations in crystals* by W. T. Read and other books, a list of which is given on pages 1 and 2.

As the author has remarked, "The amount of work on applications of dislocation theory to the understanding of the structure-sensitive properties greatly exceeds that on the pure theory itself". In the concluding chapter a few aspects of the mechanical properties of the crystals have been outlined. But a list of references to physical and chemical properties has been given on pages 80-81 for those interested in detailed study. Indeed at several places in different chapters the author has added references up to 1962, and small notes to indicate recent developments.

It is an excellent book and condenses in 91 pages the basic theory of one of the rapidly developing and spectacular fields in solid state physics.

A. R. VERMA

THE CUBE MADE INTERESTING by Aniela Ehrenfeucht; translated from the Polish by Waclaw Zawadowski (Pergamon Press Ltd, Oxford), 1964. Pp. vii+83. Price 21s.

The cube made interesting is the ninth of a series of popular lectures on mathematics that Pergamon Press is bringing out on a variety of mathematical topics by a number of distinguished mathematicians, edited by I. N. Sneddon and M. Stark. The most interesting feature of this book on the cube by Ehrenfeucht is the ingenious device of employing what are called anaglyphs instead of the more usual two-dimensional diagrams commonly employed to develop geometrical arguments. As the book explains at the very outset, anaglyphs are strange looking two-tone drawings in red and blue lines so made that the red part shows you what you see with your left eye and blue part shows what you see with your right eye. The book also has been provided with two-tone glasses with which these anaglyphs are to be seen. When an anaglyph is viewed through such two-tone glasses, each eve sees its part of the drawing and you see rising out of the two-dimensional figure on the page a three-dimensional stereoscopic picture of a solid cube made of bars. What is more is that the author manages to pull out of the cube a diversity of polyhedrons like the regular octahedrons or Egyptian pyramids by various artifices such as dividing the cube across one of its planes of symmetry and joining the centre of each of the cube's faces to the centre of each of the neighbouring faces by straight lines. You can see the inscribed octahedron inside the cube by looking at the appropriate analyph through the coloured glasses as if a solid model were placed on the page in front of you. With the aid of anaglyphs the author explores some of the most interesting properties of the cube.

He begins by classifying the cube as a member of a larger family of polyhedrons such as prisms, pyramids, tetrahedrons, and the like. As a member of this family the cube is shown to conform to the well-known theorem of Euler which requires that V+F-E=2, where V, F and E are respectively. the number of vertices, faces and edges possessed by the solid. As is well known, the cube has eight vertices, six faces and twelve edges so that Euler's equation quoted above is satisfied. But this is only a beginning. The book proceeds to show what happens when we choose to divide the cube by a plane of symmetry into two mutually symmetric parts. Through a series of anaglyphs we can actually see the various kinds of solids that can be carved out of the cube by rotating it around its axes of symmetry in various ways. In the next chapter the author describes the sections of the cube when a plane is made to cut through at least three of its faces. Since a plane is fully determined by three points, we may take three points on three of the edges of the cube. If the three points chosen are on the three edges

meeting in a vertex, the section is a triangle. But if the plane cuts through four parallel edges, the section is a parallelogram which in special cases may be turned into a rhombus, a rectangle, or a square. And so on.

The author next proceeds to amuse us by showing what one may do with a number of cubes of the same size but of different colours. The climax reaches when in the last chapter the author considers a paradoxical problem - how to make a bigger cube slide through a smaller one. Suppose we have two cubes of unequal sides. Can we bore a hole in the smaller cube so that the bigger can slide through it ? Most people will answer 'No'. However, the true problem is not to put a bigger cube completely into the smaller one which, of course, is impossible. But it is possible to cut a hole out of the smaller one so that the bigger one could only pass through, 'like a barrel through a loose hoop'. If you want to know how, you had better read the book. It will need no more than high school geometry to understand, though a certain amount of maturity in mathematical reasoning, in particular rudiments of group theory, will be necessary.

The translation into English from the original Polish is excellent.

JAGHT SINGH

X-RAY AND ELECTRON PROBE ANALYSIS — Symposium held at the Sixty-sixth Annual Meeting, ASTM, 27 June 1963 (American Society for Testing & Materials, Philadelphia), 1964. Pp. v+209. Price \$ 10.00

This book contains the proceedings of the symposium on X-ray and electron probe analysis held under the auspices of the American Society for Testing & Materials. The papers presented cover X-ray spectrochemical analysis and electron probe analysis techniques. They deal with methods of production of X-rays, X-ray and electron probe optics, detectors and counting techniques, and the applications of these techniques to analysis of metals, minerals, trace elements including thin films, and liquids and solutions, and finally trace elements in biological materials.

X-ray spectroscopy provides one more tool to the analyst. As with many other analytical procedures, special care is to be taken to avoid sources of error if one is to make the best of the particular technique. In X-ray analysis, one such pitfall is the absorption and enhancement effects. These have been adequately dealt with in the papers and methods suggested to avoid them or to evaluate them correctly. The papers also deal with efforts being made to extend X-ray methods to the lighter elements.

The electron probe method is relatively new. The papers presented give an idea of the effort made in the USA to know what one can do by this technique, its limitations and the actual results obtained to date in the field of metallography, mineral analysis and biology. Its use in detecting 0.01 per cent of an element in micron size cells and its distribution intercellularly and extracellularly opens up a vast new field of application.

The book has been well presented with neat diagrams and figures. The inclusion of discussions

makes the book more interesting. The book will be found valuable to chemists, physicists and metallurgists, and will be welcome addition to libraries of universities, colleges, scientific laboratories as well as industries.

JAGDISH SHANKAR

CHEMICAL AND BIOLOGICAL ASPECTS OF PYRIDOXAL CATALYSIS edited by E. E. Snell, P. M. Fasella, A. Braunstein & A. Rossi Fanelli (Pergamon Press Ltd, Oxford), 1963. Pp. xv+599. Price £7

The list of reactions of intermediary metabolism where the coenzyme pyridoxal phosphate plays a key role is a formidable one indeed. Such reactions include racemization of *a*-amino acids, condensation at α -C of glycine, serine, transamination, oxidative deamination, decarboxylation, elimination of substituent on B-carbon, replacement of substituent on β-carbon, β-decarboxylation, hydrolytic cleavage of γ-keto-α-amino acids or replacement of substituent on y-carbon and are responsible for the synthesis and interconversion of amino acids and sulphur containing compounds. Pyridoxal phosphate also participates in a number of non-enzymic reactions such as metal catalysed transaminations and deaminations at elevated temperatures. This property has been exploited for elucidating the mechanism of action of the coenzyme.

In a symposium on the chemical and biological aspects of pyridoxal catalysis organized by the International Union of Biochemistry at Rome in October 1962, 48 papers were contributed by leading workers of the world in this field and of these 46 have been brought together in this volume. In a prefatory paper, E. E. Snell reviews the historical aspects of the chemistry of pyridoxin with emphasis on the need for further work on model systems to elucidate the mechanism of action of pyridoxal catalysed reactions and in a concluding chapter, Braunstein presents an excellent survey of pyridoxal phosphate mediated enzymic reactions with particular reference to the binding of the coenzyme to different sites on the apoenzyme. In the intervening papers, a rich and stimulating fare is provided on subjects of such topical interest as diamine oxidases, transsulphuration, kinetics of transaminase reaction, isonictinic acid pyridoxal antagonisms, etc. The value of the contributions is enhanced by the faithful record of discussion at the end of each paper.

The volume would prove to be a very helpful companion to research workers engaged on pyridoxal phosphate mediated reaction.

C. R. KRISHNA MURTI

PROGRESS IN BIOPHYSICS AND MOLECULAR BIOLOGY: Vol. 13, edited by J. A. V. Butler, H. E. Huxley & R. E. Zirkle (Pergamon Press Ltd, Oxford), 1963. Pp. vii+328. Price 90s.

This is the thirteenth volume of the series on Progress in Biophysics and Biophysical Chemistry. The title of the present volume has been changed to suit modern trends in identifying investigations on structure and function at macromolecular level with the new discipline of molecular biology. Six well-documented reviews on radiobiological mechanisms, radiation chemistry of aqueous solutions of
nucleic acids and nucleoproteins, X-ray angle scattering of substances of biological interest, enzymic synthesis of nucleic acids, ultrastructure and kinetic aspects of solute translocation in plant stems and the mechano-chemistry of muscular contraction are included in this volume. Each review represents a wide field of experimental investigations and critical assessment of their theoretical basis, the relevant information being drawn from widely scattered sources. The reviews are of uniformly high standard and fulfil the expected function of acting as vital links between text-books and scientific journals dealing with the diverse subjects discussed. The reviewer's only regret is that the publishers have, by fixing the price at 90s, kept the book beyond the reach of the ordinary research worker.

C. R. KRISHNA MURTI

BOOK NOTES

DICTIONARY OF NUCLEAR PHYSICS AND NUCLEAR CHEMISTRY — GERMAN-ENGLISH/AMERICAN ENG-LISH/AMERICAN-GERMAN, edited by Hans Rau (Reinhold Publishing Co., New York), 1964. Pp. 351. Price \$ 8.75

Because of the addition of a large number of new words and terminologies in recent years in the field of nuclear technology, a second revised and enlarged edition of this well-known dictionary has been found necessary. The new edition includes about 8000 technical words pertaining to the various branches of nuclear physics and chemistry, and gives their meanings from German to English and vice versa. About 1500 nuclear physical and nuclear chemical symbols as well as abbreviations are also explained both in English and German. The dictionary will be valuable as a reference book to workers in research institutions and universities. It will also serve as a valuable handbook for persons engaged in translation of scientific articles.

K. S. RANGARAJAN

PUBLICATIONS RECEIVED

- NUCLEIC ACIDS: STRUCTURE, BIOSYNTHESIS AND FUNCTION (Council of Scientific & Industrial Research, New Delhi), 1965. Pp. xi+360. Price Rs 20.00; 40s. or \$ 6.00
- ROAD RESEARCH SPECIAL REPORTS NO. 1 PUZZO-LANIC CLAYS OF INDIA, THEIR INDUSTRIAL EXPLOITATION AND USE IN ENGINEERING WORKS (Central Road Research Institute, New Delhi), 1964. Pp. viii+290. Price Rs 13.00

- THE INDIAN EPHEMERIS AND NAUTICAL ALMANAC FOR THE YEAR 1966 (Manager of Publications, Delhi), 1965. Pp. xviii+462. Price Rs 14.00; 32s. 8d. or \$ 5.04
- STRUCTURE AND FUNCTION IN BIOLOGICAL MEM-BRANES: Vol. II, by J. Lee Kavanan (Holden Day Inc., San Francisco), 1965. Pp. x+760. Price § 14.75
- ENGINEERING THERMODYNAMICS by Munir R. El-Saden (D. Van Nostrand Co. Inc., New York), 1965. Pp. xv+216. Price § 5.95
 AN INTRODUCTION TO RADIATION CHEMISTRY by
- Ax INTRODUCTION TO RADIATION CHEMISTRY by J. W. T. Spinks & R. J. Woods (John Wiley & Sons Inc., New York), 1964. Pp. xi+477. Price \$ 12.75
- ADVANCING FRONTIERS IN THE CHEMISTRY OF NATURAL PRODUCTS: Vol. I (Hindustan Publishing Corp., India), 1965. Pp. xviii+311. Price Rs 35.00; 55s. or \$ 8.50
- INTRODUCTION TO THE THEORY OF RELATIVITY AND THE PRINCIPLES OF MODERN PHYSICS by Hüseyin Yilmaz (Blaisdell Publishing Co., London), 1965. Pp. xiv+216
- ADVANCES IN HETEROCYCLIC CHEMISTRY: Vol. 3, edited by A. R. Katritzky (Academic Press Inc., New York), 1964. Pp. xiii+421. Price § 13.00
- RAPID MIXING AND SAMPLING TECHNIQUES IN BIOCHEMISTRY — A Symposium of the International Union of Biochemistry, edited by Britton Chance, Rudolf H. Eisenhardt, Quentin H. Gibson & K. Karl Lonberg-Holm (Academic Press Inc., New York), 1964. Pp. xii+400. Price \$ 9.00
- QUANTUM OPTICS AND ELECTRONICS edited by C. DeWitt, A. Blandin & C. Cohen-Tannoudji (Gordon & Breach Science Publishers Inc., New York), 1965. Pp. ix+621. Price § 8.50 (paper); § 10.50 (cloth)
- CHEMICAL PHYSICS OF SEMICONDUCTORS by J. P. Suchet (D. Van Nostrand Co. Inc., New York), 1965. Pp. xii+197. Price 55s.
- BASIC THEORY OF SPACE COMMUNICATIONS by Frederick J. Tischer (D. Van Nostrand Co. Inc., New York), 1965. Pp. xix+463. Price § 11.75
- THE CHEMICAL FOUNDATIONS OF MOLECULAR BIOLOGY by Robert F. Steiner (D. Van Nostrand Co. Inc., New York), 1965. Pp. xii+468. Price § 12.00
- INTERNATIONAL SERIES OF MONOGRAPHS ON PURE AND APPLIED BIOLOGY: Vol. 4— OLIGOSACCHARIDES by R. W. Bailey (Pergamon Press Ltd, Oxford), ~ 1965. Pp. vii+179. Price 60s.

A new class of radio source spectra

Observation of the flux densities of 35 non-thermal radio sources made at the University of Michigan (using the university's 85 ft reflector) has indicated the possibility of existence of a new class of radio source spectra. When the flux densities of the radio sources measured at 8000 Mc/s. were compared with spectra of the same sources at frequencies less than 3200 Mc/s., it was found that most spectra were either straight or curved downward at the high frequency end of the spectrum. However, the radio source 3C84 which has been identified with the Seyfert galaxy NGC 1275 was found to have a flux density at 8000 Mc/s. which was four times greater than that expected from a straight line extrapolation of the spectrum observed at frequencies less than 3200 Mc/s. This is the first instance where a radio spectrum having such a pronounced upward turn in its spectrum with increasing frequency has been observed. Thus NGC 1275 may represent a new class of radio source spectra.

If the low frequency spectrum of NGC 1275 is linearly interpolated to high frequencies and subtracted from the observed composite spectrum, an isolated spectrum of a high frequency component of the source is obtained. This spectrum could be produced by thermal radiation of free-free transitions in a region of ionized hydrogen that becomes opaque near 8000 Mc/s. Based on the assumption that the high frequency component is a thermal source, it is deduced that the electron temperature (T_c) of the gas is 4500°K, and that the mass of the source (M) is $4 \times 10^{10} M_{\odot}$ (about one-tenth the mass of the galaxy). The predicted free-free and Paschen continua at optical frequencies from the above model is not inconsistent with the optical magnitude of the galaxy. However, the integrated flux density of the H line is a few orders of magnitude less than the value predicted by the above model. In order that the observed integrated flux density may agree with that theoretically deduced on the basis of the thermal interpretation of the

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radio spectrum, it is necessary to adopt a value of 1.5×10^6 °K. for T_e and $2 \times 10^9 M_{\odot}$ for the total mass. Photoelectric measurements of the H_{β} flux of the nucleus of NGC 1275 and future angular diameter measurement of the radio source at frequencies greater than 8000 Mc/s. will be able to test the validity of the above two models. It is also possible that the high frequency component of NGC 1275 is produced by a relatively flat synchrotron radiation spectrum similar to that of 3C273B but with a low frequency spectral cutoff near 8000 Mc/s. due to selfabsorption. However, synchrotron self-absorption at this high frequency requires exceptionally large magnetic fields [Nature, Lond., 205 (1965), 487].

A new logarithmic scale of temperature

A suggestion for the construction of a logarithmic scale of temperature, since the linear absolute scale of temperature does not stress the inaccessibility of the temperature 0°K., has been made from the Department of Chemical Engineering, University of British Columbia, Vancouver 8, Canada. The new scale is based on the relation $T = e^{\Psi}$ where T is the absolute temperature and $\Psi = \int g(0) d0$ and depends on the thermal properties (0) of the system. The Ψ values correspond to the values of the temperatures in the new scale. The logarithmic nature of the Ψ function assures that the zero value on the linear absolute scale (T-scale) will be reached asymptotically, that is T = 0 when $\Psi = -\infty$ and hence the inaccessibility of the absolute zero follows generically, not being subject to imagination as is the case in the linear scale [Nature, Lond., 205 (1965), 489].

Atomic definition of time

The International Committee on Weights and Measures at its XII General Conference held at Paris in 1964 tentatively adopted an atomic definition of the second, the international unit of time. The definition is based on an invariant transition of the cesium atom. This definition, which facilitates the expression of the results of high precision time and frequency measurements, is in close agreement with the definition adopted in 1956 (known as an ephemeris second). An accuracy of 1 in 100 billion (200 times that attainable by the astronomical means) can be achieved with the adoption of the new unit, precise measurements being made in a few minutes. The exact wording adopted by the conference in respect of the pro-posed definition is: "The standard to be employed is the transition between the two hyperfine levels $F = 4, M_F = 0 \text{ and } F = 3, M_F = 0$ of the fundamental state 2S1 of the atom of cesium 133 undisturbed by external fields and the value 9, 192, 631, 770 hertz is assigned " Tech. News Bull. U.S. Bur. Stand., 48 (1964), 209].

A new natural force

Physicists are speculating about the existence of a hitherto unrecognized fifth natural force, in addition to the existing four forces, viz. nuclear force, electromagnetic force, weak force and gravitation in the decreasing order. The need for the postulation of such a force arose in an attempt to explain the two-pi decay of the neutral K2 meson which otherwise leads to a contradiction of the fundamental timereversal invariance principle. The existence of such a force has been visualized independently by physicists at the European Organization for Nuclear Research (CERN) and those at the British Atomic Energy Establishment. According to them the forbidden two-pi decay is due to a new natural force that is weaker than gravity. The proposed force would have one sign (representing a basic characteristic) if produced by ordinary matter and opposite sign if produced by antimatter. Assuming that the whole of our galaxy consists of ordinary matter, the potential of the fifth force energy at the earth's surface should be almost entirely that produced by ordinary matter. If such an asymmetrical force field exists, one should expect that its effect on matter and antimatter will be different. Its strength and asymmetry would be just enough to convert an occasional neutral K_2 meson into a neutral K_1 meson, which can decay into two-pi mesons without violating the CP rule. If the fifth force exists, the number of two-pi decays should increase by a factor of 100 if the energy of the decaying particles is raised by a factor of 10. Experiments to verify the proposal are on hand at CERN and Brookhaven [Sci. Amer., 211 (No. 6) (1964), 62].

Evidence for the 'weak' force interaction between protons and neutrons

Recent observations made on the directions of spin of gamma-ray photons released during radioactive decay of hafnium-181 by Felix H. Boehm and Egbert Kankeleit of the California Institute of Technology have indicated evidence for the existence of the 'weak' force interaction between protons and neutrons. Protons and neutrons are known to interact so far only through the 'strong' force (which binds the nucleus together) while only particles like neutrinos, electrons and mesons interact through the ' weak ' forces whose magnitude is only 10⁻¹² of the strength of the electromagnetic force that binds electrons to protons and 10-14 of that of the nuclear force. It was predicted several years ago by Richard P. Feynman and Murray Gell-Mann of the California Institute of Technology that there should be also a ' weak ' force effect in the interactions of protons and neutrons. The recent observations seem to lend evidence to this prediction. In the experiments designed by Boehm and Kankeleit, the directions of spin of gamma-ray photons released in the decay of determined. hafnium-181 were This particular isotope has been selected for the reason that if there were no influence from a 'weak' force interaction between protons and neutrons, exactly half of the photons produced in the radioactive decay should emerge with a righthanded spin and exactly half with a

left-handed spin. Evidence for the 'weak' force would be indicated if these two numbers were not equal, since this would indicate a violation of parity, which is permitted for nuclear events associated with the weak force.

The gamma rays emerging from hafnium-181 were sent through a strong electromagnet, the polarity of which was reversed every 10 sec., thus making the photons to encounter electrons of alternating spin directions. When photons and electrons have opposite spins the photons would be deflected from the beam and would not reach a detector scintillation counter. If the spins were in the same direction, deflection was less likely and the photon would be counted. Photons were counted at the rate of 15 billion a day for several months, and it was found that on the average left-handed and righthanded spins did not balance out for 3 out of every 10,000 photons. Thus this observation shows that parity is not fully conserved, indicating that the 'weak' force was operative in the case of protons and neutrons to a corresponding degree [Sci. Amer., 212 (No. 2) (1965), 51].

Carbonaceous fuel cell

A significant step in the development of a practical large-scale, coalburning fuel cell system for electric power generation has been achieved by the development of an experimental 100 W. fuel cell battery at the Westinghouse Research Laboratories, USA. The fuel cell battery system consists of 400 cells of the solid electrolyte type arranged in ceramic cylinders in 20 stacks of 20 cells each and coupled to a chemical reactor which generates volatile gases from coal. The ceramic electrolyte permits an all-solid construction, eliminating liquids and paste chemical used in other types of cells. In the new system a mixture of hydrogen and carbon monoxide generated at the reactor (by passing steam over hot coal) circulates through the stacks of fuel cells, while hot air is kept circulating around the outer surface of the cells surrounding the anode. Negatively charged ions are formed when electrons removed from the anode attach themselves to the oxygen molecules in the air.

Moving through the solid electrolyte the ions collect at the negative electrode and combine with atoms of the fuel gases, freeing the electrons picked up at the anode. Such a displacement of the electrons constitutes the electric current. The fuel cell battery is housed in a heated oven to maintain the temperature at 1800°F. Cell systems developing several kilowatts, however, could generate enough heat to maintain this operating temperature without the aid of an external heat supply [Mech. Engng, 87 (No. 4) (1965), 63.

Ion-exchange technique based on reciprocating flow

Studies conducted at the Toronto University Laboratories have resulted in the development of a modified ion-exchange technique based on reciprocating flow which holds promise of extending the applicability of the technique in such areas where it was considered uneconomical so far. A typical application of the technique is in the removal of scaleforming ions from saline waters. Sea water is fed to the top of the resin column, forcing the regenerant (brine from the distillation) out of the bottom and into a reservoir. When sea water reaches the bottom, it is diverted to the distillation set-up. At the proper time, the direction of the flow is reversed by manipulating the valves and the regenerant forces sea water in the column back out of the top and through an exhaust line. Again the direction of flow is changed by manipulating the valves and sea water enters the top of the column to start the cycle. Sea water and regenerant are cycled at very high rates (30-60 sec./cvcle) which is possible because low levels of loading are used (5 per cent of the available resin capacity). This leads to a high rate of exchange, which, in turn, makes fast cycling possible. A significant feature of the technique is that mixing of sea water and regenerant does not occur. The interface is stable as it travels up and down the column during cycling. A resin bed 4 in. deep can remove 89 per cent of calcium and 55 per cent of magnesium from sea water. This volume is 0.5-2 per cent of that required in a conventional column [Chem. Engng News, 43 (8) (1965), 38].

Sub-micromethod for the determination of olefinic unsaturation

The use of bromine monochloride as an effective reagent for determining the degree of unsaturation on a sub-micro scale in a wide variety of olefins has been reported [J. chem. Soc., (1965), 1740]. The procedure for determining the unsaturation consists in the addition of a slight excess of standard bromine monochloride to 40-80 ug. of the organic material followed by an iodimetric determination of the excess of the reagent. The accuracy of the method varies from +0.4 per cent for isolated double bonds and certain less reactive olefins to +3 per cent for more reactive olefins.

A weighed sample of the unsaturated compound is dissolved in 1-2 drops of 1N sodium hydroxide (for the majority of α , β -unsaturated acids), or in 0.2 ml. of methanol. The solution is cooled in ice and 0.1N bromine monochloride solution is then added so that an excess of 20-100 per cent is present (usually between 0.02 and 0.10 ml.). The solution is allowed to stand in a desiccator containing ice until the reaction is complete. Distilled water (0.5 ml.) is then added to the titration vessel, and the solution cooled in ice again for a further 30 sec. A glass-covered rotor is added and the tip of the micrometer containing the standard 0.01Nthiosulphate placed in the solution before the addition of 2 drops of 15 per cent potassium iodide solution is made. In this way, the losses due to the volatility of the liberated iodine are minimized. The solution is titrated to a very pale yellow colour, a few mg. of thyodene are added, and the titration is continued until the disappearance of the blue colour.

With the majority of α,β -unsaturated acids, a solution of mercuric sulphate is added to advantage. After addition of the bromine monochloride reagent, 0.5*M* mercuric sulphate solution equal to 1.5 times (by volume) the volume of the bromine monochloride reagent is added. This also necessitates the addition of sufficient potassium iodide to convert all the free mercuric ion to (HgI₄)²⁻ before the titration of the excess of bromine monochloride.

Improved method for the preparation of diborane

Diborane has been produced in yields of up to 98 per cent by reacting sodium borohydride with the halides of mercury and antimony in diglyme or triglyme solution at room temperature under a near vacuum. Developed at the Department of Chemistry, University of Exeter (UK), the method is highly flexible, easily controlled, and suitable for preparing calculated quantities of diborane.

The diborane generator consists of a 500 ml. three-necked flask, fitted with an inlet tube, tap funnel and outlet tube leading to a vacuum pump via a series of traps cooled in liquid nitrogen, except the first trap which is kept at -78° C. to remove traces of volatilized solvent; diborane is collected in the other traps. In a typical experiment the stoichiometric quantity of halide needed to react with 4 g. of 95 per cent sodium borohydride is placed in the generator with 20 ml. of dried diglyme, which is stirred magnetically. The generator is swept out with nitrogen and the pressure reduced to near that of the solvent vapour. The borohydride dissolved in diglyme is now added in small portions from the tap funnel. Reaction is immediate and exothermic and does not require heating. Pumping is continued for 15 min. after the final addition to ensure complete transference of the diborane to the liquid-nitrogen traps [Chem. & Ind., (1965), 471].

New source of niobium

Investigations at the Warren Spring Laboratory in UK have indicated that pyrochlore minerals are a potential source of reactor grade niobium at lower costs. This eliminates the expensive niobium-tantalum liquid-liquid separation step required to reduce tantalum to below 0.15 per cent by weight in the preparation of reactor grade niobium from the conventional source, columbite.

Pyrochlore, a calcium niobate $(Na, Ca)_2N_2^{\circ}O_6(OH, F, O)$, has been recently investigated as a new source of niobium. Like columbite, pyrochlore is a member of an isomorphous series with pyrochlore and microlite as end

members. However, there is a difference between the two series in the way they occur in nature. Columbites always contain appreciable concentrations of tantalum, while, on the other hand, pyrochlore microbite series are close to one end or the other, so far as the niobium and tantalum contents are concerned.

The niobium in the samples was determined by decomposing sample materials by digestion into hydrofluoric acid, removing the precipitated fluorides and evaporating niobium solutions with sulphuric acid. The determinations were completed spectrophotometrically, using the colour given by niobium with hydrogen peroxide in a sulphuric-phosphoric acid solution. The tantalum was determined by measuring the activity of the separated tantalum after irradiation of the sample materials for 12 days at a neutron flux of 2×10^{12} n/cm.² sec. Then, an inactive tantalum solution was added as carrier, and decomposition effected by evaporation with hydrofluoric acid. The tantalum was precipitated from a sulphurictartaric acid solution with tannin at pH 2.3, and converted to oxide. This was dissolved in a hydrofluoric-nitric acid mixture, the tantalum present extracted into methylisobutylketone, back-extracted into hydrogen peroxide solution and precipitated with tannin at pH 2.3. The tannate was ignited to oxide, weighed and the activity of the tantalum-182 isotope measured.

Niobium/tantalum ratios as low as 500: 1 may be satisfactory for reaction grade metal and also for alloy production as in the processing of the mineral some preferential depletion of tantalum occurs. The availability of pyrochlores as a source of niobium metal can be expected to make an important contribution to an eventual reduction in the cost of this element for industrial applications [*Nature, Lond.*, **204** (1964), 867].

Use of microcrystalline cellulose in thin-layer chromatographic separation of nucleic acid derivatives

Microcrystalline cellulose, 'Avicel', has been used successfully for thin-layer chromatographic separation of bases, nucleosides and nucleotides. Avicel microcrystalline cellulose has got a number of advantages as a material for use in thin-layer chromatography over the normal unsubstituted celluloses. It requires no binder for fixing it on to the glass plate and all the solvents normally employed in paper chromatography can be used. The layer obtained is very consistent and one can even write on it with a pencil. The very white colour of the layer permits excellent detection of spots by ultraviolet light; even 5 mumoles of nucleic acid derivatives can be revealed on superfine grade Avicel. Above all, the relative positions of the spots are quite reproducible. Utilizing the two-dimensional chromatographic procedure, phosphokinases of deoxynucleotides have been successfully assayed.

The separation procedure involves the following steps. Com-Avicel micromercial grade crystalline cellulose (American Viscose Corporation, Marcus Hook, Pa; 30 g.) in 500 ml. of 5 mM versene is stirred for 10 min., the mixture filtered through a buchner funnel, and mixed with doubly glass-distilled water. Versene treatment is repeated and then the cellulose is suspended in 150 ml. of water and degassed under vacuum. On shaking, a homogeneous slurry, enough for 10 plates $(12.7 \times 16.7 \text{ cm.})$ is obtained. Superfine grade Avicel can be used as a suspension in water without any pretreatment and it will give better separations than the commercial grade. The slurry is poured on to a plate (preferably, wiped with alcohol just before use), dried overnight at room temperature and in ventillated oven at 40°C. for 1 hr. Two-dimensional chromatography is performed at room temperature (18-22°C.) in chromatographic tanks $(21 \times 21 \times 19)$ cm.) filled with the solvent to a height of 0.5-1 cm. Spots are detected with the aid of a mineralight short wave lamp [Biochim. biophys. Acta, 95 (No. 1) (1965), 1].

A new deposition technique for making high purity thin films

Refractory metal films of high purity can now be produced simply, easily and without an ultrahigh vacuum by a new deposition technique called getter sputtering developed by H. C. Theuerer of Bell Telephone Laboratories. In getter sputtering, the metal being deposited acts like a 'getter' in an electronic vacuum tube, reacting with and eliminating unwanted gaseous impurities. The new technique makes use of cathode sputtering, a process widely used to deposit thin films.

Previously, a vacuum as high as 10-12 Torr (one Torr is equivalent to 1 mm. of mercury or 1/760 of a standard atmosphere) was necessary to prevent contamination of reactive metal films formed by a vacuum deposition process. This required special equipment (the higher the vacuum, the purer the film). With getter sputtering, the same results are achieved with conventional laboratory equipment which operates at much lower vacuums ranging from 10-3 to 10-6 Torr. Getter sputtering can be used to deposit a wide range of materials that require strict control of composition, including superconducting metals, magnetic films, epitaxial semiconductors, compound films and alloy films.

Unlike conventional cathode sputtering, getter sputtering confines the deposition of material to the inside of a cylindrical container (Fig. 1). Inside the container, which serves as the anode, is a metal cathode and a thin film substrate. The entire apparatus is placed in a vacuum system. The metal cathode is bombarded by an inert ionized gas such as



Fig. 1—Schematic drawing showing the principal components used in getter sputtering

argon, causing the cathode to emit or 'sputter' in all directions.

Contaminating gases such as water vapour, carbon monoxide, oxygen and nitrogen enter the vacuum system through openings that admit the cathode leads and electrodes. However, as the gases enter the inner container, they are gettered' by some of the metal atoms being emitted from the cathode. Some of the metal atoms absorb the gases and deposit them on the wall of the container. A shutter shields the substrate from sputtered metal until proper conditions are reached and the contaminating gases have been gettered. Then the shutter is swung out of the way and cathode atoms sputter on to the substrate, forming a very thin, uniform film of high purity, that is, a film with the same composition as the cathode material [News from Bell Telephone Laboratories, 9 April 1965

Oscillopolarographic estimation of denatured DNA

Denatured DNA in amounts as small as $0.2 \mu g$, can be estimated in the presence of large excess of native DNA by an elegant technique developed at the Institute of Biophysics, Czechoslovak Academy of Sciences, Brno (Czechoslovakia). The simple and rapid method is based on the cathodic indentation on the oscillogram of dE/dt against E if denatured DNA is subjected to a.c. oscillographic polarography. Native DNA does not produce the same indentation. The appearance of the cathodic indentation on the oscillogram of DNA is a reliable sign of denaturation and can be employed both to follow the course of DNA denaturation and to measure the extent of denaturation. As little as 0.2 ml, of the sample is sufficient; protein and RNA do not interfere. Apart from a polaroscope, a specially constructed oscillograph capable of registering ' first curves' is required for the estimation of the extent of denaturation. As the electrolyte medium, a solution of ammonium formate (0.3M) and sodium phosphate (0.05M, pH 7) can be used. The dropping mercury electrode can be polarized by alternating current of sinusoidal or rectangular shape, and a frequency of 50 c/s.

Denaturation of DNA can be carried out by heating DNA in a dilute solution of sodium chloride and citrate for 10 min. at 100°C. and cooling the sample suddenly in ice. The new method compares favourably with methods based on the commonly employed techniques of ultraviolet spectrophotometry, viscosimetry, and ultracentrifugation, both in its scope and rapidity.

The oscillopolarographic method represents a new approach in the field of nucleic acid research and holds much promise to unravel further information on the properties of the DNA molecule [*Biochim. biophys. Acta*, **94** (1965), **293**].

A new immuno-electronmicroscope technique using metal chelate antibody

Immuno-electronmicroscopy, the identification of antigens made visible under electronmicroscope by combining them with electron opaque antibodies modified by conjugating with ferritin or by tetracetoxyintroducing with mercury arsanilic acid and paminophenyl mercury acetate, has been successfully employed in the studies of intracellular development of several viruses. The difficulties encountered during the interpretation of electronmicrographs due to a number of deposits of free ferritin antibodies and non-conjugated ferritin particles occurring on the background and also the nonspecific adsorption to the non-antigenic substances have been overcome by the new metal chelate antibody (MCA) technique, described by research workers at the Department of Bacteriology, School of Medicine, Kyushu University, Japan. In this technique, only the antigen-antibody complex is formed and the non-specific deposits on the background are eliminated.

Tyrosine residues of γ -globulin molecules when diazocoupled with anthranilic acid act as a chelating agent for heavy metals. Virus particles of influenza virus (type A, strain PR8) treated with MCA showed dense ring at the outer margin of the virus particle on electronmicrographs, indicating that specific antigen-antibody reaction occurs on the surface of the particle. Neither background contamination nor non-specific adsorption could be observed.

Identification of small viruses and localization of their antigenic subunits have been made possible by this new technique [*J. Electronmicrosc.*, **13** (1964), 133].

Study of membrane transport phenomena by calorimetry

The application of modern Tian-Calvet calorimeter in the study of membrane transport phenomenon, employing model systems in which the membrane constitutes one of the elements, has been suggested. Such a system employing the glucose oxidase catalysed reaction system (glucose $+O_2 \rightarrow$ gluconic acid $+H_2O_2$) as the source of heat has revealed the character of the transport or the diffusion interposed membranes.

Single cell thick lower leaf epidermis of the onion bulb quite tolerant to environmental conditions has been interposed between an enclosure containing the enzyme glucose oxidase, and a solution into which glucose solution is added to initiate the reaction. To provide an appropriate osmotic concentration prior to the addition of glucose, solutions on either side of the membrane contained L-arabinose. which is neither metabolized by the membrane nor utilized as a substrate by the enzyme. The heat evolved during the reaction gives a measure of the migration of glucose across the membrane.

This technique enables in a single reaction to study the diffusion or transport kinetics of substances through membranes [*Biochim. biophys. Acta*, **94** (1965), 302].

A method for obtaining cell monolayers from tissue surfaces using membrane filters

The difficulties encountered in obtaining the leucocytes from peritoneal surfaces of the *Pasteurella pseudotuberculosis* infected mice and guinea-pigs have been overcome by using a thin membrane filter (Millipore filter, grade HA, Lovell Chemical Co., Waterstown, Mass.), instead of the conventional method of using microscopic slides. Squares of membrane filters (0:5-1:0 cm.) placed plain side down on the omentum, peritoneal wall and visceral surface of the diaphragm adhere instantly to tissue surfaces, presumably because of electrostatic charges. Using a cotton applicator the upper surfaces of the squares are gently brushed to ensure overall contact and are then carefully peeled off and fixed by floating on formol saline. The peeled off squares are usually found to have a monolayer of cells adhering to the contact surface. The fixed squares are stained and mounted with their plain sides up for examination.

This method enables specific areas of tissue surface to be sampled with recovery of intact cell monolayers and is particularly useful in sampling the delicate tissues of omentum. The location of the bacteria, whether extracellular or intracellular in the phagocytes, can be determined by sampling animals at intervals after intraperitoneal injection [*Nature, Lond.*, **205** (1965), 1134].

Isolation of enzyme-substrate complex

A crystalline purple enzymesubstrate complex has been isolated at the University of Nagoya, Japan. Isolation of this enzymesubstrate complex stems from the study of enzyme catalysis using *p*-amino acid oxidase as the enzyme and *p*-alanine as the substrate.

In a general enzymic reaction the enzyme (E) and substrate (S) form an unstable intermediate (E-S); at this stage the substrate is activated by the enzyme to E-S'. The intermediate gives the end product (P) and the free enzyme. The enzyme-substrate complex is isolated by crystallization by bringing the reaction mixture to a condition under which it accumulates.

The flavoprotein *D*-amino acid oxidase was selected for characterizing the enzyme steps of the reaction. Flavin (the coenzyme) undergoes oxidation and reduction. The redox reaction can be followed by changes in the absorption or fluorescence of the enzyme.

In the experiment, 1 g, of the enzyme (as a benzoate complex) was dissolved in 50 ml. of oxygen-free pyrophosphate buffer (0.02M at pH 8·3) and 1 g, of D-alinine added with stirring. The enzyme reaction was interrupted by eliminating the molecular oxygen (an electron acceptor) from the reaction and by lowering the pH and temperature below the optimum. The purple crystals of the enzyme-substrate complex so obtained are hexagonal prisms with bipyramids. Excess benzoate added to the crystal solution (under anaerobic conditions) liberates free alanine molecules. But aeration in the presence of a trace of catalase gives pyruvate (P). Thus the crystals appear to be composed of a semiquinoid form of the holoenzyme and the partially oxidized substrate (E-S').

The crystalline enzyme-product complex (E-P) has also been isolated. A suspension of crystals of the enzyme-substrate complex was dialysed overnight against distilled water at 5°C. The sample gradually oxidizes during dialysis with the suspension changing from purple to yellow [*Chem. Engng News*, **42** (32) (1964), 34].

A haemoprotein from the lipid of peanuts

The Plant Industry Station of the US Department of Agriculture, Betsville, Maryland, has reported a naturally occurring haematin protein in lipid fraction of peanuts and other seeds [*Nature, Lond.*, **205** (1965), 1319].

Both dry and imbibed peanuts were ground and extracted with 0.4M sucrose, and the extract was fractionated by differential centrifugation. The only fraction that showed appreciable amount of the 635 mu absorbing material was the white lipid layer collected from the top of the centrifuge tube. The lipid also showed a carotene-like absorption band at 480 mµ. The 635 mµ pigment remained with the residue after thorough extraction of the lipid with methanol, acetone, ether, chloroform or butanol, and the extraction did not render the pigment soluble to aqueous systems. A part of the 635 mu absorbing material could be solubilized by extracting the acetone powder with 2 per cent digitonin. The concentration of the $635 \text{ m}\mu$ absorbing pigment in the lipid fraction was estimated and found to be $9 \times 10^{-6}M$.

The protein content of the digitonin-solubilized solution, measured by the biuret test after dialysis and precipitation of the protein with 10 per cent trichloroacetic acid, was 10 mg./ml. The haem content, estimated from the absorption spectrum of the solution after addition of CaCO₃, assuming an extinction coefficient of 10 mM⁻¹ cm.⁻¹ and a scatter intensification of 10, was $5 \times 10^{-6} M$. This gives a ratio of 2×10^{-6} g. protein per mole haem. The strong affinity of the protein for the lipid and the partial solubilization by digitonin suggest that the haem is attached to a lipoprotein. The digitonin-solubilized material showed moderate catalase activity and essentially no peroxidase activity. The lipoprotein, however, may not catalyse a specific reaction in vivo. In general, the action of haematin compounds in the oxidation of unsaturated fats is quite non-specific.

To ascertain how germination affects the 635 mµ pigment, absorption spectra were measured on intact peanut cotyledons from seedling plants which were germinated in the dark. There was no loss of lipid content in the cotyledons during the first 7 days. However, after that period lipid content abruptly decreased. Thus, the haemoprotein appears to be broken down as the lipid is utilized. When haematin compounds catalyse the oxidation of unsaturated fatty acids they are destroyed, presumably through reactions with lipid peroxides.

Haemoglobin could either catalyse or inhibit the oxidation of linoleic acid, depending on the ratio of the two compounds. At a concentration of $1.2 \times 10^{-5}M$. haemoglobin inhibited the oxidation of 0.017M linoleic acid, while at a concentration of $4 \times 10^{-6}M$ it was a strong catalyst with $5 \times 10^{-3}M$ linoleic acid; however, $4 \times 10^{-6}M$ haemoglobin inhibited the oxidation. The relatively high concentration of haemoprotein in peanut fat suggests that it could have a protective effect, particularly in preventing the peanut from becoming rancid during long periods of storage. However, if the degree of lipid unsaturation increased during germination, the haemoprotein might change from being an inhibition to being a catalyst of lipid oxidation [Biochim. biophys. Acta, 70 (1963), 336].

Automatic analysis of bacterial growth

Automatic instrumental analytical techniques, using Technicon autoanalyser components (Technicon Instruments Corp., Chauncey, NY) have been developed by scientists at Rutgers State University, USA, which enable the measurement simultaneously, automatically and continuously of the rate of growth and enzyme synthesis in bacteria. Employing this facility, the rates of formation of turbidity, total protein and nucleic acids (RNA and DNA) in Escherichia coli growing in simple media have been measured. Methods have also been developed for continuously monitoring the synthesis of the enzymes β-galactosidase, acid phosphatase and alkaline phosphatase.

Turbidity of the culture medium indicating bacterial growth was measured after mixing a stream of the culture with a stream containing a fixative (formaldehyde) and a surfactant (Tween-20), and passing the stream through a Technicon colorimeter flow cell. The absorbancy of solution is measured at 550 m μ and read on a recorder.

The biuret method is used for protein determination. This is carried out by partial hydrolysis of a stream of whole culture with hot alkaline tartrate to dissolve the protein. The resulting digest is filtered through filter paper using autoanalyser continuous device. The filtrate is combined with the colour developing reagent stream (copper tartrate solution). The two solutions react to form the biuret colour and the resulting coloured solution is pumped through the colorimeter flow cell and the optical density measured at 550 mµ and read on a recorder.

For nucleic acids determination, a hot acid extract of the whole culture is prepared by combining the culture stream with hydrochloric acid and passing the combined stream through a coil immersed in a bath at 95°C. The insoluble materials are docanted and the extract is split into two streams, one for RNA and the other for DNA analysis. RNA is measured using the orcinol (3,5-dihydroxy toluene) reaction. The stream for RNA is mixed with an orcinol reagent stream and heated at 95°C. to develop the colour for the determination. After cooling, the coloured solution is pumped through the flow cell of the colorimeter and the optical density measured at 660 mµ. The stream for DNA is combined with diphenylamine and also heated at 95°C. for colour development. After cooling, the coloured solution is pumped through the colorimeter flow cell and the optical density measured at 600 mµ.

Using autoanalyser components Delay and Umbreit have measured 3-galactosidase by hydrolysis of o-nitrophenyl-3-D-galactoside; acid phosphatase is determined by the hydrolysis of p-nitrophenyl phosphate at pH 4-0 while alkaline phosphatase is determined the same way at pH 8-8. For each enzyme determination the optical density of nitrophenol formed on hydrolysis is measured at 420 m μ under alkaline conditions.

The automatic analysis system has been used to determine the effects of antibiotic treatments. When streptomycin is added to an Esch. coli culture, there is a delay before the rate of turbidity formation slows down and before the protein, RNA and DNA syntheses are inhibited. But if chloroamphenicol is added, the increase in culture turbidity and protein stops immediately, and RNA and DNA syntheses continue for some time. Other studies using this system include the effect of sulphur compounds on the regulation of RNA, and protein synthesis and the effect of methionine on the protein synthesizing ability of RNA.

The disadvantages involved in the study of the bacterial growth by manual methods have been overcome by using the automatic continuous analysis system [*Chem. Engng News*, **43** (3) (1965), 38].

Mutational analysis and protein structure

Studies with the tryptophan synthetase A-protein mutants of *Escherichia coli* have revealed a structural relationship between the amino acid position and the changes associated with forward and second site reverse mutation.

It was observed that seven different amino acids could occupy the same position in A-protein. Two mutants of A-protein (A-23 and A-46) were enzymatically nonfunctional. One of the mutants, A-46, undergoes a reversion at a second site in the A-gene, which led to a change in the amino acid situated 36 residues from the position at which the original amino acid change occurred in mutant A-46. Analysis of primary structure of six proteins from second site revertants indicates that all the second site changes involve the same tyrosine-cystine replace-The studies of forward ment. mutation reveal those mutational events which lead to a loss of function and the reverse analysis reveals the spectrum of mutationally permissible changes in amino acids that can restore a functional Additional information protein. on the relation between changes in primary structure and enzyme function was obtained during reversion studies carried out on another mutant, A-187.

This mutational approach may be of considerable help in the elucidation of those tertiary structural relationships which are of significance in determining enzyme activity *in vivo* [*Science*, **146** (1964), 1593].

Role of sulphur in the genesis of petroleum

Investigations at the Petroleum Research Laboratory of Carnegie Institute of Technology, Pittsburgh, have thrown light on the possible role of sulphur in the genesis of petroleum. The amount of sulphur in the organic material from plants and animals seems to be too small to account for the large amounts of sulphur compounds in some petroleums. A thermal reaction between elemental sulphur and the organic material of the sediment may be responsible for the genesis of the sulphurcontaining compounds.

Cholesterol reacts readily with sulphur at 150°C. with the evolution of hydrogen sulphide and the product of reaction contains hydrocarbons. Some of these have a benzene, some a naphthalene and some a phenanthrene ring system as part of the molecule. Farnesol reacts with sulphur at 135°C. and cadalene has been identified as one of the products of reaction. When farnesol (25 g.) and sulphur (3 g.) were heated with stirring at 135°C. for 23 days, hydrogen sulphide was slowly evolved and the reaction product obtained as a black tar (26 g.).

Thus these studies indicate that petroleum type hydrocarbons are produced relatively rapidly by reacting cholesterol and farnesol with sulphur at temperatures no more than 50°C. above those prevailing in some sediments which are commonly regarded as source beds of petroleum. The reaction at a temperature near 100°C. would take place very slowly, but over a long period of time may be expected to produce the same or similar hydrocarbons [Science, 147 (1965), 499].

Progress Reports

Ford Foundation

The Ford Foundation has, since its inception, spent amounts totalling \$ 2.2 billion by way of grants to 5261 institutions and organizations all over the world including the USA and 76 other countries. The highlight of the last year's (1963-64) programmes was the Foundation's support to population control. Out of a total approved grant of \$235 million, nearly \$ 35 million were earmarked to programmes on population control. Aided projects include research in reproductive biology which may lead to improved birth control methods, and training facilities for personnel ranging from demographers and public health specialists to midwives and medical subprofessionals. As the branch of physiology of reproduction has not received due attention in medical research, there is a shortage of skilled scientific workers, and the Foundation in its efforts to attract more specialists has given grants to encourage talented medical and postdoctoral science students to elect careers in reproduction studies. The institutions that have been strengthened by the Foundation to be the training grounds for future personnel include the Population Council's Biomedical Division, the Zoology Department of the University of Wisconsin, the Weizmann Institute, and the Zoological Society of London, among others.

The largest beneficiary of the Foundation's programme on population studies is India. Implementing a \$ 5 million programme to reduce birth rates, the Foundation granted \$1,246,000 to help intensive projects and set up a national institute of family planning, an institute of health administration and education, and a central unit for research and training in the collection of population statistics. Work on family planning in rural communities is being carried out at Gandhigram in Madras. Grants were made to 12 research laboratories and many training centres, equipments funds, and and consultants have been provided in fields ranging from statistical analysis to contraceptive manufacture and motivational factors in the various population groups. The Foundation also helped in the establishment of essential government agencies for research coordination, evaluation and personnel development in the fields of demography and family planning. The Institute of Obstetrics and Gynecology at Madras will extend its research to use of intrauterine devices, female steriliand the zation techniques, immunological aspects of reproduction.

In the field of food production. the Foundation has given grants totalling \$ 1,012,000 for training agricultural engineers, improving irrigation and drainage systems. etc. Grants were given to the Allahabad Agricultural Institute, the Indian Institute of Technology, Kharagpur, and the Punjab Agricultural University for training agricultural engineers. Grants (\$ 1.4 million) have also been given for setting up four electronic computer centres in India and strengthening the Administrative Staff College of India and the Institutes of Management at Calcutta and Ahmedabad.

Besides grants to educational institutions, research programmes on economic development and administration, etc., several grants were made to programmes concerned with science and engineering education and reproductive biology. The problems that are being studied at various laboratories with the Foundation's grants include the use of oral contraceptives, their physiological and psychological effects; use of intrauterine devices and their physiological effects; prediction of ovulation from hormone extraction; and a method of inoculation against pregnancy.

New Periodicals

International Journal of Powder Metallurgy

The American Powder Metallurgy Institute has commenced a new quarterly International Journal of Powder Metallurgy. Devoted to basic and applied powder metallurgy, this is the first journal in the US devoted exclusively to the subject. The journal is available at \$ 10 per year from the Institute at \$ 00 East 42nd Street, New York 10017, NY, USA.

Building Science

A new quarterly *Building Science* has been commenced by the Pergamon Press Ltd, Headington Hill Hall, Oxford, England. It will carry original papers concerned with the application of science and technology to the design, construction and maintenance of buildings. The annual subscription rates are: \pounds 10 (\$ 30) for libraries, etc., and \pounds 5 (\$ 15) for individuals.

Announcements

• The Lady Tata Memorial Trust has awarded international awards of the total value of f_{c} 8100 to the

following for research in diseases of the blood, with special reference to leukaemias: J. de Maeyer (France), A. Agostoni (Italy), Q. Corneo (Italy), D. Quaglino (Italy), F. Squartini (Italy), G. Tridente (Italy), U. Buonassisi (France), J. W. Gorrod (UK) and M. Matsuyama (Japan). Indian scholarships for scientific investigations having a bearing on the alleviation of human suffering from disease have been awarded to: Fredy J. Daniel (G.S.V.M. Medical College, Kanpur), A. K. Deshpande (University of Poona), E. Lakshmi (Government General Hospital, Madras), Nirmala Lakshminarayanan (All India Institute of Medical Sciences, New Delhi), D. K. Manghani (Sir J. J. Group of Hospitals, Bombay), P. G. R. Pillai (G.S.V.M. Medical College, Kanpur), R. V. Prabhu (Department of Chemical Technology, Bombay), and R. Selvarajan (A.C. College of Technology, Madras).

 The Polynological Society of India - The Society, founded during the combined fifty-first - fifty-second session of the Indian Science Congress, offers life, ordinary and institution memberships. The Society proposes to issue two annual publications — the Polynological Bulletin and the Journal of Polynology. Details regarding membership and other particulars can be had from the General Secretary-Treasurer, Polynological Society of India, National Botanic Gardens, Lucknow.

• An International Symposium on Comparative Haemoglobin Structure will be held by the Greek Biochemical Society and the Department of Biochemistry of the Aristotelian University of Thessaloniki , in Thessaloniki during 11-13 April 1966. Enquiries may be addressed to the Secretary of the symposium, P.O. Box 201, Thessaloniki (Greece).

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MODEL 2120A

The Model 2120A AC-DC Precision Power Supply was designed particularly for use with a suitable monitoring system for standardizing and calibrating high accuracy digital, indicating and recording AC and DC electrical instruments. Accuracy is dependent upon the monitoring system used; an AC-DC transfer standard or any highly accurate indicating instrument may be employed. An internal variable radio transformer permits rapid and precise down-scale calibration of AC Voltmeters.

Fixed frequency settings of 50, 60, 400, 800, 1000 and 2400 c/s are also provided in addition to continuous frequency coverage. Rated output varies from 10 to 100 VA depending on frequency.

The model 2120A is housed in two separate aluminium cabinets. One contains the supply unit and the other the control unit which consists of a precision potential transformer, ratio transformers for matching AC instrument loads, rectifier and filter circuits for DC currents and potentials.

APPLICATIONS

The model 2120A AC-DC Precision Power Supply can be used for the testing of small motors, synchros, choppers and other electromechanical devices. It can also be used as a power amplifier for external signals from 50 to 40,000 c/s, where a powerful, variable frequency signal is required. A low internal output im-

pedance and unusually stable frequency characteristics permit unattended operation in production testing applications. When used with a suitable AC-DC transfer standard, such as the RFL models 1605 or 1605A, an instrument calibration and standardizing system of high accuracy results.

RADIO FREQUENCY LABORATORIES, BOONTON, USA

For details, please write to:

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