Journal of Scientific & Industrial Research

J. sci. industr. Res. Vol. 24 No. 12 Pp. 607-656
December 1965
Published by the Council of Scientific & Industrial Research, New Delhi

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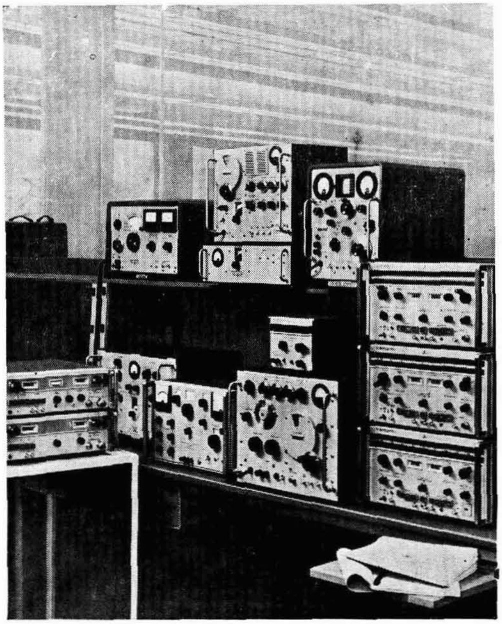

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Article entitled " Organic Semiconductors ", **24** (No. 6) (1965), pp. 282-288: The correct versions of Figs. 1, 2 and 5 appearing on pages 284 and 287 are as follows:

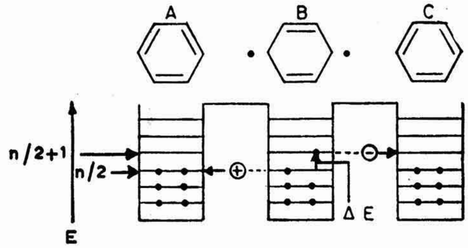

Fig. 1 — Electron **transition** in benzene molecule

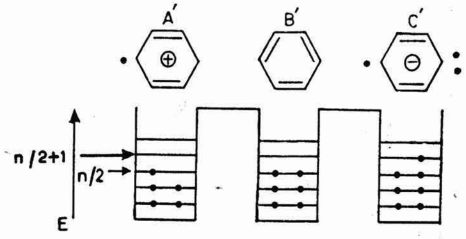

Fig. 2 — Creation of a positive hole in the benzene molecule

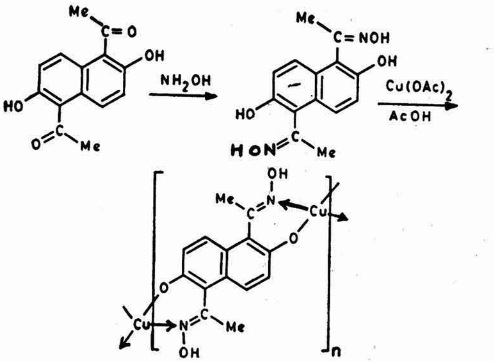

Fig. 5 — Synthesis of polymerized Cu^{II} derivative of dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene

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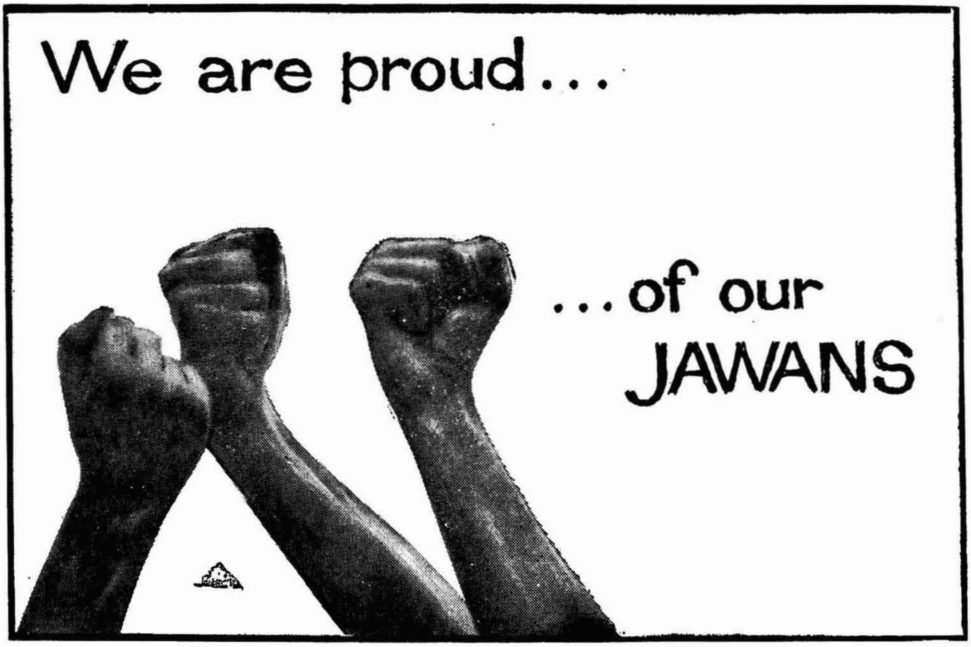
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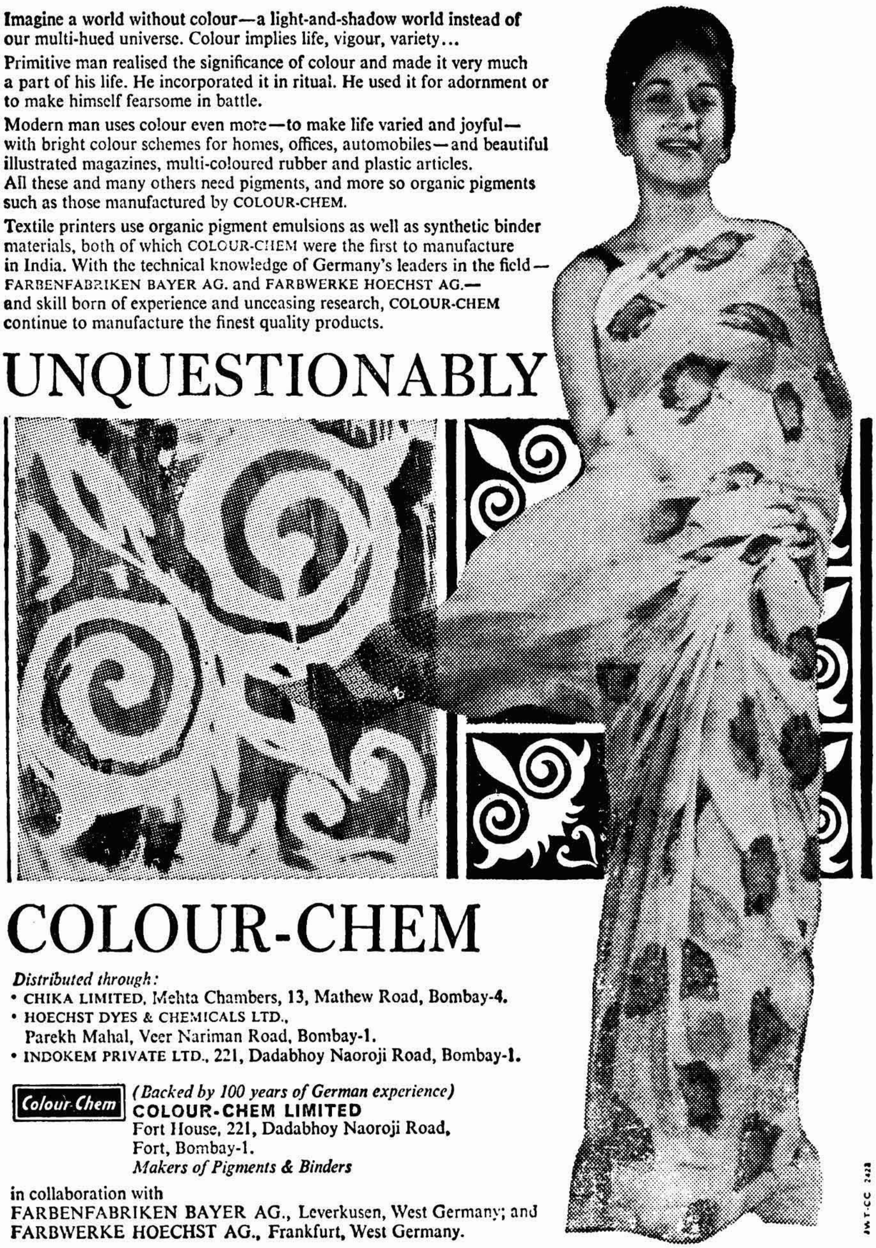

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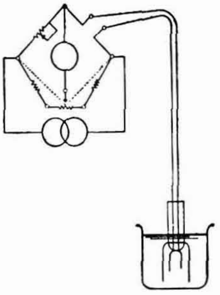

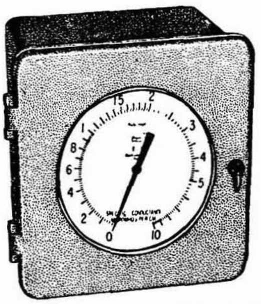

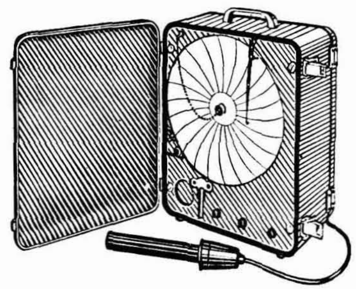

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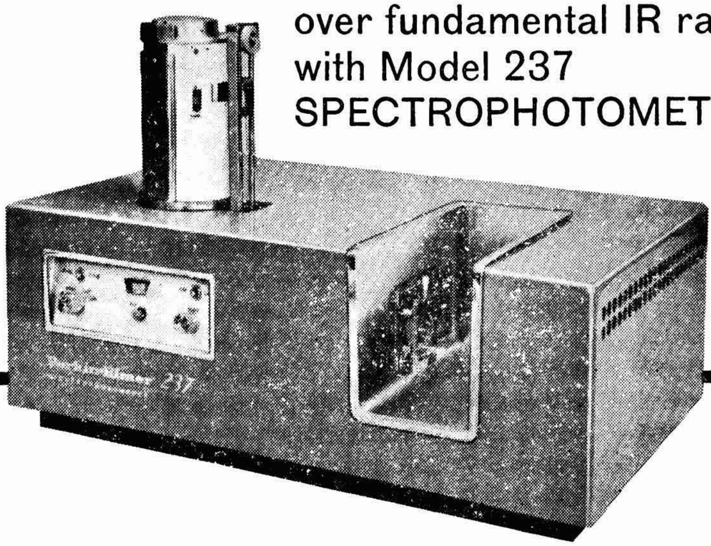

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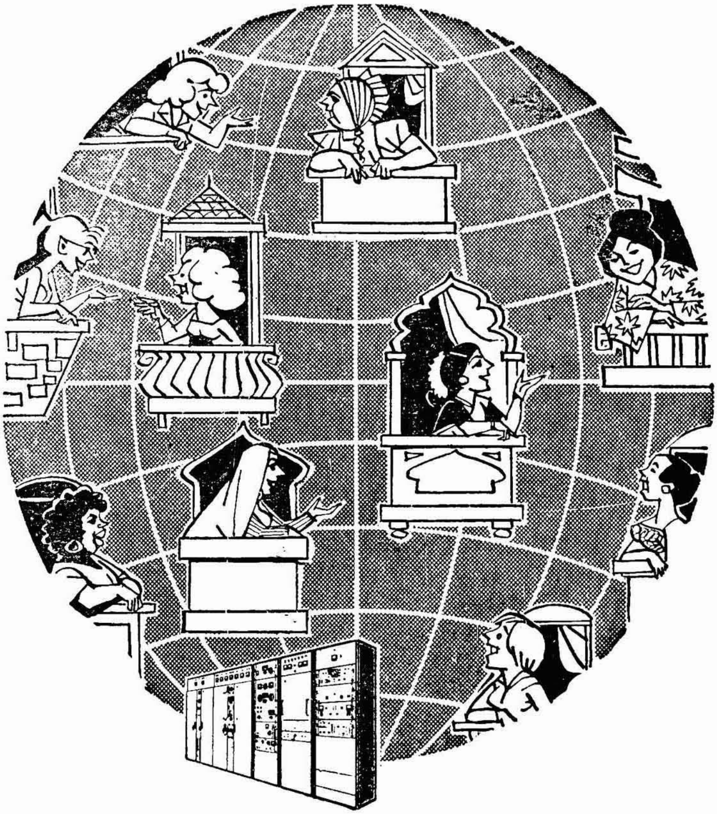

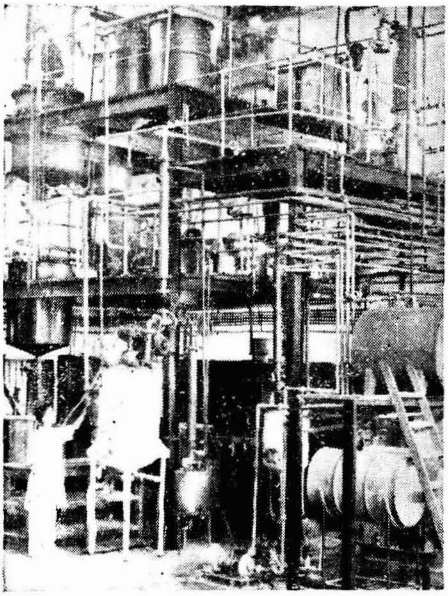

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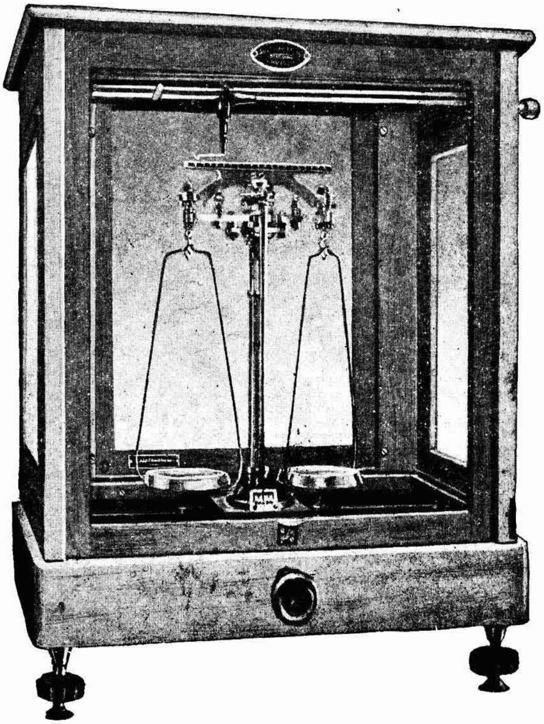

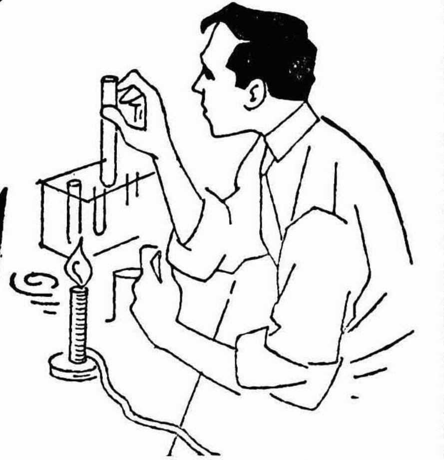

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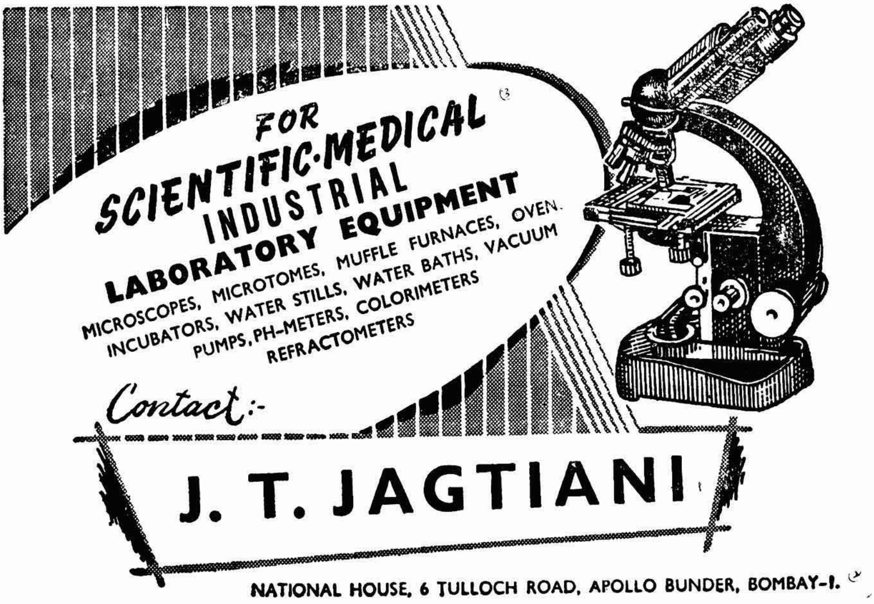

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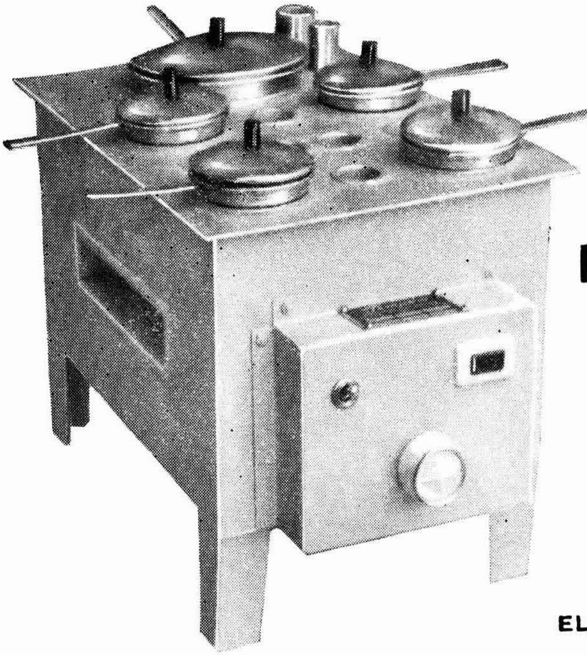

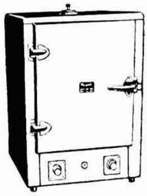

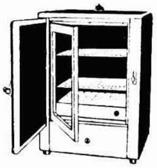

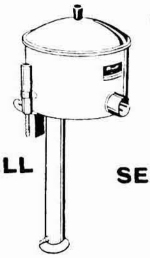

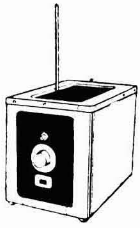

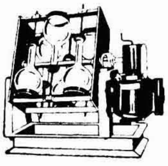

Current Topics

National & International Trends in Research in Chemistry

WHEN one looks back into the history of chemical research in India, one finds that even about two decades back, chemical research was confined to a handful of laboratories mostly in the universities. Since then scientific research in general, and research in chemistry in particular, have taken long strides in India, due mainly to the impetus given to it by the Council of Scientific & Industrial Research (CSIR). Through the national laboratories and through the schemes, units and schools sponsored by the Chemical Research Committee (CRC), the CSIR has now built a basic pattern of research in India.

To take it a step further, the future planning in research should be based on an objective survey of the current chemical research in India in the perspective of the world-wide research in general and in the perspective of the needs of India in particular. The need for such a survey was strongly felt by Dr Husain Zaheer, Director-General, CSIR, and at his initiative the CRC adopted a scheme for compiling a research directory of recent chemical research in India, the task being taken up by us in the Indian Association for the Cultivation of Science, Jadavpur. The compilation of the Research Directory in Chemistry (1960-62) is now complete and it will be published shortly; the compilation for the years 1963-64 is in progress. One main objective of such surveys was to find out areas of our deficiencies in the light of modern trends in research — areas which need more attention.

With the above objective in view the data obtained from 1964 listing of papers in the journal *Current Chemical Papers* of the Chemical Society, London, were analysed in detail.

The number of papers with at least one Indian author was about 1665 in a total of 33,760 papers. This amounts to about 5 per cent of the total. If one remembers that this estimate leaves out technological research, in which India is particularly lagging behind and that, on the other hand, countries like USA, USSR and Germany average to about 27, 19 and 8 per cent of the papers respectively[*], the figure for India would show that we have far to go to catch up with the industrially developed countries in chemical research.

TABLE 1 — NATIONAL AND INTERNATIONAL TRENDS IN RESEARCH IN CHEMISTRY IN 1964

Sl No.	Subdivision	A	B	C
1	Sub-atomics (chemical aspects)	1·0	0·8	0
2	Atomic and molecular structure	11·2	12·1	8
3	Phase structure and phase relations	5·9	4·3	1
4	Surface properties	3·2	1·8	3
5	Colloids and macromolecules	8·3	4·4	12
6	Electrochemistry	4·0	5·4	10
7	Thermodynamics	2·1	2·1	8
8	Kinetics and mechanism	8·1	5·4	13
9	Inorganic	4·8	3·6	16
10	Organometallic and organo-metalloid	8·4	9·6	5
11	Organic			
	(i) Aliphatic	5·1	2·4	0
	(ii) Amino acids and peptides	2·5	2·4	1
	(iii) Carbohydrates	1·6	1·2	1
	(iv) Homocyclic	9·2	8·5	3
	(v) Terpenes and steroids	2·5	6·0	10
	(vi) Heterocyclic	9·7	11·9	10
	(vii) Miscellaneous	1·3	4·4	16
12	Analysis	9·5	12·1	8
13	Apparatus and techniques	1·3	0·9	2

A: Number of papers in each subdivision as percentage of total number of papers. B: Number of Indian papers in each subdivision as percentage of all Indian papers. C: Number of CRC schemes.

In order to ascertain the exact areas of deficiencies a comparison was made between the national and international trends of research in the different subdivisions of chemistry. The subdivisions considered were the same as in the journal *Current Chemical Papers* and are enumerated in Table 1. A sample survey was made of the total number of papers in each subdivision as also of the total number of papers by Indian workers in it[†]. These figures, expressed as the percentage of total number of papers (total number of Indian papers in the latter case) for the different subdivisions of chemistry, have been compared in Table 1.

It is immediately apparent that the national trend of research in chemistry is more or less similar to the international trend. However, going into details one finds certain areas in which the national average is significantly below the international average.

Thus, the areas of deficiency, from the number of papers considered in the above survey, are — phase structure and phase relations, surface chemistry,

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[*] These figures are from a survey of *Chemical Abstracts* for 1961 [Baker, D. B., *Chem. Engng News*, **39** (1961), 78]. Compare also the figures for papers in physical chemistry in 1961: USA, 31; USSR, 25, Germany, 5; and India, 3·4 per cent (Bhattacharyya, K., *DRTC Seminar I*, 1963, 53).

[†] It would have been more correct to list the work done in India only in order that one can analyse the data in terms of the status of work done by chemists in India. This, however, was not possible as *Current Chemical Papers* does not include the laboratory address. We can only assume that the work done abroad will constitute but a very small percentage (in numbers) of the total number of papers by Indian workers.

colloid and macromolecular chemistry, kinetics and mechanism, inorganic chemistry, aliphatic organic chemistry, apparatus and techniques.

In the field of phase structure and phase relations, except for certain papers on the determination of crystal structure, very little is published on topics like liquid structure and single or multicomponent phase relationships.

Although colloid chemistry is known to be popular in India, the figure for research in colloids and macromolecules is very much below the international average. As surface chemistry forms an important basis for colloid chemistry, it is significant that at the same time the Indian figure for surface chemistry is also well below the international average. In the field of surface chemistry there is some work done on catalysis and related gas-solid surfaces but the other topics are neglected. Again, colloids and macromolecules, though having tremendous industrial applications are not tackled adequately. There are a number of papers on the stability of lyophobic colloids from the classical point of view. There are lots of possibilities in the quantitative studies on interparticle interactions, and their applications to biocolloids. In the field of polymers, on the other hand, most of the studies are regarding kinetics and mechanism, while topics like the physicochemical properties of polymers, their degradation characteristics and biopolymers are very much neglected.

The figures on kinetics and mechanism may be related both to surface chemistry in terms of kinetics of adsorption and catalysis, as well as to polymerization, and the dearth of papers is probably related to the deficiencies discussed in the above paragraph. Kinetics in solution is studied in several places, but some important studies like photo-chemical reactions, fast reactions, diffusion controlled reactions, perturbation methods and reactions of biochemical interest are few and far between.

In inorganic chemistry one finds that most of the papers are on complex compounds and their properties; relatively fewer papers are in ' general and inorganic chemistry '.

In organic chemistry, apart from a lack of interest in aliphatic organic chemistry, one finds a good deal of work in the other subdivisions, and work in heterocyclic compounds and alkaloids, terpenes and steroids more than compensates the above lack. The great possibilities of work on Indian medicinal plants fully justify the interest in alkaloids and indigenous plant products.

It is difficult to judge the difference between the national and international trends in the work on apparatus and techniques. From personal experience, however, one is convinced that perhaps the little difference is significant, and very little is done in devising newer methods and apparatus, keeping in mind the needs of India in particular.

The above considerations, based on the number of papers alone, leave out the questions about the quality of the papers or their relation, if any, to the needs of India. The quality or standing of a paper is difficult to judge immediately. From the references outside to papers published in Indian journals one cannot but have the feeling that much of the work published in Indian journals suffers from obsolescence if not of lack of depth. From column C Table 1 we can have a rough idea of the number of schemes of the CRC in the different subdivisions of chemistry (a better idea could have been had from the number of workers in each field). Although it may not be proper to draw far-reaching conclusions from just the number of schemes some of the figures are encouraging. Schemes, however, have to be considered individually and in the above figures a greater number of schemes could signify a greater effort being made for developing that line only if steps were taken initially to scrutinize the schemes to see that the work in its details would not fall into obsolescence but be productive and useful. Just to take an example, in the field of Indian plant products, why not consider the position of research in India in comparison with the work done in other countries, consider the exploitation of research by drug industry in India compared to that in other countries, and accordingly plan and intensify work so as to keep India ahead of other countries in this respect? An effort to make research more productive cannot but be beneficial to all the parties concerned.

The present study is incomplete to the extent that we had to leave out biochemistry and industrial chemistry *per se*, as information on these subjects is not available from *Current Chemical Papers*. A much more complete and detailed study, using *Chemical Abstracts* as the source of information, with its much more elaborate subject classification, is now in progress.

SANTI R. PALIT & SANTIBRATA GHOSH

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First International Conference on the Raman Spectra of Crystals

R. S. KRISHNAN
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THE First International Conference on the Raman Spectra of Crystals was held under the auspices of the International Union of Pure & Applied Physics in the Physical Research Laboratory of the Faculty of Sciences, University of Paris at Sorbonne, Paris, from 5 to 8 July 1965. The proceedings were held in the famous lecture hall of the Physical Research Laboratory where world-renowned French physicists like Madame Curie, Prof. Fabry, Prof. Fizeau, Prof. Cotton and Prof. Cabannes gave their lectures to the students of the university. The conference was formally opened by Prof. Zallemand, President of the French Society of Physicists, and it was followed by a welcome speech by Prof. J. P. Mathieu, the organizing Chairman of the conference. The author was given the honour of presiding over the opening session. This was in recognition of the pioneering work on the Raman spectra of crystals carried out at Bangalore. There were on the whole 30 delegates from the different countries — America, Canada, Great Britain, France and India. Of the four Indians contributing papers, only the author went from India. The remaining three are working outside India.

Historical Review

The scientific programme was divided into five sessions. The first session started with an introductory talk by Prof. E. Burstein (Philadelphia) who reviewed the milestones in the history of the scattering of light and Raman effect in crystals, and the experimental and theoretical aspects. He traced the work of Einstein, Brillouin, Raman, Rasetti, Born, Krishnan and his collaborators at Bangalore, Chandrasekharan, Gross, Stekhanov and their collaborators, Mathieu and his collaborators, Birman, Johnson, Loudon and others. He also indicated broadly the future line of work both on the theoretical and experimental aspects. He particularly referred to the work of Dr Russell (UK) on the first- and second-order Raman spectra of simple crystals using laser sources, and especially the recording of the principal Raman line of silicon by reflection. Future work on the higher order Brillouin scattering, and the Raman spectra of impurity doped crystals and of crystals under high electrostatic field in order to disturb the crystalline field was referred to by him. His talk was followed by four contributed papers.

Recent Experimental Results on Raman Spectra

The first paper was by Dr S. S. Mitra (USA) on the Raman spectrum of ZnO which has the wurtzite structure. He discussed the assignments of the single phonon branches at the critical point corresponding to $\vec{k} \approx 0(\Gamma)$ and the multiphonon branches with assumed values of Brillouin zone boundary phonon frequencies consistent with the infrared measurements. The next paper on the Raman spectrum of solid hydrogen was presented by Prof. H. L. Welsh (Canada). The vibrational line $Q_1(0)$ of solid para hydrogen is very sharp and shifted by 11·3 cm.$^{-1}$ from its frequency in the gas, the main part of the shift being caused by the isotropic intermolecular forces. The experimental results on the effect of adding ortho-hydrogen were presented. He showed that in the region of low concentrations, exciton-excitation cannot apparently be sustained by the fragmentary ortho-lattice and the components observed are due to coupling with varying numbers of ortho-molecules in the shell of nearest neighbours. Dr J. P. Russell (UK) then reviewed the recent work on the Raman spectra of crystals using gas lasers at RRE, Worcs. In this method, the crystal is placed in an external resonator built on to the laser resonator and the scattered light is examined at right angles with the aid of a spectrograph. He described the techniques together with the results obtained on GaP and CaF_2 over a wide range of temperature up to liquid helium temperature, $CaWO_4$ at room temperature and especially silicon which is practically opaque at the operating wavelength of the laser.

Interpretation of Spectra

The second session started with Prof. H. L. Welsh in the chair. The first of the three papers presented by the author was on the Raman spectrum of magnesium fluoride recorded with λ 2537 excitation. The Raman active fundamentals and their identification, the force constants taking into account the stretching and bending of the various bonds in the Matossi's model were discussed. A feature of the spectrum was the presence of two lines on the high wavenumber side, the origin of these being due to some impurity modes. In the next two papers, the interpretation of the second-order Raman spectra of GaP and CaF_2 was discussed. The critical points Γ, L, X being the representatives of the Raman supercell modes, their frequencies were obtained with the dynamics of these crystals postulated by Ramanathan. Simple selection rules were also pointed out in the assignment of these spectra. The next paper presented by Prof. E. Burstein (Philadelphia) discussed the interpretation of the second-order Raman spectra of CsI and CsBr with space group selection rules of Ganesan and the phonon frequencies at Γ, R, M and X given by Karo's calculations. The Raman and infrared spectra of CaF_2 were also discussed utilizing the experimental phonon frequencies and the space group selection rules of Ganesan and the phonon frequencies at Γ, L and X given by Ganesan's calculations. The last two papers of the session were on the Brillouin scattering in crystals. Dr L. Cecchi (France) reviewed the classical and quantum theories on the calculation of the frequencies and the intensities of Brillouin components and the experimental techniques using

Fabry-Perot interferometer. He presented the results obtained for NaCl, $NaClO_3$, quartz and the variation of the intensities as a function of temperature in quartz. Dr V. Chandrasekharan (France) pointed out that the unequal displacements of the anti-Stokes and Stokes components correspond to the quadratic relativistic Doppler effect and showed that these shifts for the longitudinal components along [111] direction for a diamond crystal, as an example, can be verified by using modern laser techniques.

Theory of Raman Scattering

The third session was presided over by Prof. E. Burstein (Philadelphia). Dr R. A. Cowley (Canada) presented the first paper of this session. He discussed the theory of Raman scattering from crystals of diamond structure with detailed shell model calculations for the frequencies of the normal modes and the matrix elements for the Raman scattering taking into account the effects of anharmonicity on one-phonon scattering. He pointed out that the details of these spectra are dependent on the polarization of the light and the orientation of crystal. Dr J. R. Hardy (UK) and Dr A. M. Karo (USA) presented their results on NaCl and CsCl type crystals with dense samples of wave vectors, neglecting the selection rules. They also discussed the spectra of RbI and its NaCl-CsCl phase transition induced by pressure. Dr R. Loudon (UK) presented a paper on the spontaneous and stimulated resonance Raman effect in crystals. The effect of the proximity of the exciting frequency to the intrinsic electronic absorption edge on the Raman scattering by electronic levels of impurity atoms and by lattice vibrations was dealt with. He showed that the optimum exciting frequency is the one at which the absorption coefficient begins to rise significantly from its zero value below the edge.

Selection Rules for Raman Effect

The next session was concentrated on papers on the space group selection rules. Dr S. Ganesan's (USA) paper which was presented by Dr Burstein dealt with group theoretical selection rules for BiF_3 and compared them with those for NaCl and CaF_2. Dr H. Poulet's (France) paper was on the representations of ZnS lattice corresponding to the symmetry points of the Brillouin zone. In the next two papers, Prof. J. L. Birman (USA) applied group theoretical methods to study the depolarization of the scattered light which could give us information on the phonons which produce the scattering. Detailed theory of the evaluation of the elements of the Raman tensor, symmetry principles of the Raman tensor including the effect of time reversal invariance and the results based on approximation better than the conventional Born-Oppenheimer approximation were also discussed. The next paper by Dr M. Nosimovici (France) was presented by Prof. J. L. Birman, who explained the space group representations for wurtzite structure and the selection rules for Raman and infrared spectra. The breakdown of the Raman selection rules and the anomalous angle dependence of the Raman depolarization ratios in low symmetry crystals were discussed in the last paper of the session by Prof. O. Theimer (USA). A general quantum theory of the phenomenon and its consequences were dealt with in detail.

Impure Crystals

The last session of the symposium was devoted to the Raman scattering from impure crystals. The first paper by Dr M. Ashkin (USA) presented experimental and theoretical results on the Raman scattering from H^- centres in CaF_2. The position and the intensities of the fundamental and the Raman active components of the first and second overtone levels were calculated for a model of the defect as a particle in an anharmonic potential which was determined from the positions of the Raman lines and compared with that obtained from infrared data. In the next paper, Dr A. A. Maradudin (USA) presented the general theory of the impurity induced first-order Raman effect in rocksalt structures, with numerical computations in the case of KCl containing U-centres. He showed that the resulting spectrum is continuous and non-zero in the range of frequencies allowed to the perfect host crystals and that it displays a structure associated with a resonance mode in the acoustic continuum but not with localized modes which are inactive. The last two papers by the Russian workers Prof. K. Rebane, Dr I. Tehver, Dr E. D. Trifonov and Dr K. Peuker considered the vibrational structure of the Raman spectra of impure crystals. The intensity distributions and the temperature dependence of the vibrational structure calculated for various models of the impurity centre and the agreement between these calculated results and the experimental results of Stekhanov and Eliashberg were discussed. The resonance Raman scattering of an impure crystal and its resemblance to luminescence spectra and the selection rules for Raman intensities were examined in detail. Due to the absence of the authors these two papers were taken as read.

The conference concluded with a critical summary by Dr R. Loudon (UK).

Summer School in Chemical Engineering

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UNDER the auspices of the Council of Scientific & Industrial Research, a Summer School in Chemical Engineering was held during 14-26 June 1965 at the Regional Research Laboratory (RRL), Hyderabad. The summer school, attended by about 50 chemical engineers from different educational, research and industrial organizations in the country, was designed to cover recent advances in chemical engineering and some allied fields. It comprised lectures and pilot plant demonstrations; 23 one-hour lectures were given by 21 Indian and 2 foreign scientists, of whom 5 were from the host laboratory. In the afternoon each day, practical demonstrations were given by the laboratory staff in the various pilot plants available and some of the analytical techniques. The school was inaugurated by Dr G. S. Sidhu (Director, RRL, Hyderabad).

Lectures

In the opening lecture, Shri N. Bhanu Prasad (Andhra Foundry & Machine Co. Ltd, Hyderabad) presented a survey of the materials used in chemical plant construction. The cost of the materials of construction in chemical industries is significant, being about 50 per cent of the total. The selection of a particular material depends upon a number of factors, most important of them being its ability to resist corrosion; besides this, compatibility, physical strength, cost and availability are also to be taken into account. In India, where choice is limited to a few materials of construction, their cost and availability become significant. Relative costs of different materials in India and USA were cited.

In addition to the availability and the cost of material, the cost of fabrication, which differs from material to material, has also to be considered. The modern trend is to use two or more different materials for the construction of a particular equipment which will couple both resistance to corrosion and enhanced physical strength. The use of clad steel, for instance, is becoming more economical for high pressure equipment.

Prof. N. R. Kuloor (Indian Institute of Sicence, Bangalore) discussed the importance of electronic computers in chemical engineering work. The computer logic was elaborated and circuit diagrams were shown for addition, subtraction, integration, etc.

Prof. M. N. Rao [Indian Institute of Technology (IIT), Kharagpur] reviewed the field of fluo-solid systems. He discussed the subject under four heads — momentum transfer, heat transfer, mass transfer and reaction kinetics. Momentum transfer was considered under four sub-heads: (i) fluid behaviour in an empty tube, (ii) batch fluidization where particles are in random motion, (iii) continuous fluidization, and (iv) pneumatic transfer. The behaviour of a flowing fluid in a conduit is well understood and equations for calculating pressure loss have been established. These equations have been modified for fluidized systems taking into account the additional factors such as bed density, porosity, particle size and shape. Equations were presented for calculating the pressure drop and size distribution in an air classifier.

In a fluidized bed there are two types of heat transfer — one from the wall to the particle and the other from particles to the surrounding fluid. The laminar film adjacent to the wall is ruptured by the random motion of the particles, thereby reducing the resistance. Another factor contributing to the increased heat transfer in a fluidized bed is that though the period of contact of the particle with the wall is very small the heat transferred to the particle by conduction is considerable.

The rate of drying in a continuous fluidized bed was shown to be related to the motion of particles and their residence time. With a few examples the complexity of the problem where chemical reactions are carried out in a fluidized bed was explained.

Dr M. V. Raghavacharya (Department of Chemical Engineering, Government Engineering College, Trichur) dealt with instrumentation and automation in chemical industries. To automatize a process, it has to be split up into different stages based on the unit operations involved. The design of automatic control equipment requires a thorough understanding of the static and dynamic characteristics of the process involved, which can be described either by mathematical equations or obtained experimentally in the form of a transient response. Different methods of control with more than one interconnected parameter and the merits and limitations of non-interacting controllers were presented.

Prof. G. S. R. Narasimhamurty (IIT, Bombay) discussed the problem of two-phase flow consisting of a gas or vapour and a liquid through circular conduits. The problem is of great interest to chemical engineers in the working of evaporators, condensers and several other two-phase contacting equipment. Flow studies have been carried out in both vertical and horizontal pipes. A limited amount of work was reported on fittings, entrance effects and mode of mixing of the two phases. For the correlation of pressure drop data, one approach is that of Lockhart and Martinelli in the form of the ratio of two-phase flow pressure drop to that of single-phase flow at the same mass flow rate, against the pressure drops of the liquid and of the gas considering each of them to flow alone at their own flow rates. Another approach is that of Bertuzzi, Tek and Poettman correlating modified friction factor based on two-phase flow with a modified Reynolds number based on an appropriate combination of individual gas and liquid Reynolds numbers. Several other workers have developed separate correlations for pressure drop estimation. Depending upon the flow rates of individual phases, different patterns of flow have been identified as bubble, plug, annular, spray and froth flow.

Prof. M. M. Sharma (Department of Chemical Technology, University of Bombay) spoke on absorption with chemical reaction of gases which are sparingly soluble in the absorbent, such as CO_2, COS and H_2S in aqueous solutions of alkalis and amines. The importance of such an absorption can be judged from the fact that in the manufacture of synthesis gas for ammonia from coal or petroleum sources, 1·2-2·2 times of CO_2 has to be removed per tonne of ammonia produced. In such cases the process is controlled by the liquid side resistance. Two theories are available to account for such liquid side resistance, viz. two-film and surface renewal theories; however, there is not much difference between the two regarding the effect of chemical reaction on the absorption coefficient. As a simplified case, an irreversible and kinetically second-order reaction is assumed between gas A and reactive species B in the solution to produce C in the solution. In this heterogeneous reaction, four limiting mechanisms are possible: (i) if the reaction is very slow the reaction rate is entirely kinetically controlled, the total interfacial area being unimportant and the scale-up of the reactor is fairly simple from small-scale experiments; (ii) if the reaction is slow, the rate will be controlled by the transfer rate of A into the liquid; thus both the interfacial area and liquid side mass transfer coefficient (k_l) will be important; (iii) in the case of fast reaction, concentration of the dissolved gas A is very small compared to the reactant B and the dissolved gas undergoes a pseudo first-order reaction; thus the transfer rate of A is independent of k_l and the scale-up can be done simply on the basis of effective interfacial area; and (iv) when the reaction is very fast, i.e. instantaneous, the process is controlled by the diffusion of the reactants to a reaction zone close to the surface where the concentration of both is zero. The scale-up of these reactions will follow the same pattern as in case (ii).

The mechanism of absorption with chemical reaction can change significantly with the hydrodynamic conditions, concentration of reactive species in the solution and partial pressure of the solute.

Dr O. P. Kharbanda (Larsen & Toubro Ltd, Bombay) discussed the usefulness of nomographs in chemical engineering calculations. The terms 'class' and 'genus' and determinant technique were explained citing practical examples.

Shri S. Fareeduddin (Atomic Energy Establishment, Bombay) emphasized the contribution of chemical engineers to the growth of atomic energy, mentioning specific areas in which chemical engineering knowledge and skill have been utilized to solve the various technological problems. These include ore processing, fuel production and reprocessing, manufacture of moderators, cladding materials and control rods, reactor design, waste disposal, etc.

Prof. Ramalingam Kaparthi (Osmania University, Hyderabad) discussed the analogy between mass, momentum and heat transport. These three important transport processes depend on molecular properties of the substances involved and the motion of eddies in a turbulent stream, hence a close relationship between them is anticipated. An analogy between the three processes has been developed from the definition of basic concepts and study of the transport phenomena in laminar and turbulent regions of flow, by considering generalized equations of change. Such an analogy helps in understanding one from a knowledge of the other well-understood process.

Dr P. K. Katti (IIT, Delhi) presented a theoretical approach to the physical properties of liquids and binary liquid mixtures, based on the principles of molecular physics. A liquid can be treated as a dense gas in which the effects of attraction forces are weak and hence there is a lack of resistance to shear stress. On the other hand, X-ray diffraction patterns of the liquids reveal structures similar to those of disordered solids referred to as quasi-crystalline. Molecular models deal with the nature and the magnitude of the forces between the molecules, relative orientation of the pairs of molecules and their relative position with respect to a particular molecule. Saturated vapour pressures, latent heats of fusion and vapourization, adiabatic and isothermal compressibilities, cubical expansion, surface tension, viscosity and thermal conductivity of pure liquids are some of the physical properties much sought after by chemical engineers and which are amenable to treatment from molecular models. When dealing with mixtures, in addition the excess properties are to be considered which are indicative of the nature and the magnitude of the forces between the pairs of unlike molecules and which account for the deviations from ideality of the mixtures. Tables of data were presented showing a remarkable agreement between the experimental and calculated values of boiling points under constant pressure, viscosity and other properties of a number of binary mixtures.

Prof. R. Bisanz (IIT, Madras) discussed chemical engineering aspects in cellulose industry, presenting a short survey of the sources, structure and chemical composition of wood and cellulose fibres. Industrial processes for the manufacture of cellulose pulp and the types of equipment used were reviewed, with stress on the purification of chemical pulp. A comparison of the methods for making nitrocellulose, acetic cellulose and viscose rayon was presented.

Prof. G. Narsimhan [National Chemical Laboratory (NCL), Poona, now at IIT, Kanpur] elaborated upon the concept and use of mathematical models in process research. A model represents a system as completely as possible by bringing together related facts and observations and correlating available data for use in the prediction of the system behaviour under unknown conditions. Two important areas of model application are those dealing with analogue simulation and scale-up and the other with process control optimization. The technique of analogue simulation helps the process designer in getting an understanding of the fundamental mechanism of the process, by combining the rate data (measured or assumed) of the chemical reactions involved in a reactor in such a manner that the operation of the reactor is simulated. Thus the pilot plant is used to obtain data for use in the simulation of the full-scale operation of the process, leading to a more reliable scale-up to the production plant.

Prof. G. S. Laddha (A.C. College of Technology, Madras) covered the field of liquid-liquid extraction dealing with the recent investigations on the effect of solute transfer on dispersed phase holdup, droplet behaviour in packed columns and relationship of holdup with overall mass transfer coefficients. He presented a new model for the interpretation of mass transfer data, involving overall mass transfer coefficients based on actual area of the dispersed phase and on superficial area of the packed column. A knowledge of the interfacial contact area may be obtained from dispersed phase holdup and the mean droplet size.

Prof. O. M. Poltorak (Unesco Expert, IIT, Bombay) discussed the theoretical and engineering aspects of the adsorbed catalyst. An adsorbed catalyst consists of an active component distributed over a surface of inactive adsorbent. It was shown that by varying the conditions of preparation of the catalyst, for instance, platinum over silica gel, it is possible to change the structure of the platinum from crystalline to molecularly dispersed layers, hence enhancing the specific surface hundred- and thousandfold compared to the crystalline adsorbed catalyst. Thus to have the same activity for a given sample a much smaller amount of expensive platinum is required. In addition, molecularly dispersed layers of platinum are much more resistant to sintering and their properties are not altered even at 500-700°C.

Dr D. V. S. K. Rao (Hindustan Lever Ltd, Delhi) dealt with the drying of solids, which is an important unit operation in the manufacture of refractories, food, textiles, paper, etc. The earlier theories of drying, i.e. diffusion and capillary, explain most of the observed phenomena, but the recent studies also take into account the effect on drying of the properties of the material such as conductivity and structure. The driers used in different industries vary in their types and designs and are developed to meet specific demands. The evolution of two new types of driers, i.e. fluidized bed and foam mat, opens new fields for investigation.

Dr Asghar Husain (RRL, Hyderabad) spoke on batch distillation which is an important technique used for the isolation and purification of substances in the laboratory or pilot plant operations, or in small-scale industries, such as the manufacture of pharmaceutical and perfumery-grade products. In view of its unsteady nature, the effect of variables is much more complicated than in continuous distillation; here holdup plays an important role, whereas it does not have any effect in continuous operation. Depending upon the values of the reflux ratio, number of theoretical plates and relative volatility of the mixture, the holdup-to-charge ratio may have an effect, either beneficial or detrimental, on separation.

A simplified method has been suggested for the design of batch distillation columns incorporating correction factors to account for the effect of holdup. More rigorous methods are based on Zuiderweg's and Buiten's theories. A two-stage concept has been presented, in the first stage the column produces concentrated fractions in more volatile component at a constant reflux ratio and in the second stage it removes traces of the same component at an increased reflux rate. Optimum conditions for both stages can be calculated from the equations derived on the basis of Zuiderweg's and Buiten's theories respectively.

The field of chemical reaction kinetics was reviewed by Dr L. K. Doraiswamy (NCL, Poona). Methods were outlined for determining the rate equations for three distinct types of reactions — vapour-phase reactions on a catalyst surface, gas-liquid reactions, and non-catalytic solid-fluid reactions. These form important groups of chemical reactions in the chemical industry. The establishment of an equation adequate to provide a plausible explanation for the effect of operating variables is much sought after by a chemical engineer. However, it must be emphasized that the development of a rate equation is only the beginning and the factors such as velocity of the feed, catalyst effectiveness, recycle, degree of backmixing and the thermal nature of the proposed operation have to be examined in the complete design of a chemical reactor.

In catalytic reactions, the catalyst operates by the adsorption of the reactants on its surface, which may be either physical adsorption in the form of thin films or an activated adsorption (chemisorption); in the latter case, the reactants are believed to be in actual chemical combination with an active centre on the catalyst surface. Any kinetic model for interpreting the rate data should obviously take into account the various steps involved, viz. diffusion and adsorption of the reactants, actual chemical reaction and desorption and diffusion of the products to the main stream. The slowest of these steps controls the overall reaction. Every possible mechanism has to be assumed and constants determined, thus eliminating all but one or two mechanisms as the most plausible. Under non-catalytic solid-fluid reactions, some of the important industrial reactions are chlorination and reduction of ores, decomposition of calcium carbonate, and Kolbe-Schmitt carbonation of phenols in a liquid medium. In such cases also equations of the form developed for reactions catalysed by a solid surface will hold good. But since the solid surface continuously decreases with time, a term will have to be introduced for the changing effective surface area of the solid.

Dr P. S. Murti (RRL, Hyderabad) spoke on heat transfer to two- and three-phase systems, which is of considerable importance in many chemical processes such as in fixed bed regenerators, fluidized and trickling bed reactors, liquid phase-solid catalysed hydrogenation, oxidation reactions, etc. The recent advances relating to interpretation and correlation of heat transfer to gas-liquid flowing systems in bare and packed tubes, and to three-phase systems where the solids are kept in an agitated state were reviewed. Areas in which further work may profitably be carried out were indicated.

Important aspects of mechanical operations which comprise a wide field of great practical and economic significance in process industries were brought out by Prof. D. Venkateswarlu (IIT, Madras). These include size reduction, size enlargement, separation, mixing, storage and transport of materials. Each of them may again be classified into several important and distinct operations. As a preliminary to their study, properties of solid particles and methods of determining particle size, shape, surface area, pore volume and surface energy are to be considered. The objectives of different operations, classification, characteristics and performance of the equipment used and factors to be considered in their selection were dealt with. The theories of Kick, Rittinger, Bond, Holmes and Harris for size reduction of materials, concept of the degree of mixing, flow properties of solids, etc., were also discussed. A good account of work on fluid-energy mill was given.

Dr P. K. Banerjee (RRL, Hyderabad) presented a comprehensive survey of mass transfer columns, mentioning the progress made in the past 30-40 years in developing various types of gas-liquid contacting equipment. Bubble cap columns, the oldest in this field, still hold a commanding position followed by the other well-known sieve plate and packed columns. The bubble cap plate construction itself has been modified in various ways to give added advantage for specific separations. During the last ten years tremendous progress has been made in the field of new column constructions to facilitate distillation of heat sensitive mixtures under high vacuum; besides the advantage of their low pressure drop are their high throughputs and better mass transfer efficiencies. The constructional features and performance characteristics of different columns including the newer trickling columns, such as plate packet nylon thread, Kirchbaum-Stora column, horizontal column, and Luwa fractionator were dealt with.

Prof. N. Gopal Krishna (Regional Engineering College, Srinagar) discussed the design aspects of fluidization columns, with emphasis on the characteristics of mixed size beds, continuous air classification technique and importance of phase diagrams in understanding the flow regions of fluid-solid systems. A correlation of the variables involved was presented.

Solid-liquid extraction, with special reference to oilseed extraction, was reviewed by Shri V. Krishnamoorthy (RRL, Hyderabad). Different types of extractors, problems related with preferential extractability of major and minor constituents of a solid feed, design principles, etc., were discussed.

Shri K. Seshacharyulu (RRL, Hyderabad) spoke on problems related to project development. The general approach to the organization of chemical engineering project, use of models in scaling up, and the influence of various design factors on the total cost of the project were elaborated. An account was given of the start-up procedures and production planning and control methods. With the help of diagrams the functions of various engineering personnel were explained.

Demonstrations

Pilot plant demonstrations were given on the following: (1) low temperature carbonization, briquetting and gasification of coal; (2) tar hydrogenation and distillation; (3) fractionation and extraction of tar acids; (4) prototype plant for the manufacture of active carbons; (5) fatty acid distillation; (6) sintering, clay washing, size reduction and sepation; and (7) processing of cottonseeds and continuous refining of crude oil.

Pilot plant experiments were arranged on batch distillation, spray-drying, solid-liquid extraction and esterification.

The analytical techniques of thin layer and gas-liquid chromatography and gas analysis were demonstrated.

Conclusion

On the closing day, comments and suggestions were invited. There was a general appreciation of the conduct and organization of the summer school, and some suggestions were made for making the future summer schools more useful. The topics assigned to some speakers were considered too vast to cover in an hour, though it was appreciated that a general coverage rather than specialized treatment of different subjects had been attempted in this first summer school.

Some Aspects of Charge Transfer Interactions in Non-electrolyte Mixtures*

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In most theories of the behaviour of non-electrolyte solutions the major contributions to the deviation from ideal mixing defined by the relation[1]

$$\Delta G_{\text{ideal}} = \Sigma_i x_i \; RT \; \ln \, x_i$$

are attributed to the dispersion forces[2]. In such theories the deviations are expected to be positive and the theories would be expected to be applicable to mixtures of non-polar molecules. Negative deviations from ideal behaviour in mixtures of molecules very different in size (e.g. solutions of polymers) can to a large extent be accounted for in terms of geometrical considerations only[3]. Large negative deviations from ideal behaviour in mixtures of similar sized molecules have long been attributed to an often unspecified ' compound formation ' between the components of the mixtures[4,5]. In many cases where there is a possibility of formation of hydrogen bonds[6] between the components this approach, which supposes that the real mixture may be regarded as an ideal mixture of the initial components A and B in equilibrium with one or more ' complexes ' formed on mixing, has been fairly successful. Among the systems whose thermodynamic properties have been correlated in this way are acetone + chloroform[7], and 1,4-dioxane + chloroform[8]. There are, however, cases such as that of 1-hydropentadecafluoro-*n*-heptane + acetone[9], where the assumption of a specific hydrogen bond interaction is inadequate and there are also large non-specific interactions to be accounted for.

The existence in the solid state of compounds formed between molecules normally regarded as ' saturated ' and between which no chemical bonds can be envisaged has been known for many years. One of the earliest such compounds reported[10] has the formula $CHI_3.3(C_9H_7N)$. Since the investigation by Benesi and Hildebrand[11,12] in 1948 of an absorption band at 2970 A. in the ultraviolet spectrum of solutions of iodine in benzene which is not present in either pure benzene or in regular[4] solutions of iodine, there has been a renewed interest, both experimental and theoretical, in the ' charge transfer interactions ' leading to such spectral behaviour. Theoretical aspects of charge transfer interaction between molecules with electron donor properties and those with electron acceptor properties have been recently reviewed by Mulliken[13] and Mulliken and Person[14] and studies of the solid complexes have been reviewed by Hassel and Romming[15]. Much of the recent interest has been in the solid complexes formed by halogen molecules. As yet less attention has been paid to the effects of this kind of interaction on the behaviour of non-electrolyte solutions and less still to solutions in which the electron transfer interaction is between electron donors and halogen atoms in molecules such as the tetrahalides.

Again, there is a long standing knowledge of solid state complexes formed between tetrahalides of group IV elements and electron donors. A brief survey of the literature[16-47] (also Kershaw, R. W. & Williamson, A. G., unpublished work) reveals evidence of more than 70 solid ' molecular complexes ' formed by tetrahalides of C, Si, Ge, Sn and Ti with ethers, amines, acid chlorides and aromatic compounds. In the case of the higher atomic weight members of group IV, there is some indication that the interaction is between the donor atom and the central atom of the tetrahalide although more investigations are needed to clarify this. In the case of carbon, however, this does not appear to be so. Rather do the interactions appear to be directly with the halogen atoms. The complexes formed by carbon tetrachloride with which much of the remainder of this paper will be concerned are summarized in Table 1.

Nearly all the evidence for compound formation comes from binary solid-liquid phase diagrams. The formation of a molecular compound, particularly one with a melting point considerably higher than the eutectic temperatures, is a reasonable but not necessarily conclusive indication of strong interactions between the two components in the liquid. The formation of the solid compound depends on geometrical considerations and it is possible, for example, to obtain compounds in which this, rather than the interactions, appears to be the main factor as, for example, in the system dioxane + anisole[48]. Further, the solid-liquid diagrams can give only a rough indication of the relative strengths of the interactions via the slopes of the solid-liquid lines and practically no direct information of their nature.

Perhaps the best indication of the nature of the interactions comes from the spectrophotometric investigations, where the appearance of a ' charge transfer band ' which is conclusive evidence of this kind of interaction, shows clearly that it is present in solution and can be used to measure its strength. The first such indication of charge transfer interactions involving halogen atoms bonded to carbon appears to be the work of Stevenson and Coppinger[49] who found a shift in the ultraviolet spectrum of solutions of triethylamine with chloroform, carbon tetrachloride, fluorotrichloromethane and bromotrichloromethane which could be attributed to interaction between the nitrogen atom of the amine and the halogen atom in the other compound. The

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*Contribution to the Symposium on Chemical and Non-chemical Interactions sponsored by the University Grants Commission and held at the University of Gorakhpur, Gorakhpur, UP, February 1965.

equilibrium constants for the assumed process

$$A + D \rightleftharpoons AD$$

are given below:

Acceptor	$CHCl_3$	CCl_4	$CFCl_3$
K/litre mole^{-1}	0·085	0·096	0·074

It is interesting to note that two different specific interactions have now been identified for mixtures of chloroform and triethylamine, the hydrogen bond interaction which can be identified and measured quantitatively from the proton magnetic resonance spectrum[50] and the charge transfer interaction mentioned above. The only other systems in which charge transfer interactions involving carbon tetrachloride appear to have been positively identified from ultraviolet spectra are CCl_4 + benzene and CCl_4 + mesitylene systems for which Anderson and Prausnitz[39] have measured the equilibrium constants shown in Table 1.

In mixtures of carbon tetrachloride + benzene the charge transfer interaction appears to be sufficiently strong to have a significant effect on the thermodynamic properties. The heats of mixing while positive and 'regular' in form are rather smaller than those for the similar system cyclohexane + carbon tetrachloride, and whereas the heat of mixing of a system in which only dispersion forces operate usually decreases slowly with increasing temperature, that for carbon tetrachloride + benzene increases rapidly with increasing temperature. Similarly, the temperature coefficient of the volume of mixing for this system is large and positive in contrast to the small temperature coefficients of systems like carbon tetrachloride and cyclohexane. Both of these properties indicate the fairly strong specific interaction between the components in the benzene + carbon tetrachloride mixtures.

It has been shown recently[40] that the heat of mixing of carbon tetrachloride and 1,4-dioxane system is completely dominated by the specific interactions between the components being large and negative (-270 *J* mole^{-1} at $x = 0{\cdot}5$) at 25°C. and having a large positive temperature coefficient. The volume charge on mixing at 25°C. for this system (Kershaw, R. W. & Williamson, A. G., unpublished work) is also large and negative although this alone should not be taken as an indication of specific interactions since it has been shown[51,52] that such negative volume changes can be explained at least for some simple systems in terms of van der Waals' interactions only. Similar results have been observed for the system poly-(propylene oxide)-dimethyl ether in which the heat of mixing and volume of mixing are negative over the whole composition range (Kershaw, R. W. & Malcolm, G. N., unpublished work). Preliminary measurements on mixtures of carbon tetrachloride with diethyl ether, triethylamine and pyridine indicate that the heats of mixing of all these systems, in which electron donor-acceptor interactions are possible, are also exothermic.

Another approach to the investigation of the charge transfer interactions in solution is via the extended lattice theory of solutions developed by Barker[52] and Barker and Smith[53]. In this treatment the quasi-chemical approximation is applied to the distribution of contact pair interactions for a lattice model in which the molecules are supposed to have various kinds of 'contact points'. An energy of interaction U_{ij}, the difference between the potential energy of interaction of an ij contact pair and the mean of the potential energies of ii and jj contacts is assigned to each unlike contact. The properties of the mixture may then be expressed as a function

TABLE 1 — MOLECULAR COMPLEXES FORMED BY CARBON TETRACHLORIDE (A)

Donor molecule (D)	Compound	m.p. or K_f	Method	Reference
Benzene	AD	−34, I, I	*P*, *P*, *P*	31, 27, 36
	A_2D	I, I, I	*P*, *P*, *P*	31, 27, 36
		$K = 0{\cdot}009$	UV	39
			H^E, V^E	36, 41
Toluene	AD	−67·2	*P*	36
p-Xylene	AD	−4	*P*	43
Mesitylene	AD	$K = 0{\cdot}113$	UV	22
Pseudocumene	AD	−43·3, −47·3	*P*, *P*	36
Diethyl ether	AD	−86·5	*P*	27
	AD_2	I	*P*	27
Anisole	AD	−57·3	*P*	36
	A_2D	I	*P*	17
Tetrahydrofuran	?	I	*P*	18
1,4-Dioxane	A_2D	−17·5, −18·2	*P*, *P*	38, 30
			H^E, V^E	40
Methyl-*m*-cresyl ether	AD	−42	*P*	17
Triethylamine			H^E	—
Pyridine	A_2D	−42·6	*P*	26
Acetone	AD	I	*P*	27
			V^E	42
Ethyl acetate	AD ? or AD_2 ?	I	*P*	26
Butyric acid	AD	—	*P*	44
Methanol	Compds ?	—	IR	25
	AD_4	I	*P*	44
Nitrobenzene	Compds ?	—	*P*	45

I = incongruent; K = equilibrium constant in litre mole^{-1}; P = phase diagram; H^E = heat of mixing; V^E = volume of mixing; UV = ultraviolet spectrum; and IR = infrared spectrum.

of the properties of the lattice, the relative numbers of lattice sites occupied by each molecule, the numbers of contact points of each type on the molecules and the values of the U_{ij}. Positive values of U_{ij} indicate that the interaction between i and j sites is weaker than the arithmetic mean of the i-i and j-j interactions and negative values indicate an attractive potential which is stronger than the arithmetic mean.

This treatment has been applied to the mixtures of carbon tetrachloride with poly-(propylene oxide)-dimethyl ether in which the polymer is assumed to have two kinds of contact point, hydrocarbon (I) and oxygen (O) and the carbon tetrachloride is supposed to have one type (Cl) (Kershaw, R. W. & Williamson, A. G., unpublished work). Since the lattice model is essentially one for constant volume, the experimental data G^E and H^E at 5°C. and 1 atm. pressure have been corrected to values of A^E and U^E at constant volume. Of the three energy parameters $U_{\mathrm{O-I}}$, $U_{\mathrm{I-Cl}}$ and $U_{\mathrm{O-Cl}}$ it is found necessary to make $U_{\mathrm{O-Cl}}$ negative in order to obtain agreement between the theory and experiment. It has also been found that the same numerical values of $U_{\mathrm{O-I}}$, $U_{\mathrm{I-Cl}}$ and $U_{\mathrm{O-Cl}}$ reproduced the data for carbon tetrachloride + dioxane system (in which the same kinds of contact point may be assumed) within about 20 per cent. The data for this system have been extrapolated to 5°C. from the experimental observations and in view of the approximations made in the extrapolation and in correcting the extrapolated values to constant volume such agreement is quite promising. The negative value of $U_{\mathrm{O-Cl}}$ required again suggests a strong attractive interaction between the oxygen (donor) and the carbon tetrachloride (acceptor).

It seems probable that the interactions between carbon tetrachloride and electron donors might be significant in a number of other systems. Dacre and Benson[54] have applied Barker's theory to mixtures of several n-alcohols with carbon tetrachloride allowing the contact points I (alkyl hydrogen), O (oxygen), H (hydroxyl hydrogen) and Cl (chlorine), and assuming that

$$U_{\mathrm{I-O}} = U_{\mathrm{I-Cl}} = U_{\mathrm{I-H}} = U_{\mathrm{O-Cl}}$$

so that only three energy parameters U_{OH}, U_{HCl} and U_{IO} were required. Although the relative magnitudes of the excess free energies and excess energies of mixing of CCl_4 with alcohols ranging from C_2H_5OH to $C_8H_{17}OH$ could be fitted fairly well with $U_{\mathrm{OH}} = -5000$ cal. mole^{-1}, $U_{\mathrm{H-Cl}} = -1800$ cal. mole^{-1} and small values of U_{IO} ranging from 0 to 13 cal. mole^{-1} the detailed shapes of the curves for U_V^E were not well reproduced. A common feature of the results was the inability of the theoretical treatment to reproduce the rapid fall in U_V^E at high alcohol concentrations and the change in sign of U_V^E in this region for the lower alcohols. Part of this failure could well be due to neglect of the special nature of the O-Cl interaction and it would be of interest to see whether an extended treatment with

$$O > U_{\mathrm{O-Cl}} \neq U_{\mathrm{I-O}}$$

would improve the agreement. Liddel and Becker[46] have suggested that the frequency shifts in the infrared spectra of very dilute solutions of methanol in carbon tetrachloride can be explained in terms of a specific interaction between the carbon tetrachloride and the methanol.

Another system in which it has been suggested[42] that charge transfer interactions may be significant but in which no detailed allowance has been made for these effects is acetone + carbon tetrachloride. The heats of mixing[55] for this system are not 'regular' having a maximum at $x_{\mathrm{acetone}} = 0{\cdot}25$ compared with the value $x_{\mathrm{acetone}} = 0{\cdot}54$ which would be expected if the system were regular[5]. The volumes of mixing are also unsymmetrical being negative over most of the composition range but changing to positive at low acetone concentrations.

There is clearly much more work both experimental and theoretical on carefully selected systems which needs to be done to achieve a thorough understanding of solutions of halogenated compounds. Spectroscopic studies will undoubtedly play a large part in this, but further studies of thermodynamic properties covering a wide temperature range are also needed. More calculations are needed based on theories such as Barker's in which the detailed interactions are considered. It is to be hoped that such studies will be undertaken by those with access to the computers which are virtually necessary in order to carry out the tedious arithmetic involved.

Summary

A search of the literature reveals evidence which suggests carbon tetrachloride might act as an electron acceptor with certain oxygen and nitrogen containing compounds, and aromatics. Most of the evidence occurs in solid-liquid phase studies, but there is also spectroscopic and calorimetric evidence available. In this review this evidence is examined, and a possible interpretation in terms of lattice theories for the interaction is discussed.

References

1. GUGGENHEIM, E. A., *Thermodynamics* (North Holland Publishing Co., Amsterdam), 1957.
2. HIRSCHFELDER, J. O., CURTIS, C. E. & BIRD, R. B., *Molecular theory of gases and liquids* (John Wiley & Sons Inc., New York), 1954, 25.
3. GUGGENHEIM, E. A., *Mixtures* (Oxford University Press, Oxford), 1952, 29.
4. DOLEZALEK, F., *Z. phys. Chem.*, **64** (1908), 727.
5. HILDEBRAND, J. H. & SCOTT, R. L., *Solubility of non-electrolytes* (Reinhold Publishing Corp., New York), 1950, 175.
6. PIMENTEL, G. C. & MCCLELLAN, A. L., *The hydrogen bond* (W.H. Freeman & Co., San Francisco), 1960, 206.
7. KEARNS, E. R., *J. phys. Chem.*, **63** (1961), 314.
8. MCGLASHAN, M. L. & RASTOGI, R. P., *Trans. Faraday Soc.*, **54** (1958), 496.
9. ANDERSON, D. L., SMITH, R. A., MYERS, D. B., ALLEY, S. K., WILLIAMSON, A. G. & SCOTT, R. L., *J. phys. Chem.*, **66** (1962), 621.
10. RHOUSSOPOULOS, *Ber. dtsch. chem. Ges.*, **16** (1883), 202.
11. BENESI, H. A. & HILDEBRAND, J. H., *J. Amer. chem. Soc.*, **70** (1948), 2832.
12. BENESI, H. A. & HILDEBRAND, J. H., *J. Amer. chem. Soc.*, **71** (1949), 2703.
13. MULLIKEN, R. S., *J. chim. Phys.*, **61** (1964), 20.
14. MULLIKEN, R. S. & PERSON, W. B., *Ann. Rev. phys. Chem.*, **13** (1962), 107.
15. HASSEL, O. & ROMMING, CHR., *Quart. Rev.*, **16** (1962), 1.
16. SISLER, H. H. & CORY, C. J., *J. Amer. chem. Soc.*, **69** (1947), 1515.

17. Sisler, H. H., Wilson, W. J., Gibbens, B. J., Batey, H. H., Pfahler, B. & Mattair, R., *J. Amer. chem. Soc.*, **70** (1948), 3821.
18. Sisler, H. H., Batey, H. H., Pfahler, B. & Mattair, R., *J. Amer. chem. Soc.*, **70** (1948), 3818.
19. Sisler, H. H., Pfahler, B. & Wilson, W. J., *J. Amer. chem. Soc.*, **70** (1948), 3825.
20. Sisler, H. H. & Mattair, R., *J. Amer. chem. Soc.*, **70** (1948), 3826.
21. Sisler, H. H., Schilling, E. E. & Groves, W. O., *J. Amer. chem. Soc.*, **73** (1951), 426.
22. Hamilton, P. M., McBeth, R., Bekebrede, W. & Sisler, H. H., *J. Amer. chem. Soc.*, **75** (1953), 2881.
23. Rolsten, R. F. & Sisler, H. H., *J. Amer. chem. Soc.*, **79** (1957), 1068, 1819.
24. Sheldon, J. C. & Tyree, S. Y., *J. Amer. chem. Soc.*, **80** (1958), 4775; **81** (1959), 2290.
25. Cullinane, N. M., Chard, S. J. & Layson, D. M., *J. chem. Soc.*, (1952), 4106.
26. Wyatt, W. F., *Trans. Faraday Soc.*, **25** (1929), 43.
27. Wyatt, W. F., *Trans. Faraday Soc.*, **25** (1929), 48.
28. Davidson, A. W., Van der Werf, C. A. & Boatright, L. G., *J. Amer. chem. Soc.*, **69** (1947), 3045.
29. Kennard, S. M. S. & McCusker, P. A., *J. Amer. chem. Soc.*, **70** (1948), 1039,
30. Kennard, S. M. S. & McCusker, P. A., *J. Amer. chem. Soc.*, **70** (1948), 3375.
31. Egan, C. J. & Luthy, R. V., *Industr. Engng Chem.*, **47** (1955), 250.
32. Goates, J. R., Sullivan, R. J. & Ott, B. J., *J. phys. Chem.*, **63** (1959), 589.
33. Goates, J. R., Ott, B. J. & Budge, A. H., *J. phys. Chem.*, **65** (1961), 2162.
34. Goates, J. R., Ott, B. J. & Mangelson, N. F., *J. Phys. Chem.*, **67** (1963), 2874.
35. Goates, J. R., Ott, J. B., Mangelson, N. F. & Jensen, R. J., *J. phys. Chem.*, **68** (1964), 2617.
36. Ott, J. B., Goates, J. R. & Budge, A. H., *J. phys. Chem.*, **66** (1962), 1387.
37. Goates, J. R., Ott, J. B. & Mangelson, N. F., *J. Chem. Engng Data*, **9** (1964), 330.
38. Ott, J. B., Goates, J. R. & Mangelson, N. F., *J. Chem. Engng Data*, **9** (1964), 203.
39. Anderson, R. & Prausnitz, J. M., *J. chem. Phys.*, **39** (1963), 1225.
40. McKinnon, I. R. & Williamson, A. G., *Aust. J. Chem.*, **17** (1964), 1374.
41. Wood, S. E. & Brusie, J. P., *J. Amer. chem. Soc.*, **65** (1943), 1891.
42. Brown, I. & Smith, F., *Aust. J. Chem.*, **15** (1962), 9.
43. Wyatt, W. F., *Trans. Faraday Soc.*, **24** (1928), 429.
44. Bordamora, M. I., *Chem. Abstr.*, **54** (1951), 183241.
45. Hrynakowski, K. & Szymt, M., *Z. phys. Chem.*, **A182** (1938), 405.
46. Liddel, U. & Becker, E. D., *J. chem. Phys.*, **25** (1956), 173.
47. Rastogi, R. P. & Nigam, R. K., *Trans. Faraday Soc.*, **55** (1959), 2005.
48. Mangelson, N. F., Goates, J. R. & Ott, J. B., *J. phys. Chem.*, **68** (1964), 1260.
49. Stevenson, D. P. & Coppinger, G. M., *J. Amer. chem. Soc.*, **84** (1962), 149.
50. Huggins, M. L., Pimentel, G. C. & Shoolery, J. N., *J. chem. Phys.*, **23** (1955), 1244.
51. Prigogine, I., *Molecular theory of solutions* (North Holland Publishing Co., Amsterdam), 1957.
52. Barker, J. A., *J. chem. Phys.*, **20** (1952), 1526.
53. Barker, J. A. & Smith, F., *J. chem. Phys.*, **22** (1954), 375.
54. Dacre, B. & Benson, G. C., *Canad. J. Chem.*, **41** (1963), 278.
55. Brown, I. & Fock, W., *Aust. J. Chem.*, **10** (1957), 417.

Recent Developments in the Spectroscopy of Uranyl Salts*

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In spite of a large number of detailed investigations on the spectra of uranyl salts by many workers, the spectra of these salts are not yet well understood due to complexity in the observed features and the difficulties in putting forward a suitable theory for their interpretation. The divalent uranyl ion (UO_2^{2+}) is chiefly responsible for the observed features in the fluorescence and absorption spectra and the fluorescence spectra are observed[1-9] in the region 4800-6500 A. while the electronic absorption spectra of these salts extend[1,4,10-14] from about 4800 to 3400 A. It is, therefore, of interest to review the progress made in the interpretation of the observed features of spectra of uranyl salts and indicate the scope for further investigation.

The UO_2^{2+} ion can be considered as a very stable intermediate product of hydrolysis reaction[15]

$$U^{6+} + 4OH \rightarrow UO_2^{2+} + 2H_2O$$

and it behaves like a molecule. From the infrared and Raman spectra[16,17] it has been established that the uranyl ion has three frequencies at about 860 (ν_1), 210 (ν_2) and 930 (ν_3) cm.$^{-1}$, corresponding respectively to the symmetric stretching, symmetric bending and asymmetric stretching frequencies of the uranyl ion. For the linear structure of the uranyl ion, one would expect the absence of ν_2 and and ν_3 frequencies in the Raman effect and ν_1 in the infrared absorption. However, experimentally all the three frequencies have been observed both in infrared absorption[16,18-20] and Raman effect[16,17] though the lines of the prohibited frequencies are weaker than the allowed ones. These selection rules are strictly valid only for free ions and do not, in general, hold good when the ions are influenced by the crystalline fields. From the X-ray diffraction studies[21-23], there is good evidence that the uranyl ion has a linear structure.

The interpretation of the fluorescence and the electronic absorption spectra of these compounds has been attempted by a few workers. Freymann and coworkers[2] analysed both the fluorescence and

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*Paper presented at the Symposium on Solid State Physics held at the National Physical Laboratory, New Delhi, in April 1964.

absorption bands as due to one electronic transition with a very weak or absent 0,0 band. On the other hand, Pant[5,10] tried to explain the spectra on the basis of two electronic transitions between two close-lying ground states and a common upper state. These two types of analyses are not satisfactory as many of the observed features in the spectra could not be explained. Dieke and Duncan[4] were the first to take up a detailed systematic investigation of the fluorescence and absorption spectra of a large number of uranyl salts in the form of crystals and powders. They have divided a large number of bands in the absorption spectra into a number of series depending on their experimental behaviour.

These different series of bands have been attributed to the different electronic transitions from the common lower state to the various excited states with their associated vibrational levels as shown in Fig. 1. The fluorescence spectrum has been interpreted on the basis of a single electronic transition from the lowest excited state to the ground state. This conclusion is based on the fact that whatever may be the wavelength of excitation from the ultraviolet to the blue region, the same fluorescence spectrum is obtained. Frequencies not only of the uranyl ion but also of the other radicals in the salts have been identified in the spectra. The above conclusions of Dieke and Duncan have been verified by Narasimham and Ramakrishna Rao, who made an independent study of the fluorescence and absorption spectra of a number of single and double uranyl salts[7,8,10-13].

The experimental arrangements to record the fluorescence and electronic absorption spectra at low temperatures have been fully described by various workers[4,5,7,24].

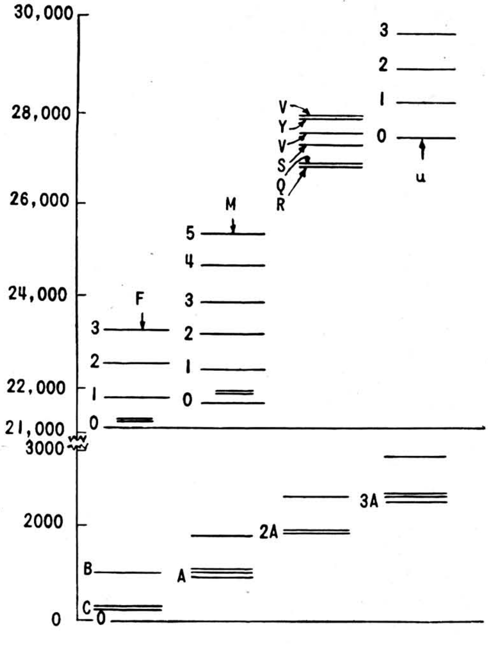

Fig. 1 — Energy level diagram of CsUO$_2$(NO$_3$)$_3$

Fluorescence Spectra

The fluorescence spectrum of UO_2^{2+} consists of about six to seven groups of lines having the maximum intensity in the second and third groups[8]. The symmetric stretching frequency ν_1 plays a vital role in all the spectra of the uranyl compounds since bands of this fundamental and its overtones are the strongest in the spectrum and other frequencies are observed only superposed on the fundamental and its overtones. The appearance of the ν_3 fundamental and its combinations with ν_1 having strong intensity may be explained as the violation of the selection rules due to the crystalline fields surrounding the uranyl ion. Bands corresponding to the bending mode of vibration (ν_2) are usually weak. In some compounds, this vibration appears with two frequencies of about 180 and 240 cm.$^{-1}$. In sulphates, more than one quanta of ν_2 vibration are observed and the intensities of the bands corresponding to this vibration are quite considerable[25].

Some weak lines are usually observed adjacent to the very strong bands of the spectrum with a separation of about ± 30 cm.$^{-1}$ from the main bands. These could be attributed to a characteristic frequency of the crystal lattice along with the frequencies 860, 210 and 930 cm.$^{-1}$ of the uranyl ion[7,11,12,14,24,26]. In addition, lines corresponding to the frequencies of other radicals in the compounds are also obtained. For example, in the spectra of the uranyl nitrate and cesium uranyl nitrate, lines of the NO_3 frequencies and in the spectra of the uranyl sulphate and potassium uranyl sulphate, lines of the SO_4 frequencies have been obtained[4,8,11]. There are some lines whose origin could not be established and they might be due to the lattice interaction with the vibrations of the uranyl ion and other radicals. Only further experiments would clear up this matter.

Detailed analyses of the fluorescence spectra have been given by Dieke and Duncan[4] for cesium uranyl nitrate and cesium uranyl chloride and by Narasimham and Ramakrishna Rao[7] and Narasimham[8] for uranyl acetate, nitrate, sulphate, anhydrous fluoride, fluoride I, fluoride II, chloride, phosphate, oxalate, potassium uranyl sulphate and ammonium uranyl sulphate.

Electronic Absorption Spectra

Unlike the fluorescence spectrum, the electronic absorption spectrum of a uranyl compound is complicated due to the overlapping of different systems. There are usually three distinct series of bands in the visible absorption region and a fourth series in the near ultraviolet, corresponding to the fluorescence, magnetic, diffuse and ultraviolet series respectively of Dieke and Duncan[4]. These four series might be considered as due to four electronic transitions from a common ground state to the different excited states. In each system, the bands can be analysed on the basis of the vibrational frequencies of the uranyl ion, the crystal lattice, and other radicals in the compounds as in the fluorescence spectrum.

To classify the absorption lines into the different electronic systems, polarized absorption experiments in different directions with single crystals of the compounds would be very helpful since the component of a given electric dipole oscillation in a given plane in the crystal is determined primarily by the two electronic states whose combination produces this oscillation. For each direction of the crystal, the spectra are recorded with the two polarized horizontal and vertical components separated. Some bands are strong in one component while they are weak or totally absent in the other component. This method has been utilized by Dieke and Duncan[4] for cesium uranyl nitrate and cesium uranyl chloride and by Narasimham and Ramakrishna Rao[27] for uranyl acetate and uranyl nitrate.

Dieke and Duncan[4] gave the detailed analyses of the absorption bands only for cesium uranyl nitrate and cesium uranyl chloride, though they have studied a large number of compounds. Narasimham[11,12,14] has proposed detailed analyses for the electronic absorption spectra of uranyl acetate, nitrate, phosphate, oxalate, chloride and three different varieties of fluorides, on the same lines of Dieke and Duncan.

The existence of a few more series in addition to the above four series cannot be ruled out since the origin of quite a few lines in the absorption spectrum could not be established. It is probable that some of them are due to the interaction of the crystal lattice with the vibrations of the uranyl ion and other radicals in the compounds.

Infrared Absorption Spectra

The infrared absorption spectra of a number of uranyl compounds have been studied by many workers including Lecomte and Freymann[28], Sevchenko and Stepanov[18], Jones and Penneman[19], Narasimham[20] and McGlynn *et al.*[29]. In all the spectra, the antisymmetric stretching frequency ν_3 appears with great intensity whereas the bands corresponding to ν_1 and ν_2 are usually weak. In addition to the uranyl frequencies, bands belonging to the vibrations of the ligands in the salts appear in the spectra.

Effect of the ligand field — It is difficult to evaluate precisely the effect of the ligand field on the uranyl ion due to an inadequate knowledge of the positioning of the ligands with respect to the uranyl atoms. Only in a few cases, the X-ray data are helpful. For example, in the trinitrate uranyl ion, $UO_2(NO_3)_3^-$, the three nitrate ions are coordinated with uranium in an equatorial plane. The two axial oxygens of the UO_2^{2+} group are in a line with the uranium atom, one directly above and the other directly below. Thus the six U-O coordination bonds lie in the plane prependicular to the two axial U-O bonds of the uranyl ion. The resultant equatorially applied field will affect the uranyl ion and modify its spectrum to some extent, but since the axial U-O distance is much shorter (1·60-1·92 A. depending on the affixed equatorial ligands) than the equatorial U-O length (~ 2·5 A.), the spectrum is primarily influenced by the axial field, the equatorial field exerting only a small perturbing influence. The changes in ligation in different uranyl compounds produce variations in the values of symmetric stretching frequency ν_1 (in the range 800-900 cm.$^{-1}$) and the antisymmetric frequency ν_3 (in the range 850-1000 cm.$^{-1}$). McGlynn *et al.*[29] who studied the ligation effects on the infrared spectrum of the uranyl ion have shown that a ligand series may be defined using the antisymmetric stretching frequency of the UO_2^{2+} and this series exhibits a remarkable parallelism with the spectrochemical series.

Isotope Substitution

Dieke and Duncan[4] have studied the effect of isotopic substitution on the spectra of $CsUO_2(NO_3)_3$ and $CsUO_2Cl_4$. When the spectra are taken with the enriched samples containing from 53 to 83 per cent U^{235}, maximum shifts of about 0·7 cm.$^{-1}$ are observed for all the ν_3 lines, agreeing with the calculated value from theory. The ν_1 lines do not show any shift as required by the theory.

The results of O^{18} substitution (1·36 per cent O^{18}) are more pronounced, as expected. Isotope shifts up to 166 cm.$^{-1}$ have been observed in the fluorescence spectrum of $CsUO_2(NO_3)_3$. Such a shift is expected for the excitation of five quanta of vibrations in the asymmetric molecule $O^{18}UO^{16}$. A shift of about 31·4 cm.$^{-1}$ has been observed for the ν_1 vibration agreeing quite well with the expected shift of 33·1 cm.$^{-1}$. As the O^{18} concentrations are still very low, the shifts of ν_2 lines are too weak to be detected with any degree of certainty. It is desirable to work with higher O^{18} concentrations as the information to be derived from the oxygen-isotope effect for the ν_2 lines would be of decisive value for their interpretation.

Zeeman Effect

The effect of the magnetic field on the uranyl spectra was investigated by Dieke and Duncan[4]. Whereas Zeeman splitting is not observed in the fluorescence spectrum, it is observed in the absorption spectra of uniaxial crystals. For the observation of the Zeeman effect in these compounds, the O-U-O direction in the crystal must be a symmetry axis. In such a case, the angular momentum around this axis is quantized (quantum number λ). Except for the states for which $\lambda = 0$ (Σ states) all other states (π, Δ, . . .) are doubly degenerate in the absence of a magnetic field. This degeneracy is removed when the magnetic field is applied parallel to the axis of the symmetry with the result one of the two coinciding energy levels will be raised and the other lowered by the amount

$$\epsilon = \frac{eh}{4mc}\lambda H = Gh\lambda$$

where G is the amount of the normal Zeeman shift.

These theoretical predictions have been confirmed experimentally[4] mainly in the absorption spectrum of $CsUO_2(NO_3)_3$. The crystals of this salt have a threefold axis of symmetry parallel to the U-O direction. When a magnetic field is applied on a single crystal of this salt with the symmetry axis parallel to the field vector, many lines are split into doublets. There is no splitting when the optic axis is normal to this field.

All the lines in the absorption spectrum do not show the Zeeman effect. Only one series of lines have been found to split into two components each and this series was called the ' magnetic series ' by Dieke and Duncan[4]. The name has also been used for an analogous series of lines in compounds, in which no Zeeman effect was noticeable.

Paramagnetism of the Uranyl Ion

The uranium atom has six valence electrons and has the electronic configuration . . . $5f^3 6d 7s^2$ according to Seaborg[30]. In the uranyl ion, twelve electrons are involved in binding, six from the uranium, four from each of the two oxygens and minus two to account for the doubly positive charge of the ion. By filling these electrons into the molecular orbitals, we have the electron configuration as follows:

$$(1\sigma_u^+)^2(1\sigma_g^+)^2(1\pi_u)^4(1\pi_g)^4$$

This configuration gives a totally symmetric singlet ground state $^1\Sigma_g^+$ for the ion[31]. As there are no unpaired electrons, the uranyl compounds are expected to be diamagnetic. But a temperature-independent paramagnetism has been definitely observed by Freed and Kasper[32] and Lawrence[33]. Van Vleck[34] attributed this paramagnetism to the matrix elements of the magnetic moment operator $\beta(L+2S)$ between the ground state and higher states. The contribution from the spin magnetic moment is zero since all spins are paired off in the ground state. As the largest orbital contribution comes from the two $5f\sigma$ bonding electrons, Eisenstein and Pryce[35] have assumed that f electrons are responsible for the magnetism of the uranyl ion. Belford[36] and Belford and Belford[37] have shown, from the orbital overlap integral calculations, that the $5f\sigma$ uranium orbitals do not overlap much with the oxygen orbitals as the $6d$ orbitals do and that considerable π bonding also might be involved.

Electronic States of the Uranyl Ion

There is little doubt from all experimental evidence that the ground or normal state of the uranyl ion is a $^1\Sigma_g$ for the uranyl ion. However, the nature of the excited states is not yet understood with any certainty. Of the various electronic transitions in the absorption spectrum, only one has shown the Zeeman splitting of the lines. In a dipole transition, the transitions for which λ remains unchanged will not be split in a magnetic field, whereas those for which λ changes by 1 will have doublets with the observed width of splitting. These considerations have led Dieke and Duncan[4] to assume that all those systems without splitting in the magnetic field are due to Σ-Σ transitions, while the upper electronic state of the magnetic series which show the Zeeman splitting might be a π state.

McGlynn and Smith[31] have made calculations of 1-electron molecular orbital (MO) energy levels of UO_2^{2+} and have come to the conclusion from group theoretical considerations and also studies on the solution absorption spectrum of $UO_2NO_3.6H_2O$ that, in the visible absorption band of the uranyl ion, there are at least three distinct electronic transitions, which are the three components of a triplet-singlet process. Thus, according to them, the lowest lying excited level is probably a $^3\pi_u$ as shown in Fig. 2. Transitions from the $^1\Sigma_g$ to the three components of the $^3\pi_u$ would give rise to fluorescence, magnetic and diffuse series in the visible region, while the transition $^1\Sigma_g$-$^1\Sigma_u$ would give rise to the ultraviolet series observed in the ultraviolet region. The absorption spectrum has been attributed by them as due to transfer of charge from the oxygens to the uranium.

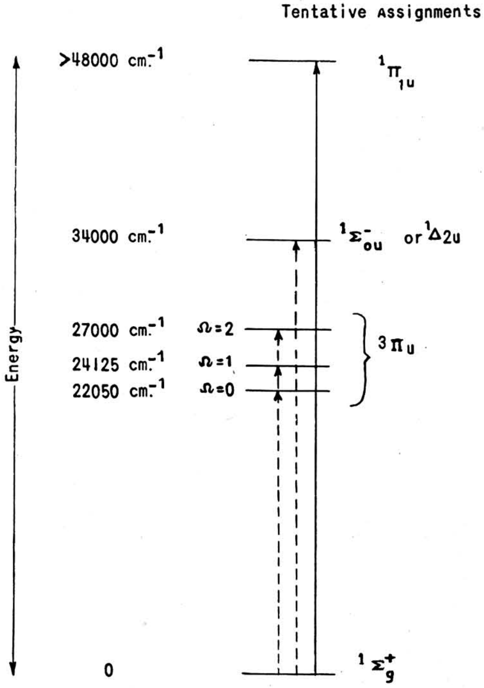

Fig. 2 — Tentative energy level scheme of the UO_2^{2+} ion spectrum

Recently, Fayt *et al.*[38] from their studies of the influence of complexation on the absorption spectra of the uranyl ion have found evidence for the idea of an excited triplet state.

Summary

The important recent advances in the spectroscopy of uranyl salts are reviewed. That the fluorescence spectrum in these salts is due to a single electronic transition from the lowest excited state to the ground state is established beyond doubt both by experiment and theory. However, the number and nature of the excited states in the absorption spectra are not thoroughly understood, though there is some evidence for an excited triplet state. No definite information is available about the extent of interaction of the crystalline field on the uranyl ion in different salts, though the fact that the ligands in the uranyl salts affect the uranyl frequencies to some extent is well established. Further experiments such as studies of various isotope substitutions, polarization characteristics in the absorption spectra, infrared spectra of compounds of spectrochemical series and the effect of the magnetic field on the spectra of a large number of compounds would clear up many of the difficulties encountered in the interpretation of the observed features of the spectra of uranyl salts.

References

1. Nichols, E. L. & Howes, H. L., *Fluorescence of uranyl salts* (Carnegie Institute of Technology, Pittsburgh), 1919.
2. Freymann, M., Guilmart, T. & Freymann, R., *C.R. Acad. Sci., Paris*, **223** (1946), 573.
3. Freymann, M., *C.R. Acad. Sci., Paris*, **225** (1947), 529.
4. Dieke, G. H. & Duncan, A. B. F., *Spectroscopic properties of uranium compounds* (McGraw-Hill Book Co. Inc., New York), 1949.
5. Pant, D. D., *Proc. Indian Acad. Sci.*, **22A** (1945), 95.
6. Samoilov, B. N., *J. exp. theor. Phys.*, **18** (1948), 1030.
7. Narasimham, K. V. & Ramakrishna Rao, V., *Spectrochim. Acta*, **18** (1962), 1955.
8. Narasimham, K. V., *Indian J. Phys.*, **35** (1961), 282.
9. Hall, L. A. & Dieke, G. H., *J. opt. Soc. Amer.*, **47** (1957), 1092.
10. Pant, D. D., *Proc. Indian Acad. Sci.*, **31A** (1950), 35.
11. Narasimham, K. V., *J. sci. industr. Res.*, **21B** (1962), 468.
12. Narasimham, K. V., *Developments in applied spectroscopy*, Vol. 2 (Plenum Press Inc., New York), 1962.
13. Narasimham, K. V., *Spectroscopia Molecular*, **11** (1962), 20.
14. Narasimham, K. V., *J. mol. Spectrosc.*, **11** (1963), 128.
15. Rabinowitch, E., *U.S. Atomic Energy Commission Reports*, ANL-5122 & ANL-5173 (Office of Technical Services, Department of Commerce, Washington DC), 1953.
16. Conn, G. K. T. & Wu, C. K., *Trans. Faraday Soc.*, **34** (1938), 1483.
17. Satyanarayana, B. S., *Proc. Indian Acad. Sci.*, **15A** (1942), 414.
18. Sevchenko, A. N. & Stepanov, B. I., *J. exp. theor. Phys.*, **19** (1949), 1113.
19. Jones, L. H. & Penneman, R. A., *J. chem. Phys.*, **21** (1953), 542.
20. Narasimham, K. V., *Indian J. Phys.*, **34** (1960), 321.
21. Fankuchen, I., *Phys. Rev.*, **43** (1933), 1048.
22. Zachariasen, W. H., *Acta cryst.*, **1** (1948), 265, 277, 288.
23. Hoard, J. L. & Stroupe, J. D., quoted by G. H. Dieke & A. B. F. Duncan in *Spectroscopic properties of uranium compounds* (McGraw-Hill Book Co. Inc., New York), 1949.
24. Ramakrishna Rao, V. & Narasimham, K. V., *Indian J. Phys.*, **30** (1956), 334.
25. Narasimham, K. V., *Spectroscopic investigations on some uranyl salts*, D.Sc. thesis, Andhra University, 1959.
26. Freymann, M., *C.R. Acad. Sci., Paris*, **226** (1948), 332.
27. Narasimham, K. V. & Ramakrishna Rao, V., *J. sci. industr. Res.*, **19B** (1960), 285.
28. Lecomte, J. & Freymann, R., *Bull. Soc. chim. Fr.*, **8** (1941), 622.
29. McGlynn, S. P., Smith, J. K. & Neely, W. C., *J. chem. Phys.*, **35** (1961), 105.
30. Seaborg, G. T., *The actinide elements* (McGraw-Hill Book Co. Inc., New York), 1954, 733.
31. McGlynn, S. P. & Smith, J. K., *J. mol. Spectrosc.*, **6** (1961), 164.
32. Freed, S. & Kasper, C., *J. Amer. chem. Soc.*, **52** (1930), 4671.
33. Lawrence, R. W., *J. Amer. chem. Soc.*, **56** (1934), 776.
34. Van Vleck, J. H., *The theory of electric and magnetic susceptibilities* (Oxford University Press, Oxford), 1932.
35. Eisenstein, J. C. & Pryce, M. H. L., *Proc. roy. Soc.*, **A229** (1955), 20.
36. Belford, R. L., *J. chem. Phys.*, **34** (1961), 318.
37. Belford, R. L. & Belford, G., *J. chem. Phys.*, **34** (1961), 1330.
38. Fayt, M. M., Vandepot, E. M. & Di Jaeger, S. A., *Nature, Lond.*, **200** (1963), 355.

Thermodynamic Criteria of the Nature of Bonding in Dye Aggregates*

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THE phenomenon of dye aggregation has been studied by many workers in relation to concentration quenching of fluorescence[1-7] and wavelength dependence of fluorescence yield[8,9]. In the case of chlorophyll, the study of the nature of stacking of molecules in the aggregate has been helpful in throwing light on energy migration in photosynthesis[10]. The evidence of aggregation has been, in general, obtained from nonconformity with the Beer's law in the light absorption property of a compound[4,11-13] from the concentration dependence of standard electrode potential of a redox system or from its electrical conductivity.

Various mechanisms have been advanced for the aggregation of dyes in aqueous solutions[4-8,13-15]. Since the process does not stop at the dimer stage, the phenomenon has been associated with the additive forces of van der Waals' type[4,6,7,13]. It has been suggested that London's dispersion forces are responsible for the stacking of dye molecules in the polymer unit in parallel orientation. From an extensive study of the heat of association of rhodamin dyes, Levschin and coworkers have suggested that intramolecular hydrogen bonding or bonding by sandwiched water molecules are involved in this phenomenon[15-17].

It has been further observed that in alcohol or glycerol solution aggregation is very small[4,6,7]. Addition of alcohol or glycerol to concentrated aqueous solution may cause disaggregation. This has been explained as due to influence of dielectric constant of the medium. That this factor is not very important has been shown by Arvan and Zaitseva[14] for a number of dyes in single and mixed solvents of identical dielectric constants. In the absence of the data on the microscopic dielectric constant around the dye ion such correlation with macroscopic dielectric constant may not always be justified. These workers ascribed a substantial role to hydroxyl groups of the solvent molecules in dye aggregation. Thus no single mechanism can be put forward to explain the forces holding the dye molecules together.

Very few attempts have been made for the study of thermodynamic behaviour of aggregation of dye molecules, as the accurate determination of the equilibrium constant of the system is difficult due to successive polymerization of the dye leading to micelle formation. Simplification has been introduced by confining to the preliminary stage of dimerization. An early attempt to study dimer equilibria and enthalpy changes on dimerization was made by Rabinowitch and Epstein[4] for the systems thionine and methylene blue. The equilibrium constant for the dimerization of fluorescein anion has been determined by Levschin and coworkers[6,7] and Lavorel[9], but a complete thermodynamic study is still lacking. Such a study is expected to be helpful in understanding the aggregation tendency of the dye and the nature of bonding involved in the aggregates.

Study of Two Typical Dyes

Two typical dyes, sodium fluorescein and rhodamin B, have been investigated. Sodium fluorescein at *p*H 12 has high quantum yield of fluorescence and aggregates at relatively higher concentrations as evident from the absorption spectra. Even in solutions of concentration $10^{-2}M$ the spectra are not visibly distorted. On the other hand, rhodamin B has low quantum yield of fluorescence and the absorption spectra are deformed considerably at a concentration of $10^{-3}M$. In each case a vibrational shoulder in the monomer spectrum is enhanced in proportion to the degree of association. This is ascribed to the dimer peak.

The equilibrium constant for the reaction

$$\text{dimer} \rightleftharpoons \text{monomer}$$

has been calculated for the two dyes from the monomer and the dimer peak heights at different gross concentrations of the dyes. The value of ΔH for the aggregating dye has been obtained from the variation of the equilibrium constant with temperature. For sodium fluorescein, the dependence of quantum yield of fluorescence on temperature has been found useful for the evaluation of the enthalpy change involved in the breaking of the dimers. From these data, free energy (ΔF) and entropy change (ΔS) have been evaluated. The data are presented in Table 1 for the dimerization process, i.e. reverse of the reaction as written above. The experimental details are given elsewhere (unpublished work).

Thermodynamic Criteria of the Nature of Bonds Involved

Hydrogen bonding — The data presented in Table 1 are very interesting. The value of ΔH and ΔS for sodium fluorescein appear to be normal values, as is expected when two monomers combine to form a dimer. The magnitude of these values suggests that, in the case of this dye, the two molecules are

TABLE 1 — THERMODYNAMIC FUNCTIONS FOR THE DIMERIZATION OF SODIUM FLUORESCEIN AND RHODAMIN B AT 30°C.

Dye	$K_{\text{ass}}^{30^\circ}$	ΔF kcal./mole	ΔH kcal./mole	ΔS e.u.
Sodium fluorescein	4·76	−0·96	−6·9	−19
Rhodamin B	$1{\cdot}43\times10^{+3}$	−4·4	−1·0	+11·2

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*Contribution to the Symposium on Chemical and Non-chemical Interactions sponsored by the University Grants Commission and held at the University of Gorakhpur, Gorakhpur, UP, February 1965.

held together by hydrogen bonding. The entropy change is negative and the value is what is to be expected for a single hydrogen bond formation. This corroborates the suggestion by Levschin and coworkers[6,7].

Hydrophobic bonding — The nearly athermal nature of dye association and positive entropy change in the case of rhodamin B is noteworthy. Many similar examples are available in the thermodynamics of protein aggregation where the reactions are even endothermic to the extent of 6-8 kcal. with large positive entropy change[18]. In many instances these reactions go in the direction they do because of their entropy change which at room temperature greatly outweighs the enthalpy effect ($T\Delta S > \Delta H$). In such cases hydrophobic bond has been suggested as one of the more important factors involved[19]. The tendency of the non-polar groups of proteins to adhere to one another in water in an attempt to avoid aqueous environment has been referred to as hydrophobic bonding. Such hydrophobic interactions provide most of the free energy that determine the stable forms of nucleic acid and certain proteins in aqueous solutions.

An analogy to this behaviour of non-polar groups is found in the thermodynamic changes involved in the transfer of hydrocarbons from a non-polar solvent to water, as discussed by Frank and Evans[20]. The process of transfer is invariably exothermic or athermal with large negative entropy change which leads to the insolubility of the compound in water. The process may be written as

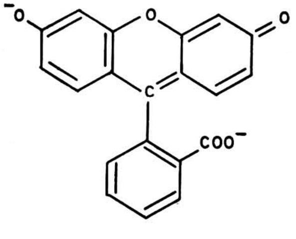
$$\text{Hydrocarbon in non-polar solvent} \rightleftharpoons \text{Hydrocarbon in water}$$

This shows that the tendency of the non-polar groups to avoid aqueous environment is governed not by enthalpy changes as would be required if hydrogen bonds were broken, but rather by the fact that by doing so, it will loose a large part of its entropy. The entropic origin of the low affinity of non-polar groups for water has long been recognized[20,21]. The positive deviation from Raoult's law observed for solutions of lower aliphatic alcohols in water suggests that the transfer of alcohol in water is accompanied by increase of free energy ($\Delta F > 0$). Yet, it is well known that addition of alcohol to a large excess of water is exothermic ($\Delta H < 0$). This can only mean that although energetically the process is favoured, the unfavourable ΔF must be due to unfavourable entropy change.

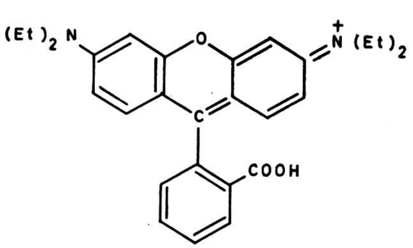
This entropy effect is also observed in molecules containing non-polar groups and have been made responsible for micelle formation by long chain molecules like soaps and detergents[22-24]. The origin of these large entropy contributions are to be found in the breaking of 'ice-bergs' in the terminology of Frank and Evans, around the non-polar molecules when they leave the aqueous environment. These 'ice-bergs' are frozen water round the non-polar groups and have a different structure than the normal ice structure. This change in the water structure has far-reaching implications in biological systems in which molecules containing non-polar groups are always found in aqueous environment. Hydrophobic interaction increases the association of water molecules. Water is almost unique in this respect since it has the highest energy per unit volume and hence the highest surface tension. Upon introduction of hydrophobic surfaces, water associates with itself in order to minimize its surface energy.

Recently, Mukerjee and coworkers[24,25] have used urea as a probe to investigate the contribution of water structure to dye association. Urea acts by breaking up the water structure thereby weakening the hydrophobic bonding, and leading to disaggregation. They have shown that metachromacy of methylene blue dye and its tendency for association are governed by the same cause, that is gain in entropy when non-polar groups leave the aqueous environment and crowd in their own non-polar regions to form hydrophobic bonds. A similar behaviour is observed for rhodamin B in the present study and, therefore, it may be concluded that the association of rhodamin B is an entropy directed phenomenon and not an enthalpy directed one. The effect of urea on the fluorescence quantum yield and the degree of association[26] also confirms the hydrophobic nature of bonding.

An indirect evidence supporting the view that dimerization in sodium fluorescein involves hydrogen bonding and that in rhodamin B hydrophobic bonding has been obtained from the nature of the absorption spectra of the dimers of the two dyes (unpublished data). This completely establishes the thermodynamic criteria of the nature of bonds involved. These conclusions are in accord with the structure (I) and (II) for fluorescein anion and rhodamin B.



Fluorescein anion



Rhodamin B

The fluorescein anion has many more sites for hydrogen bonding, whereas non-polar groups on rhodamin may induce hydrophobic bonding.

Summary

The nature of thermodynamic functions ΔF, ΔH and ΔS for the monomer-dimer equilibria in dyes, viz. fluorescein and rhodamin B, has been shown to give an indication of the type of bonding involved. It has been established that dimerization in the case of fluorescein involves hydrogen bonding, whereas in rhodamin B hydrophobic bonding is involved. The nature of the absorption spectra of the dimers of the two dyes and their structures provide additional support to the above view.

Acknowledgement

The grant of senior research fellowship to one of us (G.S.S.) by the Council of Scientific & Industrial Research, New Delhi, is gratefully acknowledged.

References

1. Walter, B., *Ann. Phys.*, **36** (1889), 502, 518.
2. Soderborg, B., *Ann. Physik*, **41** (1913), 381.
3. Levschin, V. L., *Acta phys.-chim. U.R.S.S.*, **1** (1935), 685.
4. Rabinowitch, E. & Epstein, L. F., *J. Amer. chem. Soc.*, **63** (1941), 69.
5. Vavilov, S. I., *J. Phys., Moscow*, **7** (1943), 141.
6. Levschin, V. L. & Baranova, E. G., *J. Chim. phys.*, **55** (1958), 869; *Opt. Spectrosc.*, **10** (1961), 182.
7. Levschin, V. L. & Krotova, L. V., *Opt. Spectrosc.*, **13** (1962), 457.
8. Forster, Th., *Fluorezenz organischer verbindungen* (Van den Hoek & Ruprecht, Göttingen), 1951, 245.
9. Lavorel, J., *J. phys. Chem.*, **61** (1957), 1600.
10. Brody, S. S. & Brody, M., *Nature, Lond.*, **189** (1961), 547.
11. Zanker, V., *Z. phys. Chem.*, **200** (1952), 250.
12. Zimmerman & Scheibe, *Z. Elektrochem.*, **60** (1956), 566.
13. Forster, Th. & Konig, E., *Z. Elektrochem.*, **61** (1957), 344.
14. Arvan, Kh. L. & Zaitseva, N. E., *Opt. Spectrosc.*, **10** (1961), 137.
15. Levschin, V. L. & Lonskaya, I. S., *Opt. Spectrosc.*, **11** (1961), 148.
16. Levschin, V. L. & Krotova, L. V., *Opt. Spectrosc.*, **13** (1962), 457.
17. Levschin, V. L. & Gorshkov, V. K., *Opt. Spectrosc.*, **10** (1961), 401.
18. Doty, P. & Meyers, G. E., *Disc. Faraday Soc.*, **13** (1952), 51.
19. Kauzman, W., *Advanc. Protein Chem.*, **14** (1959), 1.
20. Frank, H. S. & Evans, M. W., *J. chem. Phys.*, **13** (1945), 507.
21. Butler, J. A. V., *Trans. Faraday Soc.*, **33** (1937), 235.
22. Stainby, G. & Alexander, A. E., *Trans. Faraday Soc.*, **46** (1950), 587.
23. Bruning, W. & Holzer, A., *J. Amer. chem. Soc.*, **83** (1961), 4865.
24. Mukerjee, P. & Ghosh, A. K., *J. phys. Chem.*, **67** (1963), 193.
25. Mukerjee, P. & Ray, A., *J. phys. Chem.*, **67** (1963), 190.
26. Rohatgi, K. K. & Singhal, G. S., *J. phys. Chem.*, **67** (1963), 2844.

Use of Computers in Dissemination of Scientific Information

A two-year experimental programme sponsored by the National Science Foundation (NSF), USA, under a $ 2 million contract with the American Chemical Society provides for the establishment, by the Chemical Abstracts Service, of a computer-based registry system for chemical compounds based on chemical structure and for selected research. About 400,000 references are expected to be fed to the system each year, of which 75,000 will relate to new compounds; the system will identify any compound which has previously been processed and assign the same number to it each time it appears.

Another project sponsored by the NSF with the American Chemical Society relates to the development of an economical method of setting type in printing by computer. Special attention is being given to the problem of automatically setting into type of such unconventional items as diagrams of chemical structures, tabular material and mathematical formulae. The basic problem in computerized typesetting is the development of a simplified method of input coding to control or instruct the computer on editing. Changes in author-editor-compositor relationships that may result from increased use of computer are under study.

Dipole-Dipole Interaction & Dielectric Polarization in Polar Liquids & Solutions*

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Dipole Moment in Polar Media

ACCORDING to Onsager[1] dielectric constant of a mixture of polar components can be expressed in the form

$$\epsilon-1=4\pi\Sigma N_i\left[\frac{\mu_i^2}{9KT}\,\frac{(\epsilon_{\infty i}+2)^2.\epsilon(2\epsilon+1)}{(2\epsilon+\epsilon_{\infty i})}+a_i^3\frac{\epsilon(\epsilon_{\infty i}-1)}{(2\epsilon+\epsilon_{\infty i})}\right] \quad \ldots(1)$$

where ϵ is the dielectric constant of the mixture, N_i, μ_i and $\epsilon_{\infty i}$ are respectively the number of molecules per cubic centimetre, the dipole moment and optical dielectric constant of the ith species of the polar components, and a_i represents the radius of ith species of the molecule. The above equation can be utilized[2] for calculating the electric dipole moment of a solute dissolved in a polar solvent. Expressing N_i in g. mole/litre, and a_i^3 in terms of molar volume of the pure component and differentiating with respect to C, the gram molar concentration, one obtains for a binary solution

$$\mu_2^2=\frac{1}{A_2}\left[A_1\mu_1^2C_1^0V_2+B_1C_1^0V_2\right]+\frac{1}{A_2}\left[F\left(\frac{d\epsilon}{dC_2}\right)-B_2\right] \quad \ldots(2)$$

where

$$F=1-C_1^0\left[\frac{4\pi N_A\mu_1^2}{9000KT}\cdot\frac{(\epsilon_{\infty 1}+2)^2}{(2\epsilon+\epsilon_{\infty 1})^3}\left\{2\epsilon(\epsilon_{\infty 1}-1)+\epsilon_{\infty 1}\right\}+\frac{3V_1\epsilon_{\infty 1}}{(2\epsilon+\epsilon_{\infty 1})^2}\right] \quad \ldots(3)$$

where the subscripts 1 and 2 refer to the solvent and solute respectively, C_1^0 represents the concentration of the pure solvent, and A and B are given by the expressions

$$A_1=\frac{4\pi N_A}{9000KT}\,\frac{(\epsilon_{\infty 1}+2)^2.\epsilon(2\epsilon+1)}{(2\epsilon+\epsilon_{\infty 1})^2} \quad \ldots(4)$$

$$A_2=\frac{4\pi N_A}{9000KT}\,\frac{(\epsilon_{\infty 2}+2)^2.\epsilon(2\epsilon+1)}{(2\epsilon+\epsilon_{\infty 2})^2} \quad \ldots(5)$$

$$B_1=\frac{3V_1\epsilon(\epsilon_{\infty 1}-1)}{(2\epsilon+\epsilon_{\infty 1})} \quad \ldots(6)$$

$$B_2=\frac{3V_2\epsilon(\epsilon_{\infty 2}-1)}{(2\epsilon-\epsilon_{\infty 2})} \quad \ldots(7)$$

where V_1 and V_2 refer to the molar volume of the pure component.

The measurement of $d\epsilon/dC_2$ was carried out at a frequency of 1 Mc/s. with the help of an instrument described earlier[3,4], and the values of the dielectric constant of the solution were plotted against gram molar concentration of the solution with water[5] and pyridine[6] as solvents. The values of dipole moment obtained employing Eq. (2) are given in Table 1 along with the values of dipole moment obtained by Mizutani[7].

The value for μ for all the substances in pyridine, with the exception of sucrose, have been found by Mizutani[7] by a slightly different method of calculation. A value of 2·8 D for sucrose obtained by Landt[8] is necessarily inaccurate as no account has been taken of the interaction of the polar solvent molecules. Further, with the exception of glycine, no one has determined the μ values for these substances in water. The μ value for glycine given by Buckingham[9] has been calculated taking into account the internal field function and corresponds closely to the theoretical value. Our own value of 11·60 for glycine is 1·7 units less than 13·30 obtained by Buckingham. But this difference may be disregarded in such calculations which are necessarily approximate as no single formula gives accurate values either for the dielectric constant of a mixture of two or more polar components or electric dipole moment of one or all the components of the mixture. Buckingham's formula[9] itself gives negative values for electric dipole moment in some cases.

A close examination of the data presented in Table 1 shows that a value of 40 in pyridine for D-ribose obtained by Mizutani[7] or 39·17 in water as obtained by us cannot be correct unless

TABLE 1 — VALUES FOR ELECTRIC DIPOLE MOMENT OF SOME SUGARS AND AMINO ACIDS IN PYRIDINE AND WATER

(Dipole moment values expressed as $\mu\times10^{18}$ e.s.u.)

Substance	Pyridine		Water
	Authors	Mizutani[7]	Authors
D-Galactose	11·41	11·30	11·64
L-Arabinose	9·22	9·60	11·49
Lactose	17·69	—	17·30
Glycine*	—	—	11·60
α-Alanine	—	—	13·80
α-D-Glucose	7·99	14·10	12·05
D-Mannose	—	11·30	11·93
Rhamnose	—	—	11·30
Sucrose	12·40	(2·8)†	14·30
Maltose ($C_{12}H_{22}O_{11}$, H_2O)	10·19	—	—
D-Ribose	12·66	40·00	39·17
D-Xylose	9·19	8·10	19·80
D-Arabinose	4·02	—	—
L-Sorbose	11·39	—	—

*Value determined by Buckingham[9] in water, 13·30.
†Value determined by Landt[8].

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*Contribution to the Symposium on Chemical and Non-chemical Interactions sponsored by the University Grants Commission and held at the University of Gorakhpur, UP, February 1965.

the molecule of D-ribose forms a zwitterion. The formation of zwitterion in the case of D-ribose is not possible and hence the measurements in this case needs further investigation. Similarly, a value of 19·80 for D-xylose does not appear to be correct. Barring these few exceptions and with the exception of α-D-glucose, the values of electric dipole moment as given in Table 1 may be regarded as reasonable and the small differences observed in the values obtained in various media and by different authors may be disregarded in view of the approximations made.

Chemical and Non-chemical Interaction between Solute and Solvent

The interaction between solute and solvent molecules present here can be of two types: (i) the pure electrostatic dipole-dipole long-range interaction between the polar molecules of the solvent and the polar molecules of the solute, and (ii) the short-range interaction leading to the formation of a chemical bond (e.g. hydrogen bond). The former is already taken care of by Eq. (1) given by Onsager[10], but the short interaction or chemical interaction leading to the formation of hydrogen bonds between the solute and solvent, if present, would appear to interfere with the determination of exact values for electric dipole moment of solute molecules. This question can be settled by a study of the relaxation time of the solute molecules in the microwave region. If a number of solvent molecules are attached to the solute molecule through hydrogen bonds, the size of the solute molecules will be appreciably increased and would result in an appreciable increase of relaxation time and the diameter of the solute molecules. However, the radius of the solute molecules calculated on the basis of observed relaxation time is found to be slightly less than that expected from X-ray structure. This inevitably leads to the conclusion that the solute molecules in the present case rotate individually rather than with groups of solvent molecules attached to them.

Microwave Absorption Studies

A short introduction to the microwave study is useful although the details of measurements have been given elsewhere[6]. When a polar dielectric is placed between the parallel plates of a condenser under the influence of a low frequency field, the molecules of the dielectric rotate towards an equilibrium distribution in molecular orientation with the corresponding dielectric polarization. When the frequency of the applied field is very high, the rotational motion of the molecules is not sufficiently rapid for the attainment of equilibrium with the applied field and absorptive polarization occurs. In such cases dielectric constant is introduced as a complex quantity defined by the equation

$$\epsilon^* = \epsilon' - i\epsilon'' \qquad \ldots(8)$$

where ϵ^* is the complex dielectric constant; ϵ', the real dielectric constant; and ϵ'', the loss factor. Both ϵ' and ϵ'' are frequency dependent and may be expressed in the form

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1+\omega^2\tau^2} \qquad \ldots(9)$$

and

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1+\omega^2\tau^2} \qquad \ldots(10)$$

where ω and τ are respectively the angular frequency of the applied field and relaxation time of dielectric. At the frequency ω_m at which the loss factor becomes maximum the following equation holds good:

$$\omega_m . \tau = 1 \qquad \ldots(11)$$

Eq. (11) is usually employed for the calculation of relaxation time. The same equation is employed for calculating τ when a polar substance is dissolved in a non-polar solvent. However, there is a complete lack of exact theory for the measurement of relaxation time of one of the components when a mixture of two or more polar dielectrics is taken. Aaron and Grant[11], in the measurement of dielectric loss of glycine in water, have employed the expression

$$\lambda_S = \lambda \cdot \frac{\Delta\epsilon''}{\Delta\epsilon'} \qquad \ldots(12)$$

Here $\lambda_S = 2\pi C\tau$, where τ is the relaxation time of glycine in water, λ is the free space wavelength and C is the velocity of light, and $\Delta\epsilon'$ and $\Delta\epsilon''$ are the increments in corresponding quantities when measurements are made on pure solvent and solution.

In the present case the microwaves (λ = 3·04 cm.) were generated by a klystron oscillator which was coupled with the rectangular waveguide system containing the dielectric[6]. ϵ' and ϵ'' were measured employing the equation

$$\epsilon' = \left(\frac{\lambda}{\lambda_o}\right)^2 + \left(\frac{\lambda}{\lambda_d}\right)^2 \left[1 - \left(\frac{\alpha_d . \lambda_d}{2\pi}\right)^2\right] \qquad \ldots(13)$$

and

$$\epsilon'' = \frac{1}{\pi}\left(\frac{\lambda}{\lambda_d}\right)^2 \alpha_d . \lambda_d \qquad \ldots(14)$$

where λ_c is the cut-off wavelength; λ_d, the wavelength in dielectric; and α_d, the attenuation constant. Measurements have been confined to seven sugars dissolved in pyridine. One of the sugars, D-arabinose, does not show any perceptible absorption. The difficulty in measurement lies in the fact that the solubility of sugars is little and hence the loss increment $\Delta\epsilon''$ is small as compared to the loss of pyridine itself which is as 4·128 in the present measurement. The radius of the various sugar molecules was also calculated by employing the Debye equation

$$\tau = \frac{4\pi a^3 \eta}{KT} \qquad \ldots(15)$$

where a is the radius of the molecule and η is the viscosity of solvent. The values of the various quantities are given in Table 2.

From the data presented in Table 2 it is clear that, with the exception of L-sorbose, the values of relaxation time and the radius of molecules are in the same order as their molecular weight. As a matter of fact the values for radii are a little smaller than expected from their structural formulae.

TABLE 2 — RELAXATION TIME IN PYRIDINE AT 25°C.

Substance	Formula	$\Delta\epsilon'$	$\Delta\epsilon''$	$\frac{\Delta\epsilon''}{\Delta\epsilon'}$	$\tau \times 10^{12}$ sec.	a A.
Maltose	$C_{12}H_{22}O_{11}, H_2O$	0·6000	2·0300	3·3800	54·69	2·66
α-D-Glucose	$C_6H_{12}O_6$	0·4769	1·4220	3·1550	51·05	2·60
L-Sorbose	$C_6H_{12}O_6$	0·8200	0·5800	0·7073	11·45	1·57
L-Arabinose	$C_5H_{10}O_5$	0·2300	0·6800	2·9560	47·83	2·55
D-Ribose	$C_5H_{10}O_5$	0·5484	0·8720	1·6000	25·89	2·05
D-Xylose	$C_5H_{10}O_5$	0·9300	0·5300	0·5700	9·22	1·47

However, this definitely proves the fact that the sugar molecules rotate individually rather than with groups of pyridine molecules attached to the sugar molecules. The same conclusion has been arrived at by Aaron and Grant[11] in their measurement of dielectric loss for glycine in water. The reason for this individual rotation is that the energy required to rotate the individual molecule is slightly less than the hydrogen bond formation between solute and solvent and this is what should be expected[11] since the bond energy is the energy required to separate two molecules completely. We are, therefore, justified in assuming that the hydrogen bond formation does not interfere in the present dielectric measurements.

Summary

Electric dipole moment data for some sugars and amino acids in water and pyridine, calculated by applying Onsager's equation, have been critically examined. It has been shown that, with a few exceptions, the values of electric dipole moment thus obtained are reasonably accurate. Chemical interaction, occurring as weak hydrogen bonding between the solute and solvent molecules, does not interfere with the accurate determination of electric dipole moment of solute molecule. Dielectric loss measurements, carried out with six sugars at a frequency of 9·84 kMc/s. with pyridine as solvent, lend support to the view that in a high frequency field the sugar molecule rotates individually rather than with groups of pyridine molecules attached to it. Similar studies carried out with glycine in water lead to the same conclusion.

Acknowledgement

Two of the authors (M.L.B. and S.C.S.) are partly indebted to the Council of Scientific & Industrial Research, New Delhi, and partly to the Government of Uttar Pradesh for financing the research project whose results have been discussed in this paper.

References

1. ONSAGER, L., *J. Amer. chem. Soc.*, **58** (1936), 1486.
2. GILKERSON, W. R. & SRIVASTAVA, K. K., *J. phys. Chem.*, **64** (1960), 1485.
3. KRISHNA, B. & SRIVASTAVA, K. K., *J. chem. Phys.*, **27** (1957), 835.
4. KRISHNA, B. & SRIVASTAVA, K. K., *J. chem. Phys.*, **32** (1960), 663.
5. BALA, M. L., *Dielectric polarization in liquids and solutions*, Doctoral thesis, University of Allahabad, 1962.
6. SRIVASTAVA, S. C., *Dipole moment and molecular structure*, Doctoral thesis, University of Allahabad, 1964.
7. MIZUTANI, M., *Chem. Abstr.*, **51** (1957), 9762.
8. LANDT, E., *Naturwissenschaften*, **22** (1934), 809.
9. BUCKINGHAM, A. D., *Aust. J. Chem.*, **6** (1953), 323.
10. FROHLICH, H., *Theory of dielectrics* (Oxford University Press, London), 1949, 49.
11. AARON, M. W. & GRANT, E. H., *Trans. Faraday Soc.*, **59** (1963), 85.

Chemical Reactions Induced or Catalysed by Ultrasonic Waves: Decolourization of Dyes by Ultrasonic Waves*

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SINCE 1927 when Richards and Loomis[1] carried out a preliminary experimental survey of the chemical effects of high frequency ultrasonic waves, a large variety of chemical reactions have been found to take place under the influence of ultrasonic waves. Oxidation[2-4], reduction[5,6], decomposition[7] and hydrolysis[8] are some of the reactions that are either initiated or accelerated by ultrasonic waves. The insonation of solutions of amino acids[9], proteins and carbohydrates[10,11] leads to some interesting results, and some workers[12] have reported that even the benzene ring could be broken by ultrasonic waves. During the past few years, we have been interested in carrying out experiments on the decolourization of solutions of dyes belonging to triphenyl methane, azo, azine and phthalein groups. Some of the significant results obtained have been reviewed in this paper.

Most of the reactions taking place in liquid media under the influence of ultrasonic waves have been explained on the basis of cavitation, i.e. the formation and collapse of the cavities produced in the liquid. Various theories have been put forward to account for the activities associated with the cavitation depending upon the thermal, electrical or pressure phenomenon which are coincident with the bubble collapse. Lindstrom[13] suggested that active molecules may be formed either at the birth of the cavity, during its lifetime or during the collapse of the cavity, and also by the interaction between the surface layer of the bubble and the oscillating liquid medium. The energy released as a result of the collapse of the cavitating bubble disrupts the water molecule almost in the same way as ionizing radiations such as X-rays and γ-rays do[14]. Thus hydrogen atoms and hydroxyl radicals are produced as a result of ultrasonic decomposition of water:

$$H_2O \rightarrow H + OH$$

What happens then with the free radicals thus formed is a complicated process. The production of hydrogen peroxide, hydrogen, nitrous acid and nitric acid has been reported by several workers[3,14], and this depends evidently on the many, often very intricate, factors that influence the reactions where the chain carriers are the free radicals. The predominant reactions are probably

$$OH + OH \rightarrow H_2O + O$$
$$H + H \rightarrow H_2$$
$$H + OH \rightarrow H_2O$$
$$H + H_2O_2 \rightarrow H_2O + OH$$

When oxygen is present, the possible reaction is the formation of perhydroxyl radical.

$$H + O_2 \rightarrow HO_2$$

When nitrogen is present, NO_2^-, NO_3^- or even ammonia may be produced.

Thus the various types of chemical reactions occurring under the influence of ultrasonic waves are secondary ones caused by the active species formed in the primary reactions.

Decolourization of Dyes

The effects of exposing aqueous solutions of dyes such as congo red[15], chrysoidine[16], aniline blue[17], brilliant green[18], rhodamine B[19] and bromocresol green[20] to the action of ultrasonic waves (1 Mc/s.) for different intervals of time have been investigated, and the changes in the colorimetric readings, hydrogen ion concentration and specific conductivity of the readings have been recorded. It has been observed that the specific conductivity and hydrogen ion concentrations of the dye solutions increase with increase in exposure time. When a solution of rhodamine B ($1{\cdot}42 \times 10^{-6}M$, pH 7·1) is exposed to the action of ultrasonic waves for 30 min., the pH of the solution falls to 4·37. The specific conductivity of the solution varies from $0{\cdot}061 \times 10^{-4}$ mho to $0{\cdot}454 \times 10^{-4}$ mho. A colorimetric study of the kinetics of the decolourization process has shown that the process is unimolecular. The rate of the decolourization depends upon the initial concentration of the dye solution; in the case of rhodamine B solutions of concentrations 1·42, 1·78 and 2·13 $\times 10^{-6}M$, the time taken for complete decolourization is 30, 40 and 50 min. respectively.

When a small amount (4 per cent by volume) of ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, diacetonyl alcohol, ether, acetone, or dioxane are added to the dye solutions (e.g. bromocresol green[20] and rhodamine B[21]) before irradiation, the decolourization is almost completely inhibited. This has been attributed to the high vapour pressure, surface tension and internal pressure changes. Substances possessing high vapour pressure, low surface tension and low internal pressure have been found to suppress the breakdown of cavitation bubbles and hence sufficient energy is not available for the reaction to take place. In non-aqueous media, ultrasonic waves have not been found to initiate or accelerate chemical reactions. This has been attributed to surface tension and the fact that the values of surface tension and internal pressure for water are 4 times greater than those of most organic compounds. Higher the surface tension or internal pressure, greater will be the cavitation, and hence the energy released at the time of the collapse of the cavity will be sufficiently large leading to

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*Contribution to the Symposium on Chemical and Non-chemical Interactions sponsored by the University Grants Commission and held at the University of Gorakhpur, Gorakhpur, UP, February 1965.

various types of reactions observed in aqueous medium.

The mechanism of ultrasonic decolourization of aqueous solutions of dyes is different from that of photochemical decolourization in the sense that the primary act in ultrasonic decolourization is not the activation of the dye molecule. The decolourization reaction is a secondary reaction in the case of ultrasonic waves and is due to the free radicals produced as a result of subjecting water to the action of ultrasonic waves. Experiments carried out to find out whether decolourization is due to the formation of hydrogen peroxide have indicated that hydrogen peroxide in the concentration obtained by ultrasonic exposure of water is not effective in decolourizing the dye solutions. In relatively high concentrations, hydrogen peroxide may bring about some decolourization but the process is considerably slow. Since the amount of hydrogen peroxide produced in water exposed to ultrasonic waves is small, it is unlikely that there will be any indirect effect resulting from the formation of hydrogen peroxide. It is very likely that decolourization takes place with a more active reagent prior to the formation of hydrogen peroxide, if any.

Spectrophotometric studies of the decolourization of solutions of rhodamine B, brilliant green and bromocresol green exposed to ultrasonic waves show that the absorption maximum of the dyes does not change with the decolourization of the dye on prolonged exposure. This is because the dye molecules break up into colourless products which do not exhibit any absorption maximum. Thus the same absorption maxima obtained for the dyes on exposure for different intervals of time is due to the presence of unbroken original dye molecules.

Decolourization of dyes by ultrasonic waves has been found to be irreversible, and the colour of the dye solution is not restored either by keeping it for some time or by the addition of oxidizing or reducing agents. This shows that the dye molecules are permanently destroyed. As dyes belong to many different chemical types, it is clear that no single or simple mechanism can be put forward to explain the decolourization of dyes as a class. The decolourization of dye molecules by ultrasonic waves may involve oxidation, reduction and decomposition processes.

Summary

The results of investigations on the decolourization of aqueous solutions of some common dyes, viz. rhodamine B, bromocresol green, congo red, aniline blue, chrysoidine and brilliant green, by ultrasonic waves (1 Mc/s.) have been reviewed and the mechanism of the decolourization has been discussed. Some of the significant findings of the studies are: (i) the decolourization reaction is unimolecular; (ii) the *p*H and the specific conductivity of the dye solutions increase on exposure to ultrasonic waves; (iii) organic substances, viz. alcohols, ether, acetone and dioxane, inhibit the decolourization reaction; (iv) in non-aqueous media, ultrasonic waves have no effect on the dyes; and (v) the absorption maxima of the dyes do not change with the decolourization of the dye. It is concluded that no single or simple mechanism can be put forward to explain the decolourization reaction of dyes as they are of many different chemical types. It is suggested that decolourization of aqueous solution of dyes may involve oxidation, reduction and decomposition processes.

References

1. Richards, W. T. & Loomis, A. L., *J. Amer. chem. Soc.*, **49** (1927), 3086.
2. Virtanen, A. I. & Ellfolk, N., *Acta chem. scand.*, **4** (1950), 93.
3. Prudhomme, R. O., *J. chem. Phys.*, **54** (1957), 332.
4. Haissinsky, M. & Julien, R., *J. chem. Phys.*, **57** (1960), 664.
5. Sokolskaya, A. V. & El'piner, I. E., *Acoustics*, **3** (1957), 43, 313.
6. Mockel, P., *Chem. Tech., Berlin*, **8** (1956), 81.
7. Currel, D. L. & Zechmeister, L., *J. Amer. chem. Soc.*, **80** (1958), 205.
8. Thompson, D., Vilbrendt, F. C. & Grey, W. C., *J. acoust. Soc. Amer.*, **25** (1953), 485.
9. El'piner, I. E. & Sokolskaya, A. V., *C.R. Akad. Sci., URSS*, **123** (1958), 659.
10. El'piner, I. E. & Sokolskaya, A. V., *Biofizika*, **2** (1957), 225.
11. Topa, M. & Tokowa, K., *Roczn. Chem.*, **33** (1959), 1493.
12. Robert, R., Prudhomme, R. O. & Grabar, P., *Bull. Soc. Chim. biol.*, **37** (1955), 897.
13. Lindstrom, O., *J. chem. Phys.*, **19** (1951), 1613.
14. Lindstrom, O. & Lamm, O., *J. phys. Chem.*, **55** (1951), 1139.
15. Prakash, S. & Prakash, S., *J. acoust. Soc. Amer.*, **32** (1960), 138.
16. Prakash, S. & Prakash, S., *J. Indian chem. Soc.*, **36** (1959), 601.
17. Prakash, S. & Prakash, S., *Vijnan Parishad Anusandhan Patrika (Hindi)*, **3** (1960), 31.
18. Prakash, S. & Prakash, S., *Kolloidzschr.*, **175** (1961), 50.
19. Prakash, S. & Prakash, S., *Z. phys. Chem.*, **221** (1962), 145.
20. Prakash, S. & Prakash, S., *Kolloidzschr.*, **188** (1963), 59.
21. Prakash, S. & Prakash, S., *Nature, Lond.*, **191** (1961), 1292.

Acid Catalysed Rearrangements in the Sesquiterpenoid Series

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REARRANGEMENTS in organic compounds have indeed provided the stimuli for the creation of several new concepts and have contributed much to the general knowledge of reaction mechanism. The chemistry of natural products is a rich source of novel and interesting rearrangements which is not yet exhausted. Among the natural products, it was in terpenoids that rearrangements were earliest detected and studied. A definition of what constitutes a rearrangement has been put forward by de Mayo[1] in a practical and broad sense as follows: ' Provided a change in atomic disposition in the molecule (with concomitant bond cleavage, σ or π and reformation) has occurred, it has been accepted as a rearrangement so long as chemical interest justified it '.

The first modern attack on the theoretical problems of 1,2 rearrangements was by Meerwein and van Emster[2], who in 1920 demonstrated that cationic carbon intermediates were involved in the camphene hydrochloride-isobornyl chloride rearrangement. Although the earlier generation of chemists were baffled by the structural aspects of the rearrangements of bridged bicyclic monoterpenes (discovered by Wagner), at present, these have been reduced to order and clarity by the pioneering work of Winstein[3] and others. Thus, among the many new concepts that have been introduced in the interpretation of the mechanism of rearrangements, mention may be made of the hypothetical intermediates, which are now being called by a variety of names, such as ' mesomeric, non-classical, bridged, synartetic, complex ion ' which have replaced the classical, earlier accepted, carbonium ion intermediates.

A glance in the literature of terpenoids would reveal the abundance of several kinds of rearrangements and these may be divided into five broad types: (a) rearrangements under dehydrogenation conditions involving alkyl migration and ring formation and ring cleavage; (b) photochemical rearrangements; (c) thermal rearrangements; (d) base-induced rearrangements involving carbanion reactions and non-carbanion reactions; and (e) acid catalysed rearrangements.

This review comprises a critical survey of the acid catalysed rearrangements, observed in the field of sesquiterpenoids. Selected examples are given to emphasize a definite rearrangement in the original skeleton; cases of a mere opening of the cyclopropane ring without any further rearrangement are excluded. Since the rearrangements discussed are characteristic of a particular structure, these have been discussed under each sesquiterpene separately.

Caryophyllene

One of the outstanding characteristics of the caryophyllene molecule is its facile cyclization involving Wagner-Meerwein shifts under mild acid conditions to tricyclic compounds.

Commercial caryophyllene (I) was reported[4-6] to give on sulphuric acid treatment α-caryophyllene alcohol, clovene (II) and caryolan-1-ol (III). Recent investigations[7,8], however, revealed that highly pure caryophyllene yielded under similar conditions clovene and caryolan-1-ol only. No trace or detectable amount of α-alcohol was produced. The formation of clovene and caryolan-1-ol has been explained as shown in Chart 1.

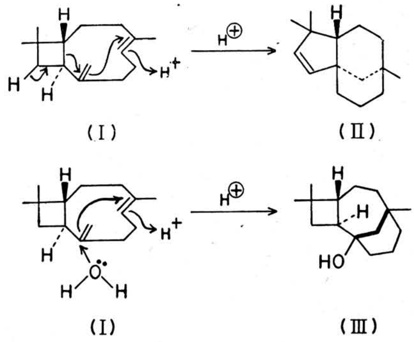


Chart 1 — Transformation of caryophyllene (I) to clovene (II) and caryolan-1-ol (III)

Dehydration of β-caryophyllene alcohol [caryolan-1-ol (III)] by acidic reagents resulted in the formation of two new tricyclic hydrocarbons[9,10]. One of these, now called pseudoclovene, has been tentatively assigned structure (IV) (Chart 2). The other hydrocarbon, isoclovene, is now represented by formula (V) on the basis of the X-ray crystallography investigations by Clunie and Robertson[11].

According to Barton *et al.*[6] the conversion of the alcohol (III) into isoclovene (V) represents an unusual problem in carbonium-ion mechanism. As a possible mechanism (Chart 3), they suggested either ring opening to a bicyclic cation followed by recyclization (b) or migrations involving 1,3 hydride shift (a). Alternative migration (c) would also lead to the same product through another cation (VIII). All these routes involve intermediates (VI) and (VIII) which are improbable and would be excluded on a strict application of Bredt's rule. But from inspection

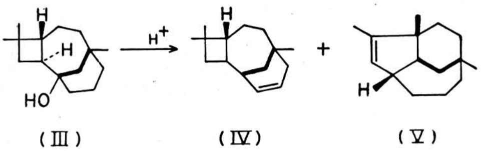


Chart 2 — Dehydration of β-caryophyllene alcohol (III) by acidic reagents and the formation of pseudoclovene (IV) and isoclovene (V)

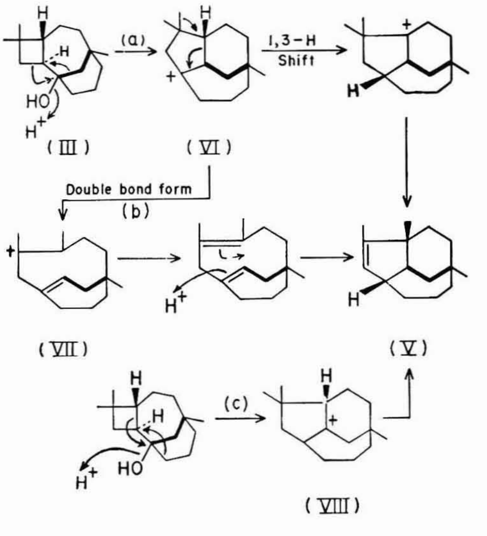


Chart 3 — Mechanism of the conversion of β-caryophyllene alcohol (III) to isoclovene (V)

of molecular models, these would seem to be not impossibly strained. Since it is known that this rule breaks down in the reaction of caryolanol, Barton *et al.* contended that this rearrangement can also be considered as to involve similar degree of unexpectedness.

It is not yet clear whether all these shifts take place in a concerted manner or follow in stepwise. According to de Mayo, this rearrangement would be an example of an ' interchange rearrangement ' of which the earliest analogous example is the conversion of santonic acid to parasantonide, reported in 1950 by Woodward and Kovach[12].

Another transformation (Chart 4) has been reported recently by Warnhoff[13] on caryophyllene oxides. An usual cyclization-rearrangement of the caryophyllene skeleton takes place when caryophyllene oxide was treated with aqueous acid[14,15]. The products comprised a C-9 epimer of the glycol which has been assigned structure (X) on spectral grounds and three carbonyl compounds, identified as aldehydes and isolated as the 2,4-dinitrophenylhydrazones. On the basis of chemical and spectral evidences, structures (XI) and (XII) have been fixed for the two carbonyl compounds (for the third carbonyl compound, no structure has so far been advanced).

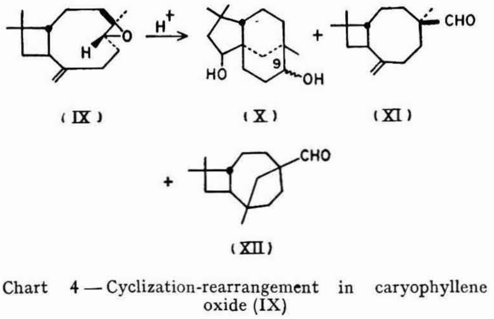


Chart 4 — Cyclization-rearrangement in caryophyllene oxide (IX)

The formation of the glycol (X) from caryophyllene oxide by mild acid catalysed hydration has been explained by Aebi *et al.*[14] as shown in Chart 5. Similarly, the conversion of iso-caryophellene oxide (XIII) to the C-9 epimer of the glycol (XIV) has also been reported.

According to Warnhoff[13] a direct rearrangement of the oxide with least structural changes results in the formation of an eight-membered carbocycle (XI). The assigned stereochemistry of the product (XI) follows from the expected inversion during oxide rearrangement.

The formation of the second aldehyde has been explained as shown in Chart 6. This mechanism received further support by the fact that the intermediate (XV), when synthesized, gave the same aldehyde (XII) in a higher yield without any trace of (XI) or the third aldehyde. The other probable structure (XVI), derivable by more complex transformations, has been ruled out on the basis of deuteration and mass spectroscopic studies.

Humulene

Acid catalysed hydration of humulene[7,16] (XVII) gave a saturated tricyclic alcohol, designated now as α-caryophyllene alcohol, and this has been recently assigned[7] structure (XVIII) on the basis of an X-ray diffraction study[8] (Chart 7).

A especially simple mechanistic explanation for the formation of α-caryophyllene alcohol (XVIII) from humulene has been given by Corey and Nozoe[17]. This transformation has been depicted as involving a prototropic rearrangement of humulene to the isomeric conjugated triene (XIX), followed by

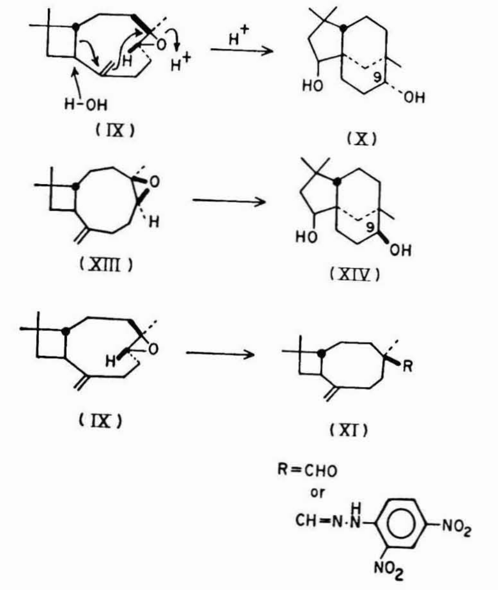


Chart 5 — Mechanism of formation of glycol (X) from caryophyllene oxide

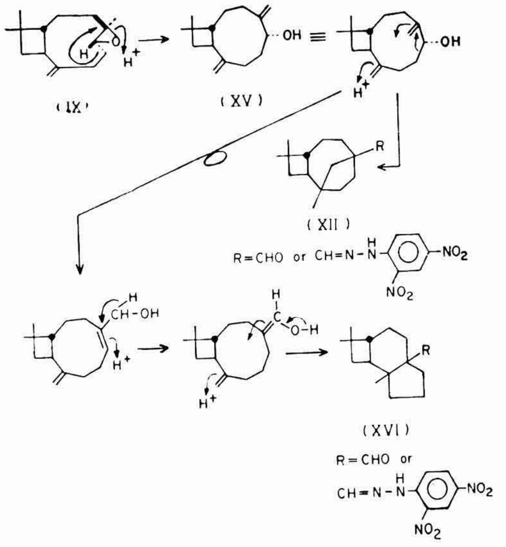


Chart 6 — Mechanism of formation of aldehyde (XII) from caryophyllene oxide

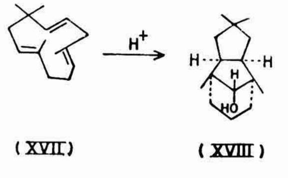


Chart 7 — Formation of α-caryophyllene alcohol (XVIII) by acid catalysed hydration of humulene (XVII)

protonation of the conjugated triene with subsequent formation of the carbonium ions (XX), (XXI) and (XXII). The final carbonium ion (XXII) would lead to the formation of α-caryophyllene alcohol as shown in Chart 8.

Longifolene

Longifolene, the tricyclic sesquiterpene with a novel ring skeleton, gave, on treatment with HCl, a solid monohydrochloride whose structure was fixed unambiguously by the X-ray crystallographic study by Moffett and Rogers[18]. This physical evidence coupled with the excellent degradative chemical study by Ourisson and coworkers[19-24] lead to the formulation of longifolene as (XXIII). From the structure of longibornyl chloride (XXIV), it is quite evident that this transformation involves a Wagner-Meerwein shift as shown in Chart 9.

However, it should be noted that while camphene (XXIX), of which longifolene may be considered as an isoprene homologue, gives with HCl isobornyl chloride (XXX), longifolene forms exclusively longibornyl chloride. So the hydrochlorination is rigorously stereospecific in the former case and stereochemically abnormal in the latter. There are other abnormalities seen in the case of longifolene, e.g. the acceleration of solvolysis rate of longibornyl chloride with respect to the bornyl and isobornyl chlorides and all these have been explained by Ourisson and coworkers as follows:

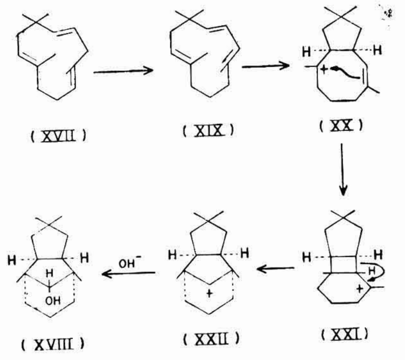


Chart 8 — Mechanism of formation of α-caryophyllene alcohol (XVIII) from humulene (XVII)

Longifolene (XXIII) can give the carbonium ion (XXV) easily and this cannot be stabilized either by the formation of the tertiary chloride (XXVII) or longi-isobornyl chloride (XXVIII) since the presence of an exo substituent with respect to the seven-membered ring at C-7 is sterically precluded on account of enormous strain which results in the proximity of exo groups. So the carbonium ion (XXV) can be stabilized only by rearrangement to (XXVI) and by the subsequent formation of longibornyl chloride (XXIV).

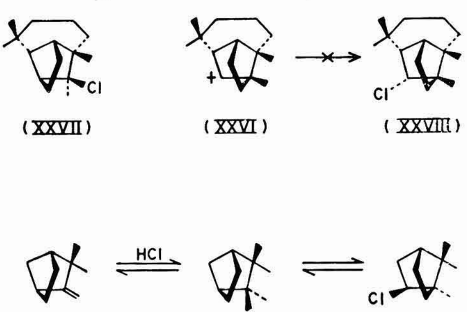


Chart 9 — Mechanism of transformation of longifolene (XXIII) and longibornyl chloride

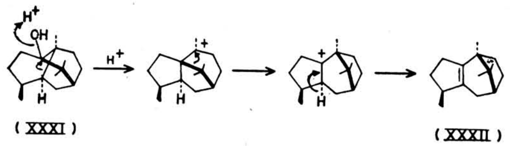


Chart 10 — Mechanism of formation of β-patchoulene (XXXII) by the dehydration using acidic catalysis of patchouli alcohol (XXXI)

Patchouli Alcohol

Patchouli alcohol has recently been assigned the structure (XXXI) on the basis of the X-ray crystallographic studies[25]. On dehydration with H_2SO_4, I_2, boric acid, formic acid or any other acidic catalysts, patchouli alcohol gave β-patchoulene which was formulated as (XXXII) on the basis of chemical evidences by Büchi and coworkers[26-28]. This transformation (Chart 10) involves a series of Wagner-Meerwein shifts, apparently facilitated by release of steric strain present in the original ring system.

A mixture of α- and ϒ-patchoulenes (XXXIII, XXXIV) was converted quantitatively to β-patchoulene (XXXII) by exposure to acids. This transformation again is accompanied by a Wagner-Meerwein rearrangement as depicted in Chart 11.

Santonin

Santonin chemistry is replete with cases of molecular rearrangements. A very interesting example is the dehydration of santonic acid. Santonic acid (XXXV), the structural elucidation of which was carried out successfully by Woodward *et al.*[29], gave on prolonged heating with acetic acid followed by pyrolysis two isomeric neutral substances, santonide and parasantonide, which have been shown to possess structures (XXXVI) and (XXXVII) respectively, by Woodward and Kovach[12]. A mechanism by which these stereoisomerides are formed has also been postulated by Woodward and Kovach (Chart 12).

A simple interchange of group attached to contiguous atoms by either of two processes (formulae XXXVIII or XXXIX as shown by arrows in Chart 12) serves to transform the santonic acid skeleton into that of parasantonic acid. But it is considered highly unlikely that such transformation could take place in such a simple fashion. So, in order to account for the change in terms of electronic processes, these authors suggested the changes symbolized by the expressions (XL) to (XLII).

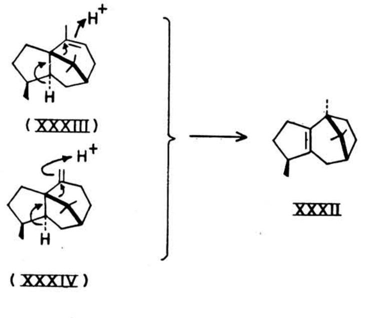


Chart 11 — Conversion of α- and γ-patchoulenes [(XXXIII) and (XXXIV) respectively] to β-patchoulene (XXXII) by exposure to acid

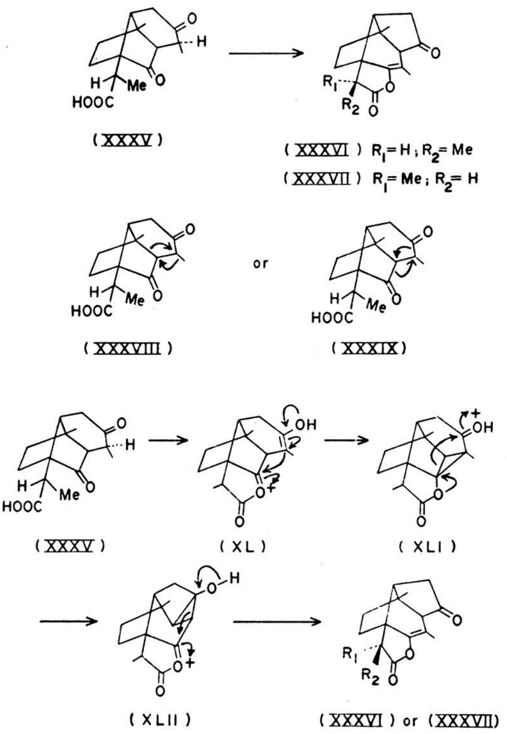


Chart 12 — Mechanism of formation of stereoisomerides santonide (XXXVI) and parasantonide (XXXVII) by the dehydration of santonic acid

The utilization of a process involving 3-membered ring intermediates may be considered unusual, but in other somewhat analogously constituted rigid systems, similar 3-membered ring compounds (e.g. tricyclene, etc.) have been isolated. Further, all these processes shown above could be concerted and hence the bonds in expressions (XLI) or (XLII) need not be considered as normal cyclopropane ring bonds.

Parasantonide (XXXVII) or the corresponding parasantonic acid gave, on treatment with either boiling hydriodic acid and phosphorus or with warm conc. H_2SO_4, a mixture of two new isomers of parasantonide, called α- and β-metasantonins. On the basis of spectral and chemical studies, α- and β-metasantonins have been assigned structures (XLIII) and (XLIV). The formation of these has been explained by Woodward and Yates[30] (Chart 13).

A series of acid catalysed changes (XXXVII→XLV →XLVI→XLIV and XLIII, arrows) having prototypes of impeccable authenticity has been postulated by Woodward and Yates and the concerted nature of

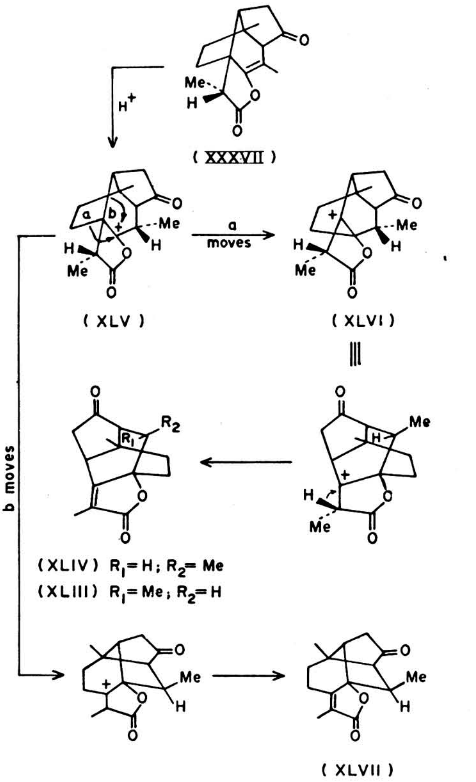
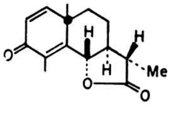


Chart 13 — Mechanism of formation of α- and β-metasantonins [(XLIII) and (XLIV) respectively] from parasantonide

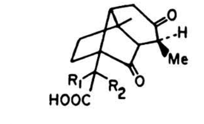
two or more of these steps has not been overlooked. Of the two probable migrations, viz. 'a' and 'b', subsequent degradative studies ruled out one of the two migrations, viz. 'b', and thus paved the way for arriving at the correct structures, viz. (XLIV) for β-metasantonin.

Santonic acid (XXXV) formed by the action of strong alkali on santonin (XLVIII) or the stereoisomeric metasantonic acid (XXXVa) gave Υ-metasantonin when treated with warm conc. H_2SO_4. Υ-Metasantonin, on the basis of spectral and chemical evidences, has been assigned structure (L) by Woodward and Yates[31]. This transformation (Chart 14) has been shown by these authors to involve a Wagner-Meerwein shift.

The tautomeric molecule (L) would be more stable than (XLIX) according to these authors and hence the former has been considered as perhaps the most likely structure for the lactone on theoretical grounds. Further spectral data confirmed the structure (L), assigned for Υ-metasantonin. The sharp contrast noticed in the behaviour of santonic acid (XXXV→L) and parasantonic acid (LI→XLIV) in the presence of warm H_2SO_4 is indeed baffling. A mechanistic explanation has been given by Woodward and Yates as shown in Chart 15.



(XLVIII)



(XXXV) $R_1 = H$; $R_2 = Me$
(XXXVa) $R_1 = Me$; $R_2 = H$

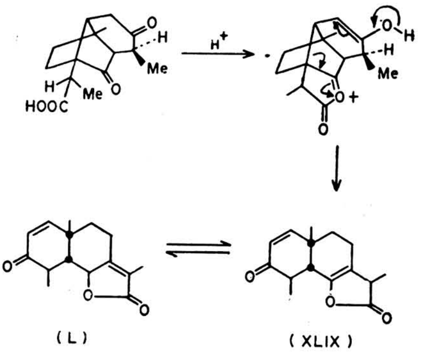


Chart 14 — Mechanism of transformation of santonic acid (XXXV) to Υ-metasantonin (L)

The relative disposition of reactive groupings in the two molecules are very similar and hence the electronic path followed in the transformations should be similar. So the divergent fates of the two substances may be attributed to some subtle stereo-electronic factors or the presence of substantially different skeletal arrangements in the acids. The relatively high degree of strain[32] in the bicyclo [2.2.1] heptane skeleton of (XXXV) favouring the observed ring cleavage in this molecule has been attributed as one of the probable reasons for this divergent behaviour. Further, the cleavage reaction shown previously must be preceded by enolization of the appropriate carbonyl system and this process may be expected to be considerably more difficult for the cyclopentanone (LI) than for the cyclohexanone[33,34] (XXXV).

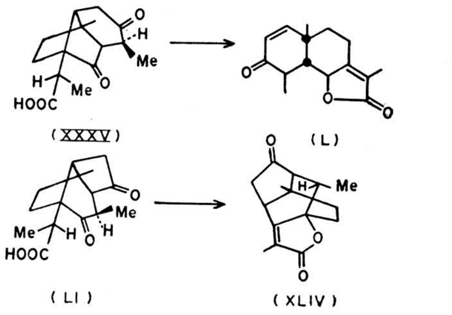


Chart 15 — Mechanism showing the difference in the behaviour of santonic acid (XXXV) and parasantonic acid (LI)

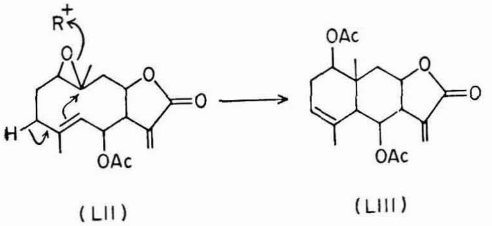


Chart 16 — Formation of cyclopyrethrosin acetate (LIII) from pyrethrosin (LII) by acetylation under acidic conditions

Pyrethrosin

Pyrethrosin, a sesquiterpene lactone, has been shown[35,36] to possess the structure (LII). The most significant single experiment on this sesquiterpene was the attempt made to acetylate the compound under acidic conditions. Treatment with acetic anhydride and *p*-toluenesulphonic acid under reflux gave in good yield a crystalline compound, cyclopyrethrosin acetate (Chart 16). On the basis of chemical and spectral evidences this derivative has been assigned structure (LIII). The mechanism of this transformation has been provided by Barton and de Mayo.

Widdrol

The preparation of widdrol from thujopsene is indeed a unique example of the acid catalysed rearrangement involving an expansion of a ring. The absolute configuration of thujopsene has now been well established as (LIV). Hydration of thujopsene[37-41] with oxalic acid furnished an alcohol, shown to be identical with widdrol (LV), the structure of which has recently been elucidated[42,43] and confirmed later by synthesis[44]. Enzell suggested that this transformation (Chart 17) involves first a *trans* diaxial addition of water to the double bond, forming the intermediate (LVI) followed by an acid catalysed opening of the cyclopropane ring.

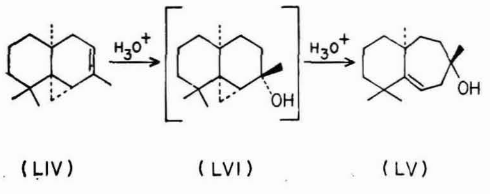


Chart 17 — Mechanism of formation of widdrol (LV) from thujopsene (LIV) suggested by Enzell[44]

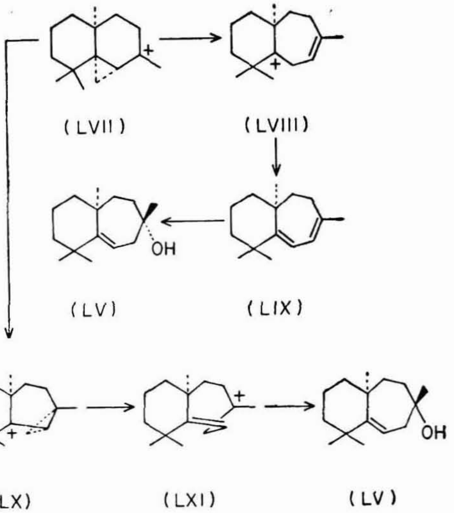


Chart 18 — Mechanism of formation of widdrol (LV) from thujopsene suggested by Dauben and Friedrich[45]

Dauben and Friedrich[45] have recently suggested another mechanism (Chart 18). The process suggested by Enzell did not find favour with these authors, since the tertiary cyclopropyl carbinol formed would rather go over to the cyclopropyl carbinyl carbonium ion (LVII) than giving widdrol by a simple opening of the cyclopropane ring. The carbonium ion (LVII) which can also be obtained by protonation of thujopsene can now rearrange in two ways, as shown in Chart 18, giving widdrol. The first pathway, which has been considered as highly unlikely, involved the formation of allylic ion (LVIII), followed by its collapse to the diene (LIX) and finally the formation of widdrol by the hydration of the diene. The other route which has been considered as more likely involves the rearrangement of the ion (LVII) to the isomeric cyclopropyl carbinyl ion (LX) first and then to homoallylic ion (LXI) and finally giving widdrol by direct hydration of the ion (LXI).

By adopting the labelling technique, these authors have succeeded to pinpoint the correct pathway, viz. that involving the isomeric cyclopropyl carbinyl ions (LVII) and (LX).

Epoxidation of widdrol[46] (LV) afforded *cis*- and *trans*-epoxy alcohols (LXIII) and (LXIV) respectively. Acid isomerization of the *trans*-epoxy alcohol gave an hydroxy ether (LXVII) as the sole product while the *cis*-epoxy alcohol yielded three diols (LXVIII, LXIX and LXX) (Chart 19).

This reaction has been extended to widdrol ethyl ether (LXII) also and here again epoxidation lead to the isolation of *cis*- and *trans*-epoxy ethyl ethers (LXIV, LXVI). Acid treatment of *trans*-epoxy ethyl ether (LXV) gave a complicated mixture from which was isolated two isomeric hydroxy ethyl ethers (LXXI, LXXII) and an unsaturated ether of unknown structure. The *cis* compound gave under similar conditions two isomeric hydroxy ethyl ethers (LXXIII, LXXIV) (Chart 20).

These studies revealed that in ethyl ethers, the migration of angular methyl group was independent of the configuration of the epoxide ring. Further, in the case of *trans*-epoxides (LXIV and LXVI), the acid catalysed isomerization could be easily visualized as occurring by a concerted mechanism. The behaviour of *cis*-epoxides (LXIII and LXV) warranted further explanation. Enzell[42] first suggested a solvated intermediate to explain the occurrence of *cis*-methyl migration. But Ito *et al.*[43]

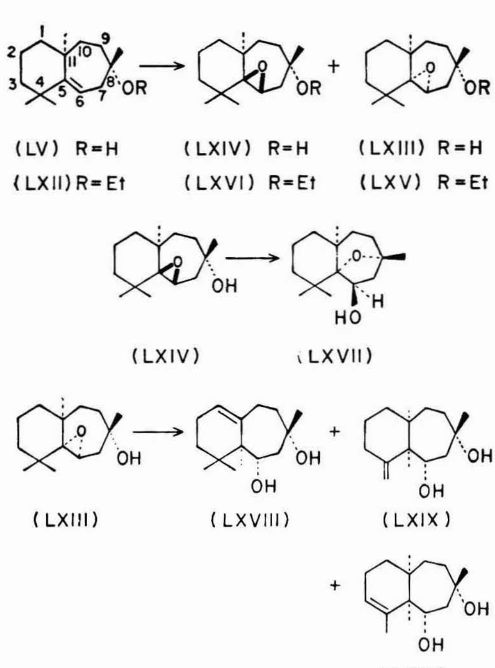


Chart 19 — Epoxidation of widdrol (LV) to *cis-* and *trans*-epoxy alcohols [(LXIII) and (LXIV) respectively] and their subsequent isomerization in acidic medium

have ruled out this possibility on the ground that such an intermediate would lead only to a triol whose formation would be highly unlikely due to triaxial interactions between the C-4 and C-11 methyls and the newly formed 6α-hydroxyl. The removal of non-bonded interactions between the C-4 and C-11 methyl groups has been considered by these authors to be the driving force for methyl migration observed in the case of *cis*-epoxides.

Finally, the non-formation of hydroxy ether in the case of *cis*-epoxide (LXIII) has been attributed to the fact that attack of the C-8 hydroxyl on the carbonium ion at C-5 does not occur here since the approach of these two centres being inhibited by the increased non-bonded interactions between the C-4 methyl and C-6 α-hydroxyl groups and the formation of intramolecular hydrogen bonding between the C-6 and C-8 hydroxyl groups.

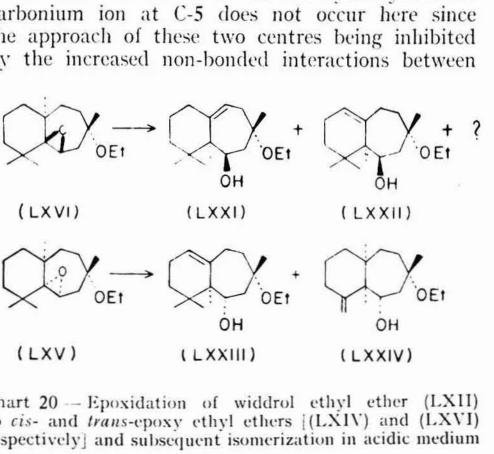


Chart 20 — Epoxidation of widdrol ethyl ether (LXII) to *cis-* and *trans*-epoxy ethyl ethers [(LXIV) and (LXVI) respectively] and subsequent isomerization in acidic medium

Summary

The acid catalysed rearrangements, observed in the field of sesquiterpenoids, have been critically reviewed and such examples have been selected which emphasize skeletal rearrangement. Cases of a mere opening of a cyclopropane ring without any further rearrangements have been excluded.

Acknowledgement

The author wishes to express his deep gratitude and sincere thanks to Dr Sukh Dev for going through the manuscript and for his advice in writing up this review.

References

1. de Mayo, P., *Molecular rearrangements*, Part II (Interscience Publishers Inc., New York), 1964, 771.
2. Meerwein, H. & van Emster, K., *Ber. dtsch. chem. Ges.*, **53** (1920), 1815; **55** (1922), 2500.
3. Winstein, S., *Proceedings of the 14th international congress of pure and applied chemistry* (Birkhauser Verlag, Basel), 1955, 137.
4. Asahina, Y. & Tsukamoto, T., *J. pharm. Soc. Japan*, (1922), 463.
5. Bell, J. & Henderson, G. G., *J. chem. Soc.*, (1930), 1971.
6. Barton, D. H. R., Bruun, T. & Lindsey, A. S., *J. chem. Soc.*, (1952), 2210.
7. Nickon, A., McGuine, F. J., Mahajan, J. R., Umezawa, B. & Narang, S. A., *J. Amer. chem. Soc.*, **86** (1964), 1437.
8. Gemmell, K. W., Parker, W., Roberts, J. S. & Sim, G. A., *J. Amer. chem. Soc.*, **86** (1964), 1438.
9. Lutz, A. W. & Reid, E. B., *J. chem. Soc.*, (1954), 2265.
10. Henderson, G. G., McCrone, R. O. O. & Robertson, J. M., *J. chem. Soc.*, (1929), 1368.
11. Clunie, J. S. & Robertson, J. M., *Proc. chem. Soc. Lond.*, (1960), 82.
12. Woodward, R. B. & Kovach, E. G., *J. Amer. chem. Soc.*, **72** (1950), 1009.
13. Warnhoff, E. W., *Canad. J. Chem.*, (1964), 1664.
14. Aebi, A., Barton, D. H. R. & Lindsey, A. S., *J. chem. Soc.*, (1953), 3124.
15. Ramage, G. R. & Whitehead, R., *J. chem. Soc.*, (1954), 4336.
16. Dev, S., *Curr. Sci.*, **20** (1951), 296.
17. Corey, E. J. & Nozoe, S., *J. Amer. chem. Soc.*, **86** (1964), 1652.
18. Moffett, R. H. & Rogers, D., *Chem. & Ind.*, (1953), 916.
19. Dupont, G., Dulou, R., Naffa, P. & Ourisson, G., *Bull. Soc. Chim. Fr.*, (1954), 1075.
20. Naffa, P. & Ourisson, G., *Chem. & Ind.*, (1953), 917.
21. Naffa, P. & Ourisson, G., *Bull. Soc. Chim. Fr.*, (1954), 1115, 1410.
22. Ourisson, P. & Ourisson, G., *Bull. Soc. Chim. Fr.*, (1954), 1415.
23. Ourisson, G., *Bull. Soc. Chim. Fr.*, (1955), 895.
24. Ourisson, G., *Proc. chem. Soc. Lond.*, (1964), 274.
25. Dobler, M., Dunitz, J. D., Gubbler, B., Weber, H. P., Büchi, G. & Padilla, O. J., *Proc. chem. Soc. Lond.*, (1963), 383.
26. Büchi, G. & Erickson, R. E., *J. Amer. chem. Soc.*, **78** (1956), 1262.
27. Büchi, G., Erickson, R. E. & Wakabayashi, N., *J. Amer. chem. Soc.*, **83** (1961), 927.
28. Büchi, G. & Maclead (Jr), W. D., *J. Amer. chem. Soc.*, **84** (1962), 3205.
29. Woodward, R. B., Brutschy, F. J. & Baer, H., *J. Amer. chem. Soc.*, **70** (1948), 4216.
30. Woodward, R. B. & Yates, P., *J. Amer. chem. Soc.*, **85** (1963), 553.

31. Woodward, R. B. & Yates, P., *J. Amer. chem. Soc.*, **85** (1963), 551.
32. Schleyer, P. von R., *J. Amer. chem. Soc.*, **80** (1958), 1700.
33. Schwarzenbach, G. & Wittwer, Ch., *Helv. chim. acta*, **30** (1947), 669.
34. Schwarzenbach, G., Zimmermann, M. & Prelog, V., *Helv. chim. acta*, **34** (1951), 1954.
35. Barton, D. H. R. & de Mayo, P., *J. chem. Soc.*, (1957), 150.
36. Barton, D. H. R., Bockman, O. C. & de Mayo, P., *J. chem. Soc.*, (1960), 2263.
37. Erdtman, H. & Norin, T., *Acta chem. scand.*, **13** (1959), 1124; *Chem. & Ind.*, (1960), 622.
38. Norin, T., *Acta chem. scand.*, **17** (1963), 738.
39. Kobayashi, H., Nagahama, S. & Akiyoshi, S., *Bull. chem. Soc. Japan*, **32** (1959), 202.
40. Nagahama, S., *Bull. chem. Soc. Japan*, **33** (1960), 1467.
41. Kobayashi, H., Nagahama, S. & Akiyoshi, S., *Bull. chem. Soc. Japan*, **34** (1961), 1123.
42. Enzell, C., *Acta chem. scand.*, **15** (1961), 1191; **16** (1962), 1553.
43. Ito, S., Endo, K., Takeshita, H., Nozoe, T. & Stothers, J. B., *Chem. & Ind.*, (1961), 1618.
44. Enzell, C., *Tetrahedron Lett.*, (No. 5) (1962), 185.
45. Dauben, W. G. & Friedrich, L. E., *Tetrahedron Lett.*, (No. 38) (1964), 2675.
46. Ito, S., Endo, K. & Nozoe, T., *Tetrahedron Lett.* (No. 46) (1964), 3375; *Chem. pharm. Bull. Japan*, **11** (1963), 132.

Pharmaceuticals & Drugs Research Committee, CSIR: Progress Report for 1964

NITYA ANAND
Central Drug Research Institute, Lucknow

THE Pharmaceuticals & Drugs Research Committee is one of the eleven research committees of the Council of Scientific & Industrial Research. It was constituted in 1940 with the main objective of 'going into the question of manufacture of important drugs in India' in order to suggest steps to overcome the shortage of some essential drugs during the war years. With this end in view the Committee sponsored research schemes for developing indigenous know-how for the manufacture of essential drugs, both synthetic and of natural origin. After the end of the war the Committee enlarged its scope to include schemes of a more fundamental nature concerned with all aspects of drug research. In addition to supporting research schemes in various universities and medical institutions, the Committee recommended setting up of a laboratory where the various disciplines involved in modern drug research could be brought together in an integrated approach to the problem of development of new drugs. On the basis of these recommendations the Central Drug Research Institute was established in 1950 at Lucknow. Later with a view to making available the more important medicinal plants the Committee, in joint consultation with the Essential Oils Research Committee, the Indian Council of Medical Research and the Indian Council of Agricultural Research, recommended the setting up of a centralized agency for the cultivation and collection of Indian medicinal plants, and this ultimately resulted in the establishment of the Central Indian Medicinal Plants Organization.

The Pharmaceuticals & Drugs Research Committee has also been sponsoring the survey and compilation of data regarding indigenous medicinal plants and the research done in the field of drugs in India. The *Indian pharmaceutical codex* and the *Glossary of Indian medicinal plants* are the outcome of schemes supported by this Committee. The preparation of two reviews, 'Clinical trials of drugs carried out in India' and 'Research done in the field of medicinal chemistry in India', has now been undertaken and these are likely to be published by the end of 1965.

The Committee has so far sanctioned about 180 research schemes on various aspects of drug research which include:

1. Pharmacological investigation of drugs
2. Chemical investigation of Indian medicinal plants
3. Synthesis of new drugs
4. Studies in antibiotics

In addition to these *ad hoc* schemes, the Committee has also been extending financial support for the creation of schools of research under the guidance of scientists of proven ability and merit. These schools encourage scientists to take up long-term problems of a fundamental nature and also help in the training of young scientists. The Pharmaceuticals & Drugs Research Committee is at present operating six such units.

In order to provide facilities for the clinical evaluation of new biologically active compounds that show promise in screening, the Committee has set up a clinical trial unit at Seth G.S. Medical College, Bombay.

With a view to utilizing the large amount of chemical work being done in the country in universities and other chemical laboratories which do not have testing facilities of their own the Committee has decided to make arrangements at certain specific centres for the systematic biological screening of all compounds synthesized or isolated from plant materials.

During the year 1964 the Pharmaceuticals & Drugs Research Committee sanctioned the continuance of 25 research schemes and three research units; in addition, two units were sanctioned in the mid-year meeting. Some of the highlights of the work done during this period are summarized below.

A new method of sequential screening for diuretics has been standardized which would help in the rapid screening of such drugs. Long-term experiments on Indian pigs have shown that at the age of 5 years they are prone to develop spontaneous atherosclerosis simulating the human disease; this may provide a suitable model for the study of human atherosclerosis and coronary heart disease. Two hypotensive drugs, phenoxybenzamin and guanethidin, have been found to possess marked antipruritic activity in atopic dermatitis. This observation may find application in the treatment of eczema and other skin infections. The chemical investigation of cobra venom has led to the isolation of a fraction which accounts for most of the lethal action of the venom. It has been observed that tetanus toxin is strongly fixed by the microsomal fraction of brain homogenates which would perhaps explain its neurotoxic action. A new dicoumarol derivative has shown strong anti-coagulant activity while a new isoquinoline shows antispasmodic action. Extracts from 20 medicinal plants and crude alkaloid fractions of another 25 plants have been screened for antibacterial and antifungal properties; two of these extracts possess antitubercular activity while three others are active against gram-negative organisms. The chemical examination of eight medicinal plants has been carried out. In a survey of natural sources for sapogenins it has been found that *Agave centella* and *A. sisalona* waste are good sources of hecogenin. The scheme entitled 'A study in chemical carcinogenesis — Synthesis of heterocyclic steroids and polycyclic hydrocarbons' has been terminated. A short résumé of the work done in this scheme is presented at the end.

Pharmacological Investigations

Screening and other studies of diuretics — A sequential analysis method based on the effect of standard diuretics in cases of oedema of various origins has been standardized for studying diuretic response in humans. An investigation of the diuretic response in rats in relation to age and body weight has shown that the best response is produced with an average body weight of 180 g. A study of the turnover of ^{24}Na in response to diuretic drugs was carried out in rats as an additional method for the screening of diuretics. A number of 5-mercapto, carboxymethylmercapto-*s*-triazines, triazoles, triazine hydrazides and urea derivatives were screened for their diuretic activity. Of these, 2-amino-4-*m*-chloroanilino-*s*-triazine was found to possess potent diuretic activity in both rats and dogs. This compound also had a saluretic action. In a limited clinical trial, however, it was found to be rather toxic (U. K. Sheth, G.S. Medical College, Bombay, 1963-64).

Effect of ganglion blocking drugs on the responses of rabbit aortic strip and tracheal chain — The action of ganglion blocking agents on the responses of various vasoactive agents on rabbit aortic strips and rabbit tracheal chain has been studied. The peripheral action of mecamylamine and chlorisondamine may be involved in the potentiation of the responses of vasoactive substances, while the action of certain other agents could not be explained in these terms. The potentiation induced by ganglion blocking agents may be the result of more than one action which still needs further investigation. During the course of this investigation, two hypotensive drugs, phenoxybenzamine and guanethidin, have been found to possess marked antipruritic activity in atopic dermatitis, and reduced significantly the severity of skin lesions in 26 patients studied in the present work (O. D. Gulati, Medical College, Baroda, 1963-64).

Role of enzymes in toxic action of venom — The purification of the lethal compounds of cobra venom and the characterization of some non-protein constituents were undertaken. It was possible to separate 8 components by electrophoresis. Two of these factors (F) and (H) were glycoproteins in nature and proved lethal to mice when injected individually. Some of the other components were by themselves ineffective but were able to enhance the lethal action of (F) and (H). The presence of a large glycoprotein fraction which had very low mobility in the electrophoresis was also observed. Further analysis of this glycoprotein fraction showed the presence of sialic acid. The lethal fraction (F) did not contain sialic acid. Purification of this fraction by treatment with acid, ammonium sulphate fractionation, and column chromatography gave a product which sedimented as a single protein in the analytical ultracentrifuge and showed a single band in the agar electrophoresis. Molecular weight determination of the above product using Sephadex gave a value of 10,000 as compared to 12,500 for cytochrome *c*. Factor (F) was found to contain galactose, fucose and hexosamine. Treatment with periodate resulted in the loss of toxicity by more than 50 per cent. Amino acid analysis showed that it contains most of the amino acids found in proteins. It was found to contain a large number of aspartic acid residues compared to glutamic acid (B. M. Braganca, Indian Cancer Research Centre, Bombay, 1963-64).

Chemical and pharmacotherapeutic studies in coumarins and related cardiovascular drugs — To study the hypothesis that the anticoagulant activity of dicoumarols is due to their ability to form a cyclic hemiacetal, a number of new dicoumarols having a phenyl ring on the bridge methylene were synthesized and screened for anticoagulant activity. It was found that compounds containing two free hydroxy groups in the 4-position were more active than those in which one of the hydroxy groups was involved in the formation of an additional ring. Among the latter group anisal dicoumarol was found to be particularly active and was, therefore, studied in greater detail. No untoward effects or tolerance to the drug were noticed.

In a search for an experimental animal in which atherosclerosis simulating the human type could be produced, a study has been made of Indian domestic pigs. It has been found that Indian pigs show spontaneous atherosclerosis after five years of age (R. B. Arora & T. R. Seshadri, All India Institute of Medical Sciences, New Delhi and Delhi University, Delhi, 1962-64).

Adrenal steroids and vitamin C in relation to diabetes — In a study of the function of the adrenal cortex in scurvy, the urinary excretion of 17-keto steroids, and sodium and potassium levels of serum have been investigated in both normal and scorbutic rhesus monkeys. Scurvy was produced by feeding scorbutogenic diet. It has been found that the adrenal cortex becomes hyperactive during scurvy.

Studies on intestinal transport of glucose *in vitro* in normal, scorbutic, insulin-treated scorbutic and ascorbic acid-supplemented scorbutic guinea-pigs by the use of everted small intestine-sac technique showed that the rate of absorption of glucose from the intestine of scorbutic guinea-pigs was double that in normal animals. Insulin treatment of the scorbutic animals did not significantly alter the glucose absorption. Ascorbic acid thus seems to play a role in the intestinal transport of glucose and this does not seem to be mediated through the associated hypoensulinism observed in scorbutic guinea-pigs (S. Banerjee, S.M.S. Medical College, Jaipur, 1963-64).

Biochemical and immunological investigation of the toxins of clostridia — With a view to studying the role of ATP in the action of the toxin of clostridia the ability by the various tissues of the susceptible species like rat as well as the non-susceptible species such as pigeon to produce ATP in the presence of tetanus toxin has been investigated. It has been found that the toxin had no action on the respiration of brain and liver mitochondria of either of the species. It, however, uncoupled the oxidative phosphorylation of rat brain mitochondria. It has no action on the swelling or shrinking of mitochondria. ATPase activity of rat brain mitochondria, measured by the increase in phosphorus content, was also not affected by tetanus toxin. A brain mitochondrial fraction was found to fix the toxin, while rat liver mitochondria was not able to do so. It is interesting that though the pigeon is resistant to tetanus toxin, its brain homogenate had the same capacity to fix the toxin as that of the rat brain mitochondrial.

Further, by studying sonicated mitochondria it was found that the intact mitochondrial structure was not necessary to fix the toxin but particulate matter was required for its fixation. Preliminary experiments with mice supported the claim that clinical tetanus could be cured by treatment of the patients in an oxygen pressure chamber. Experiments on the effects of adrenaline in mice injected with toxin showed that adrenaline *in vivo* did not protect the mice (H. I. Jhala, Haffkine Institute, Bombay, 1963-64).

Preparation and pharmacological screening of 3,4,5-*trimethoxybenzene derivatives* — Since trimethoxybenzene is a common structural feature of many centrally acting drugs such as reserpine, trimeglamide, mescaline, 3,4,5-trimethoxyamphetamine and asarone, a number of trimethoxybenzene derivatives were synthesized as simple analogues of reserpine. Of these, 3,4,5-trimethoxybenzamide and its N-acetyl derivative were found to have the most promising activity. Gross observations on intact mice and rats and avoidance behaviour studies have shown that these compounds possess CNS depressant activity, potentiate pentobarbitone hypnosis and exert a moderate effect on conditioned avoidance response of trained rats (P. C. Dandiya, S.M.S. Medical College, Jaipur, 1963-64).

Studies on Indian Medicinal Plants

Cultural and chemical investigation on brahmis and belas — Chemical investigation of *Centella asiatica* Linn. (Urb.) yielded an ester glycoside, isothankunoside, whose aglycone isothankunic acid has been found to be 3α,5α,6α,24-tetrahydroxy-urs-12-ene-28-oic acid. The conformation of the hydroxyl groups and the position C-24 for the primary hydroxyl group were arrived at through lead tetraacetate oxidation and examination of atomic models. Methyl isothankunate on oxidation and alkali treatment yielded a diketo compound. Both the diketo compound and isothankunoside show promising hypotensive and antifertility activity. *Bacopa monniera* yielded a new triterpenic saponin, monnierin. Glucose and arabinose have been shown to be the sugar components. From other chemical studies such as methylation and isolation of methylated sugars, Barry's degradation and the application of Klyne's rule, monnierin is best represented by 3-O-[α-L-arabinofuranosyl-(1→5)-O-α-L-arabinofuranosyl-(1→5)-O-α-L-arabinofuranosyl-(1→6)-]-O-β-D-glucopyranosyl-10-hydroxymethyl-20-hydroxy-16-keto-dammar-24-ene (U. P. Basu, Bengal Immunity Research Institute, Calcutta, 1963-64).

Screening of Indian medicinal plants and antibiotics — Crude extracts of some twenty Indian medicinal plants were screened for their *in vitro* antibacterial and antifungal activity. Of these *Lawsonia intermis* Linn. (leaves) and *Morinda citrifolia* Linn. (roots) were found to possess antitubercular activity while *Feronia elephantum* (fruits) and *Piper betle* Linn. (seeds) were active against *S. typhosa*, *V. cholera* and *Shigella dysentrae*.

The alkaloid fractions of twenty plants were also tested for antibacterial and antifungal activity. Only the alkaloids of *Nymphea allea* showed antitubercular activity (S. S. Bhatnagar, Caius Research Laboratory, St Xavier's College, Bombay, 1963-64).

Cardiovascular principle from certain species of Leguminosae — In view of its reported cardiotonic activity *Clitoria ternatea* Linn. was taken up for detailed chemical investigation. Cold ethanol extraction of defatted seed powder and fermentation of the extract with the enzyme present in the seeds, followed by treatment with freshly prepared lead hydroxide, gave a mixture of glycosides. Fraction crystallization of the mixture separated it into three main constituents A, B and C whose physical characteristics are described (M. P. Khare, Lucknow University, Lucknow, 1963-64).

Chemical investigation of Indian medicinal plants — From *Sarcococca pruniformis* three steroidal alkaloids were obtained, two of which have been shown to be 3-dimethylamino-20-acetylmethylamino-pregnane and 3-dimethylamino-20-acetylmethylamino-pregn-5-ene (A. R. Kidwai, Aligarh Muslim University, Aligarh, 1963-64).

Synthesis of Potential Biologically Active Compounds

Synthesis of new antispasmodics in the isoquinoline series — The work on isoquinoline derivatives has been extended to N-substituted 1,2,3,4-tetrahydroisoquinolines with a view to obtaining potent antispasmodics. Several compounds have been obtained by reacting *o*,β-bromoethyl benzylbromide with aniline, *o*-toluidine, *o*-anisidine and 4-aminoantipyrine. Similarly, 1-piperidino-3-aminoisoquinoline and 1-piperidino-3-amino-4-ethylisoquinoline have been prepared by condensing piperidine with the corresponding 1-bromoisoquinolines. All these compounds are being screened for their physiological activity. N,N-bis-(3-methyl-1-isoquinolylmethyl)-α-methyl-β-phenylethylamine, prepared earlier, has been found to possess twice the antispasmodic activity of papaverine and it also exerts a neurotropic action like that of atropine (U. P. Basu, Bengal Immunity Research Institute, Calcutta, 1963-64).

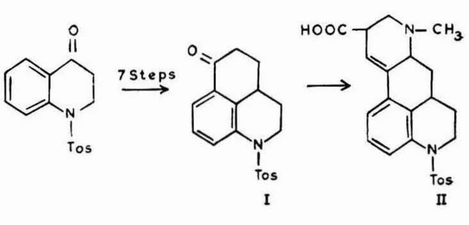
Amino acid and peptide derivatives as possible antitumour compounds — In view of the role of amino acids as the carrier moiety in alkylating agents, the synthesis of certain new amino acids and arylbiguanides and their N,N-di-β-chloroethyl derivative as potential anticancer agents has been undertaken and about 30 new N,N-bis-β-chloroethyl arylbiguanides have been synthesized. The arylbiguanides were synthesized by three different methods: (i) by condensation of N^1-aryldicyandiamide and bis-β-chloroethylamine hydrochloride; (ii) from N,N-bis-chloroethyl-dicyandiamide and the appropriate arylamine hydrochloride, and (iii) by condensation of arylguanidine and N-bis-chloroethylcyanamide. The N-carbethoxy hydrazides were synthesized from amino acid ethyl esters by condensation with N,N-bis-β-hydroxyethylhydrazine, followed by N-carbethoxylation of the amino group and treatment with thionyl chloride (A. B. Sen, Lucknow University, Lucknow, 1963-64).

Synthesis of compounds allied to pyrethrins and their biochemical mechanism of action — Some alicyclic and cyclic ketones have been prepared as starting materials for a projected synthesis of pyrethrins.

In addition, a number of 2,4-dinitroacridones have been prepared for their possible insecticidal value. These were synthesized by condensation of dinitro-*p*-chlorobenzoic acid with the appropriate amines followed by cyclization with sulphuric acid or phosphorus oxychloride (S. S. Parmar & A. K. Sen Gupta, K.G. Medical College, Lucknow, 1964).

Synthesis and studies on antidiabetic drugs — In view of the hypoglycaemic activity shown by certain sulphonyl ureas and biguanides it seemed of interest to synthesize compounds having both these chemical moieties in one structure. Eight biguanide derivatives containing a 1,3,4-thiadiazole moiety substituted at the 5-position with groups like methyl, ethyl, propyl, isopropyl, butyl, phenyl, benzyl and a 8-ethoxyquinoline ring having an ethoxy group at 8-position have, therefore, been synthesized as potential hypoglycaemic agents. These were prepared by condensation of the appropriate aminothiadiazoles with dicyandiamide (U. P. Basu, Bengal Immunity Research Institute, Calcutta, 1963-64).

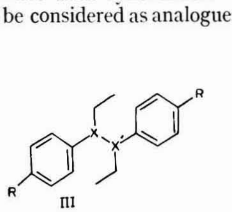
Synthesis of chemotherapeuticals related to steroids and lysergic acid — In a projected synthesis of lysergic acid analogues of the type (II), a method has been standardized for the synthesis of (I) and attempts are under way to prepare compounds of type (II).



I II

The investigation of the cyclization of 1-arylamino or arylmercapto-3-butanones using polyphosphoric acid has shown that due to intermolecular hydride transfer a mixture of the tetrahydro and the completely aromatic structure was formed. A detailed study has been made of the stereochemistry of this hydride shift. The application of this reaction to the synthesis of 6-azaequilenin and 6-azaestrone is under investigation (B. D. Tilak, Department of Chemical Technology, University of Bombay, Bombay, 1963-64).

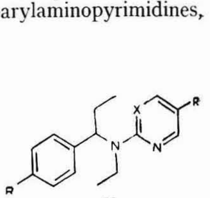
Synthesis of azasteroids — A number of aza analogues of hexesterol of the types (III), (IV) and (V) have been synthesized. These compounds can also be considered as analogues of 2-arylaminopyrimidines,



III

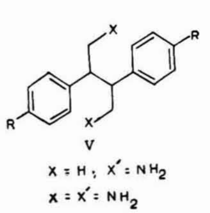
X = N; X' = CH

X = X' = N



IV

X = CH or N



V

X = H; X' = NH_2

X = X' = NH_2

some of which possess anticancer activity. These compounds have been tested and found to be inactive against lymphoid leukemia L-1210 in tissue culture and in tumours in mice (J. J. Nerukar, Ram Narain Ruia College, Bombay, 1963-64).

Preparation of steroid hormones from diosgenin — With the object of exploring the possibility of indigenous production of steroid hormones, a survey of various natural sources of steroidal saponins has been carried out. The conversion of the saponins to intermediates required for the preparation of various steroid hormones including cortisone has been studied. The yams of *D. prazeri* from Darjeeling area and of *D. deltoides* from Kashmir are particularly rich in diosgenin[1-4]. A method has been developed[5] for the preparation of diosgenin from these yams, in which the hydrolysis of the saponin and extraction of the diosgenin thus formed is carried out in one step. A study of locally available agave plants has shown that *Agave cantalla* and *A. sisalana* waste contain 0·4-0·5 and 0·2-0·25 per cent hecogenin respectively[6,7]. In the preparation of steroid hormones from these sapogenins the usual method of treatment with acetic anhydride[8] has been modified[9]. Heating with triacetin has been found to lead to the conversion of many genins to pseudogenins, which can then be easily converted to progesterone and other steroid hormones.

During these studies it was observed that Raney nickel in boiling xylene could, in addition to converting 3-hydroxy- to 3-keto steroids and hydrogenating the $5\text{-}\Delta$, also bring about the conversion of *cis* A/B ring junction to *trans*[10]. This reaction has been used for the conversion of biologically inactive etiocholon-3,17-diones into active 5α-androstan-3,17-dione[11] (R. N. Chakravarti, School of Tropical Medicine, Calcutta, 1953-64).

Heterocyclic steroids and polycyclic hydrocarbons: A study in chemical carcinogenesis — In view of the marked biological activity of many steroids the synthesis and study of various heterocyclic steroids with the hope of modifying their activity has attracted great interest and was pursued actively in the present work. The synthesis of some 6-hetero steroids has been achieved. 3-Desoxy-β-nor-6-thioequilenin and isoestradiol[12,13] were synthesized by the sequence of reactions given in Chart 1.

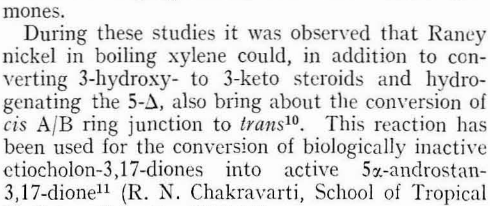


Chart 1

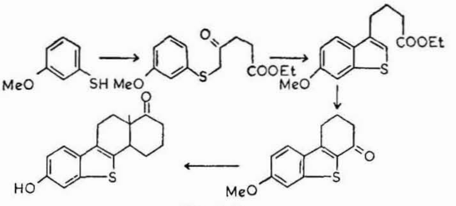


Chart 2

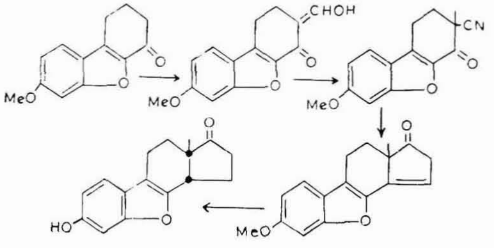


Chart 3

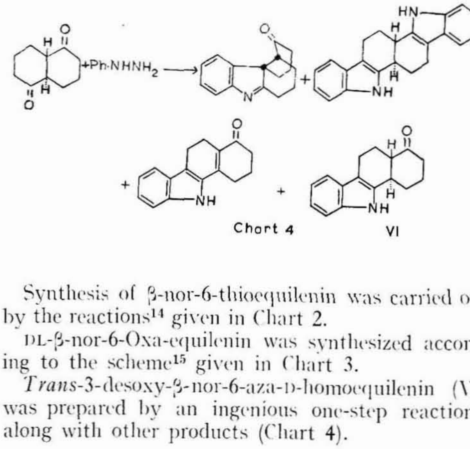


Chart 4 VI

Synthesis of β-nor-6-thioequilenin was carried out by the reactions[14] given in Chart 2.

DL-β-nor-6-Oxa-equilenin was synthesized according to the scheme[15] given in Chart 3.

Trans-3-desoxy-β-nor-6-aza-D-homoequilenin (VI) was prepared by an ingenious one-step reaction[16] along with other products (Chart 4).

References

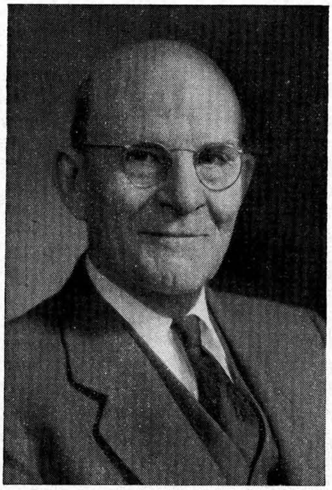
1. Barua, A. K., Chakravarti, (Mrs) D. & Chakravarti, R. N., *Indian med. Gaz.*, **88** (1953), 422.
2. Barua, A. K., Chakravarti, (Mrs) D. & Chakravarti, R. N., *J. Indian chem. Soc.*, **31** (1954), 173.
3. Barua, A. K., Chakravarti, (Mrs) D. & Chakravarti, R. N., *Bull. nat. Inst. Sci. India*, No. 4, 1956, 15.
4. Barua, A. K., Chakravarti, (Mrs) D. & Chakravarti, R. N., *J. Indian chem. Soc.*, **33** (1956), 799.
5. Chakravarti, R. N., Chakravarti, (Mrs) D. & Mitra, M. N., *J. & Proc. Inst. Chem. (India)*, **30** (1958), 106.
6. Chakravarti, R. N., Chakravarti, (Mrs) D. & Mitra, M. N., *Bull. Calcutta Sch. trop. Med. Hyg.*, **7** (1959), 5.
7. Chakravarti, R. N., Chakravarti, (Mrs) D. & Mitra, M. N., *Bull. Calcutta Sch. trop. Med. Hyg.*, **10** (1962), 3.
8. Marker, R. N., Tsukamoto, T. & Turner, D. L., *J. Amer. chem. Soc.*, **62** (1940), 2525.

9. Chakravarti, (Mrs) D., Chakravarti, R. N. & Mitra, M. N., *Nature, Lond.*, **179** (1957), 1188.
10. Chakravarti, (Mrs) D., Chakravarti, R. N. & Mitra, M. N., *Nature, Lond.*, **193** (1962), 1071.
11. Chakravarti, R. N., Mitra, M. N. & Chakravarti, (Mrs) D., *Bull. Calcutta Sch. trop. Med. Hyg.*, **12** (1964), 112.
12. Tilak, B. D., *J. Indian chem. Soc.*, **36** (1959), 509.
13. Mitra, R. B. & Tilak, B. D., *J. sci. industr. Res.*, **150** (1956), 573.
14. Bhattacharya, Mitra, R. B., Tilak, B. D. & Venkiteswaran, *Tetrahedron*, **10** (1960), 215.
15. Bhide, G. V., Tikotkar, N. L. & Tilak, B. D., *Tetrahedron*, **10** (1960), 223.
16. Bhide, G. V., Tikotkar, N. L., Pai, N. R. & Tilak, B. D., *Tetrahedron*, **4** (1958), 420.

Robert R. Williams: 1886-1965

The death on 2 October 1965 of Dr R. R. Williams, at his Summit, N.J. home, removes from the world a scientist whose achievements were only equalled by his lofty philanthropy and by his ceaseless efforts for the betterment of human existence through combat of dietary deficiency states. Born in India of missionary parents, Dr Williams' strong and abiding interest in the East was only natural. He began his career in 1908 in the Philippines after graduate training at the University of Chicago and quickly sensed the importance of studies on the nutritional basis for prevention and cure of beriberi. Though he returned to the US in 1915 and was Chemical Director of the Bell Telephone Laboratories for some 20 years from 1925, he continued unabated in his efforts at isolating the anti-beriberi factor, even under pressure of jobs in the wake of World War I. Together with his son-in-law-to-be, R. E. Waterman and other collaborators, he completed in 1936 the classic and difficult chapter in chemical research on the isolation in pure form of the life-giving substance — Vitamin B_1, thiamine — and its synthesis.

In spite of the fact that he had devoted a quarter century to this work as well as a great deal of his own funds, Dr Williams, in keeping with his philosophy, forsook the opportunity for personal wealth from his invention which, he recognized, would mean so much to the world. From out of the royalty income to his patents was born the 'Williams Waterman Fund for the Combat of Dietary Diseases' which, through more than 300 grants totalling some $ 4 million, supported a number of public health nutrition programmes, among them attacks on kwashiorkor, anaemias and other deficiency diseases in Asia, Africa and Latin America.



Dr Robert R. Williams

Dr Williams is identified with the introduction of enrichment of bread and flours and of corn meal. He spearheaded the enrichment of rice, notably by large-scale experiments in Bataan, Philippines, and elsewhere. Through the years since 1945, Dr Williams thus achieved outstanding reputation in the world of science and has been instrumental in bringing about many contributions to fundamental knowledge and public health nutrition. Not the least among these efforts are the Laboratories for Research in Nutrition at the Christian Medical College and Hospital, Vellore, now nearing completion and named for Dr Williams and his wife and life-long partner in unselfish dedication.

A great scientist and a great humanitarian, Dr Williams continued to remain active to the end and was the recipient of numerous national and international awards and distinctions. His influence will be felt around the world for a long, long time.

A. Sreenivasan

REVIEWS

RADIATION DAMAGE IN CRYSTALS by Lewis T. Chadderton (Methuen & Co. Ltd, London), 1965. Pp. xiv+202. Price 36*s*.

Although some aspects of the interaction of radiation with solids have been studied for many years, the very active interest in radiation effects in solids at the present time stems largely from the need to understand and mitigate the effects in nuclear reactor materials, and from the possibility of controlled introduction of defects by irradiation which may either be exploited in devices or else is of considerable academic interest. A large amount of information, both theoretical and experimental, has accumulated and there are some excellent books on the subject. The present monograph is an introduction to the physics of radiation damage to the exclusion of the allied field of radiation effects.

An introduction to the concept of the crystal defect, point and extended, is followed by a description of the manner of defect introduction under irradiation. The influence of the ordered lattice structure on the displacement cascade is next examined and computer simulation of radiation damage processes described. Discussions of the models for the atomic interaction potential and of range equations precede a closing chapter on some special topics and techniques. There is an appendix on the number of displaced atoms produced in bombardment with heavy energetic charged particles. A selected list of references is given at the end of each chapter.

This is a good book and should prove useful to not only the physicist but also to workers in other disciplines such as chemistry, nuclear reactor technology, metallurgy, etc. The printing and get-up are excellent, though some of the illustrations should have been drawn a little more bold.

S. R. MOHANTY

FERROMAGNETIC RELAXATION THEORY by Marshall Sparks (McGraw-Hill Book Co. Inc., New York), 1964. Pp. xii+227. Price $ 12.50

In the wake of World War II, important experimental discoveries were made in the field of magnetic resonance. The years 1945-46 gave birth to nuclear magnetic resonance, electron paramagnetic resonance and ferromagnetic resonance techniques. Each technique has been found to be of immense value in the elucidation of the structure and properties of matter involving magnetic moments (nuclear or electronic).

The interpretation of line widths and line shape of the experimentally observed resonance lines presents complex features of energy dissipation in the system. The processes responsible for energy exchange in magnetically concentrated systems (e.g. ferromagnet) were not understood until recently.

The book under review deals with the relaxation processes which have been advanced in the last eight years to explain ferromagnetic resonance (FMR) line widths. This is a book oriented towards the explanation of experimental results. The concept of magnons (quanta associated with spin waves) is introduced at an early stage. We then have an account of the properties of magnons.

In the FMR experiments, it is the uniform modes of magnons which are excited. The author discusses the various processes by which energy is transferred from the uniform mode to other modes involving collective excitations of the system, i.e. magnons and phonons. This involves the description of magnon-magnon and magnon-phonon interactions of various orders. The role of surface pits and impurities in bringing about the coupling between magnons is adequately discussed. The discussion of high radio frequency power saturation effects, which are of recent origin, will be of great value to many research workers. The book is supplemented by a fairly extensive bibliography.

There are certain aspects which have not been covered satisfactorily. The reviewer was not satisfied with the phonon-magnon interactions and some recent work in this field has not been touched. The role of magnon-conduction electrons in the line width of ferromagnetic metals and alloys has been left out. In fact, the materials selected are ferrimagnetic insulators; however, different spin wave branches for such systems ought to have been discussed.

In short, experimental research workers will find the book extremely valuable for the interpretation of ferromagnetic resonance results. Theoreticians will have to look elsewhere for satisfaction.

K. P. SINHA

CURRENT AERONAUTICAL FATIGUE PROBLEMS edited by J. Schijve, J. H. Heath-Smith & E. R. Welbourne (Pergamon Press Ltd, Oxford), 1965. Pp. viii+499. Price £ 6

The important and informative papers published in this volume were presented at the Symposium on Current Aeronautical Fatigue Problems held in Rome in April 1963. The subjects dealt with are the elevated temperature effects, the crack propagation and residual static strength, and structural fatigue testing, which are approached from the engineering point of view.

On elevated temperature effects, six papers are presented. In the first paper, B. J. Lazan discusses the importance of non-linear interactions which affect creep and strength properties under variable stress and temperature. The author emphasizes interaction studies in preference to single variable testing. In the second paper, N. F. Harpur and G. D. Sellers discuss the factors affecting fatigue life of a light alloy supersonic transport aircraft. The remaining four papers report experimental investigations of the fatigue performance of aluminium and titanium alloys in the form of small specimens and components. The testing conditions are limited to constant amplitude loading and constant temperature. R. Lachenand discusses variation in the fatigue strength of AU_2GN with temperature and frequency. Although the structural specimens are unaffected by elevated temperature up to 175°C. even after prolonged heating, the rate of crack propagation in sheet is shown to decrease with both increasing temperature and frequency. J. Heath-Smith reports in his paper the improvement of fatigue strength of L.65 notched specimens under mean tensile stress due to creep at elevated temperature. L. Locati and G. Artusio report that the fatigue strength of RR.58 compressor blades is 10 per cent lower at 155°C. C. Panseri and L. Mori report investigation of a titanium alloy at temperatures from −196° to 500°C. In this range fatigue strength reduced with increasing temperature.

Seven papers are presented on the crack propagation and residual static strength. In the first paper Jacoby reviews the techniques of fractography applicable to crack propagation problems. In the second paper, Weibull reports some results of crack propagation tests during which the stress levels were changed. Eugene develops a statistical theory of crack propagation based on a model involving accumulation of spontaneous microcracks. This is shown to agree with experimental measurements of crack propagation. The paper by Khun presents an integrated account of the effect of notches on fatigue strength and the effect of fatigue cracks on residual strength. Welbourne analyses static and cyclic crack propagation data in terms of an effective strain concentration factor for the crack. Hunt describes test programmes to investigate residual strength under biaxial stresses and the effect of crack stoppers. An analytical method for the design of biaxial test specimens is given and the redundant force method of matrix analyses is applied to residual strength problems. Finally, Capriolo describes fatigue tests on a rear fuselage structure and forging in which particular attention was paid to the development of cracking.

On structural fatigue testing four papers have been presented. In the first two papers by Melcon and McCulloch and Schijve, the equivalence between a random loading and a programmed loading sequence with respect to fatigue damage accumulation is studied. A comparison is made by performing tests with a random load sequence derived from strain records obtained in flight and tests with a programmed load sequence involving numbers of peak loads in the same proportions as the random sequence. The study of Melcon and McCulloch was made on a large number of small notched sheet specimens and the comparison was made for two values of the stress concentration factor, various types of loading (gusts, manoeuvres, ground-air-ground cycles, taxing loads and combination of them). The study reported by Schijve was conducted on a limited number of full-scale wing centre sections and for crack propagation on sheet specimens. The load sequences represented gust loads and ground-air-ground cycles. In both investigations the damaging effect of the ground-air-ground cycles was made a point of special attention. In the paper by Troughton several examples are presented, illustrating the various possibilities to introduce fail-safe characteristics in a wing structure. Since the wing was previously designed and built as a safe life structure, the author could compare both wings with respect to weight saving, production problems and costs. The paper by Herpers deals with the planning, execution and results of a full-scale test on a wing of a cargo transport aircraft.

The various aspects of aeronautical structural fatigue reported in this volume are the authoritative contributions in this field. This work will be of great use to both the industry as well as to the research workers in this field.

B. BASAVA RAJU

THE NATURE OF INDUCTION MACHINES by Philip L. Alger (Gordon & Breach Science Publishers Inc., New York), 1965. Pp. xiii+516. Price $ 25.00

The author, a frequent contributor to the Transactions of the American Institution of Electrical Engineers, needs no introduction. As the jacket says, in this book the author extends the scope and updates his earlier book, *The nature of polyphase induction machines*. There are 14 chapters and starting with the first principles of electric circuits, reactor, saturistor, the transformer and magnetic energy storage, the equivalent circuit of a motor is developed and formulae for performance calculations derived. Extensive consideration is given to the fundamental and harmonic magnetic fields produced by various types of winding. Sometimes the author writes in a loose poetical strain, which detracts the technical excellence of the work.

The various elements of motor reactance and losses are explained and extensive formulae for their calculations are given. Some analytical results are given without derivation. The clarity and correctness of expressions, sometimes, leaves much to be desired. There are good chapters on speed-torque-current relations, crawling and locking phenomena and magnetic noise. In his efforts to deal with diverse topics, the author makes some topics discontinuous and the task of the reader more difficult. One chapter is devoted to single phase induction motors and the subject is not dealt with exhaustively, especially the capacitor motor. The figure numbers are wrongly given in the note on 'The Dilemma of Single Phase Motor Theory'. Phase advancers and phase convertors have been omitted; but the use of Alnico bars in rotor slots and saturistors are treated in detail. Schrage and synchronous induction motors are very briefly mentioned. Extensive consideration is given to part-winding and split-winding starting and stepless speed control.

The book appears more like a presentation of the papers published and work carried out by the author, rather than as a text-book well adapted for the needs of any class of readers. At the end of each chapter there is a long bibliography. Some of the references quoted should be very useful for research and development workers in the particular field; but some which are more than 40 years old could have been omitted. The printing is good and the diagrams clear and informative. The book should be very useful for students of induction motor design and for research and development workers in the same field.

T. V. SREENIVASAN

ADVANCES IN HETEROCYCLIC CHEMISTRY: Vol. 3, edited by A. R. Katritzky (Academic Press Inc., New York), 1964. Pp. xiii+421. Price $ 13.00

The Katritzky series (Academic Press), *Advances in heterocyclic chemistry*, differ from the Elderfield series (Wiley) and the Weissberger series (Interscience) in several important respects. The latter two series cover various types of heterocyclic compounds in very great detail, and the Interscience volumes in particular tend to be so comprehensive in the literature survey that they are not easy to read and are more useful as literature references rather than books from which the non-specialist in a certain area may be able to make a critical assessment of synthetic methods, chemical properties and other aspects of heterocyclic types. Although the Katritzky volumes also contain some chapters on specific heterocyclic groups, usually those which are less common and more recently investigated, their special feature is the inclusion of extensive chapters on general methods and physical organic chemistry. The volume under review includes chapters on carbolines (R. A. Abramovitch and Ian D. Spenser), 1,2,3,4-thiatriazoles (K. A. Jensen and C. Pendersen) and pentazoles (Ivar Ugi). The carbolines naturally occupy about ten times the space of the thiatriazoles and pentazoles because of the large amount of work carried out on the carbolines after the discovery of serotonin and the *Rauwolfia* alkaloids. G. F. Duffin has written a most valuable chapter on quaternization, which is important in any study of heterocyclic compounds. H. H. Jaffe and H. Lloyd Jones have discussed the ways in which the Hammett equation can be applied to heterocyclic systems, giving examples of such applications and examining special problems arising in the process. The chapter which was of the greatest interest to this reviewer is on nucleophilic heteroaromatic substitution by G. Illuminati, because it includes an excellent account of the reactions of cyanuric chloride, the main intermediate for the preparation of reactive dyes. The kinetic and mechanistic aspects are fully discussed. It may be noted in passing that a considerable part of the work in this field has been carried out by Japanese chemists (K. Matsui, M. Goi and their collaborators) and access to the original papers is limited by the fact that they are all published in Japanese and one has to depend on the abstracts. Among the topics discussed by Illuminati are the course and kinetic form of the reactions, reagent and solvent effects, reactivity of the heterocyclic substrate, and inorganic heteroaromatic substitution reactions. Available kinetic data are presented in a long table as an appendix. Illuminati's treatment is from the point of view of a physical organic chemist, but it is of the utmost value for synthetic purposes.

K.V.

A GUIDE BOOK TO MECHANISM IN ORGANIC CHEMISTRY by Peter Sykes (Longmans Green & Co., London), 1965. Pp. xiii+269. Price 24*s*.

This is the second edition of the book which was first published in 1961. The great utility of the book has been well recognized by students, teachers and researchers alike during the last four years. This is amply borne out by the fact that it has already been translated into four other languages, viz. French, German, Japanese and Spanish. From personal experience, the reviewer knows that the author is an excellent teacher and it is a great satisfaction that he has produced an excellent book. The special features of the book are conciseness, clear presentation of rather a difficult and new subject, simple language, and reasonable price (Rs 19.20). Undoubtedly, this is the best available account of reaction mechanism in organic chemistry for a beginner. The reviewer, therefore, unhesitatingly recommends it strongly for B.Sc. Honours students of Indian universities. Even such teachers and researchers who had not the opportunity earlier to undergo training in reaction mechanism will also find it considerably useful.

The second edition is essentially the same as the first one; it has only 22 pages more. In the author's words, only such topics as are considered 'vital omissions' in the first edition have been added; they are nitrosation of amines, diazo coupling, ester formation and hydrolysis, decarboxylation, etc. But there is one distinct improvement over the earlier edition; Dr Sykes has taken the opportunity to clarify arguments further and to give precision to certain statements made earlier at different places.

A. C. JAIN

ORGANIC CHEMISTRY FOR GENERAL DEGREE STUDENTS: Vol. I — FUNDAMENTAL ALIPHATIC CHEMISTRY by P. W. G. Smith & A. R. Tatchell (Pergamon Press Ltd, Oxford), 1965. Pp. viii +292. Price 25*s*.

This book is the first of the three volumes on organic chemistry intended for candidates preparing for the B.Sc. general examinations of British universities and similar examinations. Besides an introductory chapter, there are thirteen chapters dealing with atomic structure and chemical bonding, paraffins, halogen derivatives of aliphatic hydrocarbons, aliphatic alcohols and ethers, structure of multiple bonds, olefins, acetylenes and diolefins, aliphatic aldehydes and ketones, aliphatic monocarboxylic acids and their derivatives, synthetic uses of Grignard reagents, β-keto esters and diethyl malonate, introduction to stereoisomerism, aliphatic nitro compounds and amines, and aliphatic sulphur-containing compounds. At the end selected questions set at various British examinations are given along with their answers.

The organization and development of the subject matter is on the usual lines but a modern approach has been adopted. The emphasis is on the chemistry of the functional groups and enough information about the general methods of preparation and properties of individual compounds is given to enable the student to understand the main points. Adequate attention is paid to processes of industrial importance. A welcome feature of the book is that theoretical aspects and reaction mechanisms are freely discussed throughout and this is in keeping with the present view that the student should be exposed to these early in his training. This not only helps him to strengthen the grasp of the subject but also convinces him that organic chemistry is not just a catalogue of facts; there is order in the behaviour of organic compounds and this can be predicted, to some extent, from their structure. The chapters on atomic structure and chemical bonding, and the structure of multiple bonds also help the student to understand the modern views on these aspects. The questions at the end will test the student's grasp of the fundamentals and also his ability to apply them to new situations.

The get-up of the book comes to the high standard of the Pergamon Press publications and it is printed in easy-to-read type. The formulae are pleasing. The book may be recommended to the first year students of the B.Sc. and B.Sc. (Hons.) classes of Indian universities.

V. V. S. MURTI

STRUCTURE AND ACTIVITY OF ENZYMES edited by T. W. Goodwin, J. I. Harris & B. S. Hartley (Academic Press Inc., New York), 1964. Pp. viii +190. Price 37*s.* 6*d.*

This timely publication contains twenty-three papers presented at a symposium organized by the Federation of European Biochemical Societies in London on 24 March 1964. The papers are arranged under four main titles: Ribonuclease, Chymotrypsin, Active Sites and Haemoglobin.

Among the more interesting papers is one by F. M. Richards on the investigations of his school on the chemical modification of ribonuclease-A and ribonuclease-S. They have concluded that a particular amino acid residue may exhibit strong interaction with other parts of the protein structure; a functional group located on this residue may or may not have altered chemical reactivity, depending entirely on the nature of the local environment and of the reagent used.

S. Moore has discussed the alkylation of the dimer of ribonuclease. Evidence is presented that the active site in each half of the dimer includes histidine-12 and histidine-119 residues from two different monomer molecules.

A. P. Mathias and his colleagues have studied the active site and mechanism of action of bovine pancreatic ribonuclease using iodoacetate to bind its two active histidine residues and cytidine 2′,3′-phosphate as substrate. Kinetic studies indicate that binding of the substrate can occur when both imidazoles of the catalytic site are in the base form. P. Venetianer and colleagues have presented the results of their investigations on the enzyme reactivation of reduced ribonuclease. They have found that dehydroascorbic acid acts as a cofactor in this reactivation and that the reactivating enzyme is not an oxido-reductase.

B. Keil and F. Sorm as also B. S. Hartley have pointed out that the amino acid sequences around two of the three histidines and around the 'active centre' serine of trypsinogen are almost identical with those in chymotrypsinogen.

B. Labouse and coworkers have shown that the activation of chymotrypsinogen to δ-chymotrypsin liberates an amino-terminal isoleucine residue whose ionization state controls both the conformation of the enzyme and its catalytic properties.

R. A. Oosterbaan and J. A. Cohen have discussed the role of serine, cystine, histidine and methionine in the active site of esterases. The unexpected high reactivity of serine is not caused by the incorporation of the serine hydroxyl into covalent ring structures.

J. I. Harris has dealt with the structure and catalytic activity of three thiol dehydrogenases, namely glyceraldehyde 3-phosphate dehydrogenase, yeast and alcohol dehydrogenases. The active forms of these enzymes are composed of an assembly of identical polypeptide chains which are held together by non-covalent bonds in such a way that each individual polypeptide chain acquires the specific three-dimensional configuration which is necessary for the manifestation of catalytic activity within the quaternary 'superstructure' of the active enzyme molecule.

E. A. Fischer has reviewed his work on the binding of vitamin B_6-coenzymes and labelling of the active site of enzymes by sodium borohydride reduction. The functional aldehyde group of pyridoxal phosphate has not been found to be necessary for it to act as a cofactor for muscle phosphorylase and the author assumes that the role of the coenzyme here is purely structural, maintaining the protein in the proper conformation for enzyme activity.

B. G. Malmström and his colleagues have studied the active site of carbonic anhydrase. They have shown that the recently discovered esterase activity of the enzyme has many properties in common with the carbon dioxide reaction and that possibly the same part of the enzyme functions as the active site in the esterase and hydrase reactions.

H. Theorell and T. Yonetaini have pointed out the possibilities opened up by the production of crystallized complexes of the enzyme with iodinated pyrazoles occupying the alcohol's active site. W. D. Stein has devised a procedure which labels the active centre of the glucose transport system of the human erythrocyte. The reversible inhibition of glucose entry by ^{14}C- and ^{3}H-labelled dinitrofluorobenzene is the basis of this study.

E. Antonini and coworkers have discussed the oxygen linked acid groups in haemoglobin. The effect of *p*H on the oxygen equilibrium (Bohr effect) is a model for *p*H effects in other proteins and enzymes and provides an important regulatory mechanism in respiration. The authors have shown that the group responsible for the normal Bohr effect in human haemoglobin is an imidazole.

Many of these papers have been published in various journals since the symposium was held and some interesting aspects on the structure and activity of enzymes like the allosteric effect and the chemical structure of haemoglobins have not been dealt with in this symposium. Nevertheless, many important papers on the subject have been compiled in one volume which will be invaluable as a reference book in any research institution interested in the mechanism of enzyme action.

T. Ramakrishnan

PUBLICATIONS RECEIVED

Photoelectronic Materials and Devices edited by Simon Larach (D. Van Nostrand Co. Inc., New York), 1965. Pp. xi+434. Price $ 12.00

Space Probes and Planetary Exploration by William Corliss (D. Van Nostrand Co. Inc., New York), 1965. Pp. ix+542. Price $ 7.75

Sillimanite by E. R. Varley (Her Majesty's Stationery Office, London), 1965. Pp. v+165. Price 15s.

Systematics of the Electronic Spectra of Conjugated Molecules — A Source Book, papers of the Chicago Group 1949-1964 by John R. Platt (John Wiley & Sons Inc., New York), 1964. Price $ 6.95 (paper); $ 10.95 (cloth)

Conformation Theory: Vol. 3 of Organic Chemistry, A Series of Monographs, by Michael Hanack (Academic Press Inc., New York), 1965. Pp. ix+382. Price $ 14.50

Food Technology the World Over: Vol. 2 — South America, Africa and the Middle East Asia edited by Martin S. Peterson & Donald K. Tressler (AVI Publishing Co. Inc., Westport, Connecticut), 1965. Pp. ix + 414. Price $ 14.00 (US); $ 15.00 (foreign)

Transition Metal Compounds: Vol. 1 — Organometallic Syntheses by R. Bruce King (Academic Press Inc., New York), 1965. Pp. xii+186. Price $ 6.50

Ulotrichales by K. R. Ramanathan (Indian Council of Agricultural Research, New Delhi), 1964. Pp. ix+188. Price Rs 21.50

Source Book on the Space Sciences by Samuel Glasstone (D. Van Nostrand Co. Inc., New York), 1965. Pp. xviii+937. Price $ 7.95

Advances in Control Systems Theory and Applications: Vol. 1, edited by C. T. Leondes (Academic Press Inc., New York), 1964. Pp. x +365. Price $ 13.00

Oriented Nuclei, Polarized Targets and Beams by J. M. Daniels (Academic Press Inc., New York), 1965. Pp. xii+278. Price $ 9.00

Introduction to Mine Surveying by W. W. Staley (Oxford & IBH Publishing Co., Calcutta), Second edition, 1965. Pp. viii+303. Price Rs 30.00

Advances in Fluorine Research and Dental Caries Prevention: Vol. 2, edited by J. L. Hardwick, J. P. Dustin & R. H. Hans (Pergamon Press Ltd, Oxford), 1964. Pp. viii+218

Engineering Physical Metallurgy by Y. Lakhtin; translated from the Russian (Gordon & Breach Science Publishers, New York), 1965. Pp. 471. Price $ 14.50

Theory of Random Functions: Vol. 1, by A. Blanc-Lapierre & R. Fort (Gordon & Breach Science Publishers, New York), 1965. Pp. xxi +432

Cells and Tissues in Culture: Methods, Biology and Physiology: Vols. 1 & 2, edited by E. N. Willmer (Academic Press Inc., New York), 1965. Vol. 1: Pp. xiv+788. Price 168s.; Vol. 2: Pp. xvi +809. Price 168s.

General Chemistry by N. Glinka; translated from the Russian (Gordon & Breach Science Publishers, New York), 1965. Pp. 694. Price $ 17.50

Organic Chemistry by B. Pavlov & A. Terentyev; translated from the Russian (Gordon & Breach Science Publishers, New York), 1965. Pp. 568. Price $ 16.00

Advances in Heterocyclic Chemistry: Vol. 4, edited by A. R. Katritzky (Academic Press Inc., New York), 1965. Pp. xiii+462. Price $ 15.00

Advances in Atomic and Molecular Physics: Vol. 1, edited by D. R. Bates & Immanuel Estermann (Academic Press Inc., New York), 1965. Pp. x+408. Price $ 13.50

Fundamentals of Dairy Chemistry edited by Byron H. Webb & Arnold H. Johnson (AVI Publishing Co. Inc., Westport, Connecticut), 1965. Pp. ix+827. Price $ 25.75 (US); $ 26.75 (foreign)

Optical Masers: Advances in Electronics and Electron Physics, Supplement 2, by George Birnbaum (Academic Press Inc., New York), 1965. Pp. xi+360. Price $ 9.50

Elementary Particle and High Energy Physics edited by M. Le'vy & Ph. Meyer (Gordon & Breach Science Publishers, New York), 1965. Pp. 362. Price $ 7.95 (paper); $ 14.50 (cloth)

Italian Physical Society Course 31, Quantum Electronics and Coherent Light edited by C. H. Townes & P. A. Miles (Academic Press Inc., New York), 1965. Pp. viii+371. Price $ 16.00

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

NOTES & NEWS

A new elementary particle

Scientists at the University of Pennsylvania have reported the experimental detection of a new elementary particle called the S^0 by using, for the first time, the neutron time of flight counting technique. The particle is reported to have a lifetime of 10^{-20} sec. About 600 S^0 particles were observed during the experiment which involved a steady run from November 1964 through February 1965 on the alternating gradient synchrotron (AGS) at the Brookhaven National Laboratory, Upton, NY.

Neutron time of flight counting technique had been used earlier in nuclear physics only and not in elementary particle physics. Thus the S^0 was the first resonance seen with a method other than the bubble chamber. The particle was detected by counters and a spark chamber.

Several properties of the particle are the same as those of a vacuum, as the S^0 has no spin or electric charge. However, the S^0 has mass and an identical mirror image. It is one of the shortest lived elementary particles known. In a bubble chamber the S^0 had been obscured previously by the presence of a nearby charged particle, the Rho meson.

The S^0 decays spontaneously into two pions. In the decay, either both particles are chargeless or one has a +ve and the other a −ve charge.

It is observed that many very short-lived particles with given spin and charge have their antiparticles. The S^0 seems to be the counterpart of the eta. All its properties except mass and mirror image are the same as those of the eta.

The decay of the eta is being studied now by the team as a few thousands of them were tracked during the S^0 experimental run [*News Release from University of Pennsylvania*, dated 24 June 1965].

Recent advances in fusion research

A concise account of the most significant advancement in the field of fusion research in recent years, viz. the theoretical and experimental investigations of Ioffe and coworkers of the Soviet Union, has been given by Albert Simon of the General Atomic Division of General Dynamics Corporation, San Diego, California, in a paper published in the *Proc. nat. Acad. Sci., Wash.*, **53** (1965), 866. Several barriers are encountered in any attempt to demonstrate the feasibility of controlled fusion reactors. One of the major problems encountered is the removal or control of the various factors that limit the plasma density, temperature or lifetime. The recent investigations of Ioffe and coworkers has tackled this problem of plasma stability from theoretical considerations coupled with experimental confirmations of the deductions made from theory. Their studies have also indicated a method of eliminating plasma instability so far as it concerns lifetime. The basis of the analysis of this problem by Ioffe and coworkers and their important deductions are as follows:

Theoretically in the absence of surface perturbation the plasma can be considered to be suspended against a gravitational force by the action of a strong magnetic field and no charge separation takes place. However, when a small perturbation produces a lump on the plasma surface a net charge separation takes place and the induced field increases the size of the lump, thus making the plasma unstable. Because the magnetic lines in a highly conducting plasma are frozen-in, this implies that the most common perturbations are those which extend uniformly along a field line and have a general shape of a flute (hence the name). In the analysis in the case of a ' magnetic bottle ', such as the mirror machine, it is not actually gravity but the centrifugal force due to the particles moving along the curved field lines bounding the plasma that has to be considered. When this field curves around the plasma, as it does in the simple mirror machine, the centrifugal force points outward and instability should result. Detailed analysis shows that the flute should move outward with a velocity proportional to the thermal velocity of the ions in the plasma.

Experimental studies made by Ioffe and coworkers have established that the flute instability is actually present in a mirror machine. Attempts were made to suppress the flute instability by reversing the curvature of the magnetic field around the plasma (in the case of magnetic mirrors by superposing a multipole field on the original mirror field). It was observed that about the point at which the field reverses at the plasma surface, there is a sharp increase in lifetime of the plasma from about 100 μsec. to about 3 msec.

Non-linear scattering of laser beams

Non-linear scattering of the radiations from a giant ruby laser by liquids or fused quartz has been observed when the laser beam was brought to a focus inside the liquid at the Scientific Laboratory, Ford Motor Co., Dearborn, Michigan. The scattered radiations (with energy about 10^{-13} of the incident energy and of nearly twice the laser frequency), which were found to occur only in the focal region of the laser beam, were due to both inelastic scattering (with frequency displacements characteristic of the material) as well as elastic scattering. Both the types of scattering, being non-linear in nature in this case, depend upon properties of material which are different from those in the case of their linear counterparts, viz. Rayleigh and Raman scattering. Thus measurements on this non-linear scattering provide an important new tool for the study of molecular structures and their interactions in liquids.

In the experiment conducted at the Michigan laboratory, a pulsed ruby laser having a plane-polarized (1 MW. peak power, 80 nsec. half width, 2 per min. repetition rate) beam was focused in water (and also in fused quartz) at *f*/10 and the scattered radiations were collected at $f/1$. Measurements on the scattered radiations were carried out at just below the threshold for dielectric breakdown or Raman laser action in the sample. The experimental observations have been found to compare well with the theoretical deductions made on lines similar to the treatment of first-order non-linear scattering by L. D. Landau and E. M. Lifshitz [*Electrodynamics of continuous media* (Addison-Wesley Publishing Co. Inc., Reading, Mass.), 1960, 377], with suitable modifications [*Phys. Rev. Lett.*, **14** (1965), 681].

A new free radical initiator

A new free radical initiator, azobisisobutanol diacetate, which may be useful for studying kinetics of polymerization at high temperature (150-200°) has been prepared in good yield. In the synthesis of azobisisobutanol diacetate, azobisisobutyronitrile is first converted to dimethyl azobisisobutyrate using dry hydrogen chloride for bringing about the conversion of nitrile groups into ester functions. The dimethyl ester is reduced with $LiAlH_4$ in ether medium to azobisisobutanol which is subsequently acetylated in methylene chloride medium using pyridine acetic anhydride to obtain the desired compound. In order to check its effectiveness as a controllable source of free radicals, polymerization of ethylene at 20,000 lb./sq. in. and 167° were carried out for 20, 40 and 60 min. using $5{\cdot}2\times10^{-5}M$/litre of the azodiacetate. The overall rates of polymerization were 7·1, 6·5 and 6·8 per cent/hr. It has been found that, kinetically, steady state polymerization is achieved and that the initiator furnishes free radicals at a constant rate [*J. org. Chem.*, **30** (1965), 1632].

Reactive hot pressing: A new ceramic process

A new ceramic process called 'reactive hot pressing' for the densification of clay materials has been reported from the Department of Metallurgy, University of British Columbia, Canada. The process does not involve high temperature sintering and gives fireclay products having a compressive strength of up to 30,000 lb./in.^{2} at 700°C. in 10-15 min. It utilizes the enhanced reactivity of a solid during a decomposition or a dissociation reaction. As such, it does not involve very high temperatures.

As typical examples, the decomposition reactions of hydroxides and carbonates have been made use of in conjunction with high pressures to obtain dense products. It has been observed that by the application of pressure (3000-15,000 lb./in.^{2}) on the reactive solid a considerable interparticle bonding can be achieved in different ceramic materials. In the case of clays and talc the following decomposition reactions have been made use of:

$$Al_2O_3.xSiO_2.yH_2O \rightarrow Al_2O_3.xSiO_2 + yH_2O$$

$$(x = 2 \text{ or } 4 \quad \text{and} \quad y = 1 \text{ or } 2)$$

$$3MgO.4SiO_2.H_2O \rightarrow 3MgO.4SiO_2 + H_2O$$

In the case of aluminium hydroxide the following reaction takes place:

$$Al_2O_3.xH_2O \rightarrow Al_2O_3 + xH_2O$$

$$\text{Brucite: } Mg(OH)_2 \rightarrow MgO + H_2O$$

A typical decarbonation reaction made use of is:

$$MgCO_3 \rightarrow MgO + CO_2$$

The reactive hot pressing is carried out in an induction heating unit. Graphite and high temperature steel dies are used which serve both as the susceptor and the hot pressing component.

The raw material is first ground in a porcelain mortar so that it can pass through a 100-mesh sieve. A hand press is used to compact the ground raw material into cylindrical form 1 cm. in diameter and 1 cm. in height approximately. The loss in weight indicates the extent of reaction taking place during hot pressing [*Nature, Lond.*, **206** (1965), 392].

Determination of the activity of viscosity-reducing enzymes

A rapid method for determining the activity of such enzymes as can be assessed by measurement of the loss in viscosity of their substrates in solution has been reported. The method has been successfully tried in the case of endo-polygalacturonase.

The initial flow rate of the mixture of substrate and buffer equilibrated to a specific temperature is noted and then a small amount (0·1 ml.) of an enzyme solution is added to the mixture. The flow times are determined at regular time intervals after the addition of the enzyme solutions, the true time of each observation being taken as the mid-point of the flow time. Plot of the decrease in viscosity against time are drawn. The initial velocity of substrate breakdown (V_0) is determined from the first portion of the plot in each case, taking care that the level of 20 per cent substrate utilization is not exceeded. Initial velocities of enzymatic action (in $c\text{P}\times10^{-2}$, decreases per min.) is then plotted against enzyme concentration, and the linear calibration curve obtained used to determine the activity present in text solutions [*Nature, Lond.*, **206** (1965), 510].

Estimation of silica in sea water

A simple and sensitive method for the analysis of soluble silica in sea water in which there is no interference from phosphates has been reported. The method consists in coverting silica in the sample to silicomolybdic acid followed by a single step extraction of the silicomolybdate in an oxygen-containing solvent, preferably ethyl acetate, and spectrophotometric determination at 3350 A. The method does not involve any filtration and 12 analyses can be completed in 1 hr.

To 30 ml. of the sample is added 1 ml. of the reagent prepared by mixing 2 parts of ammonium molybdate solution [21·5 g. $(NH_4)_6Mo_7O_{24}.4H_2O$ dissolved in 500 ml. water] with 1 part of $1{\cdot}0M$ H_2SO_4, mixed well, allowed to stand for 20 min. for silicomolybdate to form completely and then 15 ml. of 1:1 H_2SO_4 added. The mixed solution is transferred to a separating funnel containing exactly 10 ml. of ethyl acetate. The organic phase is separated and transferred to a 1 cm. spectrophotometric borosilicate glass cell and the absorbence measured at 3350 A. in a Beckman DU spectrophotometer. A calibration curve plotted by taking different quantities of a standard sodium silicofluoride solutions is used to correlate the absorbence with the quantity of silica present [*Analyt. Chem.*, **37** (1965), 764].

New method of determining melting point of powdered materials

The principle that a sudden variation of α-ray absorption is caused by melting of powdered materials has been made use of in developing a new method for determining the melting point of powdered materials, at the Ship Research Institute, Tokyo. An instrument has been designed, based on this principle, which can be used for finding melting points of powdered specimens available in small quantities and does not require any visual observation as in other methods. The instrument consists of a thin-walled differential ionization chamber and an α-ray source electroplated on a substrate which can be cooled or heated thermoelectronically. The distance between the α-ray source and the chamber is adjusted to be a little shorter than the maximum range of α-rays. The temperature is measured with a thermocouple and the ionization currents caused by absorption of α-rays are recorded against time, as the temperature of the substrate is gradually varied. When the powdered particles over the substrate begin to melt they spread into a layer whose thickness is sufficient to cut off the α-rays. Consequently, the ionization suddenly decreases, and the temperature corresponding to this phenomenon is the melting point of the powdered substance deposited over the substrate. Experiments performed with this instrument using powdered benzene and *p*-xylene as samples have shown that the method is capable of giving accurate values for the melting point [*Sci. Pap. Inst. phys. chem. Res., Tokyo*, **59** (1965), 1].

Studies on the mechanism of oxidative phosphorylation: Purification of the reduced cytochrome *c* coupling factor

Ever since Hansen and Smith [Hansen, M. & Smith, A. L., *Biochim. biophys. Acta*, **81** (1964), 214] isolated a particle from beef heart mitochondria with the same phosphorylative efficiency as intact mitochondria, attention has centred around the resolution of intact mitochondria into its component parts. The oxidative phosphorylation system of beef heart mitochondria has been further separated into two major fractions, viz. a submitochondrial particle possessing very poor phosphorylative efficiency and a soluble protein fraction which partially restores the phosphorylative efficiency of the particle [Linnane, A. L., *Biochim. biophys. Acta*, **30** (1958), 221; Pullman, M. E., Penejsky, H. & Rocker, H., *Arch. Biochem. Biophys.*, **77** (1958), 228]. Evidences have also been obtained for the existence of three distinct proteins in the soluble protein fraction, each of which can specifically restore a portion of the phosphorylative ability of the particles [Smith, A. L. & Hansen, M., *Biochem. biophys. Res. Commun.*, **8** (1962), 136; Webster, G., *Biochem. biophys. Res. Commun.*, **7** (1962), 245].

G. Webster [*J. biol. Chem.*, **240** (1965), 1365] has described the purification and some of the properties of a soluble protein from beef heart mitochondria designated as reduced cytochrome *c* coupling factor which specifically restores the phosphorylation coupled to oxidation of reduced cytochrome *c*. Purification of this coupling factor has been achieved by disrupting the mitochondria by sonic oscillation followed by centrifugation (stage I), chromatography on DEAE-cellulose (stage II), concentration by treatment with carbowax (stage III) and final chromatography on carboxymethylcellulose columns (stage IV).

The author has shown that optimal conditions for the maximal phosphorylative ability of the coupling factor are: ADP, 0·002M; Mg^{2+}, 0·01M; acetate buffer; *p*H 7·5; and temperature, 30°. The ideal condition for the preparation of submitochondrial particles is sonication for 1 min. at *p*H 7·5 in trisacetate buffer at 0°. The stability of the coupling factor progressively decreases with increasing purity of the preparation. That the reduced cytochrome *c* coupling factor is specific for the phosphorylation step coupled to oxidation of reduced cytochrome *c* has already been shown by the fact that it is completely ineffective on the phosphorylation accompanying DPNH or succinate oxidation when phenazine methosulphate is employed as electron acceptor in a system inhibited by cyanide [Webster, G., *Biochem. biophys. Res. Commun.*, **7** (1962), 245]. Using ferricyanide as electron acceptor, the author has shown that the coupling factor is ineffective on the phosphorylation coupled to oxidation of either DPNH or succinate. Similarly, the author has demonstrated that coupling factor I responsible for the phosphorylation at DPNH-flavoprotein site and coupling factor II essential for the phosphorylation at coenzyme Q-cytochrome *c* site have no effect on the phosphorylation coupled to reduced cytochrome *c* oxidation.

The purified coupling factor exhibits a single sedimentation boundary in the ultracentrifuge and has no detectable adenosine triphosphatase or adenosine triphosphate-orthophosphate exchange activity. However, it does catalyse the ADP-ATP exchange activity.— M. R. Laxman

Replication of RNA viruses

While much of our knowledge about heredity comes from the studies on DNA, very little is known regarding the mechanism of replication of RNA. A start towards evolving a mechanism of RNA replication was made by L. Shapiro and J. J. August [*J. mol. Biol.*, **11** (1965), 257] who isolated and purified viral RNA-dependent-RNA polymerase from the extracts of *Esch. coli* infected with the RNA bacteriophage f$_2$ su 11. This enzyme shows a requirement for the ribonucleoside triphosphates of adenine, uracil, guanine and cytosine; Mg^{2+} and RNA. These requirements distinguish this polymerase from the other enzymes catalysing the DNA or RNA-dependent-RNA synthesis. The viral RNA-dependent-RNA polymerase was first observed by three groups of workers [Baltimore, D. & Franklin, R. M., *J. biol. Chem.*, **238** (1965), 3395; Weissmann, C., Simon, L. & Ochoa, S., *Proc. nat. Acad. Sci., Wash.*, **49** (1962), 407; and Haruna, F., Nozu, K., Ohtaka, Y. & Spiegelman, S., *Proc. nat. Acad. Sci., Wash.*, **50** (1963), 905] following RNA virus infection. The precise role of this enzyme in the virus replicative process remains to be elucidated.

In the reaction catalysed by this enzyme, the synthesis of RNA has been shown by L. Shapiro and J. J. August [*J. mol. Biol.*, **11** (1965), 272] to be directed by the RNA added to the reaction. Based on hydrogen-bonded base pairing, a template mechanism is suggested by the dinucleotide base pair frequencies of the RNA product. The RNA product of the reaction catalysed by the polymerase using s-RNA as template is readily methylated, the reaction being catalysed by a specific s-RNA methylating enzyme. This means that the methylating enzymes recognize particular base sequences in the RNA, acting as methyl group acceptor and that the critical sequence is present in the double helical portion of the RNA product also. The RNA product of the reaction appears to have a high degree of secondary structure as indicated by its resistance to RNase and renaturation after heat denaturation.

The characteristics of the viral RNA-dependent-RNA polymerase reaction and the RNA product of the reaction favour the concept that this enzyme functions *in vivo* to catalyse the synthesis of a complementary copy of the parental single-stranded RNA to produce a double-stranded replicative form of RNA. In addition to offering a potential entry into the mechanism of RNA replication, the researches of August and Shapiro add another possible approach for designing antiviral agents. The enzyme system offers a specific assay for agents that might inhibit RNA virus through their replicative mechanism.— K. SANTANAM

Role of valyl-sRNA synthetase in enzyme repression

The synthesis of amino acyl derivatives of s-RNA by amino acyl-s-RNA synthetases has been well established. The role of these synthetases in protein synthesis has been shown by several workers with cell-free amino acid incorporation systems and also by using mutants. However, there is no report on the role of these enzymes in the regulatory system by which amino acids repress the formation of their own biosynthetic enzymes.

A naturally occurring amino acid regulates its formation either by repression or by feedback mechanism. Recently, S. Schlesinger and B. Magasanik [*J. mol. Biol.*, **9** (1964), 670] working with *Esch. coli* and *Aerobacter aerogenes* systems reported that α-methyl histidine, an analogue of histidine, blocks the activation of histidine but not its biosynthesis. During the initial stages, the growth of *Esch. coli* was inhibited by α-methyl histidine, but later growth proceeded at a slightly reduced rate. The inhibition is attributed to the blocking of histidinyl-RNA synthesis and the recovery to the increase in the histidine biosynthetic enzymes which produce more histidine to compete with the inhibitor. On this basis it must be the internal concentration of histidinyl-RNA but not the free histidine that controls the degree of repression of these enzymes in the cell. This and other reports led L. Eidlic and F. C. Neidhardt [*Proc. nat. Acad. Sci., Wash.*, **53** (1965), 539] to study whether amino acids must be activated to repress enzyme synthesis. These authors describe experiments with two strains of *Esch. coli*: (i) KB, a prototropic wild strain; and (ii) 1-9, a mutant of KB with a temperature-sensitive valyl-sRNA synthetase. The results showed that the repression of the enzymes of the valine-isoleucine pathway requires the simultaneous presence of all the four products of this pathway: valine, isoleucine, leucine and pantothenate. A limitation of anyone of the products derepresses both threonine deaminase which is involved only in isoleucine synthesis and the four enzymes which participate in the valine and isoleucine synthesis.

To determine whether valine must be activated to participate in the multivalent repression, the syntheses of the enzymes — threonine deaminase, acetolactate synthetase, α-hydroxy-β-carboxy isocaproate dehydrogenase and ornithine transcarbamylase — were studied at growth restricting temperatures in the mutant. Cultures were grown at 30° in a glucose minimal medium containing valine, isoleucine, leucine and pantothenate and samples were removed for enzyme assays. The temperature of incubation was increased to 36°, which accelerated the growth of the wild strain by 50 per cent and stopped the growth of the mutant after a short period of restricted growth. When the cultures had increased their protein content, additional samples were taken for enzyme assays. The results showed that the temperature shift caused a derepression of the two valine controlled enzymes — threonine deaminase and acetolactate synthetase — in the mutant resulting in a tenfold increase over the differential rates of synthesis in the wild strain. These two enzymes were synthesized at slightly greater rates in the mutant than in the wild strain even at 30°. The effect seems related to the fact that even at 30° the growth rate of the mutant and hence its rate of valine activation is below normal.

In another experiment the cultures were grown at 28° and the temperature raised to 36°C. at the zero time and the enzymes were assayed. The repression of the valine controlled enzyme, acetolactate synthetase, commenced in the mutant strain approximately 20 min. after the temperature shift. No change in wild strain was observed. Neither strain showed derepression of the leucine controlled α-hydroxy-β-carboxyisocaproate dehydrogenase. Chloramphenicol completely blocked the increase in the acetolactate synthetase activity, indicating that the temperature shift was not activating the preformed enzyme. Similar results were obtained when the cultures were grown on the same medium devoid of amino acids when the temperature was raised. This shows that there is no shortage of valine since valine deficiency most likely results in leucine deficiency which in turn derepresses leucine controlled enzymes.

The results presented in this paper clearly indicate that valine must be activated to repress enzyme synthesis in *Esch. coli*. It may be possible that this multivalent repression uniquely requires the participation of activating enzymes and that other amino acids need not be activated to repress their biosynthetic enzymes.— M. K. C. SRIDHAR

Conversion of shikimic acid to anthranilic acid by *Neurospora crassa*

The implication of shikimic acid as a key intermediate in the biosynthesis of aromatic amino acids has been recognized for a long time [Tatum, E. L. & Perkins, O. D., *Annu. Rev. Microbiol.*, **4** (1950), 129], although its formation from the intermediates of carbohydrate metabolism in bacteria [Srinivasan, P. R., Katagiri, M. & Sprinson, D. B., *J. biol. Chem.*, **234** (1959), 713] and *N. crassa* [Cross, S. R. & Fein, A., *Genetics, Princeton*, **45** (1960), 885] was demonstrated much later. Recent studies [Fenster, J. A., *Biochem. J.*, **85** (1962), 388; Srinivasan, P. R. & Rivera (Jr), A., *Biochemistry*, **2** (1963), 1063; Levin, J. G. & Sprinson, D. B., *J. biol. Chem.*, **239** (1964), 1142; Gibson, M. I. & Gibson, F., *Biochem. J.*, **90** (1964), 248] with bacterial mutants have indicated a sequence of reactions starting from shikimic acid towards the formation of various aromatic amino acids.

It is likely, therefore, that shikimic acid is converted to chorismic acid by three enzymic steps, which thus serves as the key intermediate in the biosynthesis of aromatic amino acids.

Genetic and nutritional studies with *N. crassa* [Ahmad, M. & Catcheside, D. G., *Heredity, Lond.*, **15** (1960), 55] indicate that the first enzyme specifically catalyses the formation of anthranilic acid from shikimic acid. J. A. De Moss [*J. biol. Chem.*, **240** (1965), 123] has investigated in detail the formation of anthranilic acid from shikimic acid in *N. crassa* extracts. The results obtained show that the extracts of *N. crassa* catalyse the conversion of shikimic acid to anthranilic acid only after the removal of an inhibitor present in the crude extracts by partial purification. This inhibitor seems to be a macromolecule, since it is not separable from the enzyme protein when passed through a column of Sephadex G-25. Moreover, it is precipitable in a narrow range during ammonium sulphate fractionation.

The enzyme reaction exhibits an absolute requirement for Mg^{2+}, ATP, phosphoenol pyruvate (PEP), TPNH and L-glutamine. Unlike the bacterial extracts which require DPNH, this enzyme shows specificity for TPNH. The very requirement for reduced pyridine nucleotide evokes considerable interest, since at least the bacterial system does not seem to involve a net transfer of electrons.

If L-glutamine is omitted from the reaction mixture, an ether-extractable intermediate accumulates which when further incubated with Mg^{2+}, L-glutamine and *N. crassa* extract forms anthranilic acid. The new intermediate is identical to chorismic acid on the basis of several of its properties. Thus, this system resembles the bacterial system in the sequence of reactions towards the formation of anthranilic acid. The conversion of chorismic acid to anthranilic acid would presumably be the first step in tryptophan biosynthesis. Although this reaction seems to be a very complex one, the enzyme activity has not been resolved into more than one component even after 83-fold purification of the enzyme. Very low concentrations of L-tryptophan completely inhibit the enzyme activity which can be reversed by chorismic acid. On the basis of such a feedback inhibition it is suggested that the initial step in tryptophan biosynthesis involves the conversion of chorismic acid to anthranilic acid. Moreover, this enzyme activity is absent from all tryp-2 mutants of *N. crassa* which are known to be blocked prior to anthranilic acid in the tryptophan pathway. It is, therefore, proposed that a single enzyme anthranilate synthetase catalyses the conversion of chorismic acid to anthranilic acid.— M. R. LAXMAN

Enzymatic hydroxylation of proline

The available evidence regarding the sequence of steps in the hydroxylation of proline indicates that proline is first incorporated into the polypeptide chain and then the hydroxylation of the proline takes place [Peterkofsky, B. & Udenfriend, S., *J. biol. Chem.*, **238** (1963), 3966]. On the contrary, evidence is also available for the presence of s-RNA-hydroxyproline in the soluble fraction of the chick embryo and carageenan granuloma system [Manner, G. & Gould, B. S., *Biochim. biophys. Acta*, **72** (1963), 243; Coronado, A., Mardones, E. & Allende, J. E., *Biochem. biophys. Res. Commun.*, **13** (1963), 75; Jackson, D. S., Watkins, D. & Winkler, A., *Biochim. biophys. Acta*, **87** (1964), 87]. The investigations of M. Univetzky, J. M. Frei and E. Meilman [*Arch. Biochem. Biophys.*, **109** (1965), 480] favour the view that s-RNA-hydroxyproline is an intermediate in microsomal collagen synthesis. However, attempts by Peterkofsky and Udenfriend to demonstrate the formation of s-RNA-hydroxyproline from proline have been futile. A more recent evidence against the involvement of an intermediary s-RNA-hydroxyproline and evidence for a peptide precursor of hydroxyproline in the synthesis of collagen has been obtained by L. N. Lukens [*J. biol. Chem.*, **240** (1965), 1661]. Recently, B. Peterkofsky and S. Udenfriend [*Proc. nat. Acad. Sci., Wash.*, **53** (1965), 335] have been able to isolate microsomal-bound polypeptide, labelled with radioactive proline which could be used as a substrate for the hydroxylation reactions.

Earlier work of these workers points out that the incorporation of proline-^{14}C into the protein-bound proline starts immediately. But this label appeared in collagen only after a 30 min. lag period. Subsequently, they could successfully employ the prelabelled microsomes as substrate for the enzymatic hydroxylation reaction in chick embryo. On assaying for protein-bound hydroxyproline-^{14}C, the proline-^{14}C has been found to be converted to hydroxyproline-^{14}C.

They suggested that two non-enzymatic factors are involved (one in the boiled supernatant and the other in the soluble protein fraction obtained by ammonium sulphate fractionation) in the reaction and also that the microsomal fraction contains the enzyme.

Puromycin, at concentrations inhibitory to protein synthesis, does not inhibit hydroxylation. It was shown earlier that the incorporation of proline-^{14}C into protein-bound proline and hydroxyproline-^{14}C is completely inhibited by puromycin. Further, anaerobiosis during the lag phase (and not after the lag phase) does not inhibit the incorporation of proline-^{14}C into collagen. These facts suggest that proline is bound in peptide linkage before hydroxylation.

The active non-enzymatic factor in the boiled supernatant appears to be ascorbic acid since ascorbic acid could be replaced for the factor. The factor contained ascorbic acid. Other hydrogen donors were also capable of replacing the boiled supernatant fraction but not as effectively as ascorbic acid. It is possible that ascorbic acid could also function indirectly by producing TPNH which is active as hydrogen donor in this system. The other factor is possibly a protein-bound metal, since ferrous ions are known to function in hydroxylases.

Thus, the labelled microsomal-bound polypeptide can be converted to microsomal-bound collagen by a system containing hydrogen donors plus another non-enzymatic factor in the soluble protein fraction and microsomes. The proline hydroxylase appears to be in microsomal fraction as evidenced by the heat lability of the microsomes with respect to the hydroxylase activity.— L. V. S. SASTRY

A new tool for study of metabolism of hormones: The radioimmunoassay

The metabolic fate of protein hormones *in vivo* has long been a subject of clinical importance and biochemical interest; yet quantitative studies on their turnover rate, excretion pattern and the tissue levels had not made much progress till the late fifties, mainly because of the difficulty in measuring the low hormone level in tissues or biological fluids, of the order of millimicrograms. With the availability of highly purified protein hormones, immunochemical techniques such as quantitative precipitin haemagglutination inhibition and complement fixation tests have come to be recognized as standard techniques. For example, as little as 2·5 μg. of growth hormone has been detected by direct precipitation with its antiserum [Li, C. H., Moudgal, N. R. & Papkoff, H., *J. biol. Chem.*, **235** (1960), 1038]. C. H. Read and G. T. Bryan [*Rec. Progr. Horm. Res.*, **16** (1960), 187] have detected 2-20 μg. of growth hormone by haemagglutination inhibition test.

Radioimmunoassay is a combination of the highly sensitive isotope methodology with the extremely specific immunochemical techniques. ^{131}I is the most extensively used isotope at present. Thus, the sensitivity of the precipitin reaction between human growth hormone and its specific antiserum has been increased as to measure 1 μg. of growth hormone by the use of radioiodinated antiserum [Greenspan, F. S., Caffel, J. C., Lew, W. & Peng, C. T., *Clin. Res.*, **9** (1961), 99].

At the low concentrations of reactants employed in the radioimmunoassay, no insoluble antigen-antibody complex is formed. Hence, various techniques have been employed to separate the hormone antigen-antibody complex from the unreacted hormone.

The soluble complexes can be immunoprecipitated by the addition of anti-γ-globulin serum. Thus J. S. Skom and D. W. Talmage [*J. clin. Invest.*, **37** (1958), 783] have precipitated insulin ^{131}I bound to human γ-globulin serum during their study of sera from diabetic patients containing antibodies that react with heterologous insulin. In their radioimmunoassay developed for human chorionic gonadotropin (HCG), C. E. Wilde, A. Hillary Orr and K. D. Bagshawe [*Nature, Lond.*, **205** (1965), 191] have precipitated the HCG-antiserum complex by adding anti-γ-globulin serum, and filtered through Oxoid filter membranes, thus achieving separation.

Another method of separation is by chromatoelectrophoresis, as applied by R. S. Yalo and S. A. Berson in their immunoassay of endogenous plasma insulin in man [*J. clin. Invest.*, **39** (1960), 1157]. Paper electrophoresis on cellulose acetate strips has been used with a high degree of success in separating the complex and unreacted hormone in their radioimmunoelectrophoretic assay for human growth hormone by W. M. Hunter and F. C. Greenwood [*Biochem. J.*, **91** (1964), 843].

Both immunoprecipitation and chromatoelectrophoresis have been successfully employed for the separation of the soluble glucagon ^{131}I-antibody complex from unreacted glucagon ^{131}I in a sensitive radioimmunoassay by R. H. Unger, A. M. Eisentrant, M. S. McCall, S. Keller, H. C. Lanz and L. L. Madison [*Proc. Soc. exp. Biol., N.Y.*, **102** (1959), 621].

^{14}C labelling seems to confer decidedly better advantages over ^{131}I labelling for radioimmunoassays. In their critical evaluation of radioiodine labelling, P. J. Collip, S. A. Kaplan, D. C. Boyle and C. N. Shimizu [*J. biol. Chem.*, **240** (1965), 143] brought out a contrast of ^{14}C labelling against ^{131}I labelling of bovine growth hormone. They have demonstrated that acetyl-^{14}C labelling of bovine growth hormone alters neither its biological activity as compared to the unlabelled hormone, nor its immunochemical behaviour significantly. It has also been shown by various workers that iodination results in a considerable loss of biological activity of hormones [Izzo, J., Rencone, A. & Izzo, M. J., *Fed. Proc. Fed. Amer. Soc. exp. Biol.*, **22** (1963), 387; Greenwood, F. C. *et al.*, *Biochem. J.*, **89** (1963), 114; Fraenkel-Conrat, H., *Methods in enzymology*, Vol. IV (Academic Press Inc., New York), 1957, 247]. Thus further studies with ^{14}C labelled hormone seem to promise a better picture of metabolism of hormones as interpreted by radioimmunoassay, considering the relationships between modification of chemical structure and alteration in biological activity.

Circulating levels of growth hormone as determined by radioimmunoassay in normal adult human subjects ranged from 0 to 50 μg. per ml. [Utiger, R. D., Parker, M. L. & Daughday, W. H., *J. clin. Invest.*, **41** (1962), 262] and 15-20 μg. per ml. were found in series of untreated acromegalic patients. After treatment, the values ranged from 0 to 27 μg. per ml. Concentrations as 0·06 IU per ml. of HCG have been detected in urine of pregnant women, and can be used as a highly sensitive immunologic pregnancy test, as well as for an early detection of choriocarcinoma [Wilde, C. E., Hillary Orr, A. & Bagshawe, K. D., *Nature, Lond.*, **205** (1965), 191]. Thus radioimmunoassay can be utilized to differentiate between the hormone levels in normal and pathological conditions or in endocrine disorders.— H. G. MADWA RAJ

Progress Reports

Applied Physics Research in Australia

The CSIRO Division of Applied Physics, which forms part of the National Standards Laboratory, presents its research activities dealing with the maintenance and improvement of standards of length, mass, barometry, time and frequency, etc., in the annual report for 1963-64.

The Division, in its investigations conducted in primary standards, developed new forms of the krypton 86 lamp to remove some of the difficulties involved in comparing two such standard sources to an accuracy of the order of 1 in 10^9. A new form of Fabry Perot scanning interferometer is being developed to enable rapid wavelength measurements to be made to an accuracy of 0·01-0·001 parts per million to help study the spectral line profiles. Work on the development of a hydrogen maser oscillator (to serve as an independent atomic frequency standard), operating at a frequency of 1420 Mc/s. was started. This will be used to control a very stable 2·5 Mc/s. quartz crystal oscillator to an accuracy of more than 1 in 10^{11}.

Towards improving the self-reliance of industrial and other laboratories in the matter of reference standards in transfer capacitors, two air dielectric parallel-plate transfer capacitors with coaxial input have been constructed. These are continuously variable from 50 to 500 pF and may be calibrated at a.f. with errors not exceeding the order of 0·2 per cent. The working frequency range as reference standard is from a.f. to the region of 100 Mc/s. The input impedances of reference standard coaxial resistive terminations using carbon film elements have been computed assuming the TEM mode as an approximation. Agreement with measured values up to 200 Mc/s. was good to about 10 per cent. The accuracy of finding the self-resonant frequencies of low-loss fixed coaxial resonators by the frequency method has been improved considerably, the absolute error being of the order of 1 in 10^5. The results and conclusions from measurements on the hardness of crystals of NaCl, KCl and LiF containing small concentrations (10^{-5} to 10^{-3} mole fraction) of divalent ions are reported.

Results of the research conducted in the current year to investigate the various factors affecting the pointing accuracy of a radio telescope are presented. The interferometric method has been developed further for the absolute measurement of small vibrations. In this method, one plate of the interferometer vibrates so that a group of fringes oscillates in the optical field. An electronic fringe detection was used dispensing with the visual counting of the fringes. The transducer was calibrated in this way at a frequency of 60 c/s. with a displacement range of 2·7-17 μ.

Under production engineering research, the results of the investigations on XK 1340 steel have shown that for general machining purposes the cold-drawn bar stock should be supplied in the fully annealed condition. Brittle fracture in the machining of zinc has been further investigated. The critical cutting speeds for cleavage fracture ahead of the tool were determined for a range of grain sizes and depths of cut and were found to be inversely proportional to the square root of the depth of cut for all grain sizes. Two 2-component dynamometers have been designed for use on automatic lathes in the laboratory. The sensing elements are air jets which measure the change in the dimension of a gap, the change being produced by the tangential and feed forces in cutting.

Textile Research Institute, Princeton

The annual report of the Institute for the year 1964 records the main achievements in its major fields of work, viz. structure and chemistry of cellulose fibres, studies on keratin fibres and synthetic fibrous polymers, thermal behaviour of textile materials, physics of fibres, properties of fibre assemblies, and processing of cotton. During the year, two new major projects were taken in hand — studies of fibre surface properties in relation to textile products, and thermoplasticity and resilience of chemically modified cotton.

Studies on chemically modified cotton undertaken with the object of elucidating the interrelation between thermoplasticity imparted by chemical means and improved resilience obtained by covalent crosslinking have led to the development of a new reaction for inducing thermoplasticity in cotton cellulose based on benzoylation of cellulose. Benzoylation imparts thermoplasticity at relatively low DS (0·7) and causes less deterioration of mechanical properties of the fibre compared to acetylation and benzylation.

A new chemical method developed for the introduction of polysulphide crosslinks, e.g. tetrasulphide and disulphide linkages, in cellulose involves the direct reaction of alkali metal sulphides with sulphorylated cellulose in either aqueous or alcoholic media. Analysis of the products obtained on the disulphide crosslinking of cellulose has suggested significant modification of, and provided new insight into the existing mechanism of, cellulose crosslinking. Studies on the mechanism by which resin treatments improve the properties of cotton, such as wrinkle recovery and resistance to microbiological degradation, have resulted in the development of new analytical methods for ascertaining the chemical structure of resin-treated cotton products. Studies on the structure of methyl cellulose, with respect to the presence of non-reducing end groups, have given rise to new methods based on gas chromatography for determining the number average degree of polymerization of polysaccharides. Studies on the structure of keratin fibres in relation to their rheological properties have provided basic information about the mechanism of permanent set, stress relaxation, swelling and supercontraction.

Studies on dependence of permanent set of keratin fibres on temperature have indicated that the transition temperature (beyond which a permanent set is achieved) depends mainly on the SH content of the fibres. Complete elimination of SH groups raises the transition temperature from its normal value (72°C.) to 85°C., reflecting the hydrolytic stability of the disulphide bonds. A programme of work has been undertaken under which the stress relaxation of a large number of synthetic fibrous materials is being studied as a function of temperature, crystallinity, orientation and other process and structure variables.

Prof. G. S. Ramaswamy

Prof. G. S. Ramaswamy has been appointed Director, Structural Engineering Research Centre, Roorkee.

Prof. Ramaswamy (b. 3 October 1923) received his BE degree in Civil Engineering in 1944 from the Madras University. After serving the Madras PWD for a brief period, he proceeded to USA and obtained his MS and CE degrees in Structural Engineering from the California Institute of Technology in 1947 and 1948 respectively. On his return to India, he joined the Government College of Engineering, Kakinada, in 1948 as Assistant Professor of Civil Engineering. In 1949, he shifted to Annamalai University as Professor and Head of the Civil Engineering Department where he started the country's first post-graduate course in Structural Engineering in 1953. He joined the Central Building Research Institute, Roorkee, in 1956 as Assistant Director and was promoted as Deputy Director in 1960. On the establishment of Structural Engineering Research Centre at Roorkee, in June 1965, he was appointed as Scientist-in-charge.

Prof. Ramaswamy's special fields of interest are structural engineering and engineering education. He is largely responsible for popularizing and promoting the use of shell structures in India. The funicular shells developed by him and his colleagues found application on a large scale in ' Operation Amar ', the Rs one-crore Defence Housing Project at Ambala involving the construction of 1700 houses. He is a member of the Executive Committee of the International Association for Shell Structures and a member of the FIP (Federation International de la Precontrainte) Commission on Prestressed Lightweight Concrete. He has been a member of the expert panels of the Building Projects Team, Committee on Plan Projects of the Planning Commission and the National Productivity Council Team on ' Factory Buildings — Layout and Construction ' and was deputed to Japan, USA and Italy in 1959. He is Chairman, Structures Group II of the Institution of Engineers (India) and member of a number of committees of the Indian Standards Institution. As Chairman of the ' Criteria for Design of Structures ' Sectional Committee, he was largely responsible for initiating standardization in the field of shell structures and folded plates. He was one of the Chairmen for the World Conference on Shell Structures held at San Francisco in October 1962, and his contributions in the field of shell structures won him international recognition. He presided over one of the sessions at the International Symposium on the Theory of Arch Dams held in April 1964 at Southampton, UK. He shared, with one of his colleagues, the John C. Gammon Prize of the Institution of Engineers (India) in 1963.

Prof. Ramaswamy is the author of over 40 research papers in the field of shell structures and prestressed concrete, and two books, *Cylindrical sheets* (National Buildings Organization) and *Analysis and design of shells and folded plates* (McGraw-Hill Book Co. Inc., New York) (under publication).

New Periodicals

Journal of Invertebrate Pathology

Beginning with March 1965 issue, the title of the *Journal of Insect Pathology* (Academic Press) has been changed to the *Journal of Invertebrate Pathology*. With this change, the scope of the journal, to be issued quarterly, has been expanded to cover the entire field of invertebrate pathology. Under the new title the journal publishes original articles and notes concerned with the nature and study of infectious and non-infectious diseases of invertebrate animals (especially insects), the suppression of these diseases in beneficial invertebrates, and their use in the control of pests. Papers on the microbiology of invertebrates (i.e. the relation between invertebrates and microorganisms) are also accepted. The annual subscription for the journal for institutions is $ 22.00; the journal is available to individual subscribers at a concessional rate.

Announcement

- *The Geochemical Society of India* — At a conference of geochemists, geologists and geophysicists held at Patna during 20-22 August 1965, the Geochemical Society of India was brought into existence, with headquarters at Patna. The principal objective of the society shall be to foster the study and application of geochemistry in national and international spheres. In pursuance of this objective, the society shall (i) work with any interested group in planning symposia and other types of meetings that are related to geochemistry; (ii) sponsor the *Journal of the Geochemical Society of India*; and (iii) appoint commissions and committees to study problems that require an all-India or international coordination.

Among the programmes of the society are the following: (i) all-India coordination of work done in earth sciences; and (ii) publication of quarterly bulletins containing abstracts and summary data of the work being done in India together with notes and news of important researches being carried out in different institutions of the country as well as abroad.

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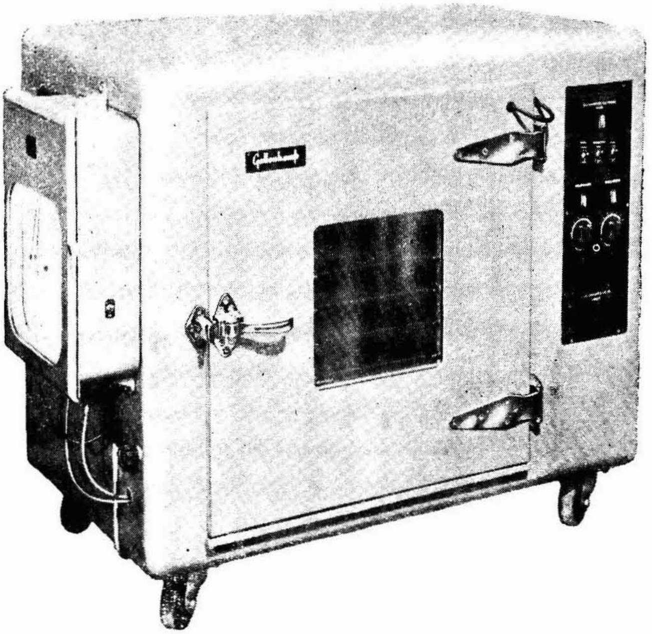

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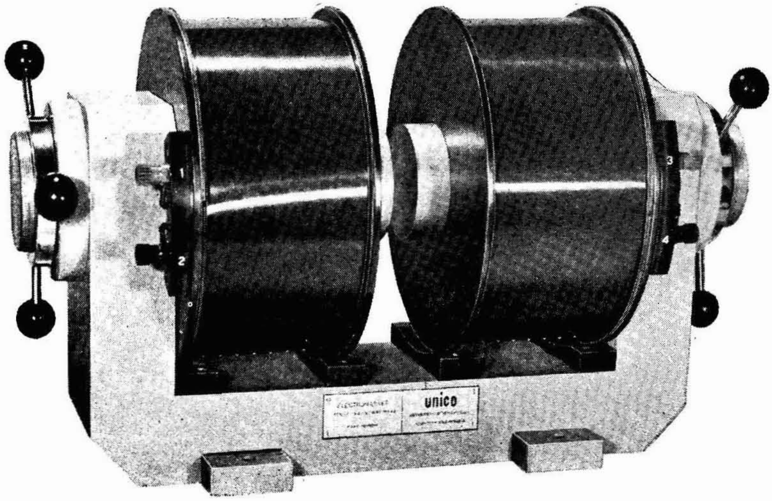
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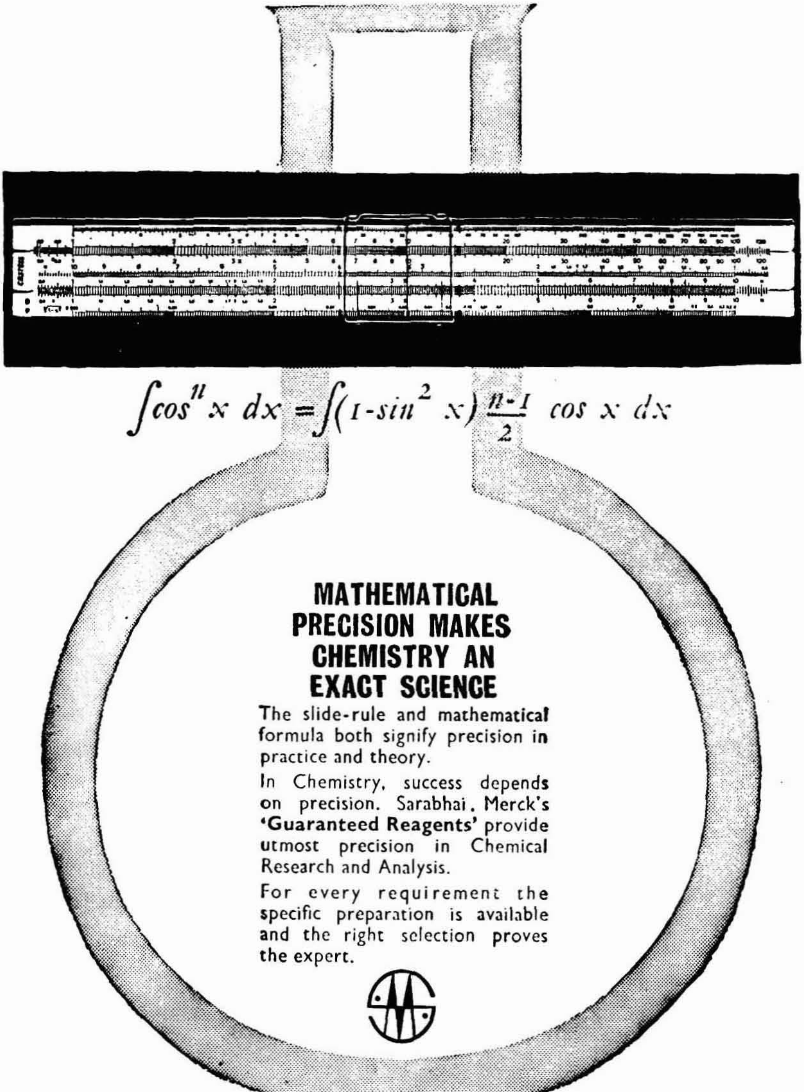


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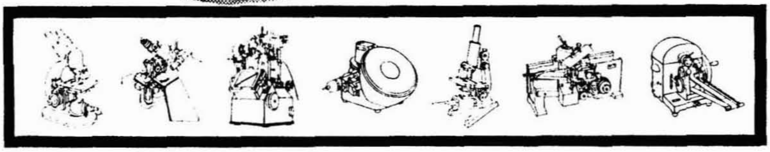

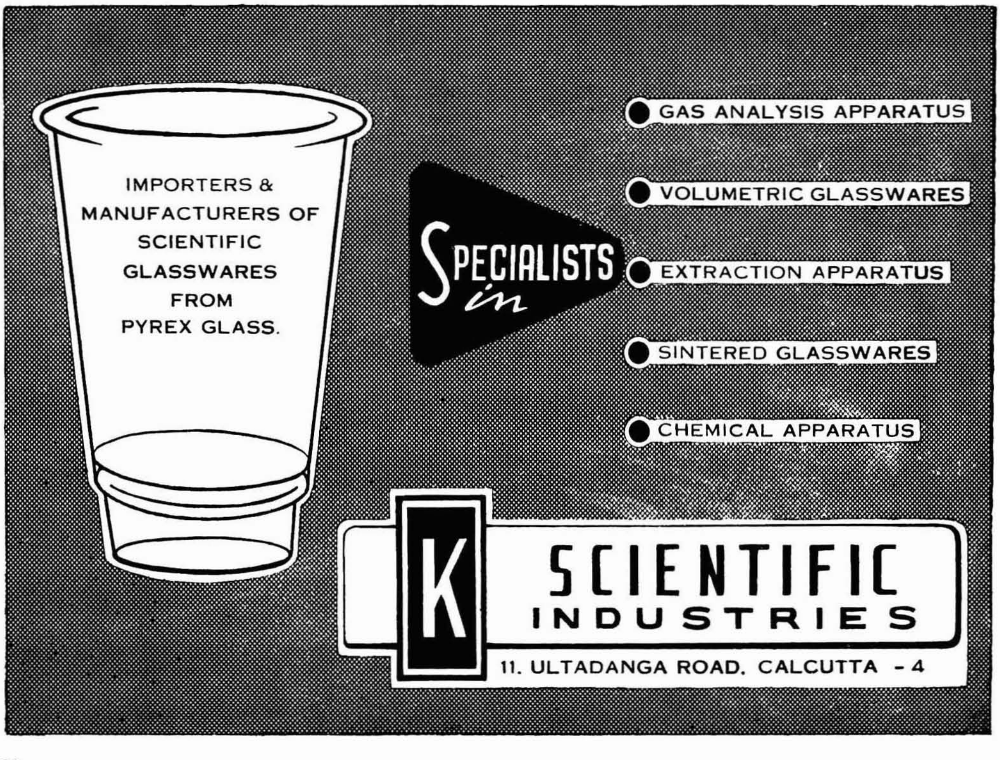

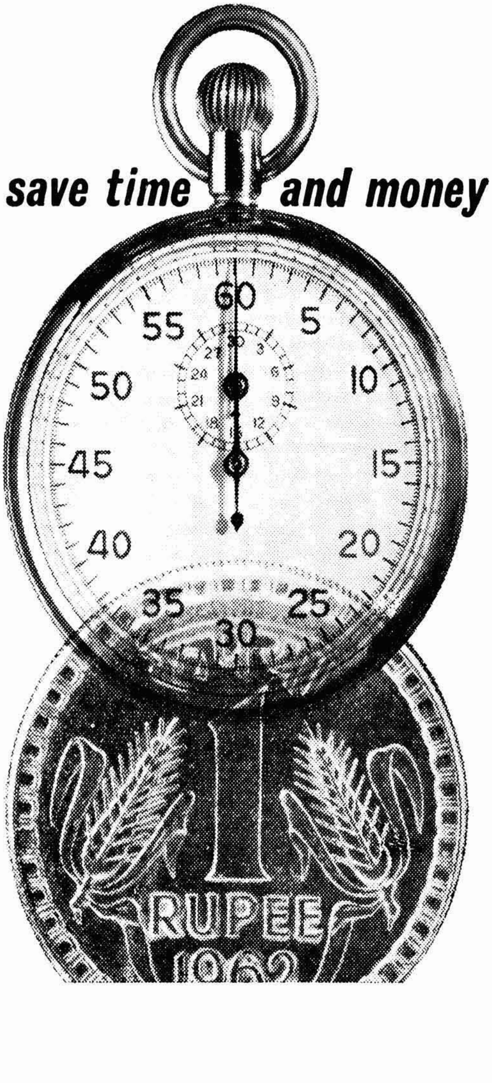
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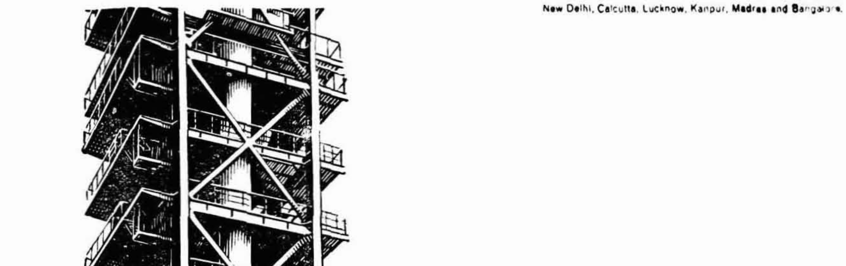
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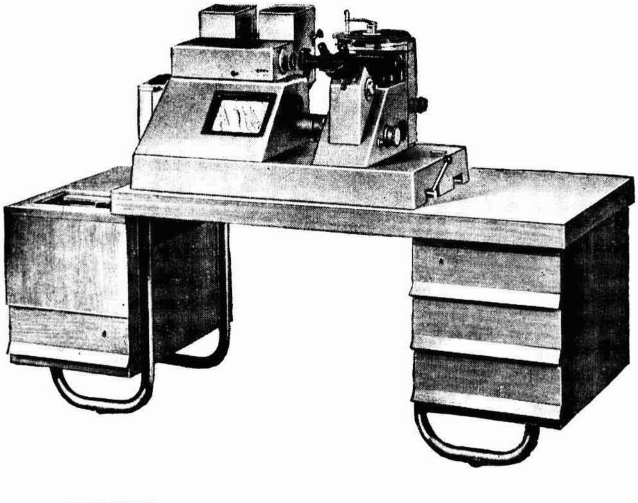

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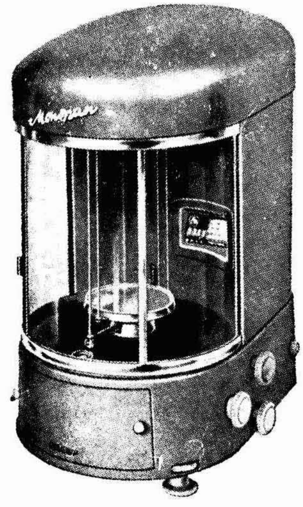
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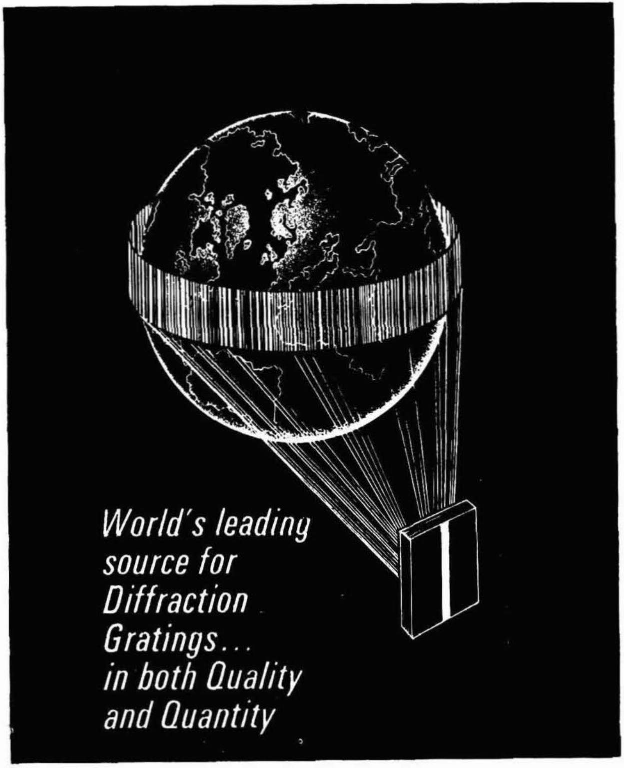

Printed and published by Shri A. Krishnamurthi, Publications & Information Directorate, Council of Scientific & Industrial Research, New Delhi, at the Catholic Press, Ranchi, India

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