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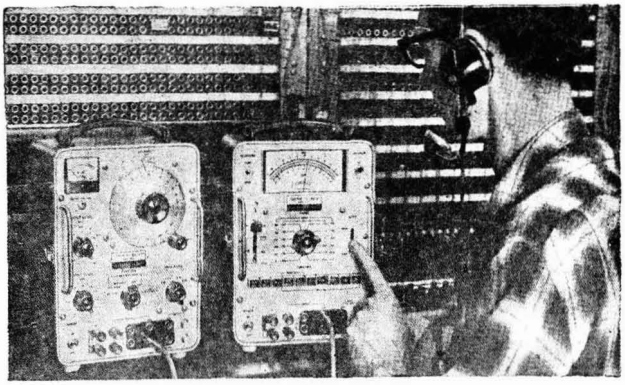

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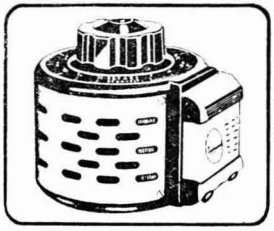

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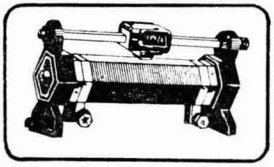

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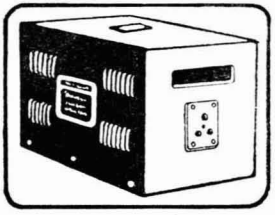

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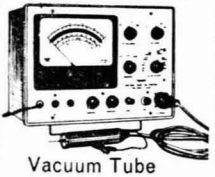

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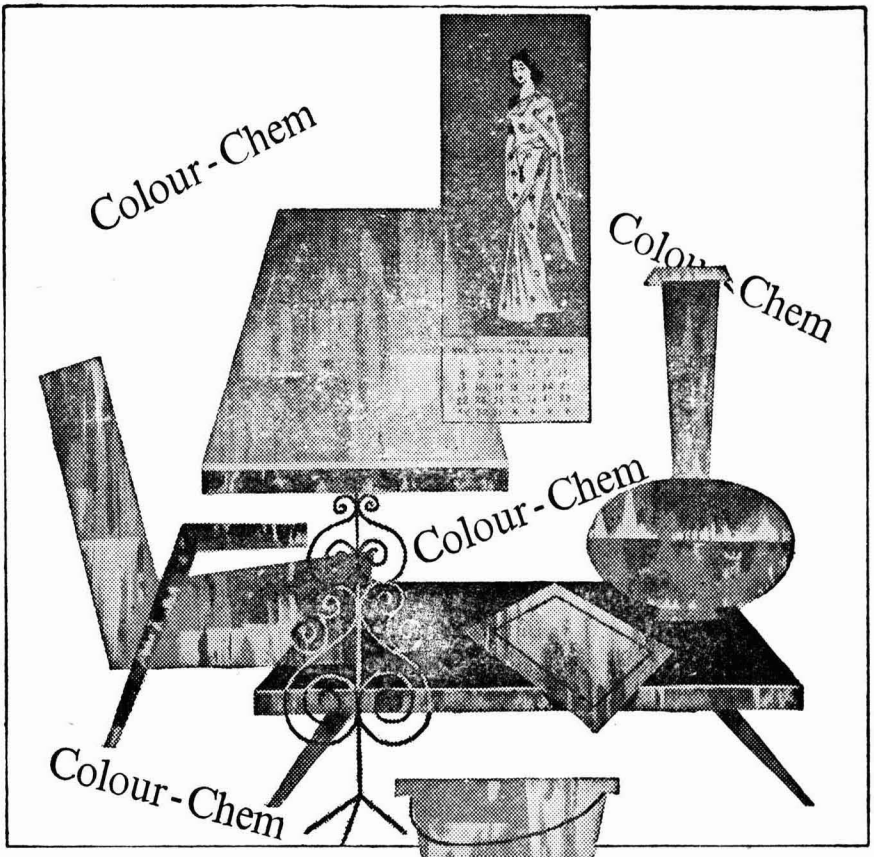

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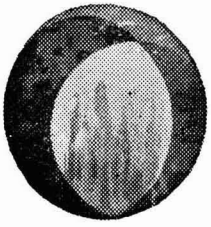

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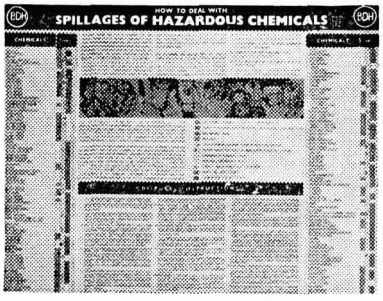

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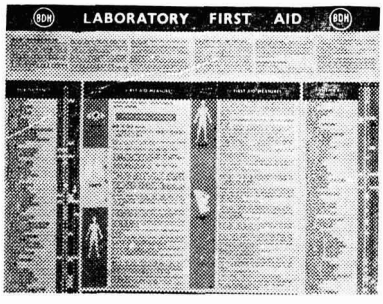

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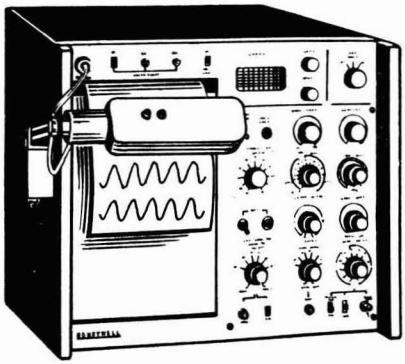

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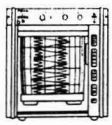

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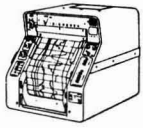

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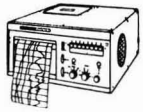

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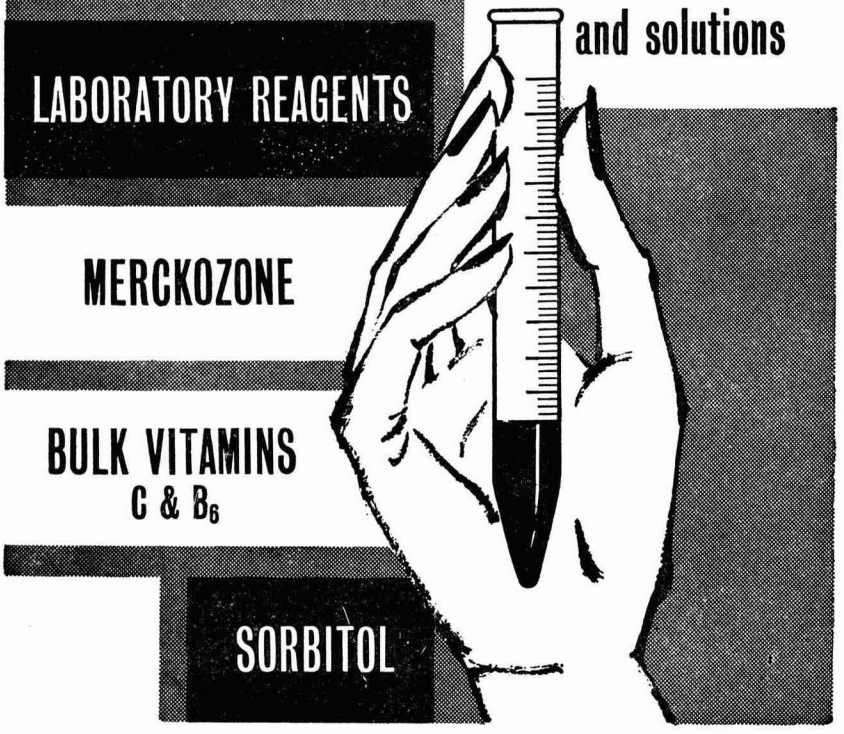

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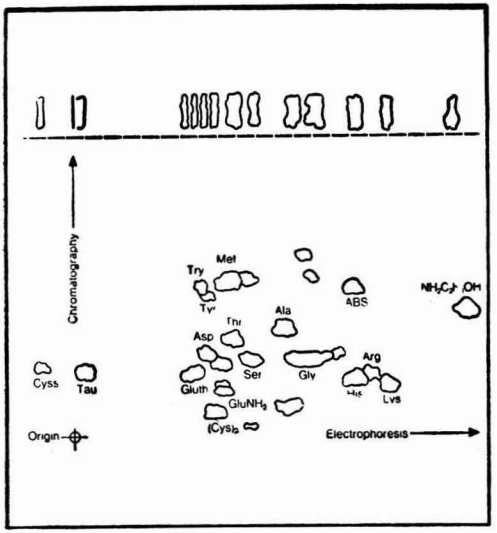

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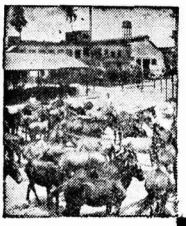

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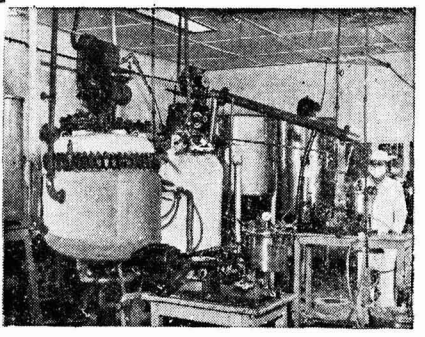

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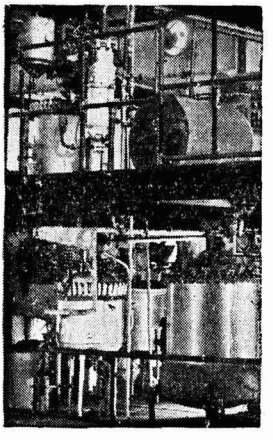

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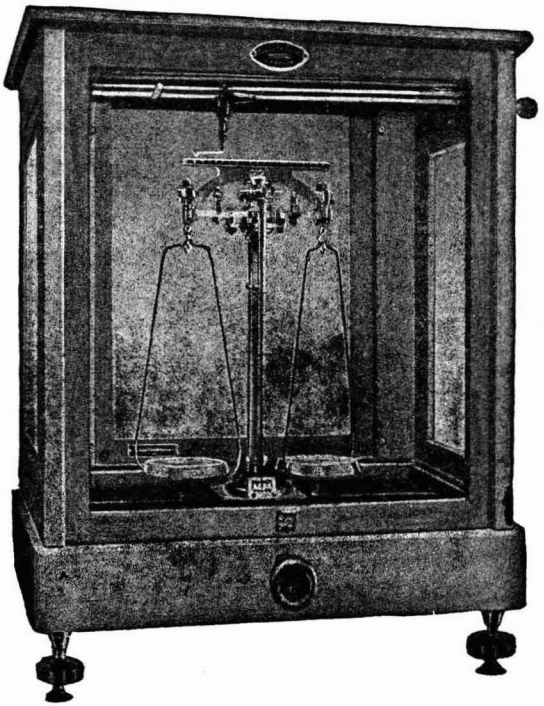

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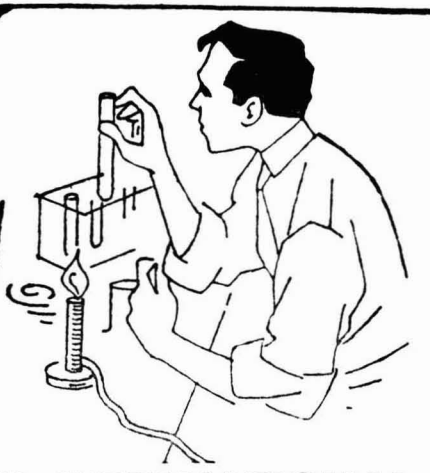

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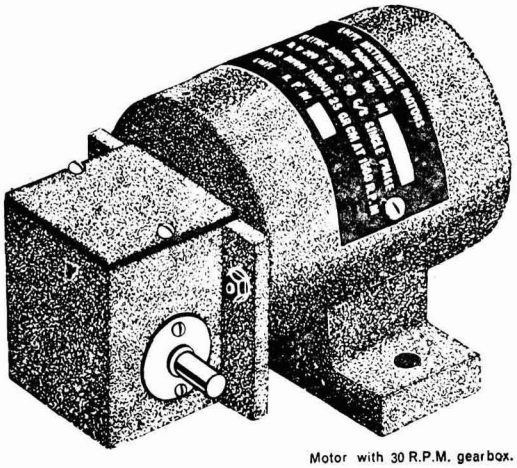

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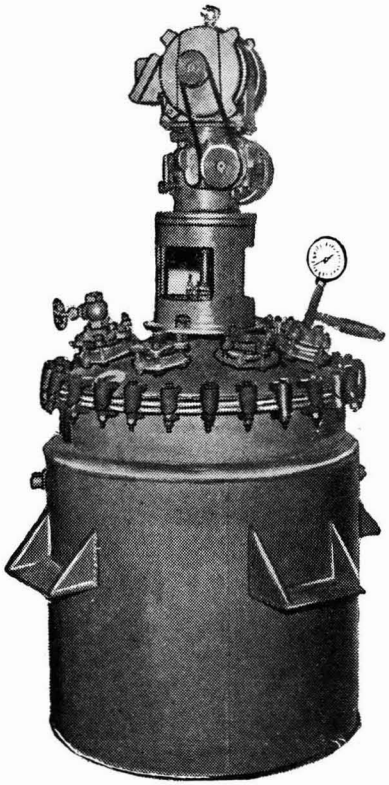

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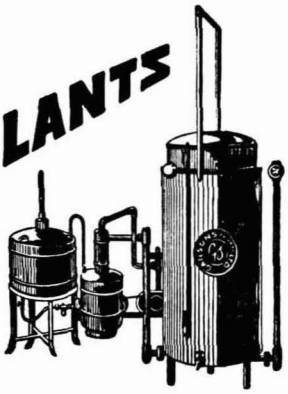

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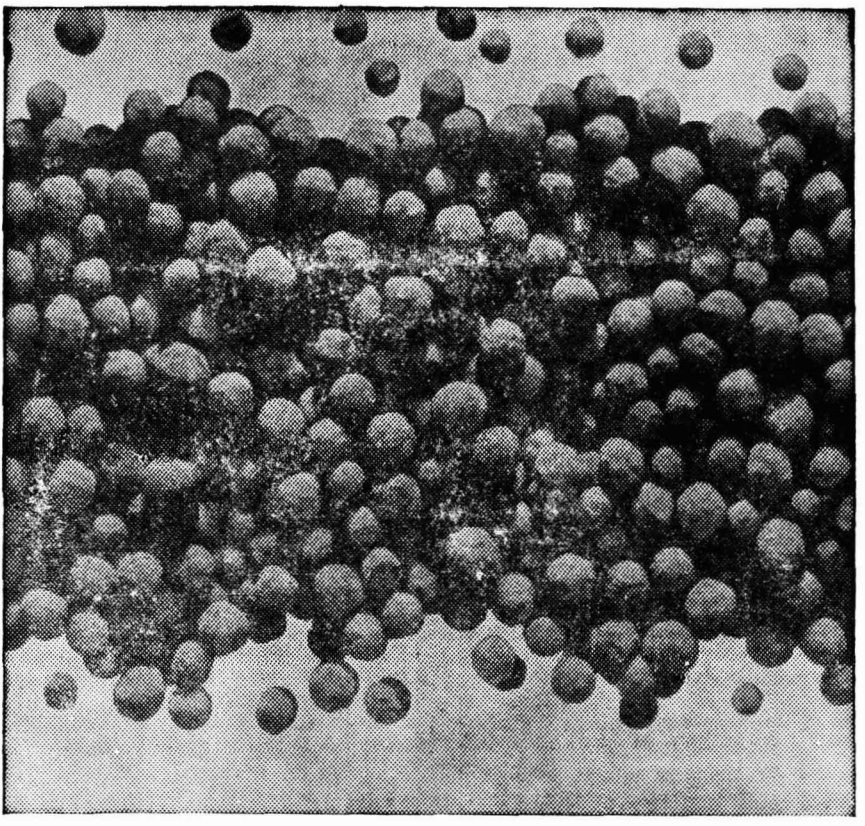

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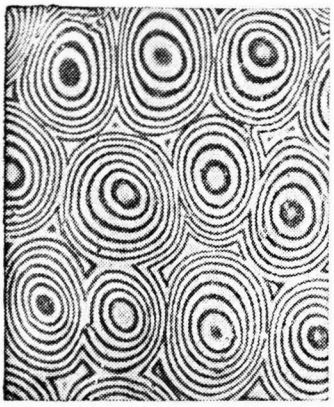

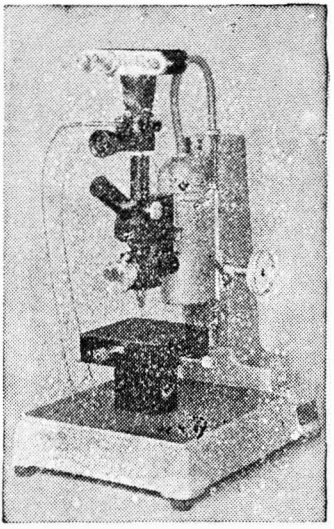

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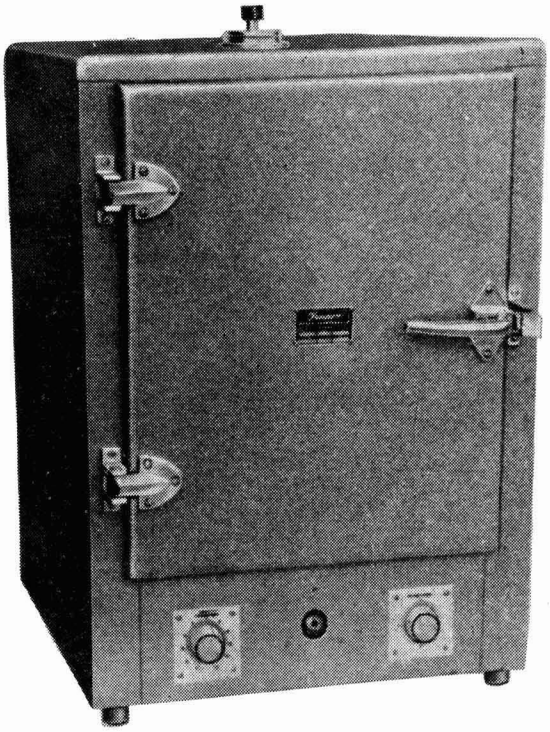

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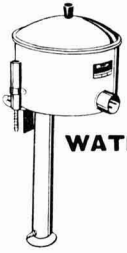

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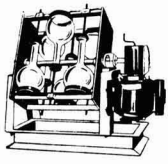

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Current Topics

Standardization of Chemical Products of Plant Origin

INDIA'S rich and varied flora provides a variety of products, both for internal consumption and export. In some products like lac India enjoys virtual monopoly in the world markets. However, the situation is fast changing due primarily to increasing competition from other supplier nations, inroads from synthetic substitutes and stringent specification requirements imposed by users. The need for a reappraisal of the pattern of exploitation of our natural resources has thus been manifest for quite some time. Of the various aspects of the problem deserving attention, the one most vital to the rational utilization of the natural products and to the retention of export markets is that of quality control. Despite the vast resources of economic plants and related materials, the work done so far in respect of quality control and standardization of products and processes is limited. It was, therefore, a welcome decision of the Indian Standards Institution to devote a separate session to standardization of chemical products of plant origin at its Eleventh Convention held at Chandigarh from 24 September to 2 October 1967, and to discuss problems which have a direct bearing on the export trade as well as internal consumption.

The papers (27) presented and discussed dealt primarily with regional practices in the handling, storage, treatment and processing techniques which influence the quality of products, such as oilseeds, rubber, resins and gums, perfumery and cosmetic materials, flavours, protein concentrates and drugs and medicinal products. Though the scope of the session was intended to be restricted to standardization, the deliberations were more broad-based and other aspects of the overall problem of rational utilization of natural products, such as alternate and more profitable uses of products and by-products, and potential uses for products considered industrially unimportant, received attention. Thus the occasion was made use of to discuss all possible aspects of the rational, scientific and economic exploitation of primary and secondary products of plant origin.

A large number of products and practices in respect of which standards need to be formulated were highlighted. Formulation of standard terminology for non-edible oils and evolution of simple testing methods for the determination of moisture, oil content, foreign matter, maturity level, etc., of oilseeds were stressed. Among the important foreign exchange earners for which lot more standardization work is yet to be done, mention was made of *kattha* and cutch, lac and modified lac products, plant gums, spices and their ready-to-use mixtures, sapogenins, etc. Though the masses in India still depend largely upon *Ayurvedic*, *Unani* and *Tibbi* systems of medicine, work on the standardization of drugs used in these systems is meagre. Formulation of purity standards for medicinal plants and their collection, storage and packaging, and reference standards for drugs manufactured in the country deserve urgent attention. The first edition of the Indian Pharmacopoeia was issued in 1955 and it has been found extremely useful. There is need for revising it at frequent intervals.

The economic potentialities of a number of products considered industrially unimportant were pointed out. It was reported that *Karanj* (*Pongamia pinnata*) oilseed cake protein, besides being a rich source of 10 essential amino acids, contains furanoflavonoids which have insecticidal properties; the cake can also find use in the manufacture of antibiotics. Typical examples of problems which could be fruitfully investigated are: (1) finding uses for non-edible oils as such or after modification; (2) finding raw materials for paper industry other than the conventional ones; (3) extension of rubber plantation to other areas like Andaman and Nicobar Islands and cultivation of improved high yielding varieties of rubber clones; (4) finding indigenous substitutes (such as mangrove extract) for imported vegetable tanning materials; (5) extending the fields of utilization of turpentine oil; and (6) investigating the possibility of using henna in cosmetics.

Considering the number of problems identified and the lines of investigation suggested, the session was indeed fruitful and the papers presented and discussed brought out effectively the importance of the subject. It is hoped that the institutions concerned will take up necessary measures so that the problems identified can be effectively solved. A prerequisite for the successful implementation of standardization practices for plants and plant products suggested is the establishment of a national herbarium, an arboretum and a museum of raw materials and industrial products of plant origin. The herbarium at the National Botanic Gardens, Lucknow, could very well be expanded into a national herbarium. Also, in view of the diversity of climatic and soil conditions in different parts of the country, the necessity of establishing regional herbaria for different regions is worth considering.

Summer School in High Voltage Laboratory Techniques

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WITH the advent of power development in India and the consequent rise in transmission voltage levels, the need for a better understanding of high voltage laboratory techniques has been felt by the electrical industry and electricity boards. To meet this demand, various educational institutions have proposed to start training facilities in high voltage engineering and these institutions have felt the need to have their staff trained in a well-established laboratory. The Department of High Voltage Engineering of the Indian Institute of Science, Bangalore, has been approached by different establishments and institutions to provide short-time but rigorous training for their staff in this important field. This laboratory with excellent facilities such as 3 MV impulse generator, 1 MV cascade transformer, 200 ka. impulse current generator, and 200 kV. d.c. generator is ideally suited for running the course. Also, this laboratory has the advantage in having a group of staff who have experience in research and testing in the field of high voltage engineering for more than a decade. It was, therefore, decided to organize a summer school in high voltage laboratory techniques, the first of its kind in this country, at this department.

The summer school was held from 8 to 20 May 1967. Though it was originally planned to accommodate only 24 participants, the strength had to be increased to 38 because of the overwhelming response from the industry, electricity boards and other institutions. There were 28 participants from electrical and allied industries, three from electricity boards, three from educational institutions and four from the Power Research Institute. The industries had sponsored senior engineers from their design, testing and development divisions.

The school was inaugurated by Prof. M. S. Thacker and Dr S. Dhawan presided over the function. In his inaugural address, Prof. Thacker stressed the importance of high voltage laboratory training in the light of the large-scale power development proposed during the Fourth Plan period. He suggested that the generating capacity had to be doubled in every five years and to meet this increased need the country has to be self-reliant in power production and distribution equipment. For this a training in high voltage laboratory techniques is essential for personnel engaged in the production and distribution.

The emphasis of the training was mainly on laboratory practice and testing procedures. However, lectures were arranged by the staff of the department to help the candidates gain the necessary background for a better appreciation of the significance of the testing procedures and importance of tests. Two lectures of one hour each were held every day followed by two laboratory experiments each extending over two and a half hours.

The lecture series was started by Prof. H. V. Gopalakrishna with a talk on high voltage research and electrical industry. In this brief résumé, he covered the various fields of research in high voltage engineering and indicated how the results of such research activities lead to new developments in the electrical industry. He then gave a talk on the phenomenon of lightning and the overvoltages that arise on transmission lines and terminal equipments due to lightning He also explained the practice of 'insulation coordination' in a power system. Shri Y. S. Venkateswaran of the Indian Standards Institution stressed the importance of standardization as applied to high voltage equipment. Dr R. S. N. Rau gave a general lecture on the problems of high voltages which are confronted both in industries and in everyday life. Dr B. I. Gururaj explained the switching overvoltages and discussed their effects on power apparatus.

The problems of earthing and shielding in a high voltage laboratory as also the principles of design and layout of such a laboratory were explained by Shri P. V. S. Rao. Dr V. Prabhashanker dealt with the production of high voltages of all kinds and explained the precautions to be observed while working with high voltages. The methods of measurements of high voltages and the sources of errors in such a measurement were discussed by Shri P. V. S. Rao. Shri N. Narayan of the Power Research Institute explained the techniques of field measurements of lightning current.

The properties of insulating materials were surveyed by Dr N. Krishnamurthy. He explained the various theories of electrical breakdown in solid and liquid insulations. The significance of testing on oils was discussed by Dr V. Prabhashanker and a critical review of the evaluation of solid insulating materials was presented by Shri D. K. Bansal of the Power Research Institute. The measurements on gaseous dielectrics with emphasis on breakdown studies was dealt with by Dr G. R. G. Raju, while the conduction of electricity through gases was explained by Dr M. N. Swamy.

The significance of tests on cables was stressed by Shri M. R. Nandagopal, while Shri H. S. Chandrasekhariah dealt with the methods and importance of tests on insulators, isolators, bushings and instrument transformers. Shri B. R. Prabhakar explained in detail the procedure for impulse tests on power transformer and discussed the methods for detecting the failure with the help of illustrations of oscillograms taken in the laboratory. The procedure and significance of testing lightning arresters was explained by Shri G. R. Nagabhushana.

The measurements of partial discharges and radio interference was dealt with by Shri P. V. S. Rao, while Dr B. I. Gururaj discussed the methods of measurement of power factor at high voltages. The lecture series were concluded with talks on processing of

data and design of experiments by Dr V. Prabhashanker and Shri S. P. Kumar.

For laboratory training, the participants were divided into six batches and six laboratory experiments were simultaneously arranged. In all 18 experiments were performed by each batch. To run such a tight programme some of the facilities of the Power Research Institute were utilized. Still ample opportunity was provided for the participants to operate all the major equipments and conduct the experiments themselves. Some of the highlights of laboratory experiments were the impulse testing of transformers, testing of lightning arresters, discharge detection in equipment, mapping of electrostatic fields, measurements of high voltages, and power factor measurements at high voltages. The experiments included the testing of insulating materials and insulators from the point of view of standard specifications and of laboratory evaluation. The ageing studies on oils, the effect of ageing on mechanical properties of sheet materials and tracking studies were also conducted in the laboratory.

In addition to the above programme, demonstrations were arranged on corona in the 400 kV. experimental transmission line and the latest model of discharge detecting equipment. Also, some technical films were screened. With difficulty it was managed to arrange visits to some of the local industries in the midst of such a tight schedule. In spite of the strain of such a concentrated course, the participants felt it to be extremely educative and useful and expressed their desire to attend similar courses in the field of high voltage engineering.

The lecture notes were distributed to the participants before the lectures so that they could study them before and follow the lectures easily. It is proposed to bring out the lectures in the form of a book.

High Resolution NMR Spectroscopy of High Polymers

B. K. PATNAIK

Shri Ram Institute for Industrial Research, Delhi 7

ALTHOUGH nuclear magnetic resonance (NMR) spectroscopy is a comparatively new technique in the characterization of polymers, its impact is already felt. In polymer chemistry NMR spectroscopy finds use in two principal areas. (i) The chain flexibility and molecular relaxation are studied with the solid or rubbery materials. This is more commonly termed as the ' broad line NMR ' spectra. Adequate number of reviews[1-7] and papers have been published on this aspect. (ii) The solutions of polymers are studied from which informations regarding polymer composition, stereochemical configuration, polymer-solvent interaction, conformational preferences, etc., can be obtained. The present review deals with the study of high polymers in the latter area.

In attempting high resolution work with polymers one is commonly frustrated by poor solubility coupled with high viscosity resulting in broadened signals of low intensity. The sizeable interactions between neighbouring molecules, the poor mobility of molecular segments and sometimes the polymer-solvent interaction cause the broadening of the spectra. In some favourable cases, it is possible to get the solutions of sufficiently low viscosity to permit tumbling to average out broadening dipole-dipole interactions and to obtain a signal to noise ratio sufficiently high to obtain spectra whose quality and interpretability approach those of simple molecules. In solutions of normal viscosity, the molecular motion is rapid in which the local field effects are nearly eliminated. The polymer interaction can be lessened by dilution, but this is accompanied by loss in intensity. An improved resolution can be achieved by raising the temperature (a temperature of 100-150°C. is often used). But, even then, some lines remain appreciably broadened, e.g. the backbone protons of vinyl polymers, because of their slower reorientation. The main chain protons exhibit broader resonance than side chain protons. In strongly coupled spectra (for example, phenyl resonance in polystyrene), a broad line is observed because of a large number of closely spaced lines, which is also observed in simple molecules. Stereochemically irregular (atactic) polymers give comparatively broader line width because of overlapping of a number of resonances differing only slightly in chemical shift. The analysis of the electron coupled spin-spin interactions is frequently very complicated. The spin coupling problem is sometimes approached through ' double resonance ' (spin decoupling) experiments. In this method one examines the spectrum of one type of protons while simultaneously irradiating the protons which give rise to the complicating multiplets. The spin coupling is effectively removed thereby.

The NMR studies in polymers have mostly been restricted to protons. The ^{19}F spectra, which are similar to the proton spectra, have also been studied to some extent in detail. Fluorine spectra are somewhat easier to study because the chemical shifts are substantially larger than those encountered with protons. Other nuclear species of interest include ^{31}P and ^{13}C.

The spectral interpretation in NMR of polymers essentially deals with the polymer composition and structure (including head to tail, head to head, and tail to tail position of monomer unit) and the stereochemical nature of the chain. The stereochemical configuration in various polymers and copolymers has been discussed by McCall and Slichter[8]. The interpretations are based on the assignments of the α-protons (or other observable α-substituents) and the methylene protons (or CF_2 group). For various assignments, the following terminology is now accepted. The α-proton (or substituent) in the central atom of an isotactic triad (*ddd* or *lll*) is denoted by *i*, that of a syndiotactic triad (*dld* or *ldl*) by *s*, and that of a heterotactic triad (*lld, ddl, dll, ldd*) by *h*. The methylene proton in a syndiotactic sequence (*dl*) is denoted by racemic (*r*) and those in an isotactic sequence (*dd, ll*) by meso (*m*). For any polymer, the summation of *i, s* and *h* as well as *r* and *m* are equal to unity.

The present review describes the results obtained with the following groups of polymers: (i) vinyl polymers; (ii) polyolefins; (iii) polyethers; (iv) polyaldehydes; (v) fluorine containing polymers; (vi) copolymers; and (vii) polyesters.

Vinyl Polymers

The vinyl polymers are the largest group of polymers that have been studied extensively. They include polymethacrylates, polyacrylates, polyacryl- and methacrylamides, polyacrylo- and methacrylonitriles, polymethacrylic acid and anhydride, polyvinyl ethers, polystyrene, poly-α-methylstyrene, polyvinyl chloride, polyvinyl acetate and polyvinyl alcohol.

Polymethacrylates

Polymethylmethacrylate (PMMA) has been studied in greater detail because of easy interpretability. The polymer solutions in chloroform, benzene, dioxane, pyridine, etc., have been studied at 35-110°C. The peaks for various observable protons appear at higher resonances in chloroform and dioxane. In general, the ester methyl resonance appears at 6·5 τ, the chain methylene at 8·16 τ and the α-methyl resonance near 9·0 τ (ref. 9-13). The tacticity is determined from the placement and multiplicity of the α-methyl and methylene resonances. The resonances for the α-methyl protons in the syndiotactic polymer appear at the highest field value because of maximum shielding and for the isotactic one, the resonances appear at the lowest in that region. Thus, when a sample is taken in chloroform, the α-methyl resonances for syndio-, hetero- and isotactic triads appear at 9·09, 8·95 and 8·78 τ respectively. Similarly, the methylene protons in a syndiotactic PMMA appear as a singlet and those in the isotactic one as a quartet.

Based on the above information it was concluded that free radical initiators give predominantly (not exclusively) syndiotactic polymers whereas anionic initiators give predominantly isotactic polymer[9]. Using free radical initiators more syndiotacticity is observed when the polymerization is carried at lower temperatures. With increasing temperatures the propagation tends towards randomness[10]. The syndiotacticity determined from NMR data compares favourably with those determined from X-ray and infrared measurements[11]. Marked narrowing of the α-methyl resonance lines occurs when the spectra are recorded at higher temperatures and that the narrowing of the isotactic α-methyl protons occurs at a lower temperature. This has been explained on the basis of the lower glass transition temperature of the isotactic PMMA compared to the syndiotactic one[12]. The distribution of iso- and syndiotactic sequence lengths in these polymers has been used in predicting the melting behaviour of each sample[13].

High syndiotacticity observed with poly-β-phenylethylmethacrylate is explained on the basis of the formation of an intramolecular π-complex resulting in the formation of a highly selective polymer redical. Bulkiness of the ester group in the methacrylate does not increase syndiotacticity but increases heterotacticity[14]. The tacticity in allyl methacrylate polymers has been reported recently[15].

Polyacrylates

Both isotactic and atactic polyisopropylacrylate have been analysed by NMR. The spectra of the isotactic polymer could be interpreted comparatively easily. The methin protons and the methyl protons of the ester group appear as heptet and doublet respectively[16]. The assignment of the position for the α- and β-protons have been made by taking deuterated samples.

Polymethylacrylate[17] has also been studied in both deuterated and undeuterated forms. The peaks observed were broadened because of deuterium couplings.

Polyacrylamide and Polymethacrylamide

Low molecular weight polyacrylamides and polymethacrylamides have been studied in aqueous solutions[18]. The doublet nature (approx. 3·0 and 2·3 τ values) of the amide proton resonance in contrast to a broad singlet observed with simple amides is attributed to the relatively slow reorientation rate of the polymer segment, permitting effective coupling of the electric quadrupole moment of the ^{14}N nucleus to the motion of the molecular framework. The doublet coalesce to a singlet at 70°C. because of free rotation around C-N bond.

Polyacrylonitrile and Polymethacrylonitrile

The stereoregularity of polyacrylonitrile (PAN) has been examined in solvents like NaSCN-D_2O (ref. 19), DMF-d_7 (ref. 20) and DMSO-d_6 (ref. 21). This has also been analysed by conversion to polymethylacrylate by hydrolysis followed by esterification. The problem has been approached both by taking α-deuterated[20,21] sample and using the decoupling technique[22]. The PAN-α-*d* gave two peaks at 7·79 and 7·76 τ in the methylene region which were attributed to the *racemic* and *meso* forms respectively arising out of syndiotactic and isotactic triads. The appearance of six peaks for the methylene protons in the undeuterated samples is ascribed to the two triplets (due to syndiotactic and isotactic units) in close proximity.

The NMR spectrum of polymethacrylonitrile has been reported after converting it to polymethyl-

methacrylate and studying the α-methyl proton resonance[23-26]. Thus tacticities of the polymers obtained under various conditions have been determined. These facts reveal that polymerization by Υ-rays at −78°C. gives a stereoblock polymer containing only isotactic and heterotactic units whereas those prepared with *n*-butyllithium, azo-bis-isobutyronitrile (AIBN) and benzoyl peroxide give products possessing similar amounts of iso-, hetero- and syndiotactic triads.

Polymethacrylic Acid and Polymethacrylic Anhydride

Polymethacrylic acid, so far, has been analysed only after conversion to PMMA. Thus methacrylic acid when polymerized by Υ-rays at −78°C. and in the presence of AIBN at 60° gives polymers having 85 and 57 per cent syndiotacticity respectively[26]. Similarly, the stereochemical configuration of polymethacrylic acid prepared by polymerization of methacrylic acid in aqueous solution is found to be dependent on the *p*H of the medium[27]. Increasing *p*H favours syndiotactic propagation.

The tacticity of polymethacrylic anhydride has also been determined only after conversion to PMMA[28-30]. Miller *et al.*[29] have reported the preparation of polymethacrylic anhydride by polymerization of methacrylic anhydride with benzoyl peroxide at various temperatures. These have been hydrolysed to the corresponding acid followed by esterification with diazomethane to give PMMA. NMR reveals that polymerization at higher temperature gives more syndiotactic polymer. Similarly, polymerization of methacrylic anhydride by UV at −50°C. is reported to give a polymer containing only syndiotactic and heterotactic units[30].

Polyvinyl Ethers

Polyvinylmethyl ether has been analysed in various solvents like chlorobenzene, CCl_4, CH_2Cl_2, CS_2, etc. Brownstein and Wiles[31] reported that the methoxy resonances appear as three peaks corresponding to iso-, hetero- and syndiotactic units, a fact confirmed by other workers[32,33]. Kern *et al.*[34] suggested that the chain methylene proton resonance was little affected by stereochemical configuration which was found to be untrue when double resonance was used. The undecoupled spectra had three regions at 6·49, 6·73 and 8·25 τ for the α-, -methoxyl and β-protons respectively. The methoxyl resonance was split into three components. The α-proton decoupled from the β-proton shows three peaks with approximately the same ratios of areas as the methoxyl component. The β-proton resonance decoupled from the α-protons consists of the overlap of an *AB* quartet and a singlet.

Poly-α-methylvinylmethyl ether[35] gives singlets for the methoxyl, methylene and the α-methyl protons under all conditions of temperature and solvent. The polymers are believed to be entirely syndiotactic.

Polystyrene

Polystyrenes of different tacticities have been studied in considerable detail[36-39]. The spectra are not as simple as that obtained with PMMA because of extensive coupling of the α- and β-chain protons. In isotactic polystyrene the α- and β-protons are partially resolved[36]. The phenyl protons appear at the lowest field (about 3·0-3·6 τ). Of the chain protons, the α-chain protons appear at a lower field (∼7·8 τ) than the β-chain protons (∼8·5 τ). In analogy with the PMMA analysis one expects to get informations on *i*, *h* and *s* from the peak of α-chain protons and *m* and *r* from that of the β-chain protons. This has been made possible from the NMR spectra of deuterated polystyrene[37,38], viz. polystyrene-ββ-d_2 and polystyrene-α-d_1. From the spectrum of polystyrene-ββ-d_2, the *i*, *h* and *s* factors have been deduced. Polystyrene-α-d_1 gives a broad peak for the β-chain protons apparently due to a multiplet centre.

The various polyhalostyrenes[38], in which the 2-, 3- and 4-positions of the phenyl ring are substituted either by Cl or I, have also been analysed. The peaks obtained from the ring, methin and methylene protons were quite broad. When the ring was substituted in the *ortho* position (poly-2-chlorostyrene), the methin protons appeared at a lower field, otherwise a very broad peak was observed at ∼8·3 τ.

Poly-α-methylstyrene

Poly-α-methylstyrene has been studied[40-42] in more detail than polystyrene because of the readily observable methyl protons. The methyl protons appear as triplet (∼9·1, 9·5 and 9·7 τ). Brownstein *et al.*[40] have regarded these as iso-, hetero- and syndiotactic units in order of increasing field strength (in analogy with those of PMMA), whereas the contrary view has been put forth by others[41,42] in which the syndiotactic units are assigned to the peak at the lowest field strength. Further work is needed to confirm these observations.

Sakurada *et al.*[41] have studied the polymers obtained with cationic, anionic and Ziegler catalysts. The polymer obtained with the cationic catalyst was quite stereoregular whereas the anionic catalysts gave a random polymer. In the polymerization of α-methylstyrene by Friedel-Crafts' catalysts[42] in various solvents, it was reported that highly stereoregular polymers were obtained with good solvents. The stereoregularity increased with increased polymer solubility in the solvent and with decreasing polymerization temperature. The polarity of the solvent and the nature of the catalyst hardly affected the stereoregularity of the polymer which is in contrast to the fact observed with PMMA.

Polyvinyl Chloride

The spectrum of polyvinyl chloride is complicated because of extensive α,β-spin couplings. Polyvinyl chloride and low molecular weight models have been analysed by a number of investigators[43-49]. The α- and β-protons appeared as quintets. Doskocilova[47], comparing the results with that of the model compounds of PVC, suggests that these are due to overlap of triplets arising due to the presence of syndiotactic and isotactic units. This supports the basic correctness of Tincher's[44] assumptions and is in accord with the results of Bovey *et al.*[32]. Bockman[49] has discussed the tacticity of low molecular weight PVC. Deuteration and decoupling experiments have also been used to simplify the spectra. The spectra of

α-deutero-PVC and PVC decoupled from β-protons support Johnsen's[43] assignments in which the syndiotactic and isotactic contents were in the ratio 2:1. In this the α-syndio peak is assigned the low field strength. The NMR signals of monomer tetrads in PVC have been reported by Yoshino and Komiyama[48]. Enomoto *et al.*[50] have recently reported the NMR spectra of various deuterated samples such as PVC-α-d_1, PVC-β-d_1, PVC-α,β-d_2, PVC-β,β-d_2 prepared at different temperatures and determined their tacticities. The various assignments which appear to be conclusive for the syndio-, hetero- and isotactic units are made after comparison with the model 2,4,6-trichloroheptane. The methylene proton resonance in PVC consists of six peaks when examined at 100 Mc. as against five when examined at 60 Mc. The origin of the additional line is yet to be confirmed. Some of the assignments in PVC need further confirmation taking polyvinyl chloride of different tacticities, which have been determined by an independent and unambiguous method.

Polyvinyl Acetate and Polyvinyl Alcohol

Tacticities of polyvinyl acetate and polyvinyl alcohol have been determined from NMR[32,51-54]. In polyvinyl acetate[32,53] (PVAc) the α-proton, CH_3 and β-protons appear in increasing field strength. The CH and CH_2 protons appear as quintet and triplets respectively. The acetate protons appear as three peaks corresponding to the different tacticities. The α-proton decoupled from the β appear in three peaks. The β-proton resonance decoupled from α is a singlet, though somewhat broadened. The CH_3 protons appear in three peaks. The assignments for the corresponding *i*, *h* and *s* factors have been made by comparing the decoupled α-proton resonances with the corresponding trifluoroacetates obtained from polyvinylmethyl ether[54] of known tacticities (by heating with hydriodic acid followed by treatment with trifluoroacetic anhydride). The assignments of the components *s*, *h* and *i* in PVAc and polyvinyl trifluoroacetate (PVTFAc) are in decreasing order of field strength, whereas the reverse is the order in polyvinylmethyl ether and polyvinyl alcohol.

Polyvinyl alcohol has been studied in D_2O and DMSO[54] and the assignments have been made after converting to trifluoroacetate. In DMSO, the α- and β-protons appeared at 6·15 and 8·53 τ respectively. The α-protons decoupled from β-protons show three components corresponding to *s*, *h*, *i* units in increasing order of field strength. The β-protons showed *m* and *r* peaks separated by 0·08 p.p.m., the latter being at higher field.

Polyolefins

The spectrum of polypropylene is quite complex because of overlapping and extensive spin-spin couplings. The earlier approaches of Satoh *et al.*[55] have been simplified by examining the proton resonance spectra of partially deuterated polypropylene[56] such as 2-d_1-polypropylene and 2,3,3,3-d_4-polypropylene. The methylene protons in the isotactic 2,3,3,3-d_4-polypropylene appear as a quartet from the intensities of which the m/r ratio can be estimated. The spectrum of 2-d_1-polypropylene shows superposition of the methyl singlet and the methylene quartet. Woodbrey[57] has measured quantitatively the tactic placements in the polymer. Ohnishi and Nukada have calculated the various coupling constants for isotactic[58] and syndiotactic[59] polypropylenes.

Polyethers

Atactic and isotactic polypropylene oxides are reported[60] to give slightly different spectra, a doublet at τ 8·87 and a complex $ABCX_3$ resonance centred around 6·55 τ. The pattern is simplified to an *ABC* system by double irradiation when the sample is decoupled from the methyl protons. The decoupled spectra of the isotactic and atactic samples are different as regards to the line width and resolution.

The proportions of oxyethylene and oxypropylene components in alkylene oxide polymers (polyethers) have been determined[61] from the intensity measurement of the methyl proton resonance in the NMR spectrum.

Polyaldehydes

NMR of polyacetaldehyde is interesting because the acetal linkages in the main chain prevents spin-spin splitting which arises in vinyl polymers. The side group can only interact with the single hydrogen of the monomeric unit and vice versa, which facilitates the location and interpretation of the spectra observed. The polymer has been analysed[62,63] in aromatic and aliphatic solvents both at 60 and 100 Mc/s. The CH protons appearing as quintet at about 5·30 τ are considered to be due to overlapping of isotactic and heterotactic triads. The polymer prepared with various catalysts such as $TiCl_4$, BF_3, $AlCl_3$, H_3PO_4, Υ-rays, etc., shows doublets corresponding to heterotactic and isotactic triads only although a very small shoulder corresponding to a syndiotactic triad was detected at 100 Mc/s.

Fluorine Containing Polymers

Fluorine (^{19}F) spectra, which in general are similar to the proton spectra, are comparatively simpler because of the substantially larger chemical shifts than those encountered with protons and choice of more common solvents, since the proton resonance does not interfere with the fluorine resonance. The fluorine shielding values are more sensitive to choice of solvents than proton shielding values. For this region, the scale[64] for fluorine chemical shifts specifies $CFCl_3$ as both reference and solvent. Whenever the polymer is not soluble in $CFCl_3$, it is used as a reference only. Most of the fluorine spectra are currently reported at 56·4 Mc/s. which corresponds to the field at 14,000 gauss.

The NMR spectrum of polytrifluorochloroethylene[65] consists of two doublets having unequal components. Those at lower field correspond to CF_2 units whereas those at higher are due to the CFCl units. In the CF_2 doublet, one component is half as intense as the other. On comparison with the spectrum of model compounds, the less intense peak of the CF_2 group is assigned to the CF_2 groups between monomer units in isotactic dyads whereas the stronger one represents CF_2 groups between monomer units in syndiotactic dyads.

Polytrifluoroethylene has also been examined[66] and the effect of progressively substituting a hydrogen by fluorine or other electronegative groups on the

fluorine resonance has been discussed. This has led to the detection of the presence of head to head and tail to tail structures in polyvinylidene fluoride.

The spectra of polyvinyl fluoride and polyvinylidene fluoride have been discussed in detail by Wilson III[67]. In polyvinyl fluoride, the head to head fractions have been determined from the NMR spectrum after decoupling from the CH_2 resonance. In polyvinylidene fluoride (PVDF), the fractions of head to head and tail to tail units have been determined after confirming their resonance from the NMR spectrum of a copolymer of ethylene and tetrafluoroethylene (1:1). The different peaks have been identified with specific local chain structures whose probabilities have been calculated from the peak intensities. These indicate that PVDF predominantly consists of head to tail units with only 5-6 per cent as head to head units.

The composition of tetrafluoroethylene-hexafluoropropylene copolymer has been determined[68] from the CF_3, CF_2 (next to CF_3), CF_2 and CF resonances which are in order of increasing field. The NMR spectrum of vinylidene fluoride-hexafluoropropylene copolymer[69] shows that certain modes of addition of monomers to the growing chain were highly preferred and that there was little tendency for homopolymerization and that there was no branching.

Copolymers

The NMR spectra of styrene-co-methylmethacrylate and α-methylstyrene-co-methylmethacrylate polymers reveal information regarding their composition and sequence distribution[70]. The copolymer (prepared with free radical and anionic initiators) compositions have been determined[70-74] from analyses of the intensities of the aromatic (or $C-CH_3$ protons in α-methylstyrene which appears at the highest field) and the methoxylic protons (of the CO_2CH_3 groups). The spectrum essentially consists of peaks in four areas: the phenyl group at 2·9-3·4 τ; the α-methyl protons of MMA units at 9·2-9·6 τ; the methoxy protons at 6·4-7·8 τ; and the chain CH_2 and CH protons at 8·2-8·5 τ. In the anionic initiated copolymer[74], the α-CH_3 protons of MMA units appear considerably downfield (~8·8 τ) partially overlapping in the region of the chain methylene and methin proton resonances. The phenyl protons of copolymers containing high mole per cent of styrene appear as two peaks corresponding to the *ortho* and *meta-para* protons. The methoxylic protons appear as three peaks. This has been attributed to the magnetic shielding of the adjacent styrene units and the stereochemical configuration of the flanking styrene units. Bovey[70] has assigned the observed multiplicity to the different triads (i.e. MMM, MMS and SMS; where M is methylmethacrylate and S is styrene). It is very difficult to account for the effect of the stereochemical configuration. The probabilities of the occurrence of these triads have been calculated. Harwood and Ritchey[72] have modified Bovey's assignments by considering pentads instead of triads.

The formation of block copolymers consisting of essentially isotactic blocks of styrene and MMA units, in the anionic initiated copolymerization[74], has been arrived at from the sharp singlet of the methoxy proton resonance appearing at 6·4 τ.

Similar observations have been made with α-methylstyrene-MMA copolymers[70,72] and styrene-methylacrylate copolymers[75].

The compositions of styrene-butadiene copolymers have been studied from analysing the spectra in terms of intensities of the $-CH=$ and aromatic protons for the butadiene and styrene units respectively[38]. When the styrene content was higher than 88 mole per cent, the phenyl protons appeared as two peaks.

The compositions of vinyl acetate copolymers[76], vinyl chloride-vinyl acetate[77], 1,1-diphenylethylene-methylacrylate[78], isobutylene-vinylidene chloride[79], ethylene-vinyl ester[80], ethylene-propylene[81] and styrene-propylene[82] copolymers have been determined from their NMR spectra.

The presence of head to head structures in vinylidene chloride sequences in copolymers of vinyl chloride and vinylidene chloride with various feed ratios have been detected by NMR[83,84].

Polyesters

The NMR studies on polyesters have provided valuable information regarding their composition, molecular weight from end group analysis and geometrical isomerism during polymerization.

The compositions of polyesters, particularly the unsaturated ones, have been identified and semi-quantitatively determined from the NMR analysis. Thus polyesters derived from isophthalic, phthalic, maleic, adipic, fumaric acids and ethylene and propylene glycols have been analysed by NMR[85]. The results agree fairly well with those determined by pyrolytic gas chromatography. Similarly, the composition in mixed polyesters derived from isophthalic and terephthalic acids and ethylene glycol containing varying amounts of isophthalic acid have been determined from their NMR spectra[86].

The molecular weight of polyesters have been determined from end group analysis. The method is based on differentiation of the CH or CH_2 groups attached to the end hydroxyl group from those attached to the ether or ester oxygen. The reported[87] error is less than 1 per cent.

The occurrence of isomerization during polyesterification of *cis-* and *trans-* 1,4-cyclohexanedicarboxylic acids and ethylene glycol has been detected by NMR[88]. The polyester was found to consist of *cis-* and *trans-* units in the ratio 2:3 no matter which isomer was taken as the starting material.

Summary

High resolution NMR spectroscopy of polymers reveal informations regarding polymer composition, stereochemical configuration, conformational preferences, etc. The present article describes its use in studies with vinyl polymers, polyolefins, polyethers, polyaldehydes, fluorine containing polymers, copolymers, polyesters, etc. The different aspects that can be studied are: tacticity and distribution of tactic sequences; the presence of head to tail, head to head, tail to tail arrangements of monomer units; composition, reactivity ratio and sequence distribution in copolymers; composition and molecular weight of polyesters; branching in polymers, etc.

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Some Novel Trends in High Polymer Research

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POLYMERS are now too familiar even to the common man in many household and industrial uses. To the scientists and technologists it has been fascinating to witness the phenomenal growth of this rather new field. The elementary processes which build high polymers, such as the almost classical bakelites, urea-formaldehydes, nylons, polystyrenes, perspex, SBR, polyethylene and so on or the more recent teflon, terylene, urethanes, polypropylene, high density polyethylene, etc., have now become too well known. The fundamental as well as applied aspects of these polymers are still under active study, but lately a good deal of researches are carried out which have some elements of novelty either in the monomer or in the process itself. These researches can be broadly classified into three thematic groups, i.e. (i) polymerization of unconventional monomers, (ii) newer polymers and copolymers, and (iii) newer initiators, and we present here a brief account of these latest developments.

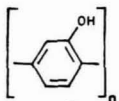
Unconventional Monomers

Benzene

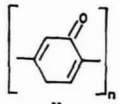
Of the unconventional monomers the rather novel is benzene whose polymerization has been discovered and is being studied for the last few years by Kovacic and coworkers[1-8]. The method is extremely simple, this being an oxidative cationic polymerization in nitrogen atmosphere with $AlCl_3$-$CuCl_2$ or with ferric chloride or with molybdenum pentachloride as initiator. The product is a rusty to dark, infusible and almost insoluble powder whose intrinsic viscosity after being made soluble by sulphonation lies between 0·2 and 0·3. It should not be too long before larger polymers of attractive properties will be obtained from this too familiar chemical.

Phenols

Ehlers[9] has reported the polymerization of phenol, catechol, resorcinol and hydroquinone by using ferric chloride-water as catalyst to produce products akin to natural polyphenols. It is also reported that the normal Kovacic catalyst system, viz. $AlCl_3$-$CuCl_2$, is ineffective with phenols and ferric chloride-water preferentially polymerizes the phenols even when benzene is present. The polymers are soluble and the polyphenols have a maximum average molecular weight of about 10000. Of the several feasible structures for the polymer the NMR evidence indicates predominantly the structure (I) with some quinonoid units (II).

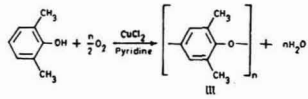


I



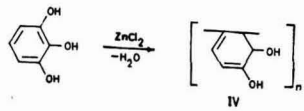
II

On the contrary, copper-pyridine catalysed oxidative polymerization of substituted phenols[10] in the presence of oxygen yields polyphenylene oxide (III), the reaction being initiated by the formation of phenoxy radicals.



III

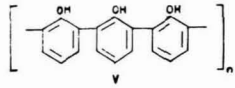
A totally different polymeric structure is obtained by the Russian chemists, Paushkinq *et al.*[11], by non-oxidative polymerization of polyhydric phenols to low molecular weight polyhydroxy phenylene (IV) using $ZnCl_2$-H_2O as catalyst. The polymers are



IV

partly soluble, the soluble fraction of molecular weight around 1840 with a softening point at 350°C. The polyconjugation is evidenced by quite a high electrical conductivity $\sigma_{50}=10^{-9}$ mho cm.$^{-1}$.

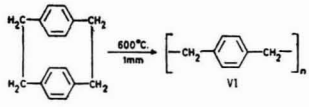
Another method to produce polyphenols and polynapthols has been developed by the Russian workers, where an organic halide (bromoform) is heated to 250-300°C. with phenols. The mechanism involved is the easy formation of radicals by halide decomposition which extracts hydrogen from phenols, naphthols, etc., and their polymers. The resulting radicals undergo polyrecombination. The molecular weight is quite low (490-1020) for the soluble fraction having the suggested structure (V).



V

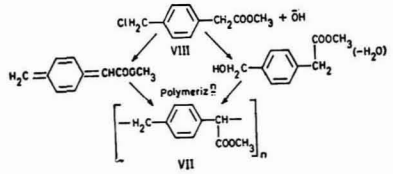
Other Aromatic Compounds

The preparation of poly-*p*-xylene (VI) by a one-step method has been reported by Gorham[12]. Di-*p*-xylylene under vacuum pyrolysis at 600°C. at 1 mm. pressure cleaves to form two *p*-xylelene molecules which polymerize in contact with a cooler surface to form a polymer. The polymer is a coherent, tough and clear film.



VI

Kadonaga *et al.*[13] reported another much simpler method of preparation of substituted poly-*p*-xylelene (VII). When *p*-chloromethyl phenylacetic esters



(VIII) and aqueous alkali are brought together, polymeric products are instantly formed by interphase reaction at room temperature. The reaction sequence may be α,α' elimination or an ordinary nucleophilic substitution followed by polymerization.

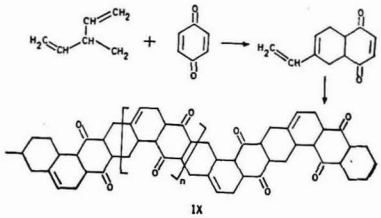
The successful polymerization of simple aromatic compounds, like nitrobenzene and aniline, has been achieved using metals and metal salts functioning as solid catalysts. The molecular weight is around 1500.

The researches described above are full of great promise, both technically and scientifically. Surprisingly, most of them can be carried out with readily available chemicals with simple equipments. These lines are, therefore, strongly commended to the Indian chemists who are looking for important lines of research amenable to study with our usual meagre laboratory facilities.

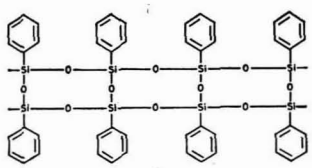
Newer Polymers and Copolymers

Spiro Polymers

Double-stranded polymers, such as the ladder polymers, have attracted interest because they have extremely high melting points due to restricted rotation. They have high degree of chemical and thermal stability and since two cleavages are required within a single ring to result in a drop in molecular weight. Houtz[14] postulated a partial ladder structure in the formation of 'black orlon' from polyacrylonitrile and the first polymer with complete ladder structure (IX) was reported by Bailey and Economy[15] by the reaction of 2-vinyl-1,3-butadiene with benzoquinone. The polymer was not very



much attractive because it was infusible and insoluble in all available solvents. Subsequently, other ladder polymers were prepared, e.g. polyphenylsilsesquioxane[16] (X).



There have been many other approaches to the synthesis of ladder polymers and they are quite well known for the last few years[17] (also Bailey, W. J. & Feinberg, B., unpublished work). On the other hand, 'spiro polymers' are new in the field. Although a number of inorganic polymers have been assigned the complete spiro structure[18-20], no spiro polymers containing only carbon, oxygen or nitrogen in the backbone have been reported. Bailey and Volpe[21] have reported the synthesis of a spiro polymer (XI) obtained by the condensation of cyclohexanedione and pentaerythritol (Table 1) in benzene solution with a trace of *p*-toluenesulphonic acid. This

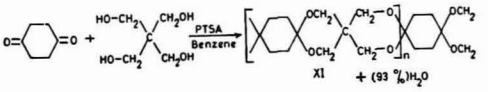
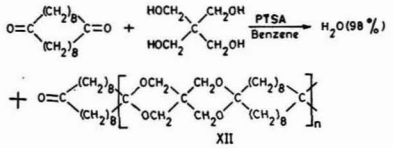


TABLE 1

Polymer from pentaerythritol	Intrinsic viscosity in hexafluoroisopropanol at 25°C.	Approx. mol. wt
1,4-Cyclohexanedione	0·049	10000
1,10-Cyclo-octadecanedione	0·092	30000
Mixture of 1,4-cyclohexanedione and 1,10-cyclo-octanedione	0·045	—

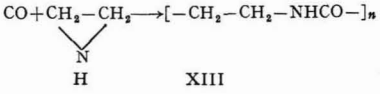
powder did not melt but began decomposing at 350°C. The polymer (XI) was insoluble in most common solvents for polymers. The introduction of a large ring increased the solubility of a ladder polymer. 1,10-Cyclo-octadecanedione and pentaerythritol were condensed to form polymer (XII). The polymer (XII)



did not melt but started decomposing at 300°C. In case of both the polymers (XI and XII), X-ray diffraction studies indicated high degree of crystallinity. Both the polymers are found soluble in hexafluoroisopropanol.

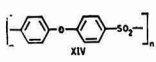
Polyamides

The synthesis of polyimines from the polymerization of aziridines by cationic catalyst has been known for some time[22]. Recently, the copolymerization of carbon monoxide with aziridines has been reported by Kagiya and Ichida[23] with the formation of polymer (XIII).



The copolymerization of carbon monoxide and aziridines takes place alternatively and produces crystalline poly-β-alanines. N-substituted aziridines also copolymerize with carbon monoxide to yield N-substituted poly-β-alanines.

The addition of olefins to these systems resulted in the production of terpolymer containing the units of $(-CH_2CH_2NHCO-)$, $(-CH_2CH_2CO-)$ and $(-CH_2-CH_2CH_2CH_2NHCO-)$ in the case of ethylene. Using various olefins such as propylene, isobutylene, pentene-1 dodecene-1 in place of ethylene, similar white powdery terpolymers containing applied olefin were obtained. Though CO and aziridines hardly polymerize with free radical initiators, the presence of a small amount of olefins remarkably produces crystalline polyamides which consists almost of poly-β-alanine structure. The polymers produced either by Υ-ray irradiation or by free radical initiator melt at a temperature around 300°C. Of other similar copolymers, diphenyl ether-sulphur dioxide copolymer (XIV) prepared by Cohen and Young[24] may be mentioned. The initiator used was Friedel-Craft in nature and the yield was 74-80 per cent and intrinsic viscosity 0·52.

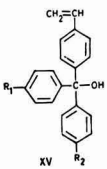


XIV

Stable Polyradicals

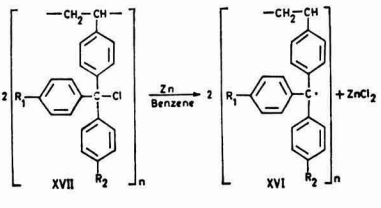
Low molecular radicals are of great significance as initiators in high polymer chemistry and some of them are quite well known. As yet, however, nearly nothing is known about polyradicals. Recently, the preparation of polyhydrazyls[25] and polyketyls[26] has been reported by Braun *et al.* More recently, the preparation of polytrityls[27] has been reported by the same authors.

Monomers having the general structure (XV) were polymerized via radical mechanism and converted to the corresponding poly-4-vinyl-trityl chloride with acetyl chloride in benzene solution. A direct polymerization of the poly-4-vinyl-trityl chloride by radical polymerization of the monomeric chloride was not possible.



XV

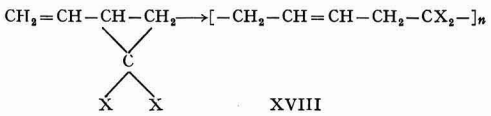
The polyradical (XVI) was obtained by treating the polytrityl chloride (XVII) with zinc in benzene under highly anhydrous condition in the presence of some alkali metal. The role of the alkali metal is to prevent the formation of the complex zinc acid by reacting with any traces of water. The number of radical centres per chain was around 100, i.e. every third or fourth carbon had a radical. The polyradicals react readily with oxygen and traces of water convert them to the corresponding polycations.



XVII XVI

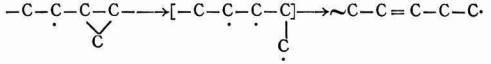
Polymerization of Vinyl Cyclopropanes

Polymerization of cyclic compounds, e.g. olefin oxide and sulphide, lactone, etc., is quite well known. Takahashi and Yamashita[28] reported a new extension — 1-5 type polymerization of vinyl cyclopropane (XVIII).

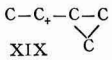


XVIII

The polymerization proceeds by opening both the double bond and the cyclopropane ring with free radical initiators. The cyclopropylcarbinyl radical rearranges itself before it reacts with the next monomer as shown below:



The polymer has high yield and a molecular weight around 1800; on the other hand, cationic polymerization through cyclopropylcarbinyl cation gives predominantly 1,2 structural unit that involves no rearrangement of the active end of propagation (XIX).

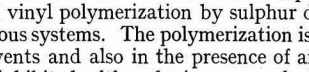


XIX

New Initiators

Polymerization Initiated by Sulphur Dioxide

The use of liquid sulphur dioxide as a co-monomer with alkanes, dienes or vinyl compounds to form polysulphones (XX) in the presence of a free radical



XX

initiator is known[29-31]. Recently, aqueous sulphur dioxide, i.e. sulphurous acid or its alkali metal salts, has been reported to initiate aqueous vinyl polymerization[32]. Ghosh and O'Driscoll[33] have reported initiation of vinyl polymerization by sulphur dioxide in non-aqueous systems. The polymerization is aided by basic solvents and also in the presence of air instead of being inhibited, although rigorous exclusion of air proves it unnecessary for the polymerization. The system is quite different from common free radical polymerization; it is neither free radical nor simply anionic in nature. Polymerization is supposed to be induced by some complex radical mechanism and is influenced by the structure of the monomer and the nature of the solvent used.

Three component initiators have been lately introduced. An example is the use of $Ni(PCl_3)_4+TiCl_4+AlCl_3$ (or $AlBr_3$) by Jenkins *et al.*[34] to effect hydrocarbon soluble *cis*-polymerization of butadiene. The combination of $Ni(PCl_3)_4$ and $TiCl_4$ is a very powerful initiator; the addition of $AlCl_3$ (or $AlBr_3$) makes it

rather controllable. Matsuda and Ishioroshi[35] reported polymerization initiated by SO_2+pyridine+carbon tetrachloride. No polymer was obtained when any of these three was missing from the system. Hydroquinone does not inhibit polymerization of methylmethacrylate or acrylonitrile but does inhibit in case of styrene or methylvinyl pyridine. It is proposed that sulphur dioxide behaves as an electron acceptor, the donor being pyridine. Other donors, e.g. quinoline, *o*-toludine and α-picoline, have also been successfully tried.

Charge Transfer Polymerization

A new type of system has lately been developed where the monomer acts as a donor and polymerization proceeds through its interaction with various organic electron acceptors. This type of process is known as charge transfer polymerization and has attracted extensive interest but has been exclusively limited with N-vinyl carbazole. Few other similar monomers have been successfully employed as donor monomers, e.g. N-vinyl carbazole, N-vinyl pyrrole, 4-vinyl pyridine, etc., the organic electron acceptors being tetracyanoethylene, *p*-chloranil, 2,5-dichloro-*p*-benzoquinone, tetranitromethane, dichlorodicyanobenzoquinone, etc. The field has received much attention lately from a number of schools[36,37].

Summary

Recent trends in high polymer research have been broadly classified into three thematic groups, viz. (i) polymerization of unconventional monomers, (ii) new polymers and copolymers, and (iii) new initiators. These have been discussed with special emphasis on some novel approaches.

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Synthetic Ion-exchange Membranes

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THE importance of ion-exchange membranes is evident from the increasing range of their applications. In an earlier review the position up to 1960-63 was surveyed[1]. The present review covers the advances in fundamental, applied and preparative aspects of the membranes reported during the period 1964-66. During this period various other reviews have appeared[2-18].

Fundamental investigations have been considered under the heads: permselective properties, membrane equilibria and potential, polarization, diffusion, conductivity, water transport, and porosity. The following topics are covered under the applied field: demineralization of water, analytical applications, applications other than water treatment, fuel cells, and preparative aspects.

Permselective Properties of Membranes

Anion-exchange membranes — Data on relative transfer rate of chloride and sulphate ions across a highly basic membrane[19] and a weakly basic membrane[20], permselectivity of various anionic radicals through commercial membranes[21], hydroxyl and chloride ion transport in mixed solutions[22] and during concentration of sea water[23] have been reported. In a mixed solution of sodium sulphate and hydroxide, the permselectivity of the hydroxyl ion has been found to be higher than that of the sulphate ion[24]. In contrast to the behaviour of a strong base membrane, a benzidine formaldehyde membrane exhibited greater selectivity for sulphate over chloride ion[25].

Cation-exchange membranes — When a cation-exchange resin was packed between cation- and anion-exchange membranes, easier permeation of barium than sodium ions through the cation membrane has been reported[26]. The variation in the composition of the membrane on selectivity has been studied[27]. The electrochemical properties of industrial cation-exchange membranes have been determined in different aqueous solutions at constant current and transport numbers have been related to conductivity[28]. The concept of a generalized mobility has been introduced in the study of transport phenomena in ion-exchange membranes[29] and transport properties and friction parameters of a system with incomplete dissociation have also been reported[30]. Permselectivity of oxalate ion through carboxylic membrane has been reported[31].

Anion and cation membranes — Data have been reported for different salt systems using a series of membranes[32]. Preferential transport in commercial membranes during electrodialysis with different salt solutions[33], specially of anions[34], has been studied. In a series of studies on the permeability of complex ions across ion-exchange membranes, the permeability of EDTA ion was observed to be maximum at *p*H 5-7 through anion-exchange membrane only[35]. However, tartaric acid permeability was observed to be minimum at *p*H 4-8 (ref. 36); the permeability of copper in tartrate, citrate or EDTA solutions showed that the order of permeability of complexing reagents was tartrate > citrate > EDTA[37]. Results of electrodialysis of sodium chloride and sodium acetate solutions with ion-exchange membranes and double membranes have shown the same trend towards transport phenomena[38].

Amphoteric membranes and liquid ion-exchange membranes — Amphoteric membranes prepared to contain both cation- and anion-exchange sites showed that transport number measurements from a mixed solution were greatly influenced by the ratio of cation to anion sites in the membrane[39]. Deviations from ideal permselectivity observed with concentration cells prepared using liquid ion-exchange membranes have been explained on the basis of solubility factors and water transport[40]. For a liquid membrane possessing high selectivity for anions, the sequence of selectivity corresponds to the Hofmeister series[41].

The need for gathering data on a wide variety of membranes for predicting permeation rates has been stressed by Rickles[42]. Kalman and Sipos[43] have experimentally verified a new mathematical expression derived for the permselectivity of ion selective membranes and this factor has been shown to depend only on the membrane potential, the concentration ratio of the solution and the temperature.

A mechanism accounting for the accumulation of alkali and acid in a five-compartment cell with two-cation and two-anion membrane has been proposed by Wood[44]. Sodium ion from the sodium chloride solution in the central third compartment migrates across the cation-exchange membrane into the adjoining second compartment wherein hydroxyl ions formed by dissociation of water in the electrode (cathode — first compartment) have migrated through the anion membrane. The hydrogen ions formed by the dissociation of water travel to the cathode and are discharged as hydrogen gas. The result is an accumulation of alkali in the second compartment. Similarly, chloride ions travel to the fourth compartment through the anion membrane and hydrogen ions from the dissociation of water of the electrode (anode — fifth compartment) migrate through the cation-exchange membrane into this chamber giving rise to acidity.

By subjecting cation- and anion-exchange membranes and bead form resin, immersed in an electrolyte solution, to an a.c. of approximately 500 ma./cm.^{2} it is reported that their electrical conductivity could be increased[45].

Membrane equilibria and potential — Donnan membrane equilibrium has been employed for determining charges on cations[46] and the influence of concentration of solutions of single salts and mixtures on membrane potentials of organic and inorganic membranes has been studied[47]. Thermal membrane potential as a function of the apparent ionic transport number for

cation and anion membranes has been evaluated[48]. Measurement of membrane potentials for a phenol-sulphonic-formaldehyde membrane yielded results agreeing with Scatchard's theory but not with those of Lakshminarayaniah and Subramanayan[49].

Kobatake and coworkers[50,51] derived an expression for membrane potential which corresponded to the limiting case in which the charge density fixed on the capillary wall was high and their results did not agree with the earlier theories of Teorell *et al.* which corresponded to the opposite limiting case where the fixed charge density was extremely low.

Equilibria and membrane potentials of two heterogeneous membranes have been studied and it was observed that the mobility ratio of counter-ions was almost equal in the membrane and in the external solution[52].

Anharmonic oscillations occurring during the determination of membrane potentials have been attributed to stirring[53]. A mathematical treatment of the properties of the steady states of a system separated by a membrane having mobile sites reveals differences from a system separated by a membrane with fixed sites. In the mobile site membrane, the current asymptotically approaches finite limiting values for high positive and negative voltages, while in the fixed site membrane the conductance approaches finite limiting values[54]. Results of test of the above theory have been reported[55]. For a uniform membrane with fixed changes an expression for membrane potential based on molecular theory has been derived and experimentally verified[56]. Bi-ionic potential and transport numbers of systems exhibiting bi-ionic specificity have been determined[57] and the data collected on an anion-exchange membrane have been explained on the basis of ion binding phenomena or the application of the Nernst or Nernst-Plank equations for the steady state[58].

Differences in bi-ionic potentials in a system after stirring and under conditions of flow have been attributed to shifts in the gradients from one phase to the other[59].

Polarization — Extensive studies have been reported on electrodialysis polarization[60-63]. The rectifying effects observed on a single permselective membrane[64] and on bipolar membranes[65,66] have been reported. The use of dipole membranes[67] and a weak base anion-exchange membrane[68] to reduce the polarization of conventional membranes has been reported. It has been observed that in the desalination of sea water it is necessary to taper the flow path in the dialysate compartment; in brackish water desalting, however, this tapering is not necessary. The differences in the two cases have been explained in terms of concentration polarization during electrodialysis[69]. A method using currentless probe electrodes has been selected for the determination of concentration polarization on ion-exchange membranes in narrow cells filled with spacer material[70]. Several other studies of importance from the point of view of practical applications have been reported[71-73].

Diffusion and conductivity — An equation representing the condition when diffusion occurs in the presence of a chemical reaction has been reported for a system where the exchange rate is very slow, as in a chelating resin[74]. The predominant effect of friction between the coion and the membrane on dialysis efficiency has been brought out for transport in charged membranes[75]. The diffusion potentials of osmotic and ion-exchange membranes have been compared[76] and an explicit approximate formula for diffusion potential derived for systems not in a condition of equilibrium[77].

The functional boundary layer thickness for ion-exchange membrane cells incorporating diffusion exchange and the influence of temperature on the rate of exchange have been reported[78]. Radiometric determination of diffusion flux across a cation-exchange membrane has revealed the interdependence of diffusion on the amount of ionogenic groups present in the membrane[79].

Electrical conductivity and some electrochemical properties of membranes in different media have been correlated to their resin constituents[80-82]. The resistance of ion-exchange membranes during electrodialysis has been measured[83]. The influence of voids in the cation-exchange membranes on their electrical conductivity in acid media and the possible utilization of conductivity data for determining the percentage of voids have been reported[84].

Water transport and porosity — The detrimental effect of water transport on electrodialysis has been studied[85]. Transport of water through commercial membranes under hydraulic pressure has been studied in a dilatometer[86] and an improved apparatus for this purpose has been described[87]. An equation has been derived which enables the determination of water transport across ion-exchange membranes; the equation relates the transport rate to the concentration difference across the membrane and membrane thickness[88]. The quantity of water transport during desalting sodium chloride solution under different experimental conditions has been studied[89] and the influence of ionic radii of cations and anions on the same during desalting has been brought out[90].

Removal of the binder in a membrane by extraction has been observed to influence its rate of exchange in terms of porosity and the rate of sorption has been found to be governed by porosity[91]. Polystyrene sulphonic acid membranes were synthesized with varying degrees of porosity by changing the alcohol group in the ester monomer and it was observed that increased permeability resulted by increasing the size of the alcohol group[92,93].

Miscellaneous studies — A membrane specially prepared to have a gradient of electric charge (hence asymmetrically charged) has been studied as a model for chemical processes displayed by biological membranes[94]. The membrane potentials of charged ion-exchange membranes have been observed to change on clamping the system in different positions; this effect has been termed 'geoelectric effect'[95]. Power consumption is found to fall if electrodialysis is conducted at higher temperatures[96,97]. Studies have been reported on electron-exchange membranes[98] and parloidon membranes[99,100]. Ionic mobility by the pile method[101] and conditions for concentrating electrolyte solutions[102] have been investigated. Theoretical studies have been conducted on thermo-osmosis in charged membranes[103] and material transport through membranes[104]. The possibilities of recovering water from urine by membrane permeation

process have been investigated[105-107]; the results are of interest for space research. A hydrogen-oxygen fuel cell capable of supplying both electric current and water for dilution in multistage electrodialysis has been developed[108].

Analytical Applications

Electrodes — The properties of different membranes have been correlated with their electrode behaviour[109-111]. Homogeneous membranes have been used as indicators in acid base and potentiometric titrations[112] and for non-aqueous potentiometric titration in acetic acid[113]. The concentration of lithium chloride in amyl alcohol has been determined with a membrane electrode[114]; calcium forms of electrodes have been used as indicators for controlled processing of calcium chloride from calcium carbonate[115]. A liquid ion exchanger in direct or indirect contact with an electrode composed of platinum wire or Ag-AgCl has been used for determining the selectivity of alkali earth ions[116]. Silicone rubber membranes for selective determination of anion activities have been reported[117,118]. The applications of specific ion electrodes have been reviewed[119].

The separation, extraction and concentration of constituents of mixtures based on exchange equilibria through membranes has been reported[120]. The use of membranes as battery separators[121,122], as gauges for determining moisture in gases[123] and for determining salt and alkali content in various solutions[124-126] has been investigated.

Improvements in methods and instruments — Improved methods for determining the characteristics of ion-exchange membranes[127], including water permeability[128], have been reported. A method has been described for determining the changes in membranes (structural, fouling and scaling) under actual service conditions[129].

Polarographic techniques have been used for diffusion studies in membranes[130]. A new method has been reported for conductivity determination[131]. A cell for measuring electrical resistance at constant flow rate of electrolyte solution has been designed[132]. An apparatus for purification of fruit juices and wine materials has been described[133].

In a process of electrodialysis described, there is no net evolution of decomposition products in the solvent; the energy used in the evolution is mostly regenerated or recovered by a subsequent electrochemical reaction, thus resulting in no waste by-product[134]. A method and apparatus are described for the reduction and oxidation of liquids and of ionic and non-ionic constituents of liquids[135]. A number of devices for improving the efficiency of the electrodialysis process have been described[136-140].

Water treatment — Improvements in cell design and modifications in the water treatment process as a whole have been attempted with the object of increasing the overall efficiency of the process and making it economically attractive.

Some novel innovations introduced in the method for electrodialytic demineralization of aqueous solutions are: recirculation of solutions in a multicell assembly with series flow[141], use of suspension of an oxidizable metal flowing from the anode zone to the cathode to reform the metal for reuse[142] and the use of a non-conducting tank containing a strong anode surrounded by a double spiral membrane[143]. In another apparatus, which helps overcome the polarization effect, spirally spaced electrodes, between which liquid passage is formed by two membranes of either sign, are used with spacers having ribbed protrusions[144]. For ease of assembling and dismantling, holes and conduits are integrated on the membranes[145]. To enable membranes to move and deform rather than rupture at water pressure in the range 60-100 lb./sq. in., a device wherein the membranes project out of the supporting gasket has been designed[146]. Specially designed gaskets have also been reported[147,148]. Frames with suitable openings are described to remove insoluble solids in electrodialysis cells[149]. A portable unit has been constructed which enables the determination of process variables involved in the technique[150].

In an examination of the electrodialysis process based on two commercial installations, Solt has considered the design features in terms of the following: thermodynamic energy necessary to effect the theoretical separation of salt from salt water, losses in the electrical resistance due to passage of the ions through a barrier and overcoming various shortcomings of the membranes and apparatus such as lack of selectivity of membranes and electrical leakage between cells[151]. The design features of a plant and the problems encountered during installation and start up have been discussed[152]. Relative cost data for different plants have been reported by Friedlander and Rickles[153].

For partial salt removal from moderately saline waters, multiple ion-exchange membrane electrodialysis has been found suitable[154] and competitive if salt concentration is 5000 p.p.m. or less[155]. The water obtained by the technique is hygienically satisfactory[156]. A demineralization apparatus containing the application of ion-exchange resins and electrodialysis has been reported[157].

Applications other than Water Treatment

Preparation of chemicals — Preparation of tetramethyl ammonium hydroxide from tetramethyl ammonium iodide[158], 20 per cent sodium sulphite solution from its 1 per cent solution[159], concentration of fluoborate[160], concentration of fluosilicic acid[161], and production of pure acids and bases from their salts[162] are among the applications of ion-exchange membranes reported. Magnesium hydroxide has been obtained as a byproduct in the concentration of sea water[163]. Electrolytic concentration of mixed solution of chromium sulphate and sulphuric acid[164] and selective concentration factor for magnesium to hydrogen ion[165] have been studied.

Purification — The influence of polarization on the desalting of glucose and glycerol solutions has been studied[166]. Fractional separation of the components of spent sulphite liquor using ion-exchange membranes has been achieved[167-169]. In a study of the separation of acetic acid from a mixture of acids it has been observed that at increasing concentration of acetic acid the losses are smaller and depend on the current density used[170]. Highly ionized inorganic and organic acids have been separated from weaker acid by dialysis using ion-exchange membranes[171].

Membranes have been used for the purification of ω amino enanthic acid[172], methanol and ethanol[173], milk, whey, sugar, juices, paint emulsions, sewage[174], the separation of solvent from an ionic solution[175], cleaning of paintings[176] and purification of hydrochloric acid[177].

Deionization of polar liquids — Acetone and other solvents have been deionized under freon atmosphere[178]. Exhaustive studies on electrodialysis of polar solvents have revealed the influence of selectivity and conductivity of the membranes on the quality of the treated solution obtained[179]. Efficient dehydration and ion-exchange techniques have been made use of in the deionization of strongly polar liquids[180].

Amino acids — Group separation of amino acids[181] using ion-exchange membranes has been studied. The rates of transfer of glycine and methionine through membranes have been determined[182], and their minimum transfer rates were observed at the isoelectric point of each amino acid and at a current density slightly exceeding the limiting value for concentration polarization.

Fuel cells — Organic and inorganic ion-exchange membranes have been used in the construction of fuel cells.

Fundamental aspects relating to power losses due to cell resistance and membrane drying up[183], electrical resistance of anion-exchange membranes[184], polarization characteristics[185] and contribution of the membrane resistance to the internal resistance of the cell[186] have been investigated.

The preparation and use of gaseous fuel cells[187], batteries with antipolar and anion-exchange membranes[188,189], combination electrolytic fuel cells with bipolar electrodes[190] have been reported.

Membranes have been used as solid electrolytes[191] and conducting media in dual membrane fuel cells[192].

A critical review of the present position regarding fuel cells indicates that the anticipated performance is not obtained due to engineering difficulties involved in the removal of product water from the cells[193]. A reversible electrodialysis technique for the removal of water from oxygen-hydrogen fuel cells has been described[194]. An apparatus has also been described for recovering water formed in fuel cells[195]. Caplan has shown that the efficiency of energy conversion in desalination processes and fuel cells depends on the degree of coupling of the flows in them. The author has described methods for determining the degree of coupling and hence the maximum efficiency of these systems. For membrane processes, since neither the transport number nor the conductivity is involved in the degree of coupling, the author suggests that uncharged membranes may offer advantages over charged membranes[196].

Preparative Aspects

Membranes based on polyethylene — Commercially available polyethylene of different densities appears to be the choice for the synthesis of membranes. It has been used widely as a binder for heterogeneous membranes and as the base for irradiation to prepare homogeneous membranes. Impregnation of polythene films with styrene, divinyl-benzene and catalyst at controlled temperature and subsequent sulphonation yielded membranes with cation-exchange property[197]. Swelling the polythene film and the reaction mixture in an inert solvent prior to polymerization is reported to minimize loss of electrical properties[198]. Sorption of styrene by low and high density polyethylene films was found to depend on temperature and time and the membranes prepared from low density polythene underwent deformation during the polymerization step[199]. Using high energy radiations, different monomers have been graft polymerized on polyethylene films of different densities and subsequent treatment has yielded cation- or anion-exchange membranes. The low levels of irradiation produced long-lived free radicals that could initiate copolymerization and crosslinking with the added monomers. Good exchange capacity and improved physical properties of the membranes have been reported[200-209].

The use of polyethylene of different grades with preformed ion-exchange resins and/or compositions capable of yielding ion-exchange resins and the influence of different reinforcing agents have been investigated. It was generally observed that increase in mechanical properties introduced by reinforcing agents lowers the electrochemical properties of the heterogeneous membranes[210-213].

Membranes based on polystyrene and its derivatives — Homogeneous membranes have been prepared from the condensation product of polystyrene sulphonic acid and polyvinyl alcohol[214,215]. Such membranes have also been obtained by heating styrene in the presence of other monomers[216] and by graft copolymerization[217]. Prior to polymerization if the films are immersed in a polymerizable monomeric or comonomeric liquid for sufficient time to allow penetration of the liquid into the film, then the resulting polymerized product is shown to have improved physical properties[218].

By polymerizing and laminating on suitable inert materials heterogeneous types of membranes have been prepared[219-221]. Thermoplastic sheets containing different proportions of polystyrene have been reacted with formalin and reagents capable of yielding ion-exchange property[222].

Membranes based on polyvinyl alcohol — Homogeneous membranes have been obtained from the reaction product of polystyrene sulphonic acid[214,215] with alkali saturated crosslinked polyvinyl alcohols[223].

Polyvinyl alcohol and different ion-exchange resins in the ratios 2:1, 1:1 and 1:2 have been used for the preparation of diaphragms[224]. Paste method has been adopted for continuous coating on film surface for membrane preparation[225].

Membranes based on polyvinyl chloride — Methods involving heating followed by chemical treatment for preparing homogeneous anion-exchange membranes have been reported[226]. Increase in crystallinity has been obtained by styrene impregnation or sulphonation[227].

Heterogeneous membranes have been prepared by coating PVC fabric with a resin-forming composition[228]. Along with a polymerizable monomer composition, PVC powder has been used and application of mixture to surface of cloth followed by heating has resulted in suitable membranes[229]. PVC has been used as a binder for preparing membranes

with synthetic ion-exchange resins in fine powder form[230].

Miscellaneous

Membranes have been obtained by allowing the reaction products of phenol and formaldehyde with different amines[231,232] to set on glass plate and by coating the reaction product of phenol sulphonic acid and formalin on orlon cloth[233]. Condensates of polyhydroxy compounds and polyamines have been cast on supporting fabrics[234] and polycarbonates containing ammonium groups have been coated on glass cloth for obtaining anion-exchange films[235].

Ion-exchange membranes have also been obtained by treatment of polyvinylidene fluoride film[236] and grafting a suitable monomer on polytetrafluoroethylene[237].

Membranes have been obtained from the copolymer of butadiene with 2-methyl 5-vinyl pyridine[238], styrene-butadiene copolymer membranes with phosphorous halide[239] and synthetic rubber latex[240].

Moulding techniques for obtaining membranes from various compositions have been reported[241-243].

Inorganic membranes deposited on glass fibre and polythene as inert support have been reported[244]. Colloidal metals, such as silver, platinum, gold, nickel or copper have been deposited on a polymeric base, such as cellophane, cotton cloth, wood pulp, etc., and then immersed in compositions yielding ion-exchange properties by grafting technique[245]. Carboxylic membranes based on PTFE[246] and styrene maleic anhydride[247] have been reported. A surface active treatment of the resin before mixing it with the binder has been reported[248].

Summary

Electrodialysis using synthetic ion-exchange membranes has proved to be a versatile technique. Besides its major application in the field of water desalination, the technique can be advantageously adopted for other applications as indicated above.

The necessity for improving both the membrane properties and the design of the electrodialysis apparatus to make the process economically attractive and operationally efficient has resulted in a wide range of investigations all over the world. The growing number of scientific contributions in this field is an index of this activity.

Newer combinations of reaction products to yield membranes with superior electrochemical properties are under investigation. With suitable membranes the designing of the apparatus has to be carefully carried out to obtain the maximum efficiency of operation based on membrane properties.

In the United States of America this technique is currently under study along with others for gathering comparative cost data to obtain fresh water from saline sources. This subject is of topical interest to India and developmental work for the preparation of suitable membranes and setting up of electrodialysis units with indigenous components is in progress.

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Biosynthesis of Deoxyribonucleotides*

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THE essential requirements for the *in vitro* biosynthesis of DNA are: (i) the DNA-template; (ii) a divalent cation, Mg^{2+}; (iii) the specific enzyme, DNA-polymerase; and (iv) the four deoxyribonucleoside triphosphates (dATP, dTTP, dGTP and dCTP). Following Kornberg's[1] demonstration that the triphosphates are the substrates for the polymerizing enzyme, considerable amount of work has been done to elucidate the enzymatic steps leading to the biosynthesis of deoxyribonucleoside triphosphates. These are formed from smaller molecular weight precursors inside the cell which are also necessary for the synthesis of cell constituents other than DNA. Of these precursors, biosynthesis of deoxyribose requires special mention because this sugar moiety distinguishes the two types of nucleic acids, the ribonucleic acid (RNA) and the deoxyribonucleic acid (DNA). In this review enzymatic evidence is presented for the origin of deoxyribonucleotides and their phosphorylated derivatives in considerably purified systems.

Biosynthesis of Deoxyribose

Racker[2] in 1952 demonstrated that deoxyribose arises by a condensation reaction between 3-phosphoglyceric acid and acetaldehyde catalysed by the enzyme, deoxyriboaldolase from *Escherichia coli*. The product of the reaction, deoxyribose-5-phosphate, could then be converted to deoxyribonucleoside through the sequential activity of the two enzymes, phosphodeoxyribomutase[3] and nucleoside phosphorylase[4], according to the following scheme:

$$\text{Glyceraldehyde-3-P} + \text{acetaldehyde} \overset{\text{aldolase}}{\rightleftharpoons} \text{deoxyribose-5-P}$$

$$\text{Deoxyribose-5-P} \overset{\text{mutase}}{\rightleftharpoons} \text{deoxyribose-1-P}$$

$$\text{Deoxyribose-1-P} + \text{base} \overset{\text{phosphorylase}}{\rightleftharpoons} \text{deoxyribonucleoside} + \text{phosphate}$$

The function of deoxyriboaldolase has not been definitely established, but the equilibrium of the aldolase reaction suggests that this constitutes the pathway for deoxyribose catabolism. However, the recent experiments of Groth and Jiang[5] with regenerating rat liver slices and tumour cells point to a role for aldolase in the biosynthesis of deoxyribonucleotides. McNutt[6] in the same year reported the presence of another enzyme, trans-N-glycosidase, which could catalyse the transfer of the deoxyribosyl group from one purine or pyrimidine to another. This enzymatic reaction has, however, not received further attention.

*The following abbreviations have been used in this article: DNA, deoxyribonucleic acid; RNA, ribonucleic acid; AMP, adenosine monophosphate; ADP, adenosine diphosphate; ATP, adenosine triphosphate; CMP, cytidine monophosphate; CDP, cytidine diphosphate; CTP, cytidine triphosphate; GMP, guanosine monophosphate; GDP, guanosine diphosphate; GTP, guanosine triphosphate; TMP, thymidine monophosphate; TDP, thymidine diphosphate; TTP, thymidine triphosphate; HMP, hydroxymethylcytidine monophosphate; HDP, hydroxymethylcytidine diphosphate; HTP, hydroxymethylcytidine triphosphate; UMP, uridine monophosphate; UDP, uridine diphosphate; UTP, uridine triphosphate; dAMP, deoxyadenosine monophosphate; dADP, deoxyadenosine diphosphate; dATP, deoxyadenosine triphosphate; NADP, triphosphopyridine; DHFA, dihydrofolic acid; THFA, tetrahydrofolic acid; FdUMP, fluorodeoxyuridine monophosphate; EDTA, ethylenediamine tetraacetate; Tris, tris (hydroxymethyl) aminomethane; and DBCC, dimethylbenzimidazolylcobamide.

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It has been known for quite some time that the deoxyribose in DNA arises by a direct reduction of the ribose of nucleoside or nucleotide. Brachet[7] used this concept to explain the reciprocal changes in the amounts of RNA and DNA which he observed during the early stages of the development of sea urchin eggs. Hammarsten *et al.*[8] injected ^{15}N-cytidine and isolated ^{15}N-deoxycytidine from rat liver DNA. It was then known that the free bases were not utilized by the rat; it was, therefore, concluded that the conversion occurred without prior cleavage of the glycosidic bond. The proof for such a reaction was provided by the studies of Rose and Schweigert[9] who injected uniformly labelled ^{14}C-cytidine into rat and found the ratio of isotope in the base and deoxyribose in the DNA deoxycytidine commensurate with the ratio of isotope in the base and ribose of the injected nucleoside. Similar results were also obtained with mammalian[10-13], avian[14-16] and microbial[17-21] systems.

The substrate level at which the conversion of ribose to deoxyribose moiety occurs was studied in greater detail by Reichard and his colleagues. They demonstrated that the reduction of ribonucleotide to deoxyribonucleotide occurred at the diphosphate stage by kinetic studies and isotope dilution experiments[22]. The conversion of CDP to dCDP was also shown to occur with a partially purified enzyme preparation[23]. Since then the biosynthesis of deoxyribonucleotides in *Esch. coli* has been extensively studied in purified enzyme preparations designated arbitrarily as B_1 and B_2. They show specific requirement for ATP, Mg^{2+} and reduced lipoic acid which acts as a reductant[24]. The enzyme fractions B_1 and B_2 have now been separated[25] and are essentially free from contaminating pyrophosphatase and kinase activities. Both purine[26] and pyrimidine[27] ribonucleotides are converted to their corresponding deoxyribonucleotides by this same enzyme system. The maximal velocity with all the four substrates (CDP, UDP, GDP, ADP) is of the same magnitude under the optimal conditions[28].

Reichard and coworkers isolated two more proteins, designated them as thioredoxin and thioreductase, which they found to be constituents of the reductase system. Thioredoxin[29] in its reduced form acts as the physiological reductant and completely replaces lipoic acid as the hydrogen donor for the conversion of ribonucleotides to deoxyribonucleotides. It has a molecular weight of 12000 and consists of a single polypeptide chain with serine as the N-terminal amino acid and cystine as one of the residues. It was apparently homogeneous on agarose when subjected to microelectrophoresis. Thioreductase[30] is a flavoprotein which catalyses the reduction of the disulphide bridge of thioredoxin to sulphydryl bonds in the presence of reduced NADP. The enzyme cannot affect the reduction of lipoic acid, glutathione and insulin, but in the presence of catalytic amounts of thioredoxin, all the three compounds are reduced. The enzyme, therefore, exhibits a high degree of specificity for thioredoxin. The data presented in Table 1 demonstrate the requirement of the four proteins and other cofactors for the reductase system. With CDP as the substrate, the overall reaction of the ribonucleosidediphosphate reductase at the physiological level can be represented[29] as in Fig. 1. Moore and Reichard[31] have shown that the requirement of reduced lipoate in Novikoff hepatoma system could be replaced by chemically reduced thioredoxin or by thioredoxin-thioreductase system in the presence of reduced NADP. The generality of this reaction remains yet to be demonstrated.

In contrast to the system in *Esch. coli*, a new reductase was reported in *Lactobacillus leichmannii* which has a specific requirement of cyanocobalamin or DBCC in addition to ATP, Mg^{2+} and dihydrolipoic acid[32]. This observation was confirmed in subsequent studies[33,34], and it was further shown by Beck and Hardy[35] that in crude sonic extracts the enzyme is active in the presence of both cyanocobalamin and DBCC, but only the latter supports the reductase activity in extracts freed of ribosomes. Blakley[36] observed that the bacterial extracts catalysed the reduction of CMP, CDP and CTP to the corresponding deoxy compounds although CDP and CTP were optimal substrates. On purification[37], enzyme specificity to substrates

TABLE 1 — REQUIREMENT OF THE RIBONUCLEOSIDEDIPHOSPHATE REDUCTASE SYSTEM*

Experimental condition	dCDP formed mμmoles
Complete system†	7·50
Omit enzyme B_1	0·06
Omit enzyme B_2	0·06
Omit thioredoxin	0·48
Omit thioredoxin reductase	2·10
Omit ATP	1·80
Omit CDP, add CTP	0·56
Omit CDP, add CMP	0·19

*From Holmgren *et al.*[25].

†The complete reaction mixture contained in a final volume of 0·13 ml.: ATP, 0·2 μmole; $MgCl_2$, 2 μmoles; Tris-HCl buffer (*p*H 8·0), 0·5 μmole; reduced NADP, 0·06 μmole; EDTA, 0·1 μmole; H^3-CDP, 0·05-0·1 μmole; dithioerythrol from enzyme B_1), 0·05-1 μmole; thioredoxin, 2 μg.; thioredoxin reductase, 3 μg.; and enzymes B_1, 15 μg. and B_2, 9 μg.

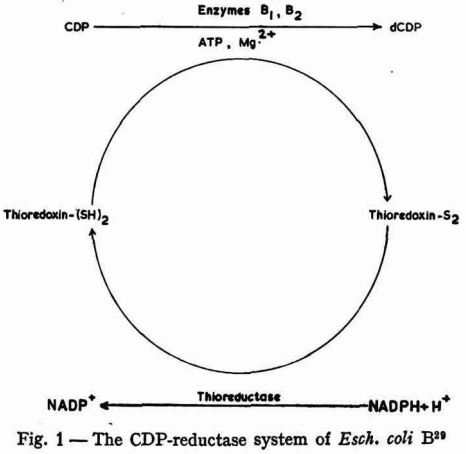

Fig. 1 — The CDP-reductase system of *Esch. coli* B[29]

altered; triphosphates were now acted on 5-10 times faster than the diphosphates and the rates with the monophosphates were the lowest. All the triphosphates, GTP, ATP, CTP and UTP, were reduced; relative specific activities being 100, 14, 10 and 3. This is in accordance with the results of Abrams[38] who also showed triphosphates to be the preferred substrates. It was observed that with partially purified enzyme the requirement for ATP and Mg^{2+} was eliminated. Blakley explained that the requirement of ATP and Mg^{2+} in crude bacterial extracts was connected with the phosphorylation of mono and diphosphates to the triphosphates[37]. Goulian and Beck[39] have isolated the reductase from *L. leichmannii* in a high state of purity; a single band is observed in the ultracentrifuge and on cellulose acetate electrophoresis, but two bands appear on polyacrylamide gel electrophoresis at *p*H 9·5. The molecular weight, estimated from sedimentation coefficient of 5·8S, is 110000. The requirement of the reaction is given in Table 2. The name ribonucleosidetriphosphate reductase was suggested by Blakley *et al.*[37], but it is only with the highly purified enzyme[39] that the products of the reaction were unequivocally identified by two-dimensional thin layer chromatography to be the corresponding triphosphates.

TABLE 2 — REQUIREMENT OF THE RIBONUCLEOSIDETRIPHOSPHATE REDUCTASE SYSTEM*

Incubation mixture	dCTP formed mμmoles
EXPERIMENT 1	
Complete system†	4·65
Minus enzyme	0·06
Minus DBC-coenzyme	0·02
Minus dihydrolipoic acid	0·00
Minus ATP	0·12
Minus Mg^{2+}	2·71
Minus Mg^{2+} plus Mn^{2+}	4·54
Minus Mg^{2+} plus Ca^{2+}	3·52
Minus DBC-coenzyme plus BC-coenzyme	2·53
Minus DBC-coenzyme plus methyl-cobalamin	0·03
Minus DBC-coenzyme plus hydroxy-cobalamin	0·00
Minus DBC-coenzyme plus cyano-cobalamin	0·02
Minus dihydrolipoic acid plus reduced NADP	0·05
Minus dihydrolipoic acid plus reduced NAD	0·05
EXPERIMENT 2	
Complete system	5·77
Minus ATP plus dATP	7·43
Minus ATP plus dTTP	0·71
Minus ATP plus GTP	0·35
Minus ATP plus UTP	0·30
EXPERIMENT 3	
Complete system	7·44
Minus Mg^{2+}	3·85
Minus ATP	0·15
Minus Mg^{2+} minus ATP	1·77
Minus Mg^{2+} minus DBC-coenzyme	0·03
Minus Mg^{2+} minus dihydrolipoic acid	0·04
Minus Mg^{2+} minus ATP plus dATP	0·80

*From Goulian and Beck[39].

†The complete system contained in a volume of 200 μlitres: CTP-2C^{14}, 52 mμmoles (10-20 mμC); DBC-coenzyme, 0·08 mμmole; dihydrolipoic acid, 600 mμmoles; ATP, 160 mμmoles; $MgCl_2$, 400 mμmoles; Tris-chloride (*p*H 7·5), 1250 mμmoles; and enzyme, 0·64 μg. of hydroxylapatite fraction.

As reported above for Novikoff hepatoma reductase system, chemically reduced *Esch. coli* thioredoxin or thioredoxin-thioreductase in the presence of reduced NADP can also replace dihydrolipoic acid as the hydrogen donor in cobamide-dependent reductase of *L. leichmannii*[40]. Orr and Vitols[41] have isolated thioredoxin and thioreductase from *L. leichmannii* which show that they are also normal components of cobamide-dependent reductase. Whether the two proteins are similar to those of *Esch. coli* must await further purification.

Studies on the effect of various ribo- and deoxyribonucleoside triphosphates on the ribonucleosidediphosphate and ribonucleosidetriphosphate reductase systems have revealed that they act as allosteric effectors. The concept of allosteric transition proposed by Monod and coworkers[42] defines an allosteric effector as one which combines with an enzyme molecule at a site other than that of the substrate resulting in a change in molecular conformation. The effectors interact with the enzyme(s) thereby yielding a conformation which either stimulates or inhibits the reduction of ribonucleotides to deoxyribonucleotides. As shown in Fig. 2, various effectors influence the ribonucleosidediphosphate reductase[28,43] and ribonucleosidetriphosphate reductase[39,40] enzyme systems in basically the same way. ATP and dGTP as effectors facilitate the reduction of either pyrimidine or purine ribonucleoside diphosphates and triphosphates to the corresponding deoxy compounds. Beck *et al.*[40] have pointed out that the real effector for *L. leichmannii* is dATP which is produced *in situ* by the reduction of ATP. dATP, however, yields with *Esch. coli* reductase an inactive state of the enzyme. dTTP is an effector *par excellence* which renders the allosteric transition ideally suited for the reduction of both purine and pyrimidine ribonucleoside diphosphates.

Little is known about the mechanism of the conversion of ribonucleotides to deoxyribonucleotides by the reductase systems of *Esch. coli* and *L. leichmannii*. The first study in this direction is that of Larsson[44] who has reported the transfer of

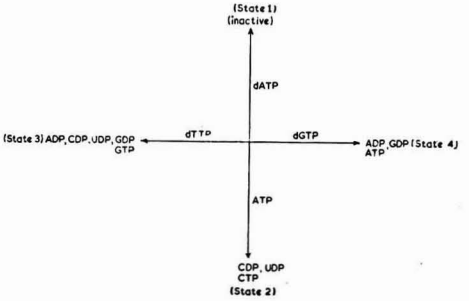

Fig. 2 — Schematic interpretation of allosteric effects in ribonucleotide reduction[28]

tritium from tritiated water to C-2′ position of dCDP by nucleosidediphosphate reductase. The reduction is affected by the transfer of hydride ion possibly through the sulphydryl reductant since it is known that hydrogen atoms exchange freely between sulphydryl groups and water[45]. Identical results were obtained when similar studies were performed with *L. leichmannii* reductase[46]. Proton magnetic resonance studies[47] have confirmed the transfer of tritium from H_2O-H^3 exclusively to 2′-pentose carbon of CTP. Beck *et al.*[48] carried out the reduction of CTP in the presence of 5′-DBCC-H^3; their results suggest the participation of the reduced form of coenzyme as an intermediate.

Biosynthesis of Thymidylic Acid

Considerable evidence is now available from isotope experiments to show that uracil, cytosine or one of their derivatives is the precursor for the thymine in DNA. The origin of 5-methyl group of thymine was traced to 1-C unit such as methyl of methionine, formaldehyde or β-carbon of serine. Crosbie[49], using a methionineless mutant of *Esch. coli*, showed that methionine could not be a methyl donor for thymine biosynthesis. As could be expected, Green and Cohen[50] also observed no uptake of $^{14}CH_3$-methionine into thymine of DNA, in a uracil-less mutant of *Esch. coli*. The available evidence pointed to the participation of THFA and formaldehyde or serine[51] in the methylation process. This view gained support through the studies of Friedkin and Kornberg[52] who showed that cell-free extracts of *Esch. coli* synthesized dTMP from dUMP in the presence of THFA, serine and ATP. The properties of the system are described in Table 3.

TABLE 3 — CONVERSION OF DEOXYURIDYLATE TO THYMIDINE TRIPHOSPHATE*

Experimental conditions	C.p.m. on Norit
EXPERIMENT 1	
Complete system†	1650
Zero time	24
Minus THFA	47
Minus serine	480
Minus ATP	51
Minus extract	212
Minus Mg^{2+}	30
Minus pyridoxal phosphate	1500
EXPERIMENT 2	
Complete system	
Plus serine plus THFA	1870
Minus serine plus THFA	470
Complete system	
Plus serine plus hydroxymethyl THFA	1650
Minus serine plus hydroxymethyl THFA	1210

*From Friedkin and Kornberg[52].

†The complete system (325 μlitres, *p*H 7·4) contained: deoxyuridine-5′-phosphate labelled with ^{32}P (2900 c.p.m.), 0·011 μmoles; ATP, 2·3 μmoles; $MgCl_2$, 5·7 μmoles; L-serine, 11·4 μmoles; THFA or N^{10}-hydroxymethyl THFA, 0·1 μmole; cysteine, 0·5 μmole; inorganic orthophosphate, 2·5 μmoles; pyridoxal phosphate, 0·1 μmole; Tris, 21 μmoles; thymidylate kinase; and an extract of *Esch. coli* treated with Dowex-1-formate.

The enzyme was named thymidylate synthetase[53] and it has been shown to affect the conversion of dUMP to dTMP in thymus[54,55], embryonic tissues[56], tumour tissues[57,58], bacteriophage-infected *Esch. coli*[53] and *Streptococcus faecalis*[59]. Blakley[60] states that deoxyuridine, rather than dUMP, is the preferred substrate for Dowex-1-treated soluble enzymes from thymus. This finding, however, has not been confirmed from other laboratories and appears less tenable.

Barner and Cohen[61] made an interesting observation that thymineless mutant, *Esch. coli* 15T⁻, on infection with the bacteriophage T_2 shows the ability to synthesize thymine. Thymidylate synthetase is not operative in the host organism[62] but is induced following viral infection. Approximately sevenfold increase in thymidylate synthetase activity was observed when wild strain, *Esch. coli* B, was infected with T_6 bacteriophage[63]. The induced enzyme required THFA and formaldehyde, with dUMP as the substrate, and was distinctly different from deoxycytidylate hydroxymethylase which was also simultaneously induced. The possibility that 5-hydroxymethyldeoxycytidylate may serve as an intermediate in the biosynthesis of dTMP was thereby excluded. Greenberg *et al.*[64] purified the host (*Esch. coli* B) and phage-induced (T_2) thymidylate synthetases on DEAE-cellulose columns and showed that they possess different properties. This evidence coupled with the inhibition studies of the enzyme with 5-FdUMP support the belief that the information for the synthesis of thymidylate synthetase induced following virus infection is contained in the phage DNA.

Mathews and Cohen[65] observed that when the enzyme was preincubated with FdUMP ($2\times10^{-7}M$) for 5 min. in the absence of substrate, enzymatic activity was irreversibly destroyed and could not be restored by addition of large amounts of the substrate. When dUMP and FdUMP were simultaneously incubated, the inhibition was of the competitive type. These workers carried out inhibition kinetics studies on thymidylate synthetase from *Esch. coli* B and from *Esch. coli* 15T⁻ infected with phage T_2. The data suggest that the two enzymes are similar. Further proof for the identity of the two enzymes would be a comparison of their properties after extensive purification.

THFA has apparently the role of a reducing agent in addition to being a carrier of 1-C unit in the methylation of dUMP to dTMP. Evidence in favour of this was provided by Friedkin[66] who obtained tritiated dTMP when he used THFA labelled with tritium. Wahba and Friedkin[67] have shown that a stoichiometric relation exists between the dTMP produced and THFA consumed in the methylation reaction. In other words, a mole of DHFA is produced for each mole of THFA oxidized (Table 4). Similar results were obtained by Humphreys and Greenberg[68]. The overall mechanism for the formation of dTMP from dUMP is represented in Fig. 3. The first step is the non-enzymatic condensation of formaldehyde with THFA giving N^5,N^{10}-methylene THFA[69,70]. A condensation between deoxyuridylate and N^5,N^{10}-methylene THFA in a subsequent step gives rise

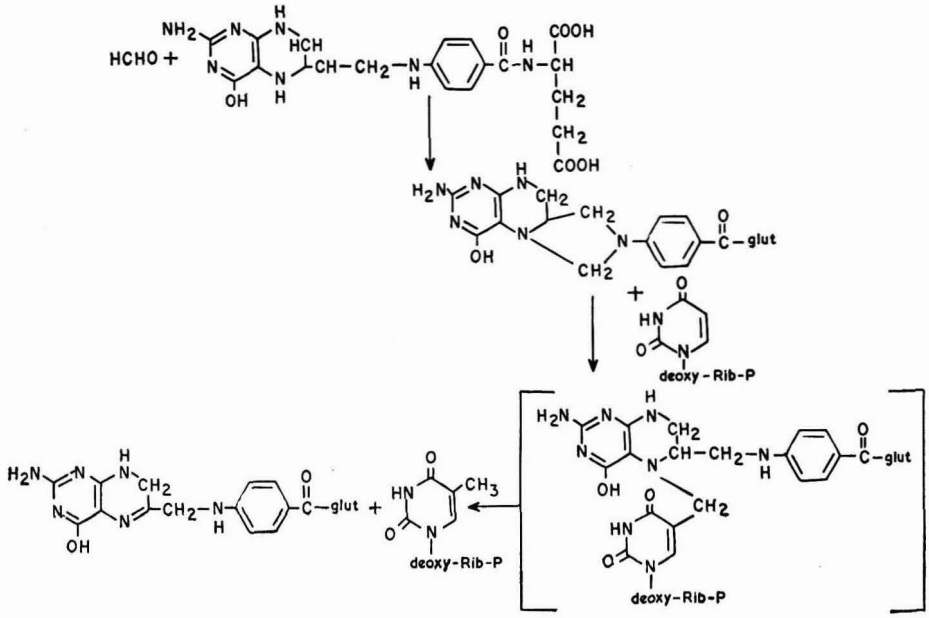

Fig. 3 — A speculative mechanism for the participation of N^5,N^{10}-methylene-THFA in the conversion of dUMP to dTMP[71]

TABLE 4 — STOICHIOMETRY OF THYMIDYLATE FORMATION FROM DEOXYURIDYLATE*†

Incubation period min.	Increase of absorbancy at 340 mμ	Dihydrofolate formed mμmoles	Thymidylate formed mμmoles	Dihydrofolate thymidylate
10	0·100	17·2	19·2	0·89
20	0·180	28·2	28·2	1·00
30	0·211	33·0	33·4	0·99
40	0·225	35·3	36·0	0·98
50	0·232	36·3	37·5	0·97
60	0·235	36·7	40·0	0·92

*From Wahba and Friedkin[67].

†The incubation mixture contained: dUMP (labelled with ^{32}P, 80000 c.p.m.), 0·04 μmole; *dl*, L-tetrahydrofolate, 0·16 μmole; and enzyme (0·2 mg. of protein) in 1 ml. of a mixture containing Tris-HCl buffer, *p*H 7·4 (40 μmoles), 2-mercaptoethanol (100 μmoles), EDTA (1·0 μmole), $MgCl_2$ (25 μmoles), and formaldehyde (15 μmoles).

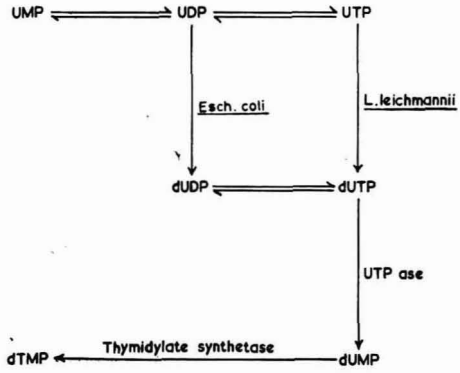

Fig. 4 — Pathways for the synthesis of thymidylic acid

to a labile intermediate which then undergoes intramolecular rearrangement to yield thymidylate and DHFA[71].

As reported earlier, Bertani *et al.*[27] have shown that UMP is converted to dUMP at the diphosphate level by the enzyme derived from *Esch. coli* while Abrams[38] demonstrated UTP to be the preferred substrate for the enzyme from *L. leichmannii*. Methylation of deoxyuridine takes place at the monophosphate level. This would mean that dUDP and dUTP would have to be converted to dUMP before they could be converted to dTMP. Bertani *et al.*[27] have shown in *Esch. coli* the presence of UTP-ase which converts dUTP to dUMP and pyrophosphate. The general scheme for the *de novo* synthesis of dTMP can then, therefore, be written as in Fig. 4.

The biosynthesis of dTMP is also accomplished by an alternate pathway which involves the deamination of deoxycytidylate by a specific enzyme, deoxycytidylate deaminase. The enzyme was first reported by Scarano in developing sea urchin eggs[72] and by Maley and Maley in young rat and embryonic tissues[56]. The enzyme is widely distributed, being present in neoplastic tissues[73], regenerating rat liver[74] and rabbit and monkey liver[75]. It is, however, absent in *Esch. coli* extracts[76] though it is readily inducible in these cells following infection with T-even coliphages[77-79]. Deoxycyti-

dylate deaminase has been purified 550-fold from unfertilized eggs of *Sphaerechinus granularis*[80], 2700-fold from monkey liver, 460-fold from rabbit liver[75], 400-fold from minced chicken embryos[81], 400-fold from T_6r^+ infected extracts of *Esch. coli*[77] and $4{\cdot}8\times10^4$-fold from donkey spleen[82]. The co-factor requirements of chick embryos deaminase are dCTP and Mg^{2+} at low substrate concentrations, but these cofactors are not required by enzyme preparations from sea urchin eggs, monkey and rabbit liver and donkey spleen. The enzyme is highly specific for 6-aminopyrimidine deoxyribonucleoside-5′-phosphate. 5-Methyl deoxycytidylate[83] and 5-hydroxymethyl deoxycytidylate[76] can also serve as substrates for *S. granularis* and rabbit liver enzyme preparations in addition to deoxycytidylate. Maley observed that 5-fluoro-dCMP and 5-bromo-dCMP were deaminated by the enzyme from extracts of rat embryos[84]. Creasey[85] has shown the deamination of 5-iodo-dCMP by tissue extracts and Kára and Šorm found that 6-aza-dCMP is a substrate for the partially purified enzyme from Ehrlich ascites cells[86].

The stability of the deoxycytidylate deaminase is markedly influenced by the presence of deoxynucleotides[87-89]. Of the triphosphates tested, dCTP is the most effective activator while dTTP is the most potent inhibitor of the enzyme derived from different sources. Recently, it has been shown that complexes of dCTP and dTTP with Mg^{2+} activate and inhibit a homogeneous preparation of the enzyme from donkey spleen[90]. Inhibition by dTTP is reversed by dCTP at low concentrations[75,91]. Maley and Maley observed that in addition to the reactivation of the enzyme in the presence of dCTP, mercaptoethanol[92] protects the enzyme from inactivation due to dilution, in the absence of dCTP and Mg^{2+}. These findings suggest the possibility that the enzyme deoxycytidylate deaminase is an allosteric protein. Deoxycytidylate and deoxythymidylate lie at the extreme end of the pathway (Fig. 5) and since the enzyme is effectively regulated by low levels of both dTTP and dCTP, feedback control is operative. Maley and Maley[92] have obtained different sedimentation constants of chicken embryos deaminase in the presence of allosteric effectors, dCTP, dTTP, and a mixture of dCTP and excess dTTP. But the sedimentation pattern of donkey spleen deaminase is not effected in the presence of dCTP.Mg and dTTP.Mg. The latter studies suggest that no dissociation of the enzyme molecule into sub-units takes place and the altered enzyme activities observed in the presence of regulatory deoxynucleoside triphosphates indicate conformational changes.

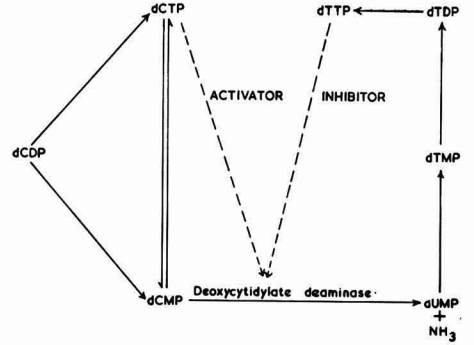

Fig. 5 — Nucleotide relationships affecting dCMP deaminase[77]

Biosynthesis of Hydroxymethyldeoxycytidylate

A unique pyrimidine, 5-hydroxymethylcytosine, has so far been shown to occur only in DNA of T-even bacteriophages (T_2, T_4, T_6) by Wyatt and Cohen[93]. The details of its biosynthesis are of special interest because of its possible relationship to bacterial parasitism by T-even coliphages. Cohen and Weed[94] demonstrated that pyrimidine ring of dHMP is derived from the cytosine of *Esch. coli* DNA. *In vivo* studies[50] indicated that the hydroxymethyl group originates from serine[94]. The synthesis of dHMP from dCMP was shown by Flaks and Cohen[53,95] to take place in the presence of formaldehyde, THFA and an enzyme preparation derived from T_6r^+ phage-infected *Esch. coli* B. The conversion, however, did not take place when deoxycytidine, cytidine, or cytosine were the substrates. The enzyme involved is deoxycytidylate hydroxymethylase and distinct from thymidylate synthetase. It is not inhibited by 5-FdUMP and is more stable in infected crude extracts than thymidylate synthetase. Deoxycytidylate hydroxymethylase[96] has been purified 40-fold by chromatography on DEAE-cellulose. The molecular weight, estimated from sedimentation and diffusion constants, is approximately 68000. Mathews *et al.*[97] infected prelabelled *Esch. coli* B (grown in the presence of ^{14}C-methionine) in non-radioactive medium. Hydroxymethylase purified from these cells was virtually non-radioactive and, therefore, essentially free of host cell proteins. The radioactivity of methionine present in the enzyme was about 0·7 per cent of that present in

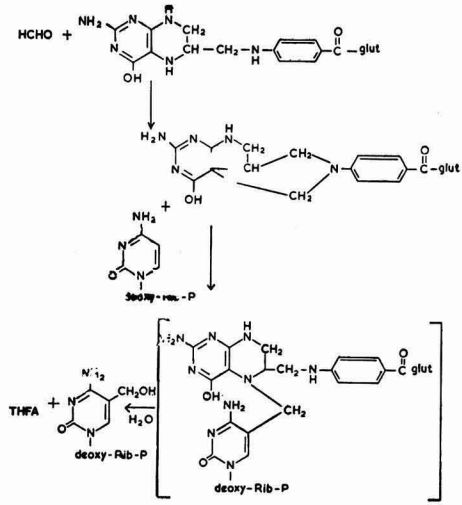

Fig. 6 — A speculative mechanism for the participation of N^5,N^{10}-methylene-THFA in the conversion of dCMP to dHMP[71]

cellular protein at the time of infection. From the foregoing evidence they concluded that the enzyme is synthesized *de novo* after virus infection.

Friedkin[71] proposed a hypothetical mechanism for the formation of dHMP from dCMP in a manner analogous to the one proposed for the synthesis of dTMP from dUMP. This involves the formation of labile intermediate between methylene THFA and deoxycytidylate, followed by hydrolysis to yield hydroxymethyl deoxycytidylate and free THFA (Fig. 6).

Phosphorylation of Deoxyribonucleotides

Deoxyribonucleosidemonophosphate Kinases

A group of enzymes catalyses the transfer of terminal phosphate from a nucleoside triphosphate to nucleoside monophosphate as follows:

$$N_1TP+N_2MP \rightleftharpoons N_1DP+N_2DP$$

where N_1 and N_2 are purines or pyrimidines.

Kornberg *et al.*[1] first studied the phosphorylation of thymidine to dTTP by the crude extracts of *Esch. coli* B. Lehman *et al.*[98] partially purified extracts of *Esch. coli* B and demonstrated that all the four deoxyribonucleoside monophosphates could be phosphorylated to higher phosphates and that the preparation, on heating, lost the ability to phosphorylate dCMP, dGMP and dTMP but not dAMP. This activity is analogous to adenylate kinase (myokinase) which uses dAMP as the substrate in place of AMP[99,100]; it was shown by Colowick and Kalckar[101] that heat stability is a characteristic property of muscle adenylate kinase. Hurwitz[102] fractionated *Esch. coli* extracts and showed that three different enzymes exist which phosphorylate dCMP, dGMP and dTMP respectively to diphosphates. The enzyme activities are, however, unspecific with respect to the sugar moiety as they could phosphorylate CMP, GMP and TMP as well. Maley and Ochoa[103] obtained a kinase preparation about 800-fold pure from the extracts of *Azotobacter vinelandii* which catalysed the conversion of dCMP and CMP to the corresponding diphosphates in the following manner:

$$dCMP+ATP \rightleftharpoons dCDP+ADP$$

At equal molar concentrations of CMP and dCMP, cytidylate was phosphorylated about 1·5 times faster than deoxycytidylate while dGMP, dAMP and dTMP could not serve as substrates. Oeschger and Bessman[104] have isolated a deoxyguanylate kinase from extracts of *Esch. coli*. This enzyme has been purified 7000-fold by gel filtration on Sephadex G-100 followed by chromatography on DEAE-cellulose. The enzyme catalyses the following reaction:

$$dGMP+ATP \rightleftharpoons dGDP+ADP$$

The specificity of the enzyme is towards the base and not the sugar as described by Hurwitz[102]. The only other purine ribonucleotide which served as the substrate was IMP which showed about 0·6 per cent activity at concentrations seven times greater than GMP. Enzyme activity[105] is stimulated in the presence of K^+ ions. Investigation of the mechanism of this activation has now revealed that dGMP interacts with the enzyme, and K^+ ions facilitate the binding of the substrates[104]. NH_4^+ ion, which also activates the enzyme, seems to have a different mechanism of action.

It was observed by Kornberg *et al.*[106] and Bessman[107] that the level of some of the enzymes involved in the biosynthesis of DNA increases when *Esch. coli* is infected with bacteriophages (T_1—T_7). A 10- to 20-fold increase in the activities of dTMP, dGMP and dCMP-kinases was observed following infection of *Esch. coli* B with T_5 phage, while with the T-even phages (T_2, T_4 and T_6) the activities of only the dTMP and dCMP-kinases increased[106,107]. A new enzyme, hydroxymethyl deoxycytidylate kinase, was also detected by Kornberg *et al.*[106] and Somerville *et al.*[108] following infection with T-even phages. The deoxynucleotide kinases induced following bacteriophages infection were different from those in the normal cells in some of their properties[109,110]. For example, dGMP-kinase in crude extracts of cells infected with coliphage T_2 has no requirement for potassium while the dGMP-kinase from normal cells requires potassium. Further, these kinases have been separated from one another by chromatography on DEAE-cellulose columns. Bessman *et al.*[111] purified deoxyribonucleotide kinase from T_5-infected *Esch. coli* B extracts 500-fold with respect to dTMP as the substrate. Concomitant with the purification of dTMP-kinase activity, fractionation of dAMP, dGMP and dCMP-kinase activities was also observed. The authors suggest that a single protein catalyses the transfer of a phosphate group from nucleoside triphosphate to the four substrates dAMP, dTMP, dGMP and dCMP. K_m and K_i values for all the four nucleotides and chromatographic properties of the four activities bear a constant relationship throughout the purification procedure. The best substrate for the T_5-induced deoxyribonucleotide kinase is dAMP which is phosphorylated 30 per cent faster than dTMP and dGMP and 3 times faster than dCMP. All the ribonucleotides are poor substrates, the specificity being thus dependent on the sugar moiety. The phosphoryl donors dATP or ATP are equally effective. The stoichiometry of the reaction is shown in Table 5. Bello and Bessman have also purified deoxyribonucleotide kinase about 200-fold from crude extracts of *Esch. coli* B infected with T_2 bacteriophage[112]. These authors have also presented evidence which suggests that the ability to phosphorylate dGMP,

TABLE 5 — STOICHIOMETRY OF THE REACTION*†: dTMP+ATP⇌dTDP+ADP

Min.	mμmoles of			
	dTMP	ATP	dTDP	ADP
10	−39	−36	+39	+39
20	−62	−51	+64	+60
40	−80	−72	+85	+74
120	−80	−78	+86	+78

*From Bessman *et al.*[111].

†The reaction mixture contained in a volume of 0·20 ml.: $dTMP^{32}$ ($4·1\times10^5$ c.p.m./μmole), 1·4 μmoles; ATP, 1·7 μmoles; $MgCl_2$, 4 μmoles; and gel filtrate, 6 μg.

dTMP and dHMP resides in a single protein. The enzyme is highly specific for deoxyribonucleotides and hardly utilizes the ribonucleoside monophosphates.

Deoxyribonucleotide kinases have also been shown to be present in animal systems. Smellie observed the formation of dATP, dGTP, dCTP and dTTP from the corresponding monophosphates in normal and regenerating rat liver[113], in extracts of Ehrlich ascites tumour cells[114] and in disrupted preparations of L-strain fibroblast grown in tissue culture; these kinase activities were similar to the enzymes from liver and kidney studied by Hecht *et al.*[115] and Sable *et al.*[116]. Canellakis *et al.*[117] and Bollum and Potter[118] found that there is no difference in the ability of normal and regenerating rat liver to phosphorylate dAMP, dGMP and dCMP. The position, however, is quite different for thymidine and thymidylate kinases which are present at very low level in normal rat liver but appear in substantial amounts in regenerating rat liver from 18 to 40 hr after partial hepatectomy. Kielley[119,120] has compared the activities of deoxynucleotide kinases in mouse liver and mouse ascites hepatoma and found that the dTMP-kinase activity is considerably higher in hepatoma.

It is clear from the foregoing studies that extracts from resting mammalian tissues have a very low level of thymidine and thymidylate kinases, but these extensively catalyse the formation of dTMP, dTDP and dTTP in growing tissues. A number of suggestions have been made to explain the low dTMP-kinase activity in resting mammalian tissues. Hiatt and Bojarski[121] found that intraperitoneal injection of thymidine or the preincubation of tissue extracts with thymidine or thymidylate stimulates the thymidine and thymidylate kinase activities of adult rat liver. This is partly due to the stabilization of the enzymes by the substrate[122]. Gray *et al.*[123] attributed the low kinase activities to the presence of interfering substances. They observed that when extracts of normal and regenerating rat liver are mixed, there is a marked inhibition of both thymidine and thymidylate kinases. The heat labile, non-diffusible inhibitory fraction, which they obtained on fractionation of rat liver had, however, no effect on dAMP, dGMP and dCMP-kinase activities. Kielley[124] has shown that the amount of thymidylate kinase in mouse liver is equal to that present in growing tissue (hepatoma) and a major part of the enzyme is present with cell particles in bound form from where it could be released. This is opposite to the view expressed by Canellakis *et al.*[117] who pointed out that the deficiency of the dTMP-kinase in rat liver may limit DNA synthesis. Friedkin[71] implies a unique role for thymidine in nucleotide metabolism.

Potter *et al.*[125] in 1957 detected the di- and triphosphates of deoxycytidine and deoxythymidine in the acid-soluble extract of thymus gland. Recently, Suggino *et al.*[126] have partially purified from calf thymus four nucleoside monophosphate kinases which are specific towards the base but not towards the sugar moiety. The purified dCMP-kinase can also catalyse the phosphorylation of CMP and UMP, but the ability to phosphorylate dCMP does not appear unless a thiol compound such as β-mercaptoethanol, glutathione or cysteine is added. dUMP is, however, not a substrate for this enzyme preparation; dUMP-kinase activity was recovered in another fraction. Of the nucleoside triphosphates tested, only ATP and dATP-served as the phosphoryl donors. A partial purification of deoxyribonucleoside monophosphate kinases from L-cells has also been carried out[127]. In this case, two distinct purine deoxyribonucleoside phosphate kinases were obtained free of each other which converted both ribo- and deoxyribonucleoside monophosphates to the corresponding diphosphates; the presence of two different enzyme activities specific for dCMP and dTMP was inferred.

Nucleosidediphosphate Kinases

Nucleosidediphosphate kinase catalyses the transfer of a terminal phosphate from nucleoside triphosphates to nucleoside diphosphates in the following manner:

$$N_1TP+N_2DP \rightleftharpoons N_1DP+N_2TP$$

where N_1, N_2 are purines or pyrimidines.

This enzyme activity was first described independently in 1953 by Krebs and Hems[128] and Berg and Joklik[129]. Since that time, this ubiquitous enzyme has been partially purified from mammalian, plant and microbial sources and the work in this respect till 1962 has been exhaustively reviewed by Weaver[130]. These studies, however, do not allow a definite conclusion to be drawn as regards its substrate specificity; little is thus known about the ability of this enzyme to phosphorylate deoxyribonucleotides. Bello and Bessman[131] compared the enzymatic activity which would phosphorylate dCDP and dHDP to dCTP and dHTP in cell-free extracts of *Esch. coli* B and T_2-infected *Esch. coli* B. Unlike the deoxynucleotide monophosphate kinases and DNA-polymerase, which showed increased levels (10- to 20-fold) of activity after virus infection, deoxynucleoside diphosphate kinase activity was unchanged. Bianchi *et al.*[132] proposed, on the basis of their studies on leukaemic mouse spleen and lymph nodes of mice, that dTTP was formed from dTMP by a one-step reaction through the transfer of a pyrophosphate group:

$$dTMP+ATP \rightleftharpoons dTTP+AMP$$

Bessman[133] suggested the possibility of dTDP as an intermediate; it was not possible by Bianchi *et al.*[132] to detect this as the equilibrium of the reaction in their experiment was in favour of dTTP formation because of high levels of the enzyme present. This suggestion has since been confirmed in leukaemic mouse spleen[134], Landschutz ascites tumour cells[135] and in a number of other systems. It is believed now that dTTP is formed by a two-step phosphorylations as follows:

$$dTMP \rightarrow dTDP \rightarrow dTTP$$

Ives have reported that nucleosidediphosphate kinase of Novikoff hepatoma[136] phosphorylates both ribonucleoside diphosphates as well as deoxyribonucleoside diphosphates. Recently, the enzyme has been isolated in a high state of purity from yeast[137]

(crystalline), calf thymus[138] (2800-fold) and erythrocytes[139] (1400-fold). All these enzyme preparations are non-specific with regards to the bases as well as the sugar moiety. ADP was converted to ATP by crystalline yeast enzyme with eight kinds of nucleoside triphosphates tested. The enzyme could also affect the transfer of terminal phosphate from either ATP or dATP to the diphosphates of uridine, guanosine, inosine and cytosine. The rate of phosphorylation observed with dCTP and dGTP was one-half of that observed with ATP, UTP and dATP. dTDP was shown to be the best phosphate acceptor with calf thymus enzyme; the rate of phosphorylation of dCDP, CDP and GDP was very much lower. The best phosphate donors were ATP and dCTP; CTP was only half as good as these when dTDP and CDP were used as the phosphate acceptors. All these enzyme preparations catalysed exchange between ADP and ATP, but not between orthophosphate and ATP.

Mourad and Parks[139] have carried out a detailed kinetic study with erythrocyte NDP-kinase and they postulate a 'ping pong' mechanism for its action, i.e. the first substrate binds the enzyme and the product formed dissociates from the enzyme surface before the second substrate adds again as before. A phosphorylated enzyme is believed to be the intermediate. This has been isolated by reacting purified NDP-kinase with ATP-β-γ-P^{32} in the presence of Mg^{2+} for 1 min. followed by chromatography on a Sephadex G-100 column. The reaction, according to Mourad and Parks, occurs in two steps:

$$N_1TP + NDP\text{-kinase} \rightleftharpoons NDP\text{-kinase}\sim P + N_1DP$$

$$N_2DP + NDP\text{-kinase}\sim P \rightleftharpoons N_2TP + NDP\text{-kinase}$$

Norman *et al.*[140] have isolated a phosphorylated enzyme as an intermediate for the NDP-kinase from Jerusalem artichoke mitochondria. Their preliminary studies suggest that histidine in NDP-kinase may be the site which accepts a phosphate group to give the phosphoenzyme intermediate. Sucrose density gradient of calf thymus NDP-kinase gave two peaks which suggest the presence of the phosphorylated enzyme. Whether the same mechanism exists for other enzymes of this class remains to be seen.

Conclusion

Two enzyme systems, one from *Escherichia coli* and another from *Lactobacillus leichmannii*, have been described in considerable detail for the synthesis of deoxyribonucleotides from ribonucleotides. A comparison of their properties is given in Table 6 for recapitulation. Two proteins, B_1 and B_2, have been partially purified from *Esch. coli* B, the presence of which is essential for the reduction of nucleoside diphosphates; these have no requirement of cobamide coenzyme and the hydrogen donor for them is reduced lipoic acid which can be replaced by thioredoxin-thioreductase and reduced NADP. Alternatively, enzyme from *L. leichmannii* is apparently a single protein catalysing the reduction of ribonucleoside triphosphates; this specifically requires cobamide coenzyme and the reductant is the same as in the case of *Esch. coli*.

TABLE 6 — COMPARISON OF RIBONUCLEOTIDE REDUCTASES OF *Esch. coli* AND *L. leichmannii*

Properties	*Esch. coli* reductase	*L. leichmannii* reductase
Protein components	Two, B_1 and B_2	One
Michaelis constant	$3{\cdot}7\times10^{-5}$ (CDP)	$1{\cdot}7\times10^{-3}$ (CTP)
Substrate specificity	Diphosphates	Triphosphates
Coenzyme requirement	None	DBC-coenzyme
Metal requirement	Mg^{2+}, Mn^{2+} (absolute)	Mg^{2+}, Mn^{2+} (relative)
Physiological reductant	Thioredoxin	Thioredoxin
Flavoprotein for reducing thioredoxin	Thioreductase	Thioreductase
Allosteric effect of dATP	Inactive	Active

The two enzymes function at different substrate levels, i.e. nucleoside diphosphates and nucleoside triphosphates respectively. It will be quite interesting to find an enzyme system with a specificity towards nucleoside monophosphates. This would simplify the synthesis of dTMP from dUMP which could then be obtained by the direct reduction of UMP. Thioredoxin has so far been detected only in *Esch. coli* B and *L. leichmannii*; before its role as the normal physiological reductant can be accepted, it is necessary that its presence be shown in other systems. It has been shown that *Esch. coli* reductase affects the transfer of hydride ion to the C-2′ carbon of ribonucleotides but how this transfer is accomplished is still unknown. Either of the two partially purified proteins B_1 and B_2 may have additional parts to play; specific functions of both of these proteins remain to be elucidated. The mechanism by which cobamide-dependent *L. leichmannii* reductase works is also not clear, although it has been suggested that reduced DBCC is the transferring agent for the hydride ion.

The synthesis of thymidylate is discussed by two enzymatic pathways which make use of deoxyuridylate and deoxycytidylate as the precursors. dUMP is methylated in the presence of formaldehyde and THFA by the enzyme, thymidylate synthetase, to give dTMP while deoxycytidylate is first deaminated to yield dUMP which is converted to dTMP as above. Enzymatic evidence is also presented for the formation of hydroxymethyl deoxycytidylate.

The deoxyribonucleoside triphosphates, a prerequisite for macromolecular DNA synthesis, are synthesized from the corresponding monophosphates, dAMP, dTMP, dGMP and dCMP, by two-stepwise phosphorylations. Deoxynucleoside monophosphate kinases convert deoxyribonucleoside monophosphates to the corresponding diphosphates by a phosphate transfer from a nucleoside triphosphate. Both ribo- and deoxyribonucleoside monophosphates serve as substrates with highly purified enzyme preparations from several sources. Only two cases are reported where the enzymes, purified following viral infection, were specific towards the sugar moiety and, therefore, could be strictly termed deoxynucleosidemonophosphate kinases. Nucleoside-

diphosphate kinase apparently catalyses the transfer of a phosphate group from nucleoside triphosphates to nucleoside diphosphates. Recently, the enzyme has been isolated from several sources in a high state of purity but does not seem to have strict specificity either towards the base or towards the sugar moiety. All the nucleoside diphosphates are phosphorylated and further the enzyme does not recognize specifically any of the nucleoside triphosphates tested as phosphoryl donors. Therefore, this group of enzymes may be more appropriately termed as nucleosidediphosphate kinase as suggested by Weaver[130]. As regards the mechanism of phosphate transfer, a phosphoenzyme has been suggested as an intermediate in the two cases.

Summary

Deoxyribonucleotides are synthesized from ribonucleotides by the reduction of ribose moiety to deoxyribose. This is accomplished by two enzyme systems which have been purified from *Escherichia coli* B and *Lactobacillus leichmannii*. Lipoic acid, or the physiological reductant thioredoxin-thioreductase, serves as the hydrogen donor with both the enzymes. However, they differ in their dependence on the cobamide coenzyme; *L. leichmannii* enzyme has an absolute requirement for this coenzyme while *Esch. coli* enzyme has none whatsoever. Both deoxyuridylate and deoxycytidylate act as precursors in the synthesis of thymidylic acid. dUMP is methylated in the presence of formaldehyde, THFA and the enzyme, thymidylate synthetase, to give dTMP. dCMP is first deaminated by deoxycytidylate deaminase to dUMP which is converted to dTMP as above. Enzymatic evidence is also presented for the formation of hydroxymethyl deoxycytidylate. The phosphorylation of nucleoside monophosphates to nucleoside triphosphates is carried out in two steps. Nucleoside monophosphates are first converted into nucleoside diphosphates which are then phosphorylated to triphosphates, both by a phosphate transfer from nucleoside triphosphate. The enzymes which affect these phosphate transfers are the deoxynucleosidemonophosphate kinases and nucleosidediphosphate kinases.

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REVIEWS

OPTICAL INTERFEROMETRY by M. Francon (Academic Press Inc., New York), 1966. Pp. xi+307. Price $ 13.50

Optical interferometry today is used extensively both in research and industry, for example, in wind tunnel aerodynamics and laser technology. This book by M. Francon, who himself has many original contributions in the field, presents the modern approach to problems in interferometry. The book has been divided into 16 chapters. The concept of coherence which has developed over the years has been dealt with in Chapter I. Without sacrificing mathematical rigour, the theoretical basis of the analysis of spatial and temporal coherence and conditions of interference have been given briefly in the beginning and this forms a very useful introduction to the later chapters on interference and partial coherence intensity interferometers and interference phenomena produced by lasers.

The chapters on interferometric measurements of the optical transfer function and interference spectroscopy require some knowledge of Fourier transformation. In all the other chapters, the emphasis is more on the experimental aspects of interference phenomena and instrumentation. The topics covered include two-beam interference, multiple beam interference, polarization interferometers, and study of wave surfaces.

The chapters on thin films and applications of interference are likely to be specially appreciated by experimental physicists, since they contain a brief and precise account of all the important uses and design features of interference instruments. The basic principles underlying optical holography have been indicated in the concluding chapter. The bibliography of other important books and original publications on the topics dealt with here will also be found useful.

The book is invaluable to researchers and engineers, since it covers even very recent developments and its clarity is such that even graduate students can use it for supplementary reading.

P. S. NARAYANAN

ADVANCES IN NUCLEAR SCIENCE AND TECHNOLOGY: Vol. 3, edited by Paul Greebler & Ernest J. Henley (Academic Press Inc., New York), 1966. Pp. xii+400. Price $ 17.50

The subjects selected for review in this volume include such diverse topics as pulsed neutron sources and physics of pulsed neutrons, synthesis methods in reactor analysis, transient radiation effects in electronics, radiation effects on inorganic solids and radiation-induced polymerization at low temperatures.

Pulsed neutron techniques have importance in studying the diffusion properties of neutrons in the medium in which they are introduced. These chapters, which review, analyse and compare the important experimental and theoretical work in this field developed over the past 15 years, are, therefore, of interest to solid state physicists in general and to the reactor physicists and engineers in particular. The review has been well written and brings together data spread over a large number of scientific journals.

The synthesis methods are of interest to the reactor physicist, as they describe a group of approximation techniques to overcome the difficulty of solving the neutron group diffusion equations in three dimensions by constructing the three-dimensional ones. Such synthesis methods — with the help of the modern computers — make it possible to predict the behaviour of a nuclear reactor under all kinds of operating conditions as well as accidental transients. The article gives a brief introduction to the subject and its applications.

The chapter on transient radiation effects in electronics is an interesting brief survey dealing not in transient effects but in effects of transient radiation on various electronic devices. Broadly speaking, radiation may be X-rays or γ-rays, electrons and neutrons. The first two are characterized by the fact that they produce ionization and the last by producing displacement of atoms and thereby producing radiation damage. This article deals mainly with the conduction and replacement effects produced as a result of ionization. The article will be of interest to all solid state physicists. The last section of this article gives typical component data which will be of interest to electronics engineers, as it gives useful information on the effects produced when, for example, a nuclear detonation takes place.

The remaining two chapters are for the chemist. The one on radiation-induced polymerization covers recent work on low temperature polymerization in liquid and solid states. The authors have emphasized on the mechanisms involved, i.e. whether it is ionic or a free radical mechanism. Various physical methods employed for this purpose are described. Photomicrographs of several polymers are also given, but the authors have not highlighted the conclusions drawn from them. On the whole, this is a useful survey.

The article on the radiation effects on inorganic components includes the results on compounds such as azides, bromates, nitrates, etc. This article reads more like a catalogue of data and the results have not been so well discussed.

The book, however, is a very useful one, as each chapter ends with full references to published work on the subject. It would have been better if the publishers had not made each volume so heterogeneous.

JAGDISH SHANKAR

ADVANCES IN HETEROCYCLIC CHEMISTRY: Vol. 6, edited by A. R. Katritzky & A. J. Boulton (Academic Press Inc., New York), 1966. Pp. xv +468. Price $ 18.50

Vol. 6 consists of six chapters, covering physico-chemical aspects, problems of substitution and

reduction, synthetic reactions leading to heterocyclic compounds, and a report of progress in the chemistry of one heterocyclic group. Nearly all the chapters make fascinating reading for organic chemists in general and those concerned with chemotherapeutic agents in particular.

Physico-chemical aspects of the chemistry of purines (J. H. Lister) — With the data collected in recent years on numerous purines synthesized as potential anti-cancer agents and on the nucleic acids, Lister has shown how this knowledge may be used to explain reactions in purine chemistry. He has briefly discussed the molecular structure of purines in the light of spectroscopic and crystallographic studies, and has dealt in detail with nucleophilic and electrophilic substitution.

Substitution in the pyridine series: Effect of substituents (R. A. Abramovitch & J. G. Saha) — The effects of substituents in the pyridine nucleus on electrophilic substitution, nucleophilic substitution (except of halogens treated in Vols. 3 and 4 of the series), and homolytic substitution are reviewed very ably. Reactions of pyridine N-oxides and pyridinium salts are included, and the chapter concludes with a brief account of intramolecular cyclizations on a pyridine ring. The mechanistic aspects of reactions are discussed in detail, drawing attention to results of doubtful value and the need for further experimental work.

The reduction of nitrogen heterocycles with complex metal hydrides (R. E. Lyle & P. S. Anderson) — Following a stimulating discussion of the mechanism of the reactions of complex metal hydrides with pyridine and pyridinium salts, supported by appropriate examples to illustrate the validity of the conclusions, the reduction of pyridine, isoquinoline, quinoline, non-aromatic heterocycles, heterocycles containing one, two and three nitrogen atoms, azoles and pteridines is discussed in turn.

Heterocyclic syntheses involving nitrilium salts and nitriles under acidic conditions (F. Johnson & R. Madronero) — The authors have carried out substantial work in the area they have reviewed. They have shown how the title compounds can be used for the synthesis of numerous heterocyclic compounds and have included 13 very useful tables. The chapter will stimulate further work on the synthetic uses of nitriles and the mechanism of the complex reactions.

Cyclic enamines and imines (K. Blaha & O. Cervinka) — Although several reviews, including one by J. Szmuszkovicz in Vol. 4 of *Advances in Organic Chemistry*, have appeared in recent years after Stork demonstrated the wide synthetic utility of enamines, the present review is welcome because it emphasizes physico-chemical properties as well as preparative methods and enamine reactions. Since enamines from aliphatic or alicyclic carbonyl compounds have been included, the authors have found it necessary to omit many recent developments. Most of the cited references are prior to 1963 and the review, therefore, concerns the basic chemistry of the 3-atom system $-\overset{|}{N}-\overset{|}{C}=\overset{|}{C}-$ in which the N atom is part of a ring, rather than the present status of the synthetic applications of enamines. A minor error is the statement that 1-morpholinocyclohexene fails to react with 1-chloro-2,4-dinitrobenzene; a synthesis of 2-aminocarbazole from the product has been described [*J. scient. ind. Res.*, **21B** (1962), 290].

Progress in pyrazole chemistry (A. N. Kost & I. I. Grandberg) — The discussion of spectroscopic and chemical properties of pyrazoles and of methods for their synthesis is useful, but the dense mass of information and 799 references have made the chapter difficult to read and digest.

K.V.

ORGANIC INSERTION REACTIONS OF GROUP IV ELEMENTS by E. Y. Lukevits & M. G. Voronkov; translated from the Russian by M. J. Newlands (Consultants Bureau Enterprises, New York), 1966. Pp. xii+413. Price $ 25.00

This is a unique book containing all the known data on the addition of organic and inorganic derivatives of silicon, germanium and tin to multiple bonds in unsaturated compounds.

The book is divided into four parts for convenience. The hydrosilylation reaction is dealt with in great detail in the first part covering Chapters 1-5. Various factors such as catalysts, initiators, solvent, structure of hydrosilane, structure of unsaturated compounds — which affect the rate and direction of the hydrosilylation reaction — are recovered in the first chapter, while the mechanism of the hydrosilylation reaction is covered in the second. Chapter 3 deals in great detail with the hydrosilylation of the C=C bond, present in alkenes, alkadienes, cyclo alkenes, bicyclo alkenes, cyclo alkadienes, aryl alkenes, halageno alkenes, alkenols and derivatives, unsaturated carbonyl, nitro, cyano and amino compounds. In addition, it also covers hydrosilylation of unsaturated hetero-organic compounds of boron and silicon. Hydrosilylation of C≡C bonds is covered in Chapter 4 and of C=O and C≡N bonds in Chapter 5.

Part 2 deals in brief with the hydrogermylation, hydrostannylation and hydroplumbylation reactions in Chapters 6 and 7. Several useful examples of preparative synthesis are presented in Part 3 in a clear and concise manner. Part 4, covering more than 200 pages, has extensive tables, followed by formulae index of the reaction products of hydrosilylation. The literature and patent references presented are up to mid-1965.

The book will prove to be a great boon to all research workers in the field as it will save them all the trouble of going through a great number of original sources (specially Russian) to discover whether a particular reaction has been carried out or to find suitable conditions and catalysts for the reaction. As such, the book is a must for every library and all other research institutions where work on organo-metallic compounds and allied fields is in progress.

B. C. SUBBA RAO

ANNUAL REPORTS IN MEDICINAL CHEMISTRY, 1965, edited by C. K. Cain (Academic Press Inc., New York), 1966. Pp. ix+342. Price $ 7.50

This is the first volume of a series proposed to be issued annually with the object of reviewing

important developments in the field of medicinal chemistry during the year. In the present volume, this rather extensive field involving a wide range of disciplines from organic chemistry to clinical medicine has been appropriately dealt with in six sections, each covering a selected area and each further divided into a number of chapters. The titles of the various sections (1. CNS agents, 2. Pharmacodynamic agents, 3. Chemotherapeutic agents, 4. Metabolic diseases and endocrine function, 5. Topics in biology, and 6. Topics in chemistry) give a very good indication of the extent of coverage. A novel feature of the review is the section ' Topics in chemistry ' which, in addition to reviewing compounds of biological interest like nucleotides, nucleosides, peptides and alkaloids, has also a chapter dealing with reactions of interest in medicinal chemistry.

" The breadth of the subject and limitations of space presented to the authors a very difficult task of selection of material and condensation of discussion " the editor-in-chief has modestly stated in the preface. The authors have, however, met the challenge admirably; almost every subject has been reviewed exhaustively and in depth. These volumes are a must not only for medicinal chemists but also for those who are in anyway connected with drug research. Medicinal chemists, like other scientists working in borderline areas, who are hard-pressed for time because they have to scan the literature of so many disciplines to keep abreast of current developments, would most warmly welcome this series and they owe a special debt of gratitude to the authors of this volume. The volume is expertly edited. Publication of future volumes will be eagerly awaited.

NITYA NAND

ACHEMA JAHRBUCH, 1965/1967, edited by D. Behrens (Dechema Deutsche Gesellschaft für Chemisches Apparatewesen e.v., Frankfurt-am-Main), Vol. 1 — European Research in Chemical Engineering, Pp. R32+1088; Vol. 2 — Technical Developments in Chemical Engineering, Pp. R53+689; Vol. 3 — Guide to Chemical Engineering in Europe, Pp. R14+62

The Achema Year-Book was founded in 1925 by Max Buchner. From 1935 to 1962 the book was edited by H. Bretschneider. Since 1963 it is being edited by D. Behrens. The present year-book is issued in three volumes. Vol. 1 deals with " European research in chemical engineering ", Vol. 2 is devoted to " Technical developments in chemical engineering " and Vol. 3 is entitled " Guide to chemical engineering in Europe ". The presentation is in three languages, viz. English, French and German. These volumes have been issued in connection with the European Convention of Chemical Engineering and the Achema Congress and Exhibition held in June 1967 in Frankfurt-am-Main.

In Vol. 1, a general section is devoted to a number of articles pertaining to activities in chemical engineering and related fields in Germany. The main section contains 319 reports in the original language from various European research institutions working in the fields of chemical engineering and allied subject, like physical chemistry, materials science and technology and nuclear engineering. These reports are highly informative and give an idea of the type of work being done in the respective organizations.

Vol. 2 contains reports by 267 companies engaged in business of interest to chemical engineering, dealing with development in new chemical engineering equipment, chemical processes and materials. A few pages are used for advertisements.

Vol. 3 is brought separately in three different languages, viz. English, German and French. The volume under review is in English. There are three sections, viz. a list of participants, a compilation entitled " Who can furnish information ", which, apart from giving the necessary information, serves as a technical dictionary giving terms employed for more than 7000 items of equipment in English, German, French and Spanish and a final section listing trade names. There is also a comprehensive alphabetical subject index.

These volumes are extremely valuable to chemical manufacturers, chemical plant fabricators, chemical and chemical plant dealers, practising chemical engineers and to research and teaching institutions connected with chemical engineering. To those chemical engineers who have the privilege of participating in the European convention and visiting the exhibition, these volumes are most valuable guides to profit most fully from the various aspects of the great convention. Non-participants by merely reading these volumes get a good picture of chemical engineering developments in Europe and can profit immensely. The production of these volumes has meant tremendous effort to the compilers and the editor is to be congratulated for the great effort.

N. R. KULOOR

LEITFADEN MODERNER METHODEN DER LEBENSMITTELANALYTIK (OPTISCHE METHODEN) by Hans Gerhard Maier (Dr Dietrich Steinkopff Verlag, Darmstadt), 1966. Pp. viii+69. Price DM 16

This " Manual of modern methods in food analysis ", in German, presents a survey of the routine optical methods used in food analysis. The aim of the author is not to produce a text-book, but to prepare a practical guide based on the experience gained by him in conducting classes in food chemistry in the University of Frankfurt. Hence, the general approach in preparing the manual is basically experimental and the author has given enough details regarding the construction and working of each one of these optical instruments so that the worker will have no difficulty in handling them and also in their routine maintenance.

In the introductory section, theories of light absorption, emission, refraction and rotation of linearly polarized light in matter have been briefly but elegantly discussed and the names of some standard books on these topics have been suggested for further reading. The major part of the remaining manual is devoted to light absorption, as the methods based on UV and IR absorptions are presumably more widely used than others.

Estimations based on fluorimetry, flame photometry and polarimetry are described in the following sections.

Each section is supplemented with useful and intelligent exercises in order to thoroughly acquaint the worker with the potentialities of the method of analysis and to focus his attention to the likely sources of error in this method. This manual will be extremely useful to students of food technology and research workers who are not fully acquainted with these optical techniques of analysis.

V. K. MOHAN RAO

THE CHLOROPHYLLS: PHYSICAL, CHEMICAL AND BIOLOGICAL PROPERTIES edited by Leo P. Vernon & Gilbert R. Seely (Academic Press Inc., New York), 1966. Pp. xv+679. Price $ 25.00

For the maintenance of life on this earth, perhaps the most important metalloporphyrin proteins are those containing the magnesium-porphyrin compounds — the chlorophylls that make possible the trapping of solar energy for the biosynthesis of carbohydrates and other compounds. The book under review brings under a single cover a fund of information about chlorophylls which are of immense interest to the chemists, physicists and biologists.

The volume contains reviews by 22 contributors divided into four sections and comprises a total of nineteen chapters. The first section deals with the isolation and chemistry and contains the chapters: (1) The chlorophylls — an introductory survey by S. Aronoff; (2) Extraction, separation, estimation and isolation of chlorophylls by H. H. Strain and W. A. Svec; (3) The structure and chemistry of functional groups by G. R. Seely; (4) Recently characterized chlorophylls by H. H. Holt; and (5) The synthesis of chlorophyll *a* by W. Lowowski. Section 2, describing the 'Physical properties in solution and in aggregates', contains chapters: (6) Visible absorption and fluorescence of chlorophyll and its aggregates in solution by J. C. Goedheer; (7) Infrared and nuclear magnetic spectroscopy of chlorophyll by J. J. Katz, R. C. Dlugherty and L. J. Boucher; and (8) Some properties of chlorophyll monolayers and crystalline chlorophyll by B. Ke. Section 3, under the title 'State of chlorophyll in the cell', includes: (9) Chloroplast structure by R. B. Park; (10) The procaryotic photosynthetic apparatus by G. Cohen-Bazire and W. R. Sistrom; (11) Spectral characteristics of chlorophyll in green plants by W. L. Butler; (12) Absorption and fluorescence spectra of bacterial chlorophylls *in situ* by J. M. Olson and E. K. Stanton; (13) Chlorophyll-protein complexes (in three parts) by J. C. Goedheer, J. M. Olson and B. Ke; (14) Protochlorophyll by N. K. Boardman; (15) The biosynthesis of chlorophylls by L. Borograd; and (16) Distribution of the chlorophylls by M. B. Allen. Section 4, dealing with 'Photochemistry and photophysics', contains: (17) Photochemistry of chlorophylls *in vitro* by G. R. Seely; (18) Photochemistry of chlorophyll *in vivo* by L. P. Vernon and B. Ke; and (19) Physical process involving chlorophyll *in vivo* by R. K. Clayton. There is a list of abbreviations, an author index and a subject index.

Most of the contributions are authoritative and generally well knit although a few, like those in Section 3, appear to be compilations of uncoordinated facts. What is the nature of the protein of chlorophyll-protein complexes? (Chlorophyllin was the name given by Rabinowitch to such complexes.) Do the pigment-proteins of different organisms show any evolutionary pattern as in the case of the well-known animal metalloporphyrin complexes like hemoglobin? We have at present only meagre information about these complexes, that too in a single photosynthetic bacterium where the pigment-protein complex has been crystallized and amino acid composition determined. We look forward for more knowledge on these aspects. The articles by Park on chloroplast structure, by Cohen-Bazire and Sistrom on procaryotic photosynthetic apparatus and by Vernon and Ke on photochemistry of chlorophyll *in vivo* are of special interest to biologists.

E. R. S. TALPASAYI

HANDBOOK OF REFRIGERATING ENGINEERING: Vol. 2 — APPLICATIONS by W. R. Woorich (AVI Publishing Co. Inc., Westport, Connecticut), Fourth Edition, 1966. Pp. xi+428. Price $ 14.50

The AVI Publishing Co. is well known for its books on food processing and preservation written by authorities in the field. The present publication, dealing with the application of refrigeration for the preservation of food (particularly perishables), by W. R. Woorich, an authority in the field, is extremely useful to those who are actively engaged in research laboratories and cold storage operators.

The book has 28 sections beginning with hospital air-conditioning and refrigeration. The second chapter dealing with refrigeration systems used by the transport carriers, for all modes of transport, serves as a good background for the subject matter covered in later sections.

Prolonging the storage life of fruits, vegetables, meat, poultry products and dairy products by refrigeration and cold storage methods is widely practised in most advanced countries. The author has compiled the available data and their presentation in different chapters, although rather disjointed, is very useful to the reader. The table on page 26 dealing with optimum cold storage conditions and the storage life of a variety of perishable foods like fruits, vegetables, fish, meat, etc., is a useful guide to cold storage operators. There are informative chapters in the book dealing with types of cryogen and their relative merits, power drives and economics, testing of refrigeration plants, instruments and controls. Dealing with cold storage as a means of preservation of food, the author has described gas storage methods as well as waxing the fruits to enhance the storage lives of fruits and vegetables. Tables dealing with chemical composition of various fruits and vegetables are a valuable addition to this section. Quick freezing of goods is dealt with exhaustively as one section and forms interesting reading. The section dealing with refrigeration of meat, fish and poultry and the one dealing with some aspects of refrigeration requirements in the dairy industry serve as useful

guides to those concerned in these fields of study. Indications given at appropriate places, although not exhaustive, make the subject matter as complete as possible. Federal standards of quality of dairy products, poultry, and sanitary control of food storage warehouses, mentioned at an appropriate section of the book, have enhanced the value of this publication.

The book is thus quite comprehensive in that it enables the reader to comprehend the diversified applications of refrigeration systems and more particularly refrigeration as a means of enhancing the storage lives of perishable products. The book is well printed, and contains a number of useful diagrams and tables. On the whole, the book is highly useful to food technologists, particularly those who are concerned with the preservation of perishables in their fresh condition. It would also serve as a valuable guide to those in charge of refrigeration plants and cold storage warehouses.

N. V. R. IYENGAR

ANTIFERTILITY COMPOUNDS IN MALE AND FEMALE by Harold Jackson (Charles C. Thomas, Publishers, Springfield, Illinois, USA), 1966. Pp. xvii+214, Fig. 33, Plates 11. Price $ 8.75

Of the many problems which confront the world today, the most important and perhaps the most serious is the population explosion. It has been claimed that if the present trends of population increase are allowed to go unchallenged, the human population, in a matter of decades, will achieve disastrous levels. Many national governments and international agencies have, therefore, not only been very actively thinking about the ways and means to check this population growth but have also promoted research on the subject. As a result of this, last 15 years have witnessed an increased tempo of research on reproductive physiology with a view to finding drugs, the occasional administration of which should produce sterility as and when desired and without interfering with sexual activity. Because of this increased emphasis on research for antifertility chemicals, the need for a book bringing together all the relevant up-to-date information has been very acutely felt. The present book fills this need admirably. The author within the 214 pages of this book has done a good job of presenting all the available information in concentrated form.

The book has been divided into two parts; Part 1 deals with the male reproductive physiology including spermatogenesis and the hormonal approach to fertility control. In this part are included two chapters on alkylating agents which are at present being used extensively for producing sterility in insect pest populations with a view to eradicating pests by what is generally known as sterile-male technique. The inclusion of a discussion on insect chemosterilant and sex pheromones has added much to the value of the book to biologists in general and entomologists in particular. Part 2 deals with female reproductive physiology, ovogenesis, non-steroids and steriods affecting ovarian function and the chemical interference with gestation. The author has also given in this section all the available information on the hazards inherent in the long-term use of steroids for population control.

The book is well printed and is free from mistakes. Dr Jackson deserves congratulations for producing the first book on the subject. The book is strongly recommended to workers actively engaged in research on various aspects of reproductive physiology.

K. N. MEHROTRA

FOUNDRY DIRECTORY, 1966, edited by K. Banerjee & R. M. Krishnan (The Institute of Indian Foundrymen, Calcutta), 1966. Pp. xciv+728. Price Rs 65.00

Detailed information regarding the Indian foundry industry is almost totally lacking at present. The present publication is a good, coordinated effort of compiling such information on the Indian foundry industry and trade by providing data on foundry raw materials, sources of supply of plant and equipment needed by foundry industry, educational facilities in foundry technology, training and research in the foundry technique, significant statistics of the industry, glossary of foundry terms, etc.

The directory is divided into three parts. Part 1 contains general information on the foundry industry and seven articles which deal with different aspects of the foundry industry and trade, the present and likely future demands for its products (specially outside the country), the plant and equipment that a foundry uses, the principal raw materials that it consumes, refractories and the standards that are applicable to different foundry processes and products, and the Indian standards for the industry. An article also deals with education and research in foundry technology. A glossary of terms used in foundry technology, which will be useful to teachers and students of foundry technology, is also included in Part 1.

The second part starts with a list of foundries in the country, arranged according to the states. The arrangement within each state is alphabetical, according to the name of the foundry. The list of each state is followed by a table giving the various metals cast by the foundries in these states. This again is followed by a list of special foundries, namely those casting malleable iron, steel and non-ferrous metals. The last section of this part gives a tabulation of the products manufactured by Indian foundries.

Part 3 lists suppliers of foundry plant, equipment, raw materials, services, etc. There is an international section at the end giving lists of classified suppliers for various items of interest to the foundry industry including plants, equipment, furnaces, testing equipments, etc.

As a first publication, the book is splendid and enormous efforts have been put by the various experts in the field in writing the different chapters.

The editors, in their preface, have expressed hopes to improve upon the edition of this directory in future and the following comments are made here only to help them in this improvement.

1. In the chapter ' Demand production — Future plans and potentials ', pages 11-14, no mention has been made about forgings. Though it is an established fact, specially in steel castings, that,

as the demand for a particular item goes up, the casting is likely to be replaced by forging depending on cost. As there is no mention of forgings, it is presumed that the demand for castings also includes those used for forgings.

2. In the chapter 'Export of foundry castings and machinery', pages 31-38, there should have been some mention about the export of non-ferrous castings and its future scope, specially of aluminium alloy die castings. As a large percentage of its cost includes labour charge, which is still cheap in India, it is likely to be competitive in the export market.

3. In 'Statistical tables', pages 105-120, the name of Mukand is found on page 110 in serial No. 3 'Predominantly engineering railway works', but its name is missing on page 111 in serial No. 6 'Railway castings and jobbing work (existing)'. In the reviewer's opinion this sort of anomalies can be avoided, if the names of the foundries are given capacity-wise with a remark column giving some idea of their variety of production.

4. The chapter 'Glossary of terms', pages 121-140, leaves a lot to be desired. Whereas involved terms like 'austempering' and 'bainite' are dealt with, the simple term 'acicular' is not dealt with separately and is written in a way as if the structure appears only in grey cast iron. Whereas 'cope' is defined, there is no mention of 'drag'. The common term 'bob riser' does not appear.

5. In Part 2, there is a table at the end of the list of foundries in each state. The table is entitled 'Metal cast by foundries'. The number of various products can be reduced profitably by shortening as exact information is not available for the range of product of the foundries so easily.

There are a number of anomalies in pages 320 and 321. According to the directory, Indian Standard Metal Co., Bombay, does not manufacture non-ferrous castings in aluminium, brass, bronze, gun-metal, light alloys, etc., and this also applies to Bombay Metals & Alloys, Bombay. In fact, both these companies mainly manufacture non-ferrous castings. The same applies to the list 'Indian foundry products' in pages 509-638.

6. Numbering of pages in Part 3 should have been a continuation from Parts 1 and 2.

The defects mentioned above can be avoided in future publication by adopting the same procedure as adopted by the American Society for Metals for their publications. It means, over and above the General Publication Committee, each subject is to be entrusted to a committee of experts and their names should also be published along with the book. This procedure, apart from improving the contents, will safeguard against any possible lapses.

The above comments are made by the reviewer only as suggestions to improve the publication in future. The publication is a splendid effort and is very attractive, with a beautiful cover. The volume contains a variety of information of interest to the foundry technologist and the book can be recommended as a source of reference to all those interested in the subject of foundry technology as well as the foundry trade.

G. S. TENDOLKAR

ROSTER OF INDIAN SCIENTIFIC AND TECHNICAL TRANSLATORS (Indian National Documentation Centre, New Delhi 12)

The importance of the role of technical translators in the scientific and technological development of a country needs no special mention in the present days. However, in order that authentic and accurate translation of scientific publications in different languages may be obtained, it is necessary that technical translation assignments are given to the most competent persons in the field. The roster compiled by the INSDOC with this end in view represents the first attempt towards assessing the translation potential in India for scientific and technical subjects and gives the subject and language specializations along with the addresses of about 600 translators. A section on Indian language expertise is also included. Being the first attempt, naturally, the compilation cannot be expected to be complete. The compilers themselves hope that the publication of the first edition will help to draw the attention of potential translators and thus make the later editions complete and up to date. In view of the growing specializations in scientific fields and the use of a number of new technical expressions which are being coined every day to convey specific concepts in different fields, it is necessary for technical translators to have a good knowledge of the field of study of the passage translated, a familiarity with the technical expressions current in the field (in both the languages) and a good command of the language in which the translation is made. The aim of a technical translator should be to present an accurate account of the information found in the foreign language in English (or other Indian languages) in a form, as though it was originally written in English (or in the Indian language). The choice of the most suitable translator for a particular assignment of translation work can be made only when complete details of the scientific and technical qualifications, research experience and experience in technical writing and editing of the translators are known. The usefulness of the roster can be increased by incorporating these details as well as the degree of proficiency of the translators in the languages. Further, the subject specialization as given in the present edition is too general (being physics, chemistry, etc.). It is necessary to specifically mention the fields of specialization like electronics, solid state physics, etc., under subject classification. It is hoped that these points will be attented to while revising the roster.

K. S. RANGARAJAN

PUBLICATIONS RECEIVED

ELECTROCHEMISTRY OF SEMICONDUCTORS by V. A. Myamlin & Yu. V. Pleskov (Plenum Press Inc., New York), 1967. Pp. xxii+430. Price $ 19.50

ELEVENTH SYMPOSIUM (INTERNATIONAL) ON COMBUSTION (The Combustion Institute, Union Trust Building, Pittsburgh, USA), 1967. Pp. xxi +1200. Price $ 42.00

NOTES & NEWS

A new interferometer with gratings as beam-splitters

A new type of beam-splitter, in which two special gratings have been combined to form a Machzehnder interferometer system, has been developed at the Department of Applied Physics, Nagoya University, Japan. In ordinary interferometers, transparent plates covered with semi-reflecting films are used as beam-splitters. Plastic films and wire meshes are employed in the far infrared region where ordinary materials become opaque and unusable. But the characteristics of such devices have a strong frequency dependence which is troublesome in operation. The new device proposed is essentially a parallel strip type mirror working as both reflection and transmission grating at the same time. The sketch of the interferometer is shown in Fig. 1.

One-half of the incident light passes through the narrow slit apertures of the beam-splitters while the other half is reflected at the reflecting strip of the splitter. When the grating constant of one of the gratings is twice that of the other, the overlapping of different orders is avoided and the emergent light consists of only the zeroth order beams and the whole system works just like an ordinary interferometer.

A wire grating constructed by winding a plastic fibre of uniform diameter around a metal frame is placed on the surface of a plane glass plate, which is then aluminized by vacuum evoporation. When the wire grating is removed, the grating obtained on the glass plate functions simultaneously as a reflection and as a transmission grating. In practice, the aluminized mirrors shown as M_1, M_2 and M_3, M_4 in Fig. 1 are replaced by reflecting prism systems. The performance of the interferometer had been tested in the visible region and the interferograms have been observed to depict the beat phenomenon of different spectral lines of mercury and cadmium lights. The performance has been found to be satisfactory [*Sci. Lt., Tokyo*, **15** (1966), 131].

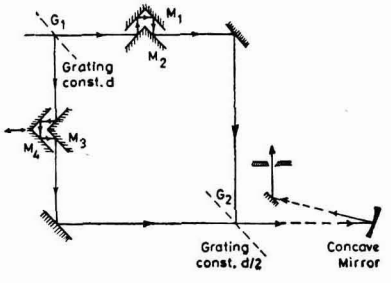


Fig. 1 — The new interferometer

Nylon-platinum catalysts with unusual characteristics

Interesting and unusual results have been reported [*Ind. Engng Chem.* (*Fundamentals*), **6** (1967), 161] in a study of hydrogenation of benzene over unique catalysts prepared by the interaction of various nylons with platinum. The catalysts have been prepared by the interaction of chloroplatinic acid with different nylons. Unlike all the previously known platinum catalysts the catalysts with nylon 6, nylon 66 and nylon 610 as supports gave the intermediate, partially hydrogenated cyclohexene as one of the products. Of the other nylons tested, nylon 3-platinum catalyst has been found to be active but it does not yield any intermediate, while Nomex has been found to be inactive. Also, contrary to the performance of the common platinum catalysts, the reaction over nylon-platinum catalysts has been found to be directly proportional to the benzene pressure and independent of hydrogen pressure. To explain these differences a geometric factor has been postulated based on an arrangement of platinum corresponding to the position of amide groups in the nylon crystal.

Simulation of fractional liquid-liquid extraction

A new laboratory method, utilizing Craig apparatus or a set-up operating in an analogous manner, for the simulation of large-scale countercurrent liquid-liquid extraction systems has been reported [*Ind. Engng Chem., int. Edn*, **59** (No. 3) (1967), 14]. Mathematical expressions are developed to calculate the number of transfers required during the operation for a required yield of the required components of a system or vice versa. This scale-down procedure is useful for the preparation of typical production materials from small amounts of the starting material, for the early evaluation of fractional liquid-liquid extraction as a processing alternative, and for the design of fractional liquid-liquid extraction processes. The method is applicable to any experimental system, irrespective of the type of the solvent. However, the usual restrictions are maintained permitting use of the approximations to calculate component profiles in the transient state distribution.

Enzyme regulation

The dynamic equilibrium characteristic of all living organisms is the resultant of well-regulated chemical reactions mediated by enzymes. Besides the innumerable reactions involved in the trapping of energy from food, in the synthesis of building materials of the cell and in their assembly into macromolecular structures, the efflux and influx of sodium, potassium, calcium and magnesium ions which control intracellular and intercellular transport, muscle contraction and transmission of the nerve impulse are all dependent on the proper functioning of enzymes. As long as enzymes play their part in a disciplined manner, order is maintained in the system by the phenomenon of homeostasis. When enzymes begin to misbehave, manifesta-

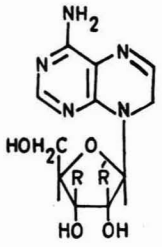
tions of disorder make their appearance leading to pathological symptoms. An extreme case of disorder is represented by the cancerous cell embodying a situation where the enzymes have gone almost completely out of control by the host.

There is obviously an urgent need to understand the mechanism of control and regulation of enzymes at all levels of cellular organization. The experimental approaches to the problem of enzyme regulation in mammalian tissues have become now well defined with the advent of the concepts of allosteric modification of proteins, the operon theory, enzyme induction and repression and feedback control — all of which have emerged out of extensive studies on metabolic regulation in unicellular organisms. In addition to the genetic and environmental factors, the regulation of enzyme activity in the living animal seems to be inseparably linked to the function of hormones. The precise mechanism of action of hormones and their specificity of action are challenging subjects of study currently.

The field of enzyme regulation studies has attracted the attention of several investigators. Scientists have used a variety of enzyme systems as objects of intensive exploration. The following problems can be identified in the unexplored region: regulation in the cancer cell and in oncogenesis, the regulation of enzymes in cardiac and associated vascular diseases, glucogenesis and glycolysis control in the liver and kidney and the regulation of metabolism by sex hormones in the process of embryogenesis. The Pharmacology Division of the Indiana University, School of Medicine, Indianapolis, USA, has played host to annual symposia on enzyme regulation in the last four years, the proceedings of which have appeared as the well-known *Advances in enzyme regulation* brought out by Academic Press, New York. This year's symposium reviewed by G. Weber in *Science* [**155** (1967), 1137] discusses among other subjects the role of coenzymes in enzyme regulation, biosynthesis of nicotinyl adenine nucleotides, relative mechanism of regulation in different tissues, *in vitro* action of hormones at enzyme level, role of isoenzymes, etc. It is to be hoped that the vast information which is being made available by these studies would provide us the clue to understand first the normal or healthy cell and equipped with the humility born of that knowledge approach the enigma of disease or malfunction.

Synthesis of biologically active branched-chain sugar nucleosides

Two biologically active nucleosides [2′-C-methyladenosine (I) and 3′-C-methyladenosine (II)] containing branched-chain sugars have been reported, for the first time, from the laboratories of Merck, Sharp & Dohme, Rahway, New Jersey. Both the compounds at a concentration of 10 μg./ml. are inhibitory (65-80 per cent) to the growth of KB cells in culture and show resistance to the action of calf intestine adenosine deaminase, thereby indicating their high therapeutic value. The details of the synthesis of (I) are provided [*J. Am. chem. Soc.*, **88** (1966), 4524].



I, R=H; R′=CH_3
II, R=CH_3; R′=H

2-C-Methyl-D-ribono-Υ-lactone after conversion into 2,3,5-tri-O-benzoyl derivative was reduced with bis (3-methyl-2-butyl) borane to produce an anomeric mixture of 2,3,5-tri-O-benzoyl-2-C-methyl-D-ribofuranose as the main product. Benzoylation of the mixed anomers with benzoyl chloride in pyridine produces 1,2,3,5-tetra-O-benzoyl-2-C-methyl-α(β)-D-ribofuranose. Following chromatography, one of the anomers was isolated as a crystalline solid and the other as a pure syrup. The two anomers were then converted to the chloro-sugar with ethereal hydrogen chloride. Reaction of the chloro-sugar with chloromercuri-6-benzamidopurine gave 9-(2,3,5-tri-O-benzoyl-2-C-methyl-B-D-ribofuranosyl)-6-benzamido-purine as an amorphous solid which was purified by chromatography on silica gel. Removal of the benzoyl blocking groups from this compound in the methanolic sodium methoxide gave crystalline 2′-C-methyladenosine (I).

Use of a detergent-acid mixture to rupture tissue culture cells

The use of a quaternary ammonium bromide ('Cetavlon', cetrimide, Imperial Chemical Industries), in acid solution (0·1*N* hydrochloric acid, *p*H 1·0) has been suggested, as an alternative to the ultrasonic vibration method for releasing mycobacteria from cell cultures for enumeration [*Nature, Lond.*, **214** (1967), 624]. The method is free from aerosol formation, an objectionable feature of the ultrasonic vibration method.

Cetrimide ruptures the cell, releasing the intracellular contents, including the bacilli into the supernatant fluid, while leaving the nuclei intact. The nuclei released into the supernatant fluid do not interfere with the counting of the bacteria. In neutral solutions, only partial rupture of the cells is obtained. The recovery of bacilli after exposure to cetrimide is checked with a suspension of *Mycobacterium lepraemurium* prepared in 0·1 per cent albumin in saline solutions. At 0·025-0·1 per cent concentrations of cetrimide the recovery of bacilli is satisfactory. At concentrations higher than 0·1 per cent, there is significant loss of bacilli from the slides prepared for counting. This loss is not prevented by coating the slides with gelatine-phenol, or by diluting the cetrimide solution tenfold with water. Neutralization of the acid with *N* sodium hydroxide results in more even drying of the drops sampled, and the distribution of the bacilli on the slides is consequently better.

The application of this method for making total bacterial counts

of *M. tuberculosis* in mouse peritoneal macrophages, and of *M. lepraemurium* in a continuous line of rat fibroblast has been tested. Viable counts of bacilli are also possible with *M. tuberculosis*, because this species, unlike many other bacteria, is not killed by cetrimide at *p*H 1·0 even after exposure for several hours. Since the detergent is somewhat lethal to tubercle bacilli at neutrality, its initial concentration should be kept as low as is effective for disruption and dilutions of the disruption mixture made fairly rapidly before plating on culture medium.

New method for isolating ribosomal RNA

A simple method for the isolation of ribosomal RNA reported from the Children's Cancer Research Foundation, Boston, involves the use of soluble sulphonated polystyrene (mol. wt 100000) for the complete dissociation of protein from RNA. The yield (90 per cent) of RNA, by this method, is comparable to that obtained by the phenol method. Protein contamination is only 1·5 per cent. RNA obtained by this method has hydrodynamic properties and approximate molecular weights similar to those of RNA prepared by the phenol method.

The method consists in treating 50S ribosomes with sulphonated polystyrene (0·8 per cent) in 5 m*M* Tris HCl (*p*H 7·4)-0·1 m*M* Mg^{2+} at 4-8°C. for 16 hr followed by isolation of RNA by differential precipitation with NaCl (0·01*M*) and alcohol (52 per cent); the concentration of alcohol is critical. Further purification up to 5 per cent protein contamination is achieved by redissolving and reprecipitating with alcohol (56 per cent) [*Biochemistry*, **6** (1967), 983].

Pasteur Institute, Coonoor

Among the main achievements of the institute recorded in its annual report for 1966 are those relating to the development of Semple vaccine for the treatment of rabies, production of vaccine against small-pox, development and improvement of methods for the cultivation of influenza and other respiratory viruses and their concentration. Five per cent Semple vaccine produced at the institute has been found to reduce the mortality rate of patients bitten by proved infective animals from 2·9 to 0·18 per cent.

In view of the general belief that post-infection antirabies treatment of dogs, cattle and other animals is of no value, a series of investigations were carried out, and it has been found that 39 per cent of presumably rabid animals contain the virus in the salivary glands and are capable of transmitting the infection. Considering the mortality rate among the infected animals, post-infection treatment has been found to be of significant value.

The results of an investigation aimed at improving the antigenicity of the antirabies vaccine show that the antigenicity of vaccine prepared from suckling mouse brain is higher than that of the vaccine prepared from sheep brain. Highest antigenicity is obtained when β-propiolactone is used for inactivation instead of phenol. There is a drop in antigenicity after lyophilization.

Studies have been in progress to improve the medium V_2 so as to increase the titre of influenza virus obtained in CAM cultures *in vitro*. The effect of adding certain compounds, such as sodium succinate, calcium hexosediphosphate and *i*-inositol has been studied. These compounds appear to have a beneficial effect on the growth of the virus. Based on egg titrations, sodium succinate and *i*-inositol, either singly or in combination, promote the growth of the virus. Higher titres of the virus are obtained in cultures when the initial inoculum is low.

Basic data on the incidence of poliomyelitis, the type of virus prevalent, the age at which the children come in contact with the virus as judged by the appearance of antibodies and the other enteric viruses prevalent among them, which are likely to interfere with live virus vaccination have been collected. The isolation rate for poliovirus types 1, 2 and 3 is 20·7, 12·0 and 5·4 per cent, while the infection rate is 22·9, 12·0 and 6·0 per cent respectively. The susceptible age to infection with type 1, 2 and 3 poliomyelitis viruses has been found to be 7, 5 and 5 years respectively. Efforts at preparing live oral poliomyelitis vaccine (Sabin) are in progress.

During the year attempts were made to improve the growth media V_1 and V_2 used for the preparation of cell cultures from kidney and medium V_3 used for the cultivation of the Russian strain of vaccinia virus. The period of trypsinization could be reduced further from 4 to 1·5 hr. The viability of the cells improved when Hank's basal salt solution was used for the preparation of trypsin (0·2 per cent) instead of GKN.

Studies have been undertaken to determine the effect of incorporating several compounds into nutrient agar medium at neutral *p*H on the growth of *V. cholerae*. The inhibitory concentrations of rosolic acid, cetavlon and sodium lauryl sulphate on *V. cholerae* have been found to be 0·005, 0·002 and 2·0 per cent respectively. Preliminary studies indicate that the administration of copper sulphate reduces the severity of the lesions in experimental cholera infection in guinea-pigs even when the challenge is severe.

Laboratory of the Government Chemist, London

The annual report of the Government Chemist for 1965 lists the following among the major topics on which investigations have been completed during the year: (i) determination of the residue level of agricultural pesticides in foodstuffs, milk, water, animal tissue, etc.; (ii) determination of non-ionic detergent traces in water supplies; (iii) determination of trace levels of oestrogens, e.g. stilboestral; and (iv) assessment of the concentration of toxic substances.

A simple testing scheme involving density staining and a simple chemical test has been developed for the identification of the various synthetic tissues used in the manufacture of fishing nets.

A standard of cleanliness for feathers used as the dividing line between taxable and non-taxable feather has been worked out and a number of samples analysed.

Methods based on condensation between formaldehyde and

certain phenolic nuclei present in the tanning extracts followed by measurement of the fluorescence of flavonoids present in and characteristic of quebracho are being developed for determining the quality of tanning materials.

A new technique based on attenuated total reflectance has been successfully applied for *in situ* examination of coated fabrics, thereby making the classification of even the inseparable coatings possible.

The determination of denaturants in preparations made from industrial methylated spirits has been facilitated by the development of a rapid gas chromatographic method enabling classification of the samples.

A rapid and convenient method for the extraction of cetrimide, a widely used denaturant, consists in shaking 1 ml. of the sample with 5 ml. of chloroform and 10 ml. of a conc. solution of ammonium cobaltothiocyanate followed by separation, drying and spectrophotometric estimation of cetrimide at 618 mμ.

Investigations on the analysis of potable and illicit spirits have led to the development of a gas chromatographic procedure for the direct estimation of furfuraldehyde. A method employing a hydrostatic balance to measure specific gravity of the calibrating liquid by weighing a rhodium-plated sphere in air, in water and in solution has been devised for calibrating Skies hydrometers to be used as ' standards '.

The major part of the work of the Food, Drugs, Agricultural and Water Division of the laboratory was devoted to the development and improvement of methods for the determination of vitamin D, folic acid, oestrogen and hexoesterol in foods, drugs and agricultural chemicals. A simple means of reducing oxygen to a negligible amount in dehydrated foods, thus increasing their storage life, has been developed. As a result of investigations on the gas chromatographic analysis of head space gases in canned foods, a sampling unit with two adsorption columns containing a molecular sieve and silica gel for the analysis of oxygen/nitrogen and carbon dioxide respectively has been designed. The unit enables these gases to be determined rapidly.

A method based on the reaction of phloroglucinol with pentoses in mild condition has been found practicable for the rapid estimation of neomycin. Investigations are in hand on the development of a standard test to assess the biodegradability of synthetic anionic detergents.

Among the investigations undertaken by the General Analytical and Advisory Chemistry Division are: (i) the development of a short colour film capable of illustrating various operations in the testing of aerosils for inflammability and explosive properties; (ii) extraction of iodine, a toxic material, from parts of an artificial kidney machine employing polyester resin reservoir, as the dithizone complex and a subsequent photometric determination using nitroso R-salt; (iii) the development of new and more rapid methods based on the ion-exchange separation of the cations followed by ethylenediaminetetracetic acid filtrations for the analysis of the dental setting liquids; (iv) the development of an electrostatically focused image converted with appropriate camera front and narrow-band optical filters, together with a microscopic eyepiece for visual examination of the forged documents, intensity and spectral nature of the infrared illumination; (v) the development of technique employing rapid thawing of deep frozen vegetable tissues for complete extraction of entrained residues and separation of systematic from contact pesticides; (vi) the development of thin layer chromatographic procedure for the determination of dimethoate, phorate and disulphoton together in vegetable tissue; and (vii) the development of a complete method employing loose-layer chromatography on alumina for the detection, determination and identification of organochlorine pesticide residues in samples of fatty nature.

Improvements in the instrumentation for atomic absorption spectrophotometry are in progress. These when completed will incorporate a.c. amplification and a read-out system which will enable evaluation down to 10 absorption to be attained with an acceptable degree of reliability.

Some preliminary work has been carried out to investigate the possibility of checking the authenticity of hair samples held by museums. In one study two samples of hair, one taken in 1953 and the other in 1965, from a male subject were examined by irradiating the samples for 3 days in a neutron flux of 10^{12} neutrons/cm.^{2}/sec. and the gamma spectra obtained after various periods of time were very similar except for a gold-198 (half-life 2·6 days) peak at 0·40 MeV. which was more prominent in the earlier sample.

Announcement

▪ *The Second International Conference on Thermionic Electrical Power Generation* sponsored by the European Nuclear Energy Agency will be held at Stresa (Italy) during 27-31 May 1968.

The main purpose of the conference is to review current research on thermionic processes for direct conversion of energy into electricity. The topics for discussion at the conference are: (i) convertor performance (including related theory), (ii) plasma and surface phenomena, (iii) materials (including nuclear fuels), (iv) in-pile studies, (v) heat pipes and related devices, and (vi) integrated system.

Enquiries concerning the conference should be addressed to the European Nuclear Energy Agency, 38 Boulevard Suchet, Paris 16e, France. Provisional titles and abstracts of papers should reach the Direct Conversion Division, Euratom CCR, Ispra (Varese), Italy, by 15 December 1967, and full texts by 31 March 1968.

The proceedings of the first conference held in London in 1965 have been published (March 1967) by the Institution of Electrical Engineers, London.

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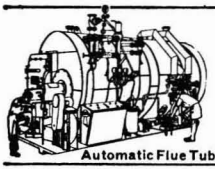
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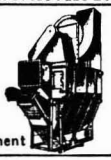
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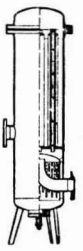
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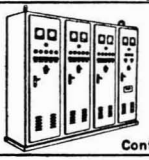
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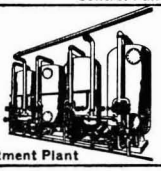
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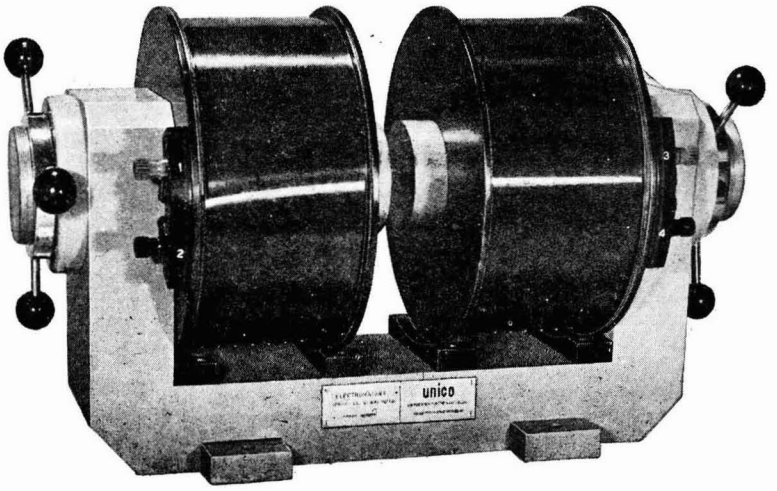

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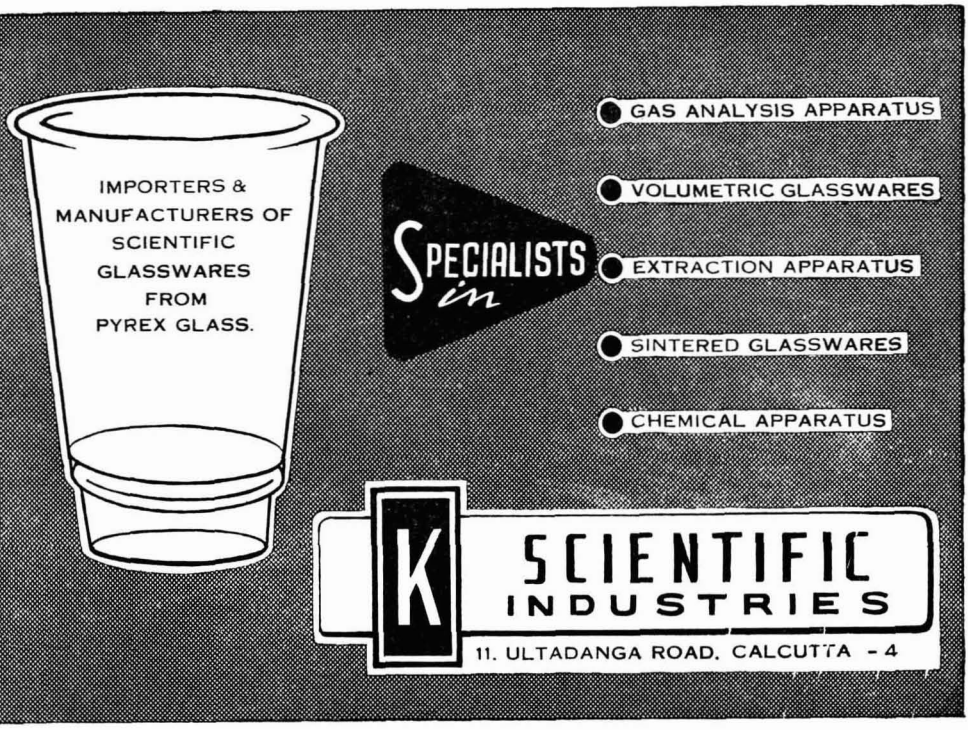

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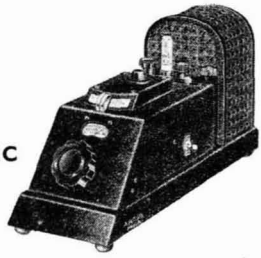

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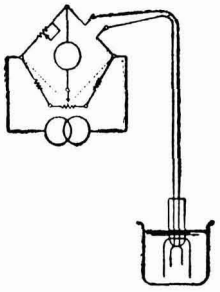

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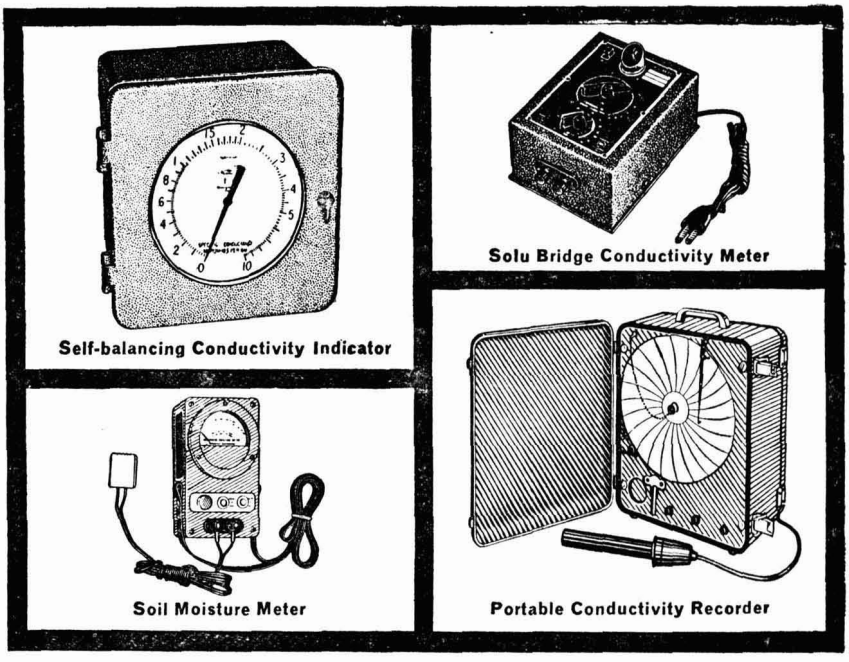

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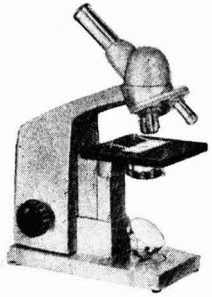

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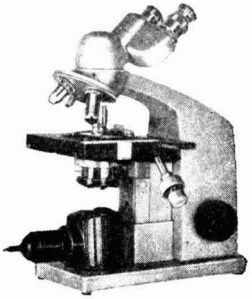

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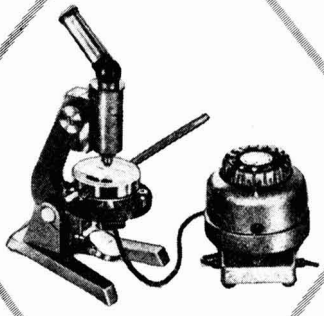

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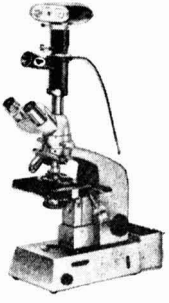

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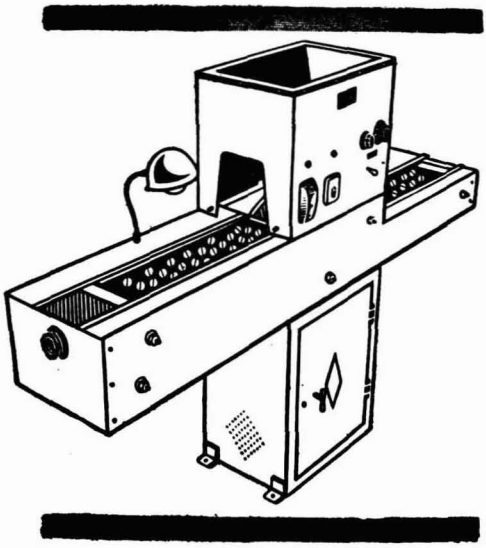

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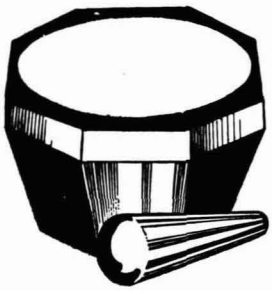

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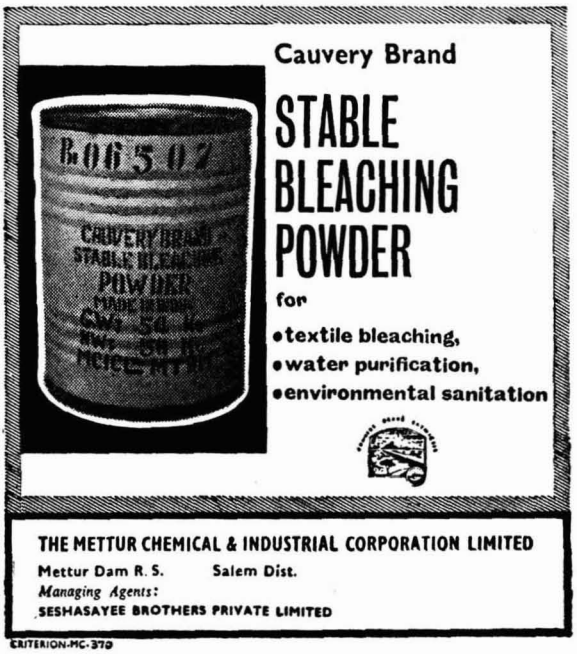

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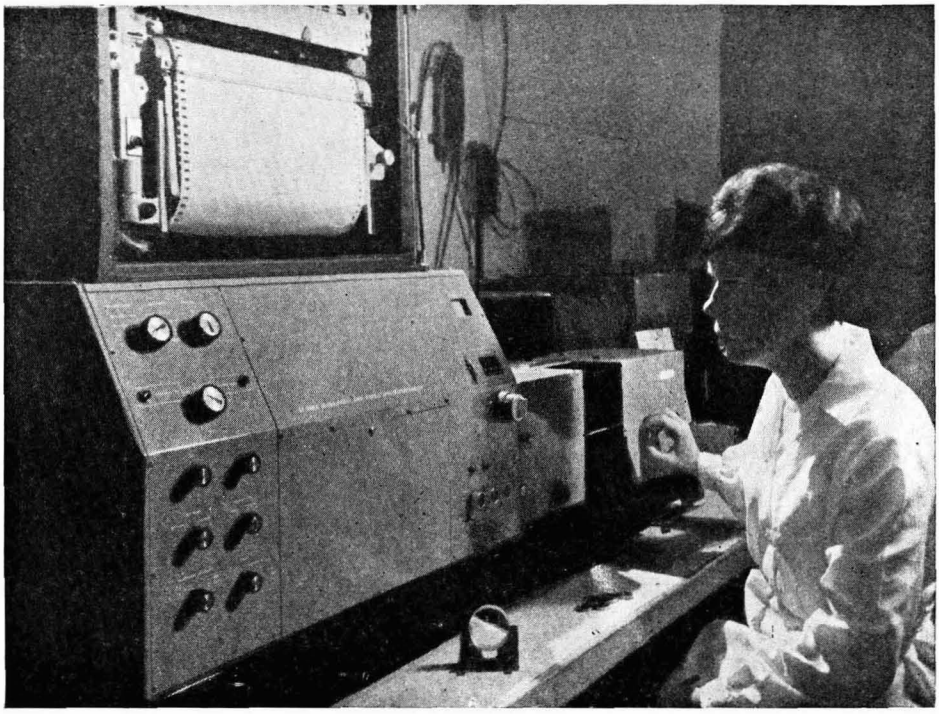

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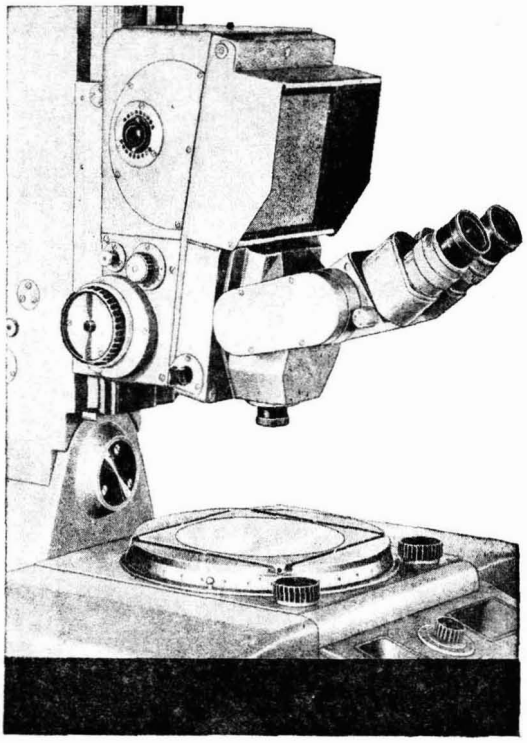

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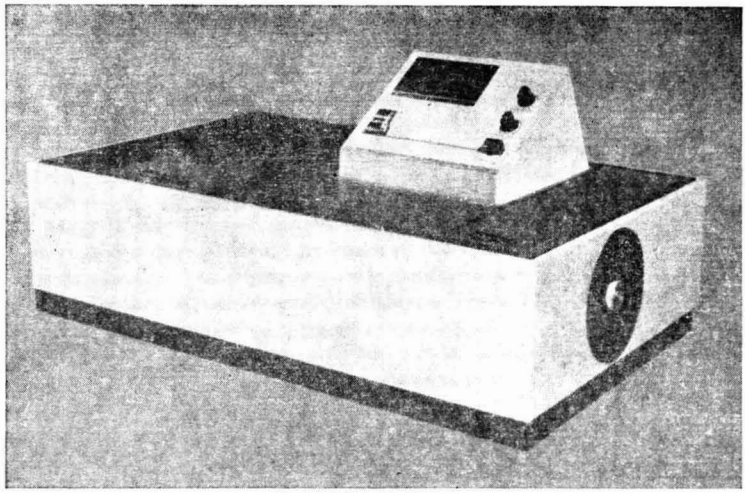

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