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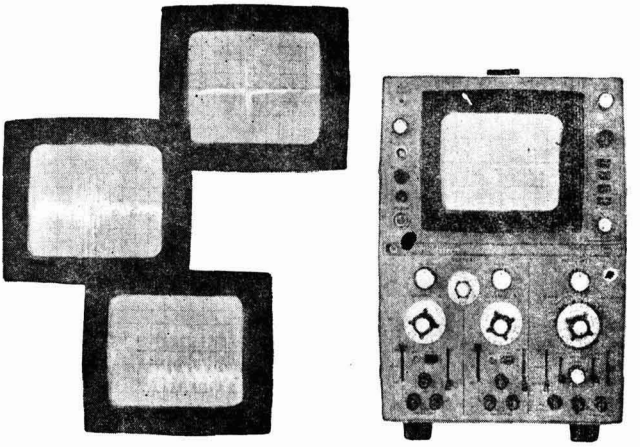

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CONTENTS

For Index to Advertisers, see page A13

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Current Topics

Scientific Research in the Fourth Plan

THE draft outline of the Fourth Five Year Plan finalized by the Planning Commission estimates the total expenditure (both plan and non-plan) during the plan period by the main organizations concerned with scientific research, viz the Council of Scientific & Industrial Research, the Department of Science in the Ministry of Education and the Department of Atomic Energy, at Rs 270 crores, which is substantially higher than the total expenditure (Rs 230 crores) incurred on research during the 15-year period (1951-66) covering the three previous five-year plans. The plan outlay proposed for the Department of Atomic Energy, the Council of Scientific & Industrial Research and the Department of Science in the Ministry of Education is Rs 50, 46 and 24 crores respectively. An additional expenditure of Rs 160 crores (with a plan outlay of Rs 70 crores) is envisaged for the other ministries in the Government of India having under them scientific organizations with research responsibilities. The R & D expenditure expressed as percentage of the gross national product (termed as research ratio) works out to 0·35 at the end of the Fourth Plan period, the corresponding figures for the first three plan periods being 0·06, 0·16 and 0·26 respectively.

Pointed attention is drawn in the draft outline of the plan to the disproportionately low level of participation of industry towards R & D expenditure. While in the advanced countries this figure is of the order of 60-70% of the total non-military R & D expenditure, in India it is only about 5%. This is indicated as an important factor responsible for the failure of R & D effort to make the desired impact on the process of economic growth. Another equally important factor has been the country's continuing weakness in respect of design and development work and dependence on imports for foreign designs and technical know-how. The draft emphasizes the need for allotting specified objectives and time schedules to projects of applied research, particularly those of design and development character. A strong plea is also made for the utilization of as large a part as possible of R & D staff and facilities in government agencies and in higher educational and technological institutions to promote research, design and development work within, or in collaboration with, industrial establishments in both public and private sectors. It is also considered necessary for scientists in government and other research agencies to participate in the activities of educational and technological institutions.

Attention is drawn to the rapid growth in the number of R & D scientists and technologists, and its bearing on the quality of research. From about 9000 scientists and technologists at the end of the Second Plan, the number has gone up to 15,000 at the end of the Third Plan. In order to maintain a high rate of growth of research, it is considered necessary to initiate a long-term programme of training for research personnel, with due emphasis on basic research, and an outlay of Rs 15 crores is proposed for this purpose. The inadequacy of the existing training facilities for research personnel is attributed partly to the weakness of basic research in higher educational and training institutions and partly to the lack of instruments, accessories, equipment, stores and other facilities. The specific purpose of the additional outlay is to give selective financial support, on merit, to individuals, projects, or institutions to strengthen basic research in science and technology associated with research training in any subject field independently of the existing administrative channels or institutional affiliations. It would also be used to correct disparities which have arisen through imbalances in the allocation of resources and lack of adequate support of non-government institutions and scientists.

The draft outline of the plan lays down broad guidelines in the fixation of priorities in the formulation of research programmes of the main research organizations. Thus, it proposes that the effort in the Department of Atomic Energy should be directed mainly to the atomic power programme, with special emphasis on import substitution of hardware, maintenance and replacement parts, and on the use of atomic energy for other peaceful purposes. In the case of the Council of Scientific & Industrial Research, highest priority is indicated for projects relating to food, import substitution and export promotion, and to the promotion of research and development within industry through the collaboration of its own staff with industrial enterprises and the establishments of cooperative research associations. The Survey of India would be strengthened for the systematic preparation of maps as an essential prerequisite for hydroelectric power, irrigation, flood control, minerals development, etc. Anthropological, botanical, sociological and other scientific activities of the Department of Science, Ministry of Education, would concentrate on consolidation and utilization of development schemes taken up in the Third Plan. A special provision of Rs 5 crores has been made for the support of high priority programmes in connection with food, import substitution and export promotion, especially within, or in collaboration with, industry.

Discussing the important problem of Indian scientists working abroad, the draft outline attributes the insignificant success achieved in attracting the bulk of these scientists to work in India, despite the establishment of the 'Scientists Pool', to the fact that a career in scientific research in India is not yet sufficiently attractive. The two problems identified as being highly crucial to the achievement of best results from the R & D effort are: (1) how to make scientific research sufficiently attractive to men of talent and ability, and (2) how to use applied research and development to promote economic growth.

Mathematical Methods in Science & Technology: Conference Series

The Council of Scientific & Industrial Research will be sponsoring conferences, seminars and symposia on 'Mathematical Methods in Science and Technology (MASTECH)' at various centres in India. Prof Alladi Ramakrishnan, Director, Institute of Mathematical Sciences, Madras, will be the general convener of the series of conferences. He will be assisted by a steering committee appointed separately for each conference.

The main objectives of the conferences are: (i) to foster original work in mathematical sciences; (ii) to bring creative mathematicians into direct contact with the scientists engaged in industry and technology; (iii) to stimulate new applications of mathematical methods in various fields ranging from biology to industry; and (iv) to survey the state of the subject and to discover new topics for research and improve methods for research in progress.

The number of participants for each conference will be approximately 30, some 6 of them being invited lecturers who would survey the state of the subject. The lecturers are expected to give comparative and critical accounts of the developments in the field in which they have made original contributions. The participants should present original papers (hitherto unpublished) and are expected to join discussions in the scientific meetings. Those intending to present papers should send them to any of the members of the steering committee.

The first 'MASTECH' conference will be on 'Matrix and Combinatorial Analysis in Science and Technology' at the National Aeronautical Laboratory, Bangalore, for 3 days some time in August 1969. The members of the steering committee for this conference are Dr S. R. Valluri, Director, National Aeronautical Laboratory, Bangalore; Prof G. S. Ramaswamy, Director, Structural Engineering Research Centre, Roorkee; and Prof J. N. Kapur, Professor of Applied Mathematics, Indian Institute of Technology, Kanpur.

The subjects of some of the conferences to follow will be: Numerical Analysis; Differential Equations; Stochastic Theory; and Operational Research.

Seminar on Food Irradiation

WITH population growth continuously outstripping agricultural production, food remains a major problem in large parts of the developing world. Besides the inevitable economic disturbances in the region, this imbalance is causing enormous damage in terms of human health. It has been estimated that over 50% of the world's population suffers from hunger or malnutrition, or both. Lending urgency to this problem is the alarming prospect of feeding an additional 4·6 billion mouths over the present 3·4 billion, just 41 years away. This increase, according to UN experts, will be mostly in the developing countries, some of which are already experiencing chronic food shortages.

The solution lies partly in increasing the food output coupled with an aggressive drive to retard population growth. An important complement to these efforts is conservation and preservation of food. This means making a larger portion of the produce available for human consumption or, in other words, preventing a large portion of the food from becoming unfit for people.

For almost two decades, research has been going on in several countries on the use of nuclear energy for food preservation to supplement and, in some cases, to replace traditional methods. Presently, some 76 countries, constituting 80% of the world's population, are already engaged in research, or are planning to initiate food preservation programmes. In a few countries, notably the USSR, Canada and Israel, some items of irradiated food have already been cleared for human consumption.

In India, work in this area has been going on for some time at the Food Irradiation and Processing Laboratory of the Bhabha Atomic Research Centre (BARC), Trombay. Here, emphasis has been placed mainly on four aspects of immediate relevance to the country, viz grain disinfestation, sprout inhibition in potatoes and onions, extension of shelf-life of sea-foods and flesh foods, and delaying of maturity in mangoes and bananas.

The progress of research at BARC was brought out in a number of status reports presented at a seminar on Food Irradiation held at FIPLY on 13 and 14 January 1969.

The seminar, organized jointly by the BARC, the International Atomic Energy Agency (IAEA) and the Food and Agricultural Organization (FAO), brought together specialists and research workers in food sciences and technology and representatives of industry and government departments, for exchange of information and discussions with IAEA experts and BARC scientists. Shri H. N. Sethna, Director, BARC, inaugurated the seminar. The deliberations began with opening remarks by Dr A. Sreenivasan, Head, Biochemistry and Food Technology Division, BARC, who outlined the current and the projected research programmes of the BARC in the field of preservation of food by irradiation.

Apart from the reports of BARC scientists, informative lectures on the fundamentals of food irradiation were delivered by three international experts: Dr Harry E. Goresline, Food Irradiation Specialist, IAEA; Dr Maurice de Proost, Head, Food Preservation Section, Joint FAO/IAEA Division of Atomic Energy in Food and Agriculture, Vienna; and Dr Walter M. Urbain, Professor of Food Science, Michigan State University, USA. These lectures provided a useful background to the proceedings, of particular benefit to several of the participants not actively engaged in food irradiation.

Speaking on planning for a research programme in food irradiation, Dr Goresline enumerated the various factors that have to be considered to ensure that the process is feasible and economical. In the actual planning of the experiments, he stressed that so far as is possible, the number of variables to be studied should be kept to a minimum in the interest of economy of time, material and effort. He held that uncontrolled fluctuations in pretreatments, actual process of irradiation or post-irradiation storage conditions, could cause as much variability in the results as any of the experimental factors being investigated.

Dr Goresline also brought out that the acceptable minimum radiation dose for any product has to be established on the basis of the microbiological, entomological and enzymological objective of the treatment in stabilizing the product.

Describing food irradiation as a process, Dr W. M. Urbain said that generally there is a minimum dose requirement, and the average above the minimum is usually controlled by legal requirements, practical considerations and economics. Speaking on the economics of food irradiation, he said that since there is no commercial radiation processing experience in the food industry, estimation of costs is particularly difficult. He held that many of the factors involved in the costing of any conventional food process also applied to food irradiation. It is important to bear in mind, he said, that since much of the cost of irradiation is of a fixed nature and is incurred whether the facility is used or not, it is necessary to operate the unit as fully as possible for economy. Ordinarily, a single shift of 8 hr provides 2000 hr of operation per year and a three-shift operation with about 6000 hr per year is usually the maximum one can expect to obtain.

The technological aspects of food irradiation were briefly described by Dr M. de Proost with emphasis on the choice of suitable sources, dosimetry and safety systems. According to him, though initial research work can be done in small units of 1-3 litres capacity, when interest grows to the stage of industrial application, the work must be carried out in large units to obtain information on a scale that would have validity when extrapolated to commercial production. Pilot plants are necessary for working out problems of implementation, mechanical handling on large scale, continuity of operation and likely economics of the process.

Dr de Proost also reviewed the food irradiation programmes of the Joint FAO/IAEA Division of

Atomic Energy in Food and Agriculture, and summarized the status of present research on disinfestation, pasteurization and sterilization of foods through ionizing radiations, as well as aspects of legislation and clearance of irradiated food.

Shri D. R. Bongirwar spoke on design and problems of dosimetry in connection with the two pilot scale ^{60}Co irradiators installed in the Food Irradiation and Processing Laboratory at Trombay. He said that one of the main considerations in the design of the package irradiator had been the need to obtain variable throughputs and dose rates to allow flexibility of operation for multipurpose usage.

The package irradiator (100,000 curies ^{60}Co), consisting of large and small source racks, he said, was being used for experimental and developmental work for gamma irradiation of fruits, vegetables, sea-foods, flesh and dairy foods as well as for the sterilization of medical supplies.

The through-flow irradiator (28,000 curies ^{60}Co) was being used to test various irradiation conditions and technological problems peculiar to the application of radiation for disinfestation of grains in India. Shri Bongirwar disclosed that plans had been completed for comparative studies of post-disinfestation behaviour during storage of irradiated and fumigated grains in experimental silos of 2-tonne capacity, under fabrication.

Recounting the problems encountered in the dosimetry of the package irradiator, he said that the high overdose ratios of about 1·8 and 2·6 respectively for the large and small sources obtained initially after installation had been reduced to 1·25 and 1·5 respectively by effecting several modifications in the design of the source, reducing the area of the product box and increasing the number of passes for the product boxes around the source racks.

Shri S. D. Dharkar spoke on his work on the delaying of ripening in tropical fruits, especially mango and banana, by the use of gamma rays. Describing his studies, Shri Dharkar reported that a combination of skin coating and irradiation extended the shelf-life of mangoes up to 16 days. This would be of considerable help in transporting the fruit within the country. For despatch to distant countries, he said, the fruit would in addition require storage in refrigerated holds.

He also reported on the differences observed when mangoes were kept covered by either paper cuttings or dry paddy straw. Irradiated mangoes covered in this way showed twice the storage life (90 days) of the uncovered irradiated ones (40 days).

One of the main objectives of irradiation is protection of the produce during transit, and in this context, Shri Dharkar described studies on transportation of irradiated mangoes over long distances. It was observed by him that the combination process of skin coating and irradiation was the best.

Shri Dharkar reported observing a similar delay in ripening of four Indian varieties of bananas by exposure to low-dose irradiation.

Another area of emphasis at BARC is inhibition of sprouting in potatoes and onions. Shri Dharkar said that low-dose irradiation can be used to considerable advantage in preventing the losses due to sprouting, while evaporative losses can be minimized by skin coating.

In a typical study, onions were exposed to irradiation in the range 6-10 krads, and subsequently stored at ambient (26-32°C) or subroom (10°C) temperatures. Almost 100% of the control bulbs stored in cold and ambient temperatures sprouted within 2·5 months, and after 6 months were completely spoiled and unsaleable, whereas the irradiated ones stored at both temperatures were found to be still in marketable condition.

Sarvashri K. S. Karnik and P. N. Joglekar of the Department of Atomic Energy, Bombay, read a paper on the economics of potato and onion preservation by the use of irradiation. They held that even very preliminary investigations had established the economic viability of the commercialization of the irradiation process.

In India, they said, only 7 tonnes out of every 10 tonnes of potatoes and onions grown are actually available for consumption, 3 tonnes being lost due to sprouting, dehydration, spoilage, rot, etc.

Dr U. S. Kumta reported on the status of the programme relating to the preservation of sea-foods by radio-pasteurization. Programmes in this area at BARC, Dr Kumta stated, had been undertaken with two objectives: (i) to develop radiation pasteurization procedures for tropical sea-foods, especially those which have defied other methods of preservation, and (ii) to use appropriate combination of conventional preservation techniques with irradiation, so as to minimize limitations of either method, improve product quality and extend shelf-life.

In the case of Bombay duck, he said the storage life of fillets at 10-12°C could be extended to 21 days by 0·5 Mrad in contrast to rapid deterioration of unirradiated fish within 3 days. The radiation pasteurization process, he maintained, was of considerable technological significance for Bombay duck, since hitherto this fish has not been readily amenable to canning or freezing.

Dr Kumta also said that semi-dried shrimps and Bombay duck with 40% moisture which spoil within seven days, could be stabilized for room temperature storage for about 3 weeks by irradiating the products with 0·25 and 0·5 Mrad respectively.

Dr Kumta stated that promising results so far obtained were being scaled up with a view to testing the merits of the processes in commercial practice and these studies were being carried out with the active collaboration of the Central Institute of Fisheries Technology, Veraval and Bombay sub-stations.

Dr P. L. Sawant reported on the preliminary findings on radiation pasteurization of lamb meat, a process which appears promising. Lamb meat, packed in polythene bags and subjected to gamma irradiation in the dose range of 0·25-0·90 Mrad at melting ice temperature, gave extension of storage life up to a maximum of 90 days when stored at 0°C. While no radiation odour was noticeable in samples irradiated up to 0·25 Mrad, it was found tolerable in those irradiated at 0·5 Mrad, and was quite pronounced in samples given 0·9 Mrad. The radiation odour was, however, found to be

transient and disappeared during subsequent storage of samples at 0°C or 10-12°C; samples irradiated at 0·9 Mrad had normal odour within three weeks post-irradiation storage at 0°C.

In a paper on grain disinfestation with gamma rays jointly prepared by Shri G. W. Rahalkar and Miss Anne J. Lewis, it was stated that there was enough data available to demonstrate that radio-sensitivity, measured either as sterility or lethality, was dependent upon the stage of insect development at irradiation.

Describing their studies, Shri Rahalkar and Miss Lewis said four radiation dose levels — 5, 10, 15 and 20 krads — were selected, and the response of various developmental stages of insects as regards inhibition of development or induction of sterility was measured. Adult emergence was the main parameter selected for the assessment of radio-sensitivity and, whenever adult emergence was observed, their reproductive potential was evaluated on the basis of total progeny produced.

Based on the experience gained, studies have been planned to carry out large-scale disinfestation of stored wheat by the use of gamma rays from ^{60}Co in a specially designed through-flow irradiator (28,000 curies) with a capacity to irradiate 500 lb per hr at 15,000 rads. The merits of the process would be compared with the currently practised fumigation process in experimental storage bins of 2- to 3-tonne capacity installed in the open.

Dr (Smt) U. K. Vakil presented data on the effects of ionizing radiation on the physico-chemical properties of starch and protein in wheat, and on the activities of amylase and protease, since these are important parameters in determining the quality for bread-making. It was observed that irradiation results in increased initial reduction of sugars and siastatic activity and that amylose is more vulnerable to radiation damage than amylopectin. There is a significant decrease in glutenin and gliadin with concomitant increase in peptides and free amino acids as a result of irradiation.

She added that detailed investigations of various textural characteristics of dough indicate that irradiated wheat offers better resistance to stretching and uses more energy to extend the dough stability. These results suggest that the elasticity of gluten and the potential backing volume are improved in irradiated wheat.

In another report, Dr Vakil stressed the importance of knowledge on the wholesomeness of irradiated foods to avoid recognized hazards to health, and detailed long- and short-term feeding studies with rats and mice.

Wheat, irradiated at the insect disinfestation dose level of 20 krad or at ten times this dose, was included at a high level (75%) in otherwise nutritionally adequate diets and fed to the experimental animals for four generations, besides the parent generation. In addition to physiological studies on growth, reproduction, lactation and longevity, detailed studies on tissue function, hematology, histopathology and characteristics of intestinal microflora were carried out. No changes in any of these parameters were apparent in the animals fed the irradiated wheat, when compared to controls.

Similarly, no significant differences were observed between groups fed either unirradiated or irradiated (0·25 Mrad) shrimps as sole source of protein in diet in parent and first generations. Short-term studies (12-15 weeks) on rats fed on irradiated complete diets (20 and 200 krad) also did not reveal any differences in growth, feed and protein efficiency ratios as compared to controls.

Dr A. S. Aiyar referred to reports on the cytotoxic effects of irradiated sugar solutions and other media on cell cultures and lower forms of life which had been interpreted by some to indicate a potential hazard in the use of irradiated foods. Detailing a series of experiments with irradiated sucrose solution, he pointed out that while it was found to impair oxidative phosphorylation and energy dependent biochemical processes at the cellular and sub-cellular levels *in vitro*, judged by various parameters, it was without any effect in the whole animal when fed orally. Similar *in vitro* toxicity was also observable with autoclaved sucrose solution. In a further study, it was observed that, when fed orally to rats, the components in irradiated sucrose solution responsible for *in vitro* toxicity are rapidly metabolized and excreted with no detectable retention in the tissues of the animal beyond 30 hr. These studies clearly point to the invalidity of extrapolations of findings with *in vitro* systems to whole animals endowed with efficient physiological and metabolic processes, such as digestion, absorption, detoxification and excretion besides numerous hormonal and other regulatory control mechanisms.

International Symposium on the Metabolic Function of Vitamin A

J. GANGULY
Department of Biochemistry, Indian Institute of Science, Bangalore 12

AN international symposium on the Metabolic Function of Vitamin A was held in the Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge (Mass.), USA, during 25-27 November 1968. The chairman of the conference was Prof George Wolf, Associate Professor of Physiological Chemistry in the same department.

The symposium was broadly divided into four sessions. In Session I, papers on absorption, transport and storage of vitamin A were presented, while Session II was devoted to metabolism and the 'active form' of vitamin A, and the conversion of β-carotene to vitamin A. Session III was divided into three parts as follows: Part 1 — vitamin A and enzymes; Part 2 — vitamin A and membranes; and Part 3 — vitamin A, differentiation and reproduction. Session IV was on clinical aspects of vitamin A deficiency, as related to metabolic function. In all 20 invited papers of half an hour duration each were presented by 19 guest speakers, while there were 15 official discussants participating at the various sessions.

During the first session, Prof DeWitt S. Goodman (New York) presented his latest work on the isolation and properties of the protein that transports retinol in human plasma. Long ago the present author had suggested that retinol is transported in plasma by a specific carrier protein[1,2]. It was, therefore, gratifying to note that such a carrier protein has now been isolated. Prof I. Ascarelli (Israel) presented various aspects of his work on the absorption of vitamin A in chickens, including the effect of protein malnutrition. Here also, it was gratifying to note that Prof Ascarelli's work on chickens was in full agreement with the earlier work from this laboratory with rats. The present author then discussed the latest work on the absorption of retinol, retinyl esters, retinal and retinoic acid. He showed that retinoic acid is absorbed entirely through the portal route and is rapidly excreted through the bile of rats. But what appeared most interesting was that quite a bit of dietary retinol and retinal are absorbed through the portal route and are excreted through the bile as retinoic acid, which is quite contrary to the currently accepted concept that vitamin A is absorbed entirely through the lymphatic system of rats.

Session II was opened by Prof Hector F. DeLuca (Madison, Wis.), who presented his already published work on the possible pathways of degradation of retinol and retinoic acid inside the rat. This was followed by Prof J. A. Olson's (Bangkok) review of his work on the *in vitro* conversion of carotenes to vitamin A with mucosal and liver enzymes, and on the *in vitro* oxidation of different apo-carotenals by the same enzymes. Prof DeWitt S. Goodman (New York) then described his recent work on the carotene cleavage enzyme isolated from pig intestine.

In Part 1 of Session III, Dr Joseph Carroll (Dublin) reviewed the existing information in support of, and against, any role of vitamin A in sulphate metabolism and admitted that their earlier work on the *in vitro* effect of retinol and retinoic acid in the sulphotransferase of the livers of newly born baby rats could not be reproduced. They attributed this to a change in the dietary history of their rats and also to the possibility of their retinol derivatives forming peroxides during prolonged storage. Dr Charles A. Pasternak (Oxford) reiterated his earlier claims that vitamin A deficiency does not affect sulphate metabolism in rats. Dr Rene Grangaud (Rennes, France) reviewed with extensive illustrations his sustained work carried out over a period of years on the relationship between vitamin A and steroid hormones, and fully confirmed the observations we have made in this laboratory regarding the effect of vitamin A deficiency on the $\Delta^5,3\beta$-ol steroid dehydrogenase activity in rat adrenals. The final participant in this part of the session was Dr William E. Rogers (Jr) (Bethesda) who tried to review the existing information on the effect of vitamin A deficiency on (i) sulphurylation, (ii) $\Delta^5,3\beta$-ol steroid dehydrogenase, and (iii) γ-gulunolactone oxidase in rats. In these attempts of his, which were backed by virtually no convincing work of his own, he tried to draw the conclusion that vitamin A deficiency does not affect any of these three enzyme systems.

During Part 2 of Session III, Prof Oswald A. Roels (New York) presented his work on artificial membranes prepared with various lipids, including retinol, while Prof Jack A. Lucy (London) discussed theoretical aspects of the role of vitamin A in electron transport and in membrane formation.

Part 3 of Session III was opened by Dr J. N. Thompson (Liverpool and Ithaca) who extensively reviewed the work on the effect of retinol and retinoic acid on the growth and development of chick embryo, while Prof B. Connor Johnson (Oklahoma City) discussed the possible relationships between vitamin A and nuclear RNA synthesis and Dr Luigi DeLuca (MIT) discussed similar possible relationships between vitamin A and protein synthesis in rat intestinal mucosa. This session ended with a paper from Prof H. D. Eaton (Storrs) who reviewed the work he and his colleagues have been carrying out over a period of years on the effect of vitamin A deficiency on the cerebrospinal fluid pressure in farm animals.

The concluding session of the symposium was devoted to clinical aspects of vitamin A deficiency, as related to metabolic functions. During this session Dr V. N. Patwardhan (India) spoke on the epidemiology of xerophthalmia, Dr H. A. P. C. Oomen (Netherlands) on vitamin A deficiency: the

clinical picture, and Dr G. Arroyave (Guatemala) on the interrelations between protein nutrition and vitamin A metabolism; finally, Dr Edward G. High (Nashville, Tenn.) discussed some aspects of nutritional vitamin A levels in pre-school children of Beaufort County, South Carolina.

The main purpose of the symposium was to find leads regarding the mode of action of vitamin A. Outside its well-known role in vision the proper understanding of the metabolic function of vitamin A has been alluring us for a long time. From this point of view, commendable attempts were made by the organizers of the symposium at reviewing, and at focusing attention on, various aspects of the biochemistry and physiology of vitamin A. As in the case of many other vitamins, work on the effect of vitamin A deficiency on various enzyme systems should have been of considerable significance. Indeed, lately considerable amount of work has gone into such attempts and it has been shown that several enzyme systems, viz Δ^5,3β-ol steroid dehydrogenase, γ-gulunolactone oxidase and ATP-sulphurylase, are affected by vitamin A deficiency in rats. However, as already mentioned, Dr W. E. Rogers (Bethesda) tried to prove that vitamin A deficiency has no such effects. It is interesting to recall that even a year ago Rogers[3] had recognized that gulunolactone oxidase is depressed in the liver of vitamin A-deficient rats. The results presented at the symposium by the same author on this enzyme system were of a very preliminary nature and certainly could not be considered to be of great significance.

Regarding the steroid dehydrogenase, Grangaud and his colleagues have demonstrated over a period of years the superiority of pregnenolone over progesterone in prolonging the life of vitamin A-deficient rats. More recent work from our laboratory has produced direct evidence showing a loss in the activity, in the tissues of vitamin A-deficient rats, of the enzyme system Δ^5,3β-ol steroid dehydrogenase, which is involved in the conversion of pregnenolone to progesterone. In the symposium, Grangaud presented extensive data fully confirming our observations, while the results of Rogers indicated that the deficiency has no such effect on this enzyme system. Recently they have published this work[4]. But scrutiny of this paper clearly shows that most of their rats had grown between 200 and 250 g, before they had become deficient and had begun to lose weight. In contrast, the deficient rats used by us, as well as by Grangaud, seldom exceeded 100 g in weight. Even more striking was the weight of the adrenals. Thus, while the adrenals of our deficient rats usually weighed 18-30 mg, those used by Rogers were between 30 and 80 mg. It is now a moot question as to whether a comparison of the enzymes from such sources will be strictly valid.

As regards the sulphurylase, it is now generally recognized that it is quite sensitive to variations in dietary treatments, age, sex, etc, of the rats[5]. This point was rather clearly brought out by Prof B. Spencer (Dublin) when he tried to explain their failure to reproduce their earlier observations on the effect of vitamin A deficiency on ATP-sulphurylase in rats. According to them, this was mainly due to a change in the diet and in the housing of the rats. It may be recalled in this context that in their work Pasternak and his colleagues[6] found no difference in the sulphurylase activity in the tissues of vitamin A-deficient and normal animals. The present author[7] had raised the question that they had not produced sufficient evidence to show that their animals were deficient, but Pasternak was rather emphatic at the symposium that their animals had lost weight. An examination of their paper[6] will not only reveal that they made no mention of the loss of weight of their animals, but also that they did not use pair-fed controls. The latter point assumes great significance, because it is well known that vitamin A deficiency does affect food consumption and that starvation affects ATP-sulphurylase, in which case these authors should have found some difference in the enzyme activities between their control (which were not pair-fed) and deficient animals (if at all they were deficient).

The general concensus of the symposium was that the reported effects of vitamin A deficiency on the several enzyme systems are probably not directly related to any metabolic function of vitamin A, but are rather indirect effects brought about by prolonged deficiency.

I think another interesting point to emerge from the discussions in the symposium was the general recognition of the fact that the history of the treatments the animals receive before use cannot be ignored. As already discussed, some of the participants mentioned this point. To the present author this point assumes considerable significance because of the lack of uniformity in the procedures used for obtaining vitamin A-deficient rats. I have already mentioned that, while our deficient rats seldom exceed 100 g in weight, there are laboratories where they are much bigger.

Several years ago, we[8] had conclusively shown that ascorbic acid synthesis is markedly reduced in the vitamin A-deficient rats and that the life span of such rats can be prolonged by giving them ascorbic acid. We had, therefore, suggested that in order to obtain pure vitamin A deficiency, free of ascorbate deficiency, ascorbic acid should be included in the vitamin A-deficient diet of the rats. But this procedure is not recommended by the USP and, therefore, we have never used it. It was, nevertheless, interesting to note that Geison *et al*[5] had included 0·01% ascorbate in their vitamin A-deficient diet.

Yet another procedure that is being considered for obtaining the deficient rats consists in maintaining rats on a vitamin A-free diet supplemented with retinoic acid. As soon as retinoic acid is withdrawn from such a diet, the rats rapidly lose weight. Here again this procedure is not according to the USP specifications and it is also another moot question as to whether retinoic acid might change the physiology of the rats to any significant extent, because it is known that it does have profound effects on the metabolism of hormones in rats of both sexes.

This brings me to the interesting work presented by Dr Bieri at the symposium on the induction of vitamin A deficiency in germ-free rats. Apparently

such rats take much longer time (as compared to the conventional ones) to reach the weight-plateau stage, after which they continue to live for a considerable length of time without losing much weight. While this observation confirms the existing concept that vitamin A-deficient rats ultimately die of infection, it has not been clear as to what causes the ultimate death of these rats. Be that as it may, my point is that, here we have yet another parameter for obtaining vitamin A-deficient rats. It seems almost certain that such rats will show a completely different set of changes in their enzymes, when compared to those made deficient by the conventional method.

Therefore, we are now faced with the peculiar situation as to which type of rats should be called vitamin A-deficient rats. According to strict definition all of them are. But according to the USP specifications they should neither receive retinoic acid nor ascorbic acid, nor should they be germ-free. I think now somebody should come forward and re-define a vitamin A-deficient rat. Till that is done, it will save us a lot of unnecessary work and confusion, if the different laboratories at least try to follow the existing specifications given by the USP. Even here, unless the age, weight and sex of rats of different laboratories are comparable, the chances of disagreement will always be there. I need hardly comment on the importance of pair-feeding in the work with vitamin A-deficient rats. In the past, several workers had made the mistake of not using proper pair-fed controls, and as mentioned above, Pasternak and his colleagues also did not use such pair-fed controls. But I think there is a general recognition now that the control animals should be pair-fed.

If the main objective of the symposium was to find indications regarding the metabolic functions of vitamin A, it has sadly missed the most important and promising area. Recent work on the effect of retinoic acid in reproduction in both male and female rats has been most interesting and during the symposium, Dr J. N. Thompson ably reviewed their work with chick embryo. The present author[9] has just published the results of extensive work from his laboratory on the effect of injection of several steroid hormones in the prevention of gestation-resorption in the retinoic acid-fed pregnant rats. It seems almost certain that retinol is somehow required for the biogenesis of steroid hormones in the female rats. Had proper emphasis been placed on this topic and had meaningful discussions taken place, perhaps the symposium would have made a significant contribution by opening up this entire area. It is rather unfortunate that such an opportunity was missed.

Note added in proof: Since this manuscript was sent to the press, two papers have appeared in print that substantiate the points developed here. Thus, in the paper by D. B. Thomas and C. A. Pasternak [*Biochem. J.*, **111** (1969) 407], retinoic acid was used for obtaining the vitamin A-deficient rats. Weanling male rats were fed a retinoic acid-supplemented diet for 2-3 months, at which time they weighed 200-300 g. Vitamin A-deficient animals were obtained by withdrawing the retinoic acid supplementation at this stage. Clearly, these rats had become adults by the time they lost weight and, moreover, retinoate supplementation must have changed their metabolic patterns, because retinoic acid does affect the synthesis of steroid hormones. Therefore, a comparison of the results obtained under these conditions, with those obtained under conventional conditions, cannot be strictly valid.

More significant has been the report by J. Clausen [*Eur. J. Biochem.*, **7** (1969), 575], where he has not only demonstrated a pronounced effect of vitamin A deficiency on sulphate metabolism in rat brain, but has also pointed out that unless the stress of the deficiency is applied before myelination is complete, the effect of the deficiency may not be perceptible. This is in conformity with our opinion that, unless the stress is applied during the early phases of rapid growth, similar effects may not be noticeable in other tissues and other enzymes also.

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Study of Fast Events

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DURING the last two decades, a variety of instruments and techniques have been developed for studies on explosives, armaments and other fast events. The techniques commonly used are high speed photography, oscillography and flash radiography. Excellent bibliographies on high speed photography have been published by Garvin[1] and Tapia[2] giving references to 1892 articles. The techniques of high speed photography used at the Lawrence Radiation Laboratory, University of California[3]; Aberdeen Proving Grounds, USA[4]; Laboratoire Central de l'Armement, France[5]; AWRE, Aldermaston, UK[6]; RARDE, Fort Halstead, UK[7]; and CARDE, Canada[8], have been discussed. The developments in respect of high speed photographic cameras have been reviewed by Fatora[9] and Singh[10]. The techniques employed for missile photography have been described by Waddell[11] and Economou[12].

Since many of the techniques developed for the study of fast events are not well known, this article attempts to provide a general summary of these techniques and their capabilities. Some typical records taken using the specialized equipments are also presented.

Multiple-spark Photography

The principle of the multiple-spark camera, based on the optical system due to Cranz and Schardin[13], is to obtain a purely optical image separation by successive illumination by a series of spark gaps. The shadow of a non-luminous object is recorded on a stationary photographic film. The blur in the shadowgraph is eliminated due to the extremely small size and short duration of the light source. The photographs are taken at a framing rate of about a million pictures per second and the exposure time is about 0·25 μsec. Hyzer[14], Chesterman[15] and Jones[16] have discussed the spark photographic technique. The layout of a typical spark range is discussed by Hills[17]. Schardin[18] has developed a multiple-spark camera which can take 5000 pictures at the rate of 500,000 pictures per second.

A typical shadowgraph of a projectile in flight, taken by a set-up similar to that discussed by Hills[17], is shown in Fig. 1. The airflow pattern around the projectile is visible in the shadowgraph. Fig. 2 is a shadowgraph of a projectile after it has penetrated a mild steel plate.

Ultra High Speed Photography

Fast shutters — The Kerr cell[19] uses the birefringent liquid nitrobenzene as a shutter. The shutter unit employs two polaroid filters which are 'crossed', so that normally no light can be transmitted through them. Located between these is a hermetically sealed Kerr cell filled with purified nitrobenzene in which are immersed a pair of planar electrodes. The application of a high voltage pulse to the electrodes induces birefringence in nitrobenzene rotating the plane of the polarized light passed by the first polaroid, so that it will be passed by the second. The duration of this transmission condition is determined by the duration of the voltage pulse and can be made as short as 5×10^{-9} sec[20].

Kerr cell photography was used by Dunnington[21] for the study of early stages of spark discharge, by Anderson[22] for the measurement of velocity of light, by Froome[23] for cathode spot formation in arc discharge, by Quinn *et al*[24] for ballistics study, by Pugh *et al*[25] for photography of high speed phenomena, and by Chase *et al*[26] for studies on exploding wires.

A hemisphere of a service high explosive weighing 200 g was placed at the bottom of a water tank (30×30×30 cm), whose two opposite sides were fitted with glass. The charge was initiated at the

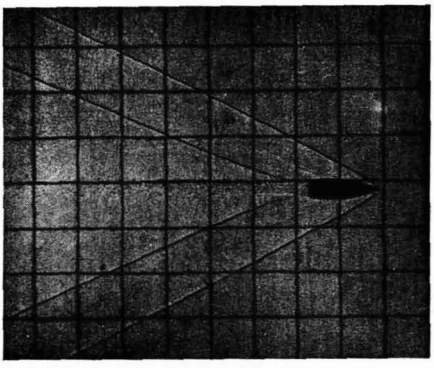

Fig. 1 — A typical shadowgraph of a bullet in flight [The phenomenon is stationary except in and around the wake]

Fig. 2 — A typical photograph of a projectile after it has penetrated a mild steel plate

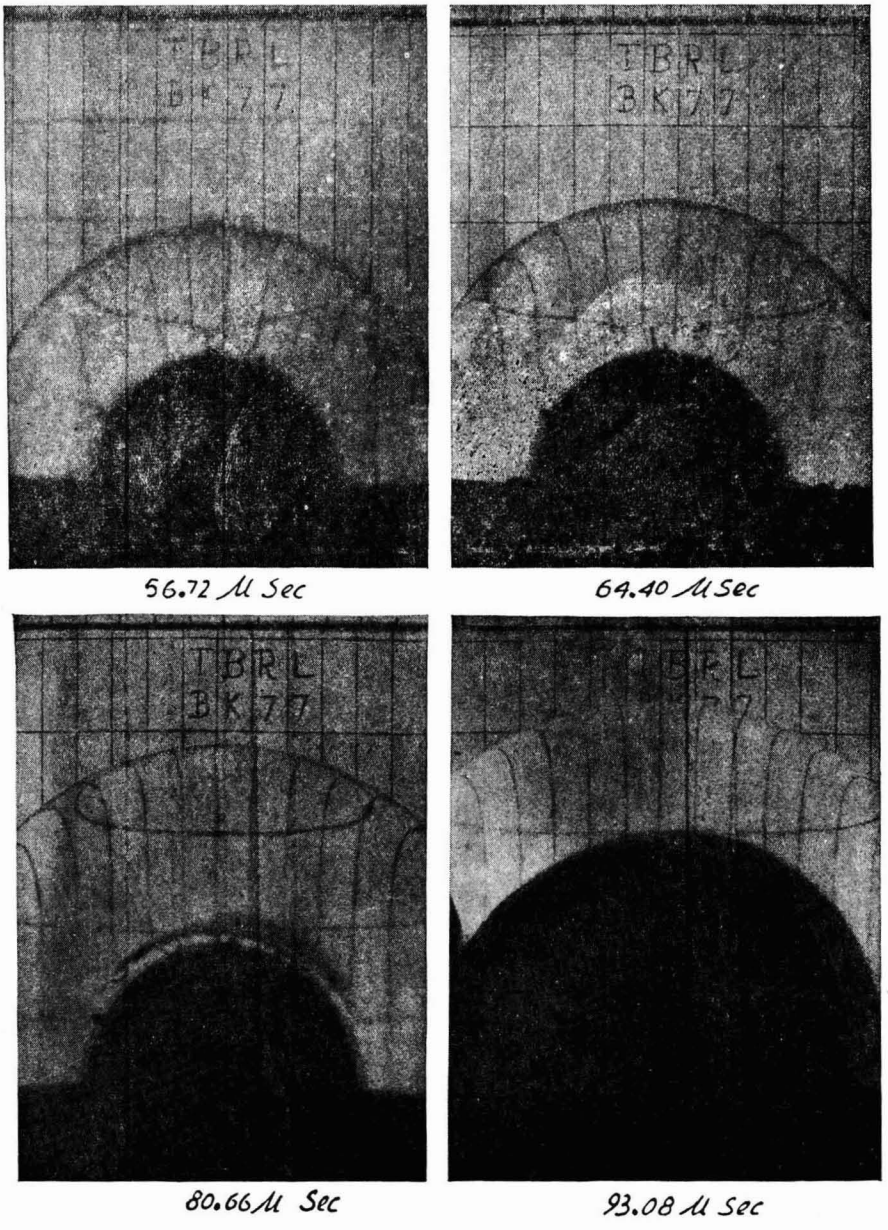

Fig. 3 — Photographs taken with the Kerr cell camera showing the travel of a shock wave in water and bending of the grid lines [Zero time has been taken from the point of initiation of the charge. Exposure time for each photograph, 0·1 μsec]

centre. The water tank was back-lighted by an argon flash bomb having a translucent grid of 2×2 cm. Some typical Kerr cell camera photographs taken at preset times and with an exposure time of 0·1 μsec are shown in Fig. 3. The grid lines are distorted as the light passes through the shock-compressed water. The vertical lines in the centre are less distorted, but those on the sides spread out more and have become blurred due to irregularities in the wavefront and refractive dispersion.

High speed framing photography — Most developments in the field of high speed photography have followed the original ideas put forward by Miller[27] in 1946 and 1949. In general, the framing camera reduces the phenomenon in the field of view into a set of data of X and Y coordinates in the film plane. Since it is a discrete recording instrument, some loss of data between successive pictures is obvious. The object field is imaged on the rotating mirror face and is re-imaged through relay lenses on the stationary film. These cameras were developed by Skinner[28] at AWRE, UK, and by Brixner[29] at Los Alamos. Several models of these cameras are currently in production in USA[30], UK[31,32], USSR[33,34], France[5] and Sweden[35]. The Beckman & Whitley, USA, model 189A records 25 high resolution 35 mm pictures at rates varying from $4{\cdot}8\times10^4$ to $4{\cdot}08\times10^6$ pictures per sec, and model 189B records 120 pictures at rates varying from 25×10^4 to $20{\cdot}3\times10^6$ pictures per sec.

The framing camera was used by Zernow[36] for the study of electrode behaviour in spark and disintegration of electrically exploded wires; Field[37] used it for the determination of fracture velocity in diamond. Napadensky and Savitt[38] studied the dynamic response of explosives to very high rates of loading. In general, the framing camera provides qualitative information about the irregularities of initiation, jet formation, shock wave structure and other fast events.

Some typical frames taken with the Beckman & Whitley camera model 189A at $4{\cdot}8\times10^5$ pictures per sec of the collision of two aluminium pellets (5 cm diam ×2·5 cm thick) propelled by two high explosive charges initiated simultaneously are shown in Fig. 4. The explosive charges were of 5 cm diam and 15 cm long. These were initiated simultaneously and also back-lighted by an argon flash bomb. Both the aluminium pellets were propelled by the hot detonating gases and these collided in the centre producing intense light.

High speed streak photography — The streak camera provides a high precision in the measurement of time. It has a distinct advantage over the framing cameras in that it allows a continuous time resolution of the order of nanoseconds by abstracting a narrow segment by means of a rotating mirror along a strip of photographic film. To a first approximation, the image motion in a streak camera may be considered to be a linear function of time. To obtain excellent continuous time resolution by a streak camera, space resolution in one direction is sacrificed and the records are often difficult to interpret. In other words, the framing camera gives good space resolution at the cost of time resolution, whereas the streak camera gives good time resolution and sacrifices space resolution. In certain respects, both the cameras supplement each other and the data from both of them give more or less a complete picture of the event under study. Rotating mirror streak cameras are currently in production in USA[30], UK[31,32], France[5] and Sweden[35].

The streak camera, developed by Skinner[39], has been used for the study of ' theta pinch ' in plasma. Cook[40] used this camera for detonation and wave-shape measurements in explosives. Stresau and Napadensky[41] developed a technique, using the streak camera to study the behaviour of porous materials under high rates of loading. Recently, Beckman & Whitley have introduced a simultaneous streak and framing camera (maximum framing rate, $7{\cdot}84\times10^6$ pictures per sec and maximum streak recording rate 27·6 mm per μsec). Bagley[42] has discussed the numerous applications of this camera. In general, the streak camera is well suited to provide quantitative information, such as initiation delay times, detonation, shock velocity and other fast events.

A streak record taken at 3·34 mm per μsec of the set-up shown in Fig. 4 and taken simultaneously with the framing camera is presented in Fig. 5. The velocity of the aluminium pellet is about 1·64 mm per μsec. At the point of collision, intense light is also produced.

Oscillography

The electrical conductivity of the ionized detonation front of an explosive is quite high. When a pair of closely spaced wires are located in the explosive, they experience a shorting contact on arrival of the ionized front. This high speed switching action can be used for very accurate measurement of short time intervals. This technique is commonly known as pin oscillography and has been discussed in detail by Cook[43]. Campbell *et al*[44] made use of this technique for precise measurement of detonation velocity in liquid and solid explosives. Minshall[45] studied shock wave propagation in metals employing this technique, while Costello[46] determined the yield strength of steel. Buchanan *et al*[47] reported the data on shock wave transmission through non-metallic solids like perspex.

A typical set-up for measuring the wave profile of a detonating high explosive is shown in Fig. 6. The probe carrier was made of perspex and was mounted at one end of the charge where the wave profile determination was required. Probe tips were all ensured to be in the same plane to an accuracy of 0·0025 mm. Pulse outputs from the pulse forming RC networks were fed to the recording multichannel high velocity oscilloscope through independent channels. This oscilloscope comprises a set of cathode ray tubes having independent signal input sockets but a common time base and power supply. The characteristics of this type of oscilloscope are almost identical to those discussed by Buchanan *et al*[47]. Time markers of 0·1 μsec duration and a common reference pulse were also fed into all the channels. Typical records obtained in channels I, III and VIII are shown in Fig. 7.

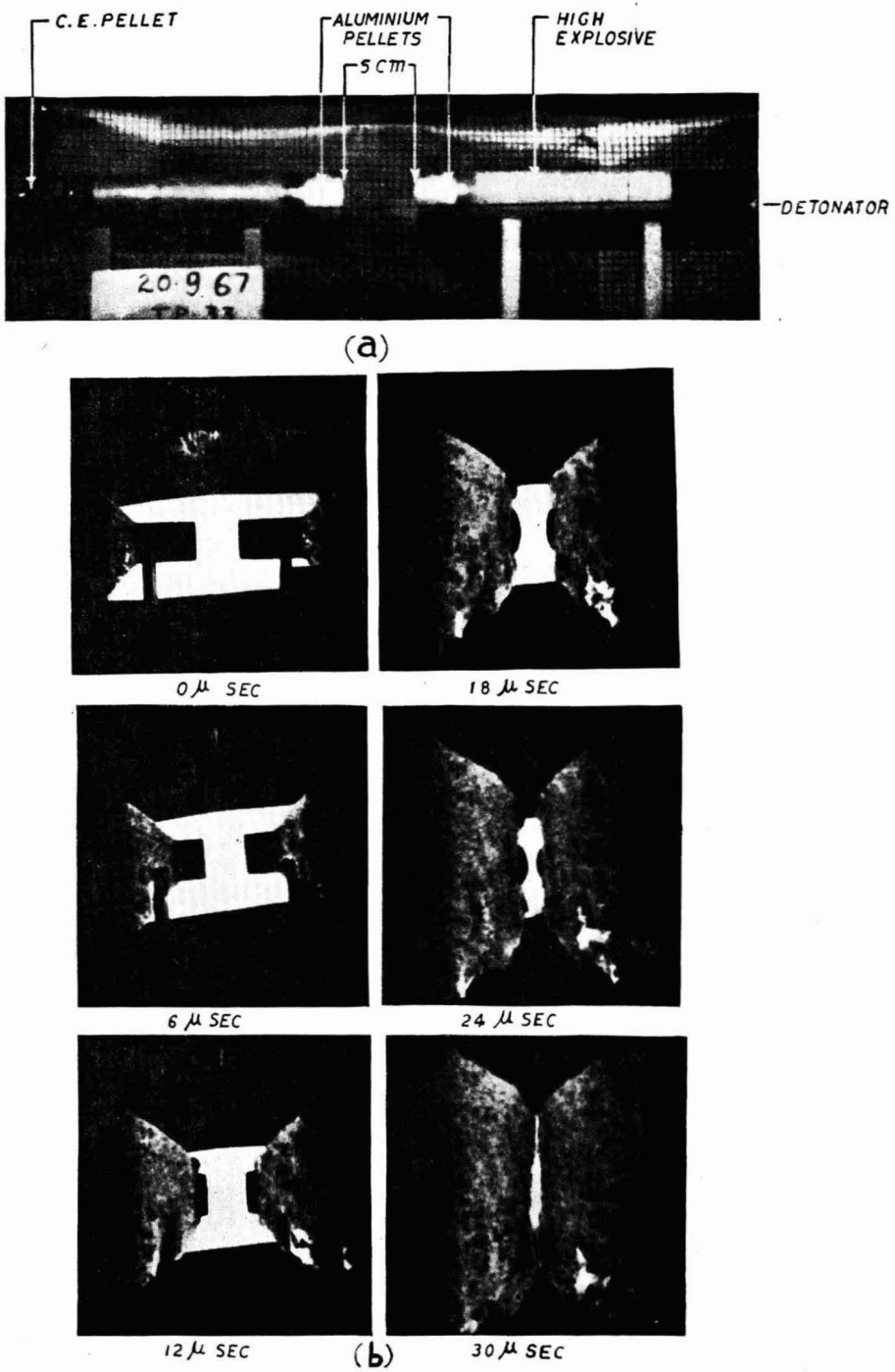

Fig. 4 — (a) Static photograph of the charge set-up; and (b) typical pictures taken with the Beckman & Whitley framing camera model 189A [The timing of each frame is given underneath the respective pictures]

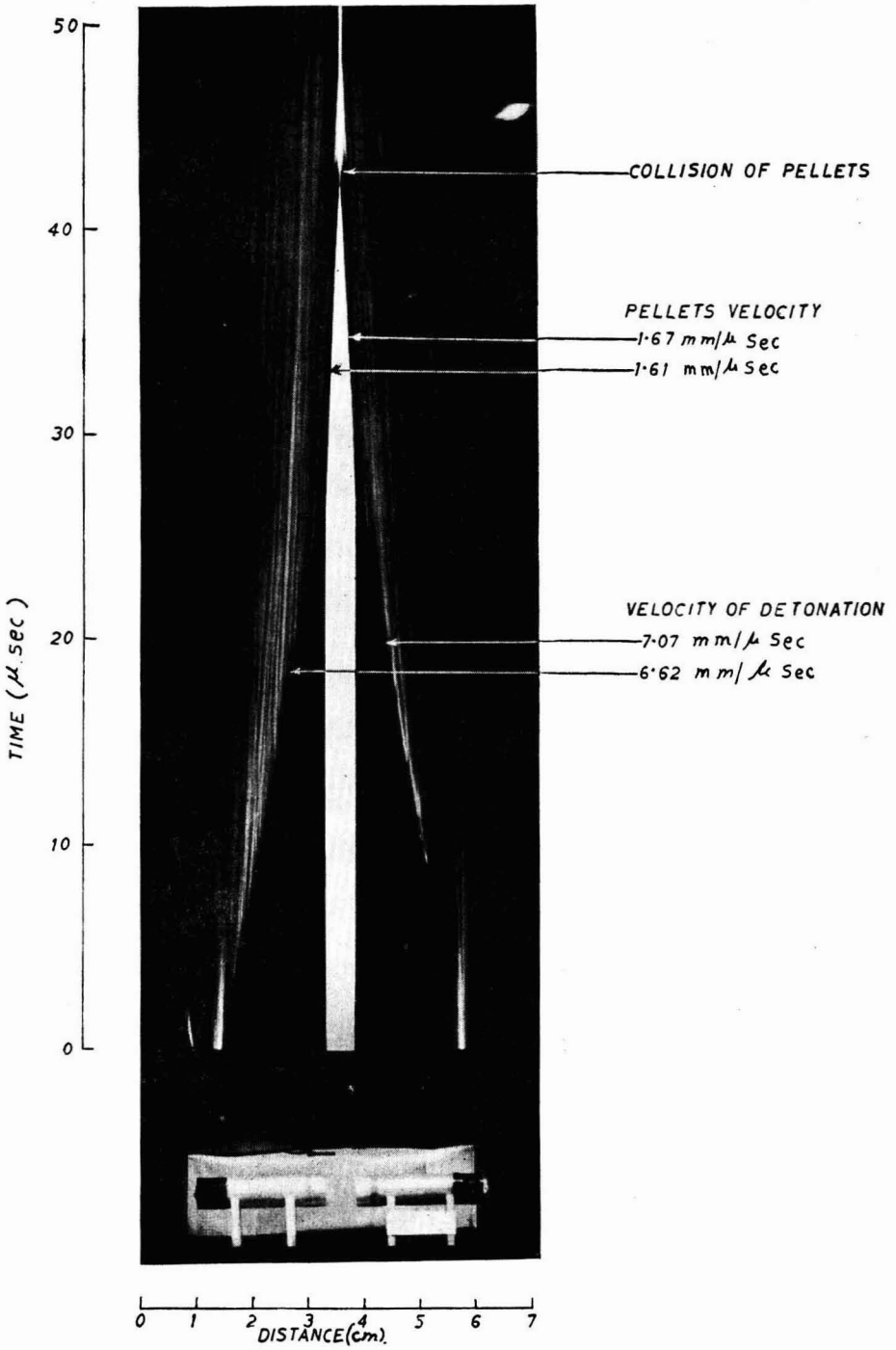

Fig. 5 — Photograph of two colliding aluminium pellets taken with the Beckman & Whitley model 770 streak camera

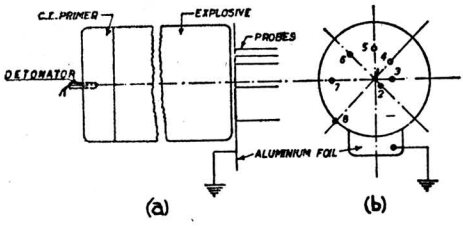

Fig. 6 — (a) Layout for determining the wave profile of a high explosive by pin oscillography (explosive cylinder diam, 7·62 cm; length, 12·7 cm); and (b) sectional view of the charge showing the location of the pins [The numbers indicate different channels]

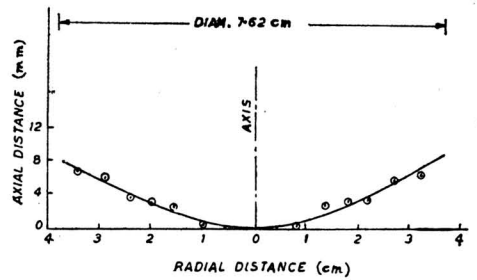

Fig. 8 — Wave profile of the explosive charge shown in Fig. 6

The time interval between the event pulse and the common pulse in each record is measured and the wave profile is worked out. The wave profile obtained in the case of a typical cylindrical charge is shown in Fig. 8.

Flash Radiography

When the phenomenon under study is hidden by the reaction products of the explosive, or occurs in an opaque medium (eg shock waves in solids), or is an intense source of light, flash radiography may be the only convenient method for its study. The flash X-ray tubes (Fexitron) use a field emission cold cathode and are designed for studies involving high intensity radiation from a small source, eg Fexitron X-ray tube, model 515, operates at peak power of 420 MW, the source size is 6 mm in diam and the dose rate at the tube surface is 10^8 r/sec. The X-ray equipment using the field emission techniques have been discussed by Dyke and Charbonnier[48] and Dyke[49]. A 50 mμsec flash X-rav equipment has been discussed by Grundhauser *et al*[50], a 30 nsec radiographic equipment capable of taking frame rates up to 10^6 by Dyke *et al*[51], and a megavolt flash radiographic equipment by Meakin[52]. The installation for triple X-ray equipment at 600 kV has been discussed by Viard and Beaudouin[53]. Gehring[54] used these equipments for hypervelocity impact studies. Recently, the Field Emission Corp, USA[55], has produced a new equipment called Febetron. The pulser voltage may be adjusted continuously from 600 kV to 2·3 MV. The electron currents are generally in the range 4000-7000 amp. This gives rise to very short pulse length (3 nsec) and long life (6400 shots). The use of this equipment can be extended to the production of X-rays.

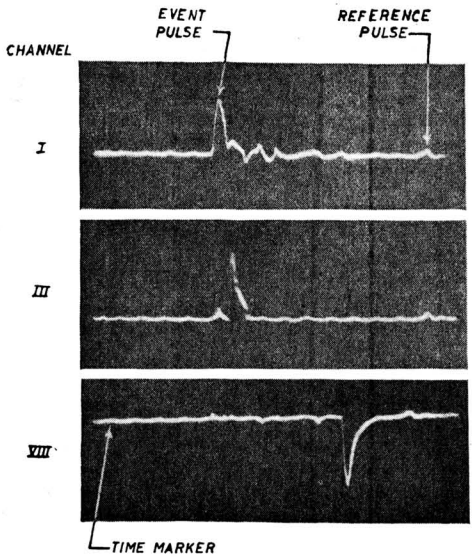

Fig. 7 — Typical records obtained in channels I, III and VIII [Sweep length, 2·0 μsec; duration of time markers, 0·1 μsec]

Flash X-ray photographs of the collapse of a cone and the high velocity jet from a standard shaped charge equipment used by Eichelberger and Pugh[56] are shown in Fig. 9. A trigger signal was taken from the base of the cone and 250 kV X-rays were used to radiograph the event. The radiograph shows the collapse of the cone, lengthening of the jet due to velocity gradients and break-up of the jet into particles.

Blast Wave Characteristics

Kinney[57] and Norris *et al*[58] have discussed the pressure, duration and impulse of a blast wave produced by detonating high explosives. Generally, piezoelectric materials, eg quartz (X-cut) or tourmaline (Z-cut), are used for measuring these quantities. The electric charge developed is fed to an amplifier system and the output is recorded on a cathode ray oscillograph. A typical layout for the measurement of blast wave characteristics is shown in Fig. 10. A typical record taken by detonating a cylindrical high explosive charge weighing 1 kg is shown in Fig. 11. The record shows the peak over-pressure, duration and impulse.

Davidson[59] measured the velocity of the blast wave using high speed photographic technique, whereas Stoner and Bleakney[60] used cathode ray oscillograph to measure this parameter. They calculated the peak over-pressure from the pressure-velocity relation derived from the Rankine-Hugoniot equations. The velocity of the shock wave is also measured by a pair of shock arrival gauges having lead zirconate crystals, and their output is recorded by a microsecond counter. The peak over-pressure

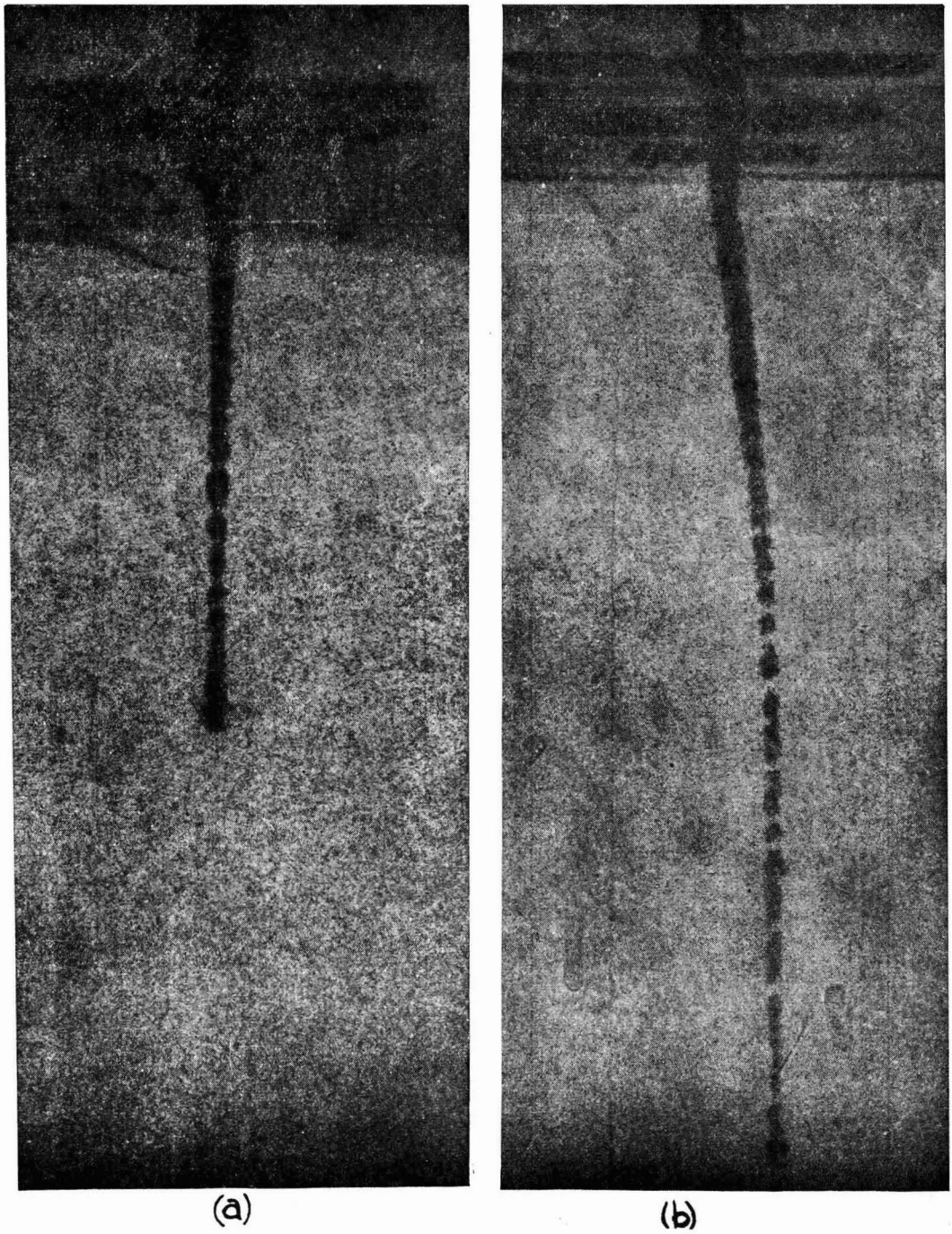

Fig. 9 — Radiograph of a jet in flight (a) after 10 μsec, and (b) after 25 μsec [Exposure time, 0·1 μsec; zero time taken from the base of the cone]

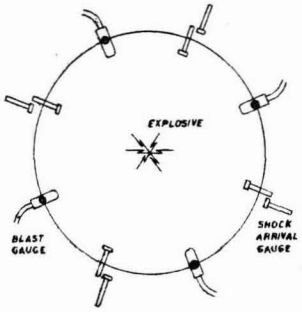

Fig. 10 — Layout for measuring the blast wave characteristics [The blast gauges and shock arrival gauges house X-cut quartz and lead zirconate crystals respectively]

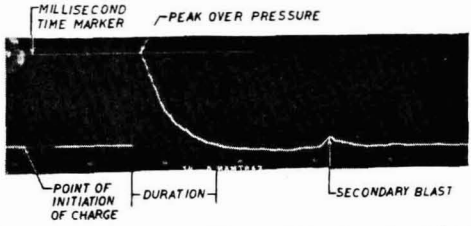

Fig. 11 — A typical record taken at 2 m from the point of detonation of the explosive cylinder [Weight of cylinder, 1 kg; diam, 5 cm; and length, 29·3 cm]

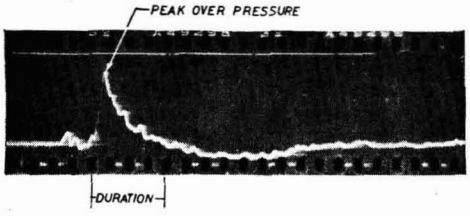

Fig. 12 — A typical record taken at 1·5 m from the point of detonation of 135 g of high explosives confined in a 0·5 cm thick steel tube

measured by this technique is of the same order and magnitude as measured by the blast gauges. The main limitation of the technique lies in the fact that pressure-time history data in the blast wave are not obtained, but only the peak overpressure.

The detonation of a cased high explosive charge gives rise to high velocity fragments in addition to the blast waves. The metallic container (gauge) housing the piezoelectric materials is protected against the fragment hits by means of an appropriate barrier. A typical record obtained by detonating 135 g of high explosive and confined in a 0·5 cm thick steel tube is shown in Fig. 12. The oscillations before the arrival of the blast wave are due to the shock waves accompanying the fragments moving faster than the blast wave. The oscillations down slope are due to the shock waves accompanying the fragments, which are slower than the shock waves.

Problems Encountered in Explosive Research

Preparation of explosive charges — High precision determination of explosion characteristics or any instrumented studies on detonation in solid explosives present special difficulties, not generally associated with liquid and gaseous explosives. In particular, the problem of homogeneity with respect to uniform density and composition and also particle size distribution are peculiar to solids. The explosives are melted in double jacketed steam-heated stainless steel pans fitted with suitable stirrers. The melt is poured into preheated moulds. The rate of cooling of the moulds is controlled by circulating hot water in the jacket around the mould. Generally, the cast charges are further processed through the machining operation. The technique of machining of explosives is basically the same as employed in the machine tool industry, but certain additional safety precautions are observed. The explosive swarf is not allowed to fall on the machine, but is removed by suction. Care is also taken that there is no sparking by incidental striking of the tool portion against any other part of the machine. At times, copper beryllium tool bits are used. Copper beryllium tools are fitted in a hollow shank connected to the suction line. For turning operation on the lathe, the maximum peripheral speed is fixed at 64 m/min. The maximum feed rate permissible is 0·1 mm per machining revolution and the depth of cut is less than 2 mm.

Safety of personnel and equipment — An explosion does not provide the most favourable circumstances for photography. The camera and related gear are exposed to shock, vibration and flying fragments. Generally, the high explosives are fired in the open and the equipment is housed in RCC bunkers[43].

Artificial illumination — The common techniques of producing short duration, high intensity light are the electrical spark discharge[61], vaporization of metal wire by electrical energy[62-64] and subjecting a gas, eg argon to explosive-induced shocks. Pressman[65] and Gerson and Stressau[66] have discussed the design and characteristics of argon flash bombs. The design parameters, eg explosive quantity, length and cross-section of the bomb, are determined to give the optimum illumination and the required duration for the event under study.

Summary

The photographic, oscillographic and radiographic techniques for studies of explosives, armaments and other fast events are discussed. The time resolutions possible with these techniques are indicated.

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Ellipsometry & Thin Film Studies*

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ELLIPSOMETRY has come to stay as a powerful tool in understanding some aspects of solid state physics with particular reference to thin films[1]. The method, essentially consisting of the analysis of the polarization characteristics of the reflected light from any surface, is applicable, by way of determining the optical constants, to the study of both thin film growth on bulk substances like an oxide film and the changes that occur in thin films prepared by vacuum evaporation, sputtering or any other method.

STUDY OF SURFACES AND THIN FILMS

Problems of oxidation, ageing, adsorption, desorption and allied phenomena affect the performance of a wide variety of components produced by thin film technology and single crystals. In general, the optical properties of these layers are different from those of the original surface. Space charge layers on the surfaces of semiconductors and in insulating layers also come into the same category. Similarly, diffusion of impurities into surface layers may manifest itself in a change in the optical properties of the layers. Accurate data on these lines are essential for the development of the technology for various types of optical components and active and passive electronic devices, especially in connection with integrated electronics.

There are three optical methods useful for the study of surfaces and films:

Photometry — This method[2] consists of measuring the amount of light reflected or transmitted and is used for the determination of optical constants, location of absorption bands, etc.

Interferometry — This includes single and multiple beam interferometry. The method[3] is useful in determining the thickness of films and surface topography.

Ellipsometry — This method consists of determining the changes in the characteristics of a polarized beam of light caused by reflection at the test surface.

Of these three methods, ellipsometry offers the following advantages over the other two methods: (i) greater sensitivity (which is quite high for films even a few angstroms thick), (ii) the sample need not be prepared specially, and (iii) the method is non-destructive.

Though the basic principles of the method have been established in the nineteenth century by Drude[4], it is only in recent times that the experimental and theoretical developments have been receiving greater attention[5-9]. The present review gives a detailed account of the theory of ellipsometry, design of the ellipsometer in general and specially the one fabricated by the authors, and some typical results.

*A brief outline of the contents of this paper has been presented at the convention organized by the Physical Research Committee of the Council of Scientific & Industrial Research at the Andhra University, Waltair, in February 1968.

CHARACTERISTICS AND REPRESENTATION OF POLARIZED LIGHT

Polarized Light

Barring the trivial case of partial polarization, three types of polarization are usually recognized: linear, circular and elliptical. Two simple harmonic motions with a phase and amplitude difference can be compounded to give an elliptic vibration, the end point of the radius vector moving clockwise or anticlockwise along an ellipse. The circular and linear polarizations can be considered as two extreme cases of the general case of elliptical polarization. Distinction is also made between the right-handed and left-handed nature of the elliptical vibration.

If the two vibrations along the X and Y axes are represented as

$$\left.\begin{aligned} E_p &= a_1 \cos(\tau+\delta_p) \\ E_s &= a_2 \cos(\tau+\delta_s) \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots(1)$$

the locus of the end point of the resultant of these two will be an ellipse given by

$$\frac{E_p^2}{a_1^2}+\frac{E_s^2}{a_2^2}+\frac{2E_pE_s}{a_1a_2}\cos\delta = \sin^2\delta \quad \ldots \quad \ldots \quad \ldots(2)$$

where E_p and E_s are the instantaneous amplitudes of the two light beams polarized mutually orthogonally; a_1 and a_2, the maximum values of amplitudes; δ_p and δ_s, the phases of the two ($\delta = \delta_p - \delta_s$); and τ represents the variable part of the phase factor.

The ratio $a_1/a_2 = \tan\alpha$ and δ the phase difference determine the amount of ellipticity and its inclination to the X axis. When the phase difference is equal to $(2n+1).\pi/2$ where n is an integer, the axes of the ellipse coincide with the coordinate axes. If in addition $a_2 = a_1$, the ellipse reduces to a circle, resulting in circular polarization. When $\delta = 0$ or $2n\pi$ the ellipse degenerates to a straight line, a_2 becoming zero for $(a_1)_{max}$ and a_1 becoming zero for $(a_2)_{max}$. In all other conditions the resulting vibration is elliptical, with various eccentricities and azimuths of inclination to the X axis.

Regarding the direction of rotation the following convention is generally accepted[10]. If the end point of the electric vector appears to describe the ellipse in a clockwise sense, when viewed in the direction of propagation of the beam, the polarization is right-handed. In this case, $\sin\delta > 0$ or $0 < \chi < \pi/4$. Anticlockwise rotation and the conditions $\sin\delta < 0$ and $\pi/4 < \chi < 0$ give the left-handed polarization.

The same ellipse can also be represented by another notation in coordinate geometry referring to the eccentricity and specified with a particular inclination ϕ of the major axis of the ellipse, with the X axis of reference. As the two modes of representation refer to the same ellipse the following relationships hold:

$$\left.\begin{aligned}\tan 2\phi &= \tan 2\alpha \cos \delta \\ \sin 2\chi &= \sin 2\alpha \sin \delta\end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots(3)$$

Stokes Parameters and Stokes Vector

Any beam of polarized light can be described by a set of parameters — the well-known Stokes parameters — given by

$$\left.\begin{aligned}S_0 &= a_1^2+a_2^2 \\ S_1 &= a_1^2-a_2^2 \\ S_2 &= 2a_1a_2 \cos \delta \\ S_3 &= 2a_1a_2 \sin \delta\end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(4)$$

The above four Stokes parameters are ultimately represented in the form of a Stokes vector (a column vector). Any polarized light, except partially polarized light, can be represented by this factor as

$$\begin{vmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{vmatrix}$$

These Stokes vectors are tabulated for a number of commonly occurring cases of polarization[11,12]. The Stokes vector can be used to understand the behaviour of any two incoherent beams of any polarized light. The action of polarizers and retarders on any given beam can also be predicted. The Stokes vector, however, is not useful in the case of coherent radiation.

Jones Vector

An alternative and more compact method of representing polarized light, applicable to the addition of coherent beams, is the Jones vector. This vector, however, fails in the case of unpolarized or partially polarized light.

The Jones vector is a two-element column vector; each element describing one component of the electric vibration. The upper element deals with the amplitude and phase of the X component and the lower element with the Y component similarly. The elements are written as

$$\begin{vmatrix} a_x & e^{i\phi_x} \\ a_y & e^{i\phi_y} \end{vmatrix}$$

where a is the amplitude along the axis and ϕ is the phase. This vector can be normalized and written in the appropriate form to represent various polarizations.

Mueller Matrices

Using Stokes vectors, Mueller developed various matrix forms for all the known types of polarizers and retarders. All the matrices are 4×4 as the Stokes vector is a 1×4 vector.

The multiplication of a Stokes vector, representing a particular polarized beam, by a Mueller matrix of any particular retarder or polarizer gives the nature of polarization of the emergent beam. In fact, this process can be telescoped into a sequence of operation and the final effect of a number of retarders on a polarized beam could be correctly predicted by a sequential multiplication of these vectors and matrices according to the normal rules of matrix algebra. The emergent vector is given by $V_E = V_i(M_AM_BM_C \ldots)$, where V_i represents the incident vector and M's are the Mueller matrices for retarders A, B and C. The process of this matrix multiplication has to follow the experimental set-up.

On similar lines, the Jones matrices are developed from the Jones vector. The matrices are obviously 2×2 corresponding to the 2×1 Jones vector. The calculus follows the same pattern as Mueller calculus, and matrices are available in literature[11,12].

Poincare Sphere

Another useful method of representation of polarized light is by the Poincare sphere. The Stokes parameters S_0, S_1, S_2, S_3, etc, can be connected with the quantities ϕ, χ, α and δ described earlier, as follows:

$$\left.\begin{aligned}S_1 &= S_0 \cos 2\phi \cos 2\chi \\ S_2 &= S_0 \sin 2\phi \cos 2\chi \\ S_3 &= S_0 \sin 2\chi\end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots(5)$$

$$\left.\begin{aligned}S_1 &= S_0 (1-\tan^2 \alpha)/(1+\tan^2 \alpha) \\ S_2 &= 2S_0 \tan \alpha \cos \delta/(1+\tan^2 \alpha) \\ S_3 &= 2S_0 \tan \alpha \sin \delta/(1+\tan^2 \alpha)\end{aligned}\right\} \quad \ldots \quad \ldots(6)$$

Eq (5) can be identified with the Cartesian coordinates of a point on a sphere of radius S_0. The radius vector makes an angle of 2χ with the X-Y plane and 2ϕ with the Y-Z plane (Fig. 1).

The S_1, S_2 and S_3 vectors can be fixed along the X, Y and Z axes respectively.

Any polarized light of intensity S_0 can, therefore, be represented by a point P (Fig. 1) on the sphere at a distance of S_0 from the centre of the sphere.

The equatorial plane X-Y represents the condition $S_3 = 0$ with finite values for S_1 and S_2. These two parameters represent only plane polarized light of various azimuths. The intersection of

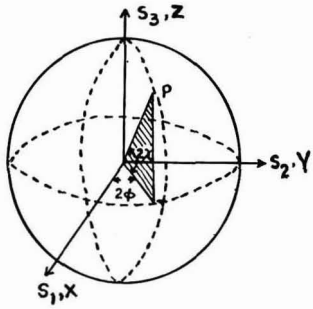

Fig. 1 — The Poincare sphere [S_1, S_2, S_3 are the three axes of reference; P is the point representing the state of polarization]

the positive S_1 axis (X axis) with the sphere represents horizontally plane polarization and a diametrically opposite point will represent a vertical polarization (the angles ϕ and χ in the coordinate system are doubled in this representation on the Poincare sphere). The intersection of the positive S_2 axis (Y axis) represents light plane polarized at a 45° azimuth. The north and south poles of the sphere are mutually orthogonal and are represented by $S_1 = S_2 = 0$ and $S_3 = \pm S_0$.

The two points, therefore, represent circularly polarized light. Other points, away from the poles and the equatorial plane, represent an infinite number of types of elliptically polarized lights with various eccentricities. Points in the southern hemisphere represent left-handed polarization. This representation of the polarized light proposed by Poincare is very convenient for the study of polarized light through various types of retarders. This sphere is called the Poincare sphere and is designated by Σ. The polarization effects produced by metallic reflection can be represented on the above sphere.

Reflection at a Plane Boundary: Electromagnetic Theory

The well-known laws of reflection and refraction may be directly deduced from the vector wave equation of Maxwell's theory

$$\nabla^2 A - \sigma\mu \frac{\delta A}{\delta t} - \epsilon\mu \frac{\delta^2 A}{\delta t^2} = 0 \quad \ldots \quad \ldots \quad \ldots \quad \ldots(7)$$

where A is either the electric or magnetic vector; ϵ, the time independent dielectric constant; μ, the permeability; and σ, the conductivity.

Fresnel's coefficients of reflection, for the components parallel and perpendicular to the plane of incidence follow from the same equation if we apply the relevant boundary conditions, and are:

$$r_{12p} = \frac{\tan(\theta_i - \theta_t)}{\tan(\theta_i + \theta_t)}; \; r_{12s} = \frac{-\sin(\theta_i - \theta_t)}{\sin(\theta_i + \theta_t)} \quad \ldots \quad \ldots(8)$$

the terms θ_i, θ_t being respectively the angles which the incident and transmitted rays make with the wave normal at the point of incidence.

Reflection at a dielectric surface — For the condition $(\theta_i + \theta_t) = 90°$, r_{12p} is zero and r_{12s} is observed as a completely plane polarized beam for any type of incident light. (θ_i is the Brewster angle $= \tan^{-1} n_2/n_1$). If the incident beam is plane polarized, the reflected beam will also be completely plane polarized at an azimuth different from that of the incident beam.

Phase considerations — In addition to the amplitude variation resulting in the intensity variation, due to reflection, the phase considerations are of considerable importance in the study of reflected light. The magnitude and sign of the phase change on reflection play a great part in these studies. In this context reference must be drawn to the papers by Shklyarevskii *et al*[13].

It can be seen from Eq (8) that the reflected s component is always out of phase by π with the incident s component. The reflected p component is in phase with the incident one as long as $(\theta_i + \theta_t) < \pi/2$, ie up to the Brewster angle. When $(\theta_i + \theta_t) > \pi/2$ it is also 180° out of phase with the incident p component. Thus the phase difference between the p and s components in the reflected beam is π up to the Brewster angle and 0 after that.

At normal incidence the p and s components are identical as no plane of incidence exists. At grazing incidence both the reflected components will have the same intensity as the incident components while both will be out of phase by π with respect to the incident component.

The reflectivity of a glass ($n_2 = 1{\cdot}5$) surface in air at normal incidence can be seen to be $r_{12p} = r_{12s} = \pm 0{\cdot}2$. The intensity ratio is 4%.

All dielectrics are treated as transparent and non-magnetic so that $\mu = \mu_0 = 1$ and the refractive index $n = \sqrt{\epsilon}$ referring to the free space. Here n is a real number and this is the optical constant of the dielectric.

Reflection at a metallic surface — When plane polarized light is incident at a metallic surface, under no circumstance will the reflected light be plane polarized, except in the extreme cases of 0 or $\pi/2$ azimuth. There is no value of the angle of incidence for which r_{12p} is zero, though it touches a minimum. When the azimuth of the incident polarization is somewhere between 0 and $\pi/2$, the reflected beam is always elliptically polarized. When the incident azimuth is $\pi/4$, the p and s components of the incident beam will be equal in intensity. So this experimental set-up is invariably used in the study of the reflected light. This behaviour of metallic surfaces can be explained if we assume a complex refractive index $n = n + ik$ where k is the absorption coefficient of the material, and n and k are related to μ, ϵ and σ by the following relations:

$$n^2 = \frac{\epsilon_r}{2}\left[1 + \left(1 + \frac{\sigma^2}{\omega^2\epsilon^2}\right)^{\frac{1}{2}}\right] \quad \ldots \quad \ldots \quad \ldots \quad \ldots(9)$$

$$k^2 = \frac{\epsilon_r}{2}\left[1 - \left(1 + \frac{\sigma^2}{\omega^2\epsilon^2}\right)^{\frac{1}{2}}\right] \quad \ldots \quad \ldots \quad \ldots \quad \ldots(10)$$

The use of a complex index of refraction in case of conducting media is necessitated by the absorption characteristics of the material. The complex trigonometric functions that result from the Fresnel coefficients are related to the inhomogeneous nature of waves in the absorbing medium where the planes of constant amplitude do not necessarily coincide with the planes of constant phase. An outstanding feature to be noted is that the reflected p and s components are given by a value different from 0 and π. The transmitted wave is rapidly attenuated within a few skin depths of the material and most of the incident intensity is reflected; hence the high value of reflectivity for metals.

Phase considerations — The variation of the phase difference δ, between the p and s components of the reflected beam is continuous between π and 0 for angles of incidence 0 to $\pi/2$ and thus passes through $\pi/2$. The angle at which δ becomes $\pi/2$ is called the principal angle of incidence for the material. At this angle the elliptically polarized reflected light has its major axis along the Y axis. At angles close to this angle the intensity of the

reflected p component is a minimum, though not zero as in dielectrics. In spite of δ being equal to $\pi/2$, the reflected beam is not circularly polarized at the principal angle of incidence because of the amplitude difference between the p and s components.

Azimuth of the reflected beam — From the Fresnel coefficients the reflected amplitudes can be written as

$$\left.\begin{aligned} R_p &= \frac{\tan(\theta_i-\theta_t)}{\tan(\theta_i+\theta_t)} A_p \\ R_s &= \frac{-\sin(\theta_i-\theta_t)}{\sin(\theta_i+\theta_t)} A_p \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(11)$$

In relations (11), θ_i and the phase factor in the dielectric are real but θ_t and the reflectivities are complex.

If δ_p and δ_s are the phase changes and ρ_p and ρ_s are the absolute reflection coefficients, the complex reflection coefficients can be written as

$$\left.\begin{aligned} r_p &= \frac{R_p}{A_p} = \rho_p e^{i\delta_p} \\ r_s &= \frac{R_s}{A_s} = \rho_s e^{i\delta_s} \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(12)$$

if α_i and α_r are the azimuths of the incident and reflected beams, we have

$$\tan^{-1}\frac{A_s}{A_p} = \alpha_i$$

$$\tan^{-1}\frac{R_s}{R_p} = \alpha_r$$

Let us define

$$\left.\begin{aligned} \Delta &= \delta_p - \delta_s \\ P &= \frac{\rho_p}{\rho_s} = \tan\Psi \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(13)$$

Then, $\tan\alpha_r = 1/P\, e^{i\Delta} \tan\alpha_i = \tan(90-\Psi) e^{i\Delta} \tan\alpha_i$. α_r is real in two special cases:

(1) for normal incidence, $\theta_i = 0$, $P = 1$, $\Delta = \pi$
$\tan\alpha_r = -\tan\alpha_i$

(2) for grazing incidence $P = 1$, $\Delta = 0$
$\tan\alpha_r = \tan\alpha_i$

The azimuth of the linearly polarized light is unchanged in its absolute direction in both cases. At the principal angle of incidence, however, $\Delta = \pi/2$. If in addition $1/P \tan\alpha_i = 1$, then the reflected light is circularly polarized. It is interesting to note that if $\alpha_i = \pi/4$ at the principal angle.

$$\tan\alpha_r = 1/P\, e^{i\Delta} = e^{i\Delta} \tan(90-\Psi) \quad \ldots \quad \ldots(14)$$

The above cases are represented diagrammatically in Figs. 2(a) and 2(b).

In the case of metals, the optical constants of interest are the refractive index n and absorption coefficient k. If we write the complex refractive index in the form $n(1+ik)$, k is known as the extinction coefficient. The other physical parameters like σ and ϵ are the values at optical frequencies, generally different from the low frequency values.

The optical constants of metals can obviously be studied only by reflected light as the transmitted beam vanishes in effect for any appreciable thickness. The penetration of electromagnetic radiation for a metallic surface is of the order of 6×10^{-7} cm (the value for copper) even for infrared radiations.

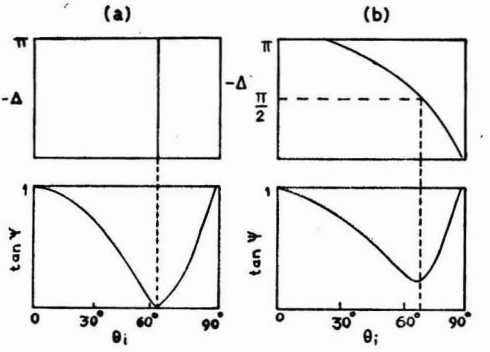

Fig. 2 — Representation of reflection at an interface. Curves showing the variation of Δ and tan Ψ with angle of incidence [(a) Reflection at a dielectric surface; and (b) reflection at a metallic surface]

Representation of Reflection on the Poincare Sphere

Reflection at a metal surface can be represented[14] on the Poincare sphere as shown in Fig. 3.

Reflection at a metal surface changes $|\delta_p-\delta_s|$ by a value Δ and the amplitude ratio by a factor tan Ψ. Thus the ratio between the reflection coefficient of the two components is given by

$$\frac{r_p}{r_s} = \tan\Psi e^{i\Delta} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(15)$$

Then the Stokes parameters of the reflected beam are given by

$$\left.\begin{aligned} S_1' &= \frac{1-\tan^2\alpha\cot^2\Psi}{1+\tan^2\alpha\cot^2\Psi} \\ S_2' &= \frac{2\tan\alpha\cot\Psi\cos(\delta+\Delta)}{1+\tan^2\alpha\cot^2\Psi} \\ S_3' &= \frac{2\tan\alpha\cot\Psi\sin(\delta+\Delta)}{1+\tan^2\alpha\cot^2\Psi} \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots(16)$$

S_0 being assumed to be unity, the reference.

In Fig. 3(b), I_p is the point $S_1 = 1$, $S_2 = 0$, $S_3 = 0$, on the sphere, representing the plane of incidence.

Suppose P in Fig. 3(a) represents the incident plane polarization. The point is rotated about the S_1 axis through an angle Δ to get the point L,

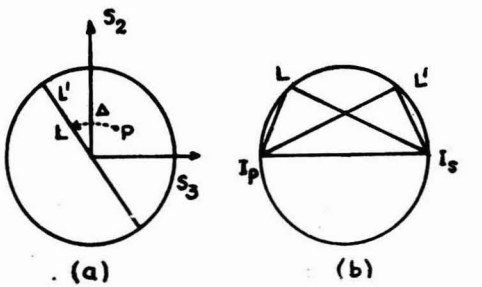

Fig. 3 — Representation of metallic reflection on the Poincare sphere [P represents the incident polarization and L' represents the final state of the beam]

represented by

$$\left.\begin{aligned} S_1' &= \frac{1-\tan^2\alpha}{1+\tan^2\alpha} \\ S_2' &= \frac{2\tan\alpha\cos(\delta+\Delta)}{1+\tan^2\alpha} \\ S &= \frac{2\tan\alpha\sin(\delta+\Delta)}{1+\tan^2\alpha} \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(17)$$

Now because of the change in the amplitude ratio this point is further shifted to L' having the coordinates S_1'', S_2'', S_3''. From the values of S_1', S_2', S_3' and S_1'', S_2'' and S_3'', it can be seen that both L and L' lie on a circle which has $S_3/S_2 = \tan(\delta+\Delta)$. This circle will be given by the intersection of a plane passing through L and normal to the S axis with the sphere. Referring to Fig. 3(b) which represents this circle, $I_p = (1, 0, 0)$ and $I_s = (-1, 0, 0)$, L is the point (S_1', S_2', S_3'), we can write

$$\left.\begin{aligned} I_pL &= \frac{2\tan\alpha}{(1+\tan^2\alpha)^{1/2}}; \quad I_sL' = \frac{2}{(1+\tan^2\alpha)^{1/2}} \\ \therefore \quad I_pL/I_sL &= \tan\alpha \end{aligned}\right\} \quad \ldots(18)$$

The tangent of the angle I_pI_sL' givest he ratio of the amplitudes of the components of the reflected polarized light which is equal to $\tan\alpha \cot\Psi$. By calculating this angle we can determine the position of L'.

Therefore, starting from the point P we determine the point L' as follows. We move the point P on the sphere along a plane normal to the S_1 axis through an angle Δ. The chords are measured and $\tan\alpha$ calculated. Then from the $\tan\Psi$ value we can know the angle I_pI_sL' and locate L'.

Reflection at a Thin Film Surface

Considering a thin film as a plane parallel plate between two different media, it is possible to apply Airy's formula for reflectivity. The formula takes into account the various multiple reflections that take place within the surface and gives the total sum of the effects as[15]

$$D^2 = \frac{4R\sin^2\delta/2}{(1-R^2)+4R\sin^2\delta} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(19)$$

where D^2 is the reflected intensity; R, the reflection coefficient of each surface; and δ, the phase difference.

However, the formula gives the ratio of the intensities of the incident and reflected beams and does not give any indication of the direction of the reflected amplitude leading to the phase difference. Fry[16] proposed a method of superposition of a number of cases and taking the sum effect which will be identical with the Airy's expression. In this particular case, Fry's method can be applied as follows.

The case of the film given by Fig. 4(a) can be identified with the sum of the effects of the cases shown in Figs. 4(b), (c) and (d). Figs. 4(b) and (c) are self-explanatory. In Fig. 4(d) the amplitudes and phases of the beams are so chosen that the reflected intensity from E_3 and the transmitted intensity from E_7 interfere destructively so that there is no resultant intensity in the direction E_1. On applying the method the reflectivity of the film

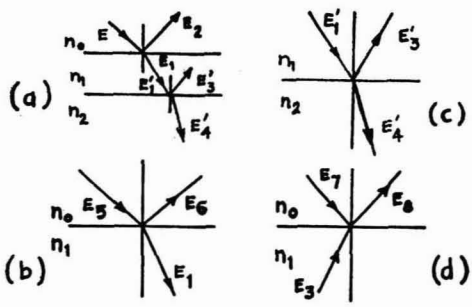

Fig. 4 — Representation of reflection at a thin film surface (a), and Fry's equivalents [(b), (c), (d)] [$E_5+E_7 = E$ and $E_6+E_8 = E_2$]

surface is obtained as

$$R_{12} = \frac{r_{12}-r_{23}e^{-2i\beta_2}}{1+r_{12}r_{23}e^{-2i\beta_2}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(20)$$

This gives the amplitude ratio and gives the Airy's formula when squared. The subscript numbers refer to the media and interfaces as indicated in Fig. 4(a), the r's are the normal reflectivities of the surfaces and β_2 is a term introduced to take into account the damping of the electromagnetic wave in an absorbing medium. It is given by $\beta_2 = 2\pi n_2 \cos\phi_2\, d_2/\lambda_0$, n_2 being the refractive index of the medium, ϕ_2 the angle of propagation in that medium, d_2 its thickness and λ_0 the wavelength in vacuum. So it is obvious that β_2 is the term which introduces the thickness into the consideration of the reflectivities. This expression can be used for either the p or the s wave.

Effects of multiple films can be evaluated by successive application of this formula to each film and using the result for r_{23} afterwards.

Matrix Notation

An elegant way of representing a thin film is by the matrix notation[17,18]. The representation of a thin film by a matrix follows from Maxwell's equations. For a wave linearly polarized with its electric vector perpendicular to the plane of incidence, let us consider that the yz plane is the plane of incidence, z being the thickness dimension of the film. The solution for the second order differential equation in E_x is of the form

$$E_x = U(z)e^{i(k_0\alpha_y - t\omega)} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(21a)$$

where $U(z)$ is a possibly complex function of z, $k_0 = \omega/c = 2\pi/\lambda_0$ and α is a constant[16]. H_y and H_z are given by similar functions

$$H_y = V(z)e^{i(k_0\alpha_y - \omega t)} \quad \ldots \quad \ldots \quad \ldots(21b)$$

$$H_z = W(z)e^{i(k_0\alpha_y - \omega t)} \quad \ldots \quad \ldots \quad \ldots(21c)$$

The functions U and V are interrelated by first order differential equations

$$\left.\begin{aligned} \frac{dU}{dz} &= ik_0\mu V \\ \frac{dV}{dz} &= ik_0\left(\epsilon - \frac{\alpha^2}{\mu}\right)U \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(22)$$

On elimination using these two relations, the final second order equations in U and V are obtained as

$$\left.\begin{aligned}\frac{d^2U}{dz^2}-\frac{d}{dz}(\log\mu)\frac{dU}{dz}+k_0^2(n^2-\alpha^2)U=0\\ \frac{d^2V}{dz^2}-\frac{d}{dz}\left[\log\left(\epsilon-\frac{\alpha^2}{\mu}\right)\right]\frac{dV}{dz}+k_0^2(n^2-\alpha^2)V=0\end{aligned}\right\} \quad ...(23)$$

The equations for the p wave can be obtained by interchanging E and H and ϵ and μ.

These equations will in general have two solutions U_1, V_1 and U_2, V_2. These are coupled again by Eqs (22) as

$$\left.\begin{aligned}\frac{dU_1}{dz}=ik_0\mu V_1\,; \qquad \frac{dU_2}{dz}=ik_0\mu V_2\\ \frac{dV_1}{dz}=ik_0\left(\epsilon-\frac{\alpha^2}{\mu}\right)U_1\,; \quad \frac{dV_2}{dz}=ik_0\left(\epsilon-\frac{\alpha^2}{\mu}\right)U_2\end{aligned}\right\} \quad ...(24)$$

which give

$$\frac{d}{dz}(U_1V_2-U_2V_1)=0 \qquad ... \quad ... \quad ...(25)$$

which implies that the determinant

$$\begin{vmatrix}U_1 & V_1\\ U_2 & V_2\end{vmatrix}$$

is a constant. The solutions for equations given by (23) may be chosen as

$$\left.\begin{aligned}&U_1=f(z)\,;\ U_2=F(z)\,;\ V_1=g(z)\,;\ V_2=G(z)\\ &\text{such that}\\ &f(0)=g(0)=0 \text{ and } F(0)=G(0)=1\end{aligned}\right\} \quad (26)$$

The determinant of the matrix

$$\begin{bmatrix}g(z) & -f(z)\\ -G(z) & F(z)\end{bmatrix}=M$$

is a constant from Eq (25) and is unimodular from the solutions given by Eq (26).

It can be seen that if $Q_0=\begin{vmatrix}U_0\\ V_0\end{vmatrix}$ represents the X and Y components of the wave in the plane $Z=0$ and $Q=\begin{vmatrix}U\\ V\end{vmatrix}$ those in the plane where Z has an arbitrary value, then

$$Q_0=MQ \qquad ... \quad ... \quad ... \quad ... \quad ... \quad ...(27)$$

M is known as the characteristic matrix of the thin film since if we know its value for a particular film we can determine its effect on a plane monochromatic wave incident at its surface.

It now remains to calculate the values of U_1, V_1, U_2, V_2 for the thin dielectric films. The parameters ϵ, μ and n are constants. If the wave makes an angle θ with the Z axis, α is given by $n\sin\theta$.

Eqs (23) are now to be written as

$$\left.\begin{aligned}\frac{d^2U}{dz^2}+k_0^2n^2\cos^2\theta U=0\\ \frac{d^2V}{dz^2}+k_0^2n^2\cos^2\theta V=0\end{aligned}\right\} \qquad ... \quad ... \quad ...(28)$$

The solutions satisfying conditions (22), (26) and (28) are

$$\left.\begin{aligned}U_1=f(z)=i/p\ \sin\beta\\ U_2=F(z)=\cos\beta\\ V_1=g(z)=\cos\beta\\ V_2=G(z)=ip\ \sin\beta\end{aligned}\right\} \qquad ... \quad ... \quad ... \quad ...(29)$$

where $\beta=2\pi n\cos\theta\ d/\lambda$, d being the thickness of the film.

$p=\sqrt{\epsilon/\mu}\cos\theta$ for s waves and

$=\sqrt{\mu/\epsilon}\cos\theta$ for p waves

Thus the characteristic matrix of the film can be seen to be

$$M(z)=\begin{vmatrix}\cos\beta & -i/p\ \sin\beta\\ -ip\ \sin\beta & \cos\beta\end{vmatrix} \qquad ... \quad ...(30)$$

In the case of an absorbing film n is complex and all the four terms will become complex. The matrix representation can be extended to multiple films by successive application. For example, the characteristic matrix of a system of an adjacent films, the first extending from $z=0$ to $z=z_1$, the second from $z=z_1$ to $z=z_2$ and so on is given by

$$M(z_n)=M_1(z_1)M_2(z_2-z_1)\ldots.M_n(z_n-z_{n-1}) \quad ...(31)$$

where M_1, M_2, etc, are the matrices of the individual films.

The reflection coefficient of a film characterized by a matrix

$$\begin{vmatrix}m_{11} & m_{12}\\ m_{21} & m_{22}\end{vmatrix}$$

can be obtained as

$$r=\frac{(m_{11}+p_3m_{12})p_1-(m_{21}+p_3m_{22})}{(m_{11}+m_{12}p_3)p_1+(m_{21}+p_3m_{22})} \qquad ... \quad ...(32)$$

the p's being the values for corresponding media.

By substituting the actual expressions for m_{11}, etc, and simplifying it can be seen that the expressions reduce to Eq (20).

If we study Eq (20) a striking similarity to the transmission line equations $dV/d_2=-zI$ and $dI/dz=-YV$ can be noticed. This only emphasizes the similarity of the two disciplines since both the transmission lines and films are means to propagate electromagnetic waves. In fact, some workers[19] have developed the theory of the matrix representation of thin films by analogy with the transmission lines and networks.

FUNDAMENTAL EQUATION OF ELLIPSOMETRY

Solutions of the Reflectivity Equation

From the expression for the reflectivity of a thin film surface it is obvious that the reflectivity is dependent on the film thickness and the refractive index. The problem here is to calculate these two quantities from reflectivity measurements. Thus it is necessary to solve the reflectivity equation for these two terms. For this purpose Eq (15), namely

$$r_p/r_s=e^{i\Delta}\tan\Psi \qquad ... \quad ... \quad ... \quad ... \quad ...(15)$$

is utilized. This is the fundamental equation of the method since all calculations and measurements are based on it.

The Fresnel coefficients in this equation can all be expressed in terms of the optical constants of the media and the angle of incidence. The expressions for Δ and Ψ can be obtained by separating the real and imaginary parts, the only unknown quantities remaining being the film parameters.

The optical constants of a reflecting film-free surface can be obtained by solving expression (15) for n and k. The following expressions are obtained:

$$\left.\begin{aligned} n^2-k^2 &= \\ \sin^2\theta_i\left[1+\frac{\tan^2\theta_i\,(\cos^2 2\Psi-\sin^2 2\Psi\sin^2\Delta)}{(1+\sin 2\Psi\cos\Delta)^2}\right] & \\ 2nk &= \frac{\sin^2\theta_i\tan^2\theta_i\sin 4\Psi\sin\Delta}{(1+\sin 2\Psi\cos\Delta)^2} \end{aligned}\right\} \ldots(33)$$

θ_i is the angle of incidence.

In the case of film calculations, however, if the refractive index is not known, it is necessary to solve the equation for both the refractive index and the thickness and some of the methods adopted are as follows. Values of Δ and Ψ are experimentally determined for various thicknesses of the film and are plotted in a complex plane. These values are also calculated theoretically and for various thicknesses and for an arbitrary value of $\bar{n}$ are plotted again in a complex plane (Fig. 5). Similar curves are prepared for a number of $\bar{n}$ values and the curve giving the best fit with the experimental curve is taken to give the exact $\bar{n}$ value; the plot can be used as a nomogram for further work. If $\bar{n}$ is known, the nomogram can be directly prepared and used.

It is obvious that this type of calculation is extremely cumbersome. But when done by a computer, curves with exact fit may be obtained. Graphical methods can also be used, where computers are not available.

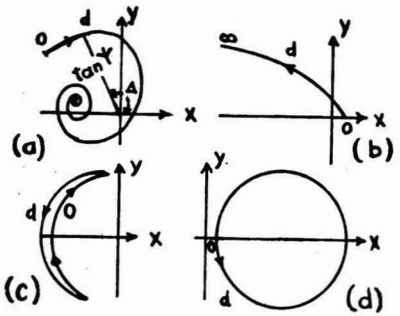

Fig. 5 — Δ versus tan Ψ curves plotted in a complex plane [The thickness parameters are marked along the curve as shown; (a) is for an absorbing film on absorbing substrate; (b) is for an absorbing film on a transparent substrate; (c) is for a transparent film on an absorbing substrate; and (d) is for transparent film on a transparent substrate]

Approximations

Very thin films — However, it is not always necessary to use these rigorous expressions. For in cases of the very thin films ($d \ll \lambda$) second and higher order terms in d/λ can be neglected. Using this approximation, Drude[4] has shown that the values of $\Psi-\Psi_0$ and $\Delta-\Delta_0$ are directly proportional to the thickness at any angle of incidence, Δ_0 and Ψ being the values with the film-free substrate and Δ and Ψ the values with the film-covered surface. Drude's values are given by[20]

$$\left.\begin{aligned} \Psi-\Psi_0 &= \alpha\, d/\lambda_0 \\ \Delta-\Delta_0 &= \beta\, d/\lambda_0 \end{aligned}\right\} \quad \ldots\ \ldots\ \ldots \ldots(34)$$

where

$$\alpha = \frac{2\pi}{\lambda_0}\left[\frac{\cos\theta_i\sin 2\Psi\sin^2\theta_i\, a[1-n_1^2\cos^2\theta_i(1/n_1^2-1)]}{(\cos^2\theta_i - a^2)+a_1^2}\right]$$

and

$$\beta = \frac{4\pi}{\lambda_0}\left[\frac{\cos\theta_i\sin^2\theta_i\,(\cos^2\theta_i-a)(1/n_1^2-1)}{(\cos^2\theta_i-a)^2+a_1^2}\right]$$

a and a_1 being functions of n_2.

Thick absorbing films — In the case of thick absorbing films also we can expect some sort of approximation since it is reasonable to expect that only a single reflection in the film is effective[21]. So we take that

$$r_{23}\frac{e^{-2i\beta}}{r_{12}} \ll 1 \quad \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots(35)$$

Now, if we expand the original expression for the reflectivity of the filmed surface binomially, we obtain

$$R = r_{12}+[1-(r_{12})^2]r_{23}e^{-2i\beta} \quad \ldots\ \ldots\ \ldots(36)$$

The deviation of this expression from the exact value decreases as the film becomes thicker.

McCrackin *et al*[14] have shown that it is not strictly necessary to prepare plots of Δ and Ψ. They obtained an expression

$$C_1\,(\exp\beta)^2+C_2\exp(\beta)+C_3 = 0 \quad \ldots\ \ldots(37)$$

where C_1, C_2 and C_3 are constants to be calculated from the values of the refractive indices and r values, and solved the expression for β. This can again be done for various $\bar{n}$ values if the film characteristics are completely unknown and the value of $\bar{n}$ which gives the smallest imaginary term in the thickness value is to be taken as correct.

Vasicek[22] applied this method to thin dielectric films on glass also, on the assumption that such films also introduce a slight ellipticity while reflecting plane polarized light. He derived expressions from which the Δ value can be calculated from the Ψ value, the expression involving n_2. So using three or four n_2 values and the measured Ψ value, he determined corresponding Δ values and plotted them against n_2 values. The correct n_2 value can be extrapolated from this n_2-Δ curve. If the calculation is continued, a different thickness value can also be obtained from each n_2 value. The correct thickness can now be extrapolated from the n_2 value in the n_2-d_2 curve.

DESIGN, FABRICATION AND EVALUATION OF THE EQUIPMENT

Measurement of Δ and Ψ

From the foregoing account of the solutions of the reflectivity equation, it is obvious that the quantities to be measured are Δ, the differential phase change and tan Ψ, the ratio of the reflectivities of the p and s components, introduced by reflection at the film surface.

Equipment requirements — The problem thus reduces itself to the analysis of elliptically polarized light produced as a result of reflection at the film surface at known angles of incidence. The equipment, therefore, should consist of the following basic units:

1. A source of well-collimated beam of polarized light with provision for changing the azimuth of polarization.
2. A system for analysis of the reflected beam, together with a telescopic system for viewing the parallel beam.
3. Provision for setting at various angles of incidence.
4. A suitable mount for the reflector.

The basic unit is obviously a spectrometer, to which the polarizing units are attached. The entire instrument with the above attachments is called a polarizing spectrometer or an ' ellipsometer '.

Methods for measuring Δ and Ψ — Several procedures for measuring Δ and Ψ with this set-up are proposed[7] and are discussed in the following.

1. One of the simplest ways is to make use of Eq (14) which indicates that if plane polarized light at an azimuth $\pi/4$ is incident at the principal angle of incidence and the phase difference introduced by reflection ($\Delta = \pi/2$) is compensated, then the azimuth of restored polarization is equal to $(90-\Psi)$. The set-up to be adopted in this case is indicated in Fig. 6(a). The compensator C serves to compensate the phase difference. This procedure requires the minimum amount of numerical calculation. However, the method requires the accurate determination of the principal angle by a separate experiment[23].

2. In another method, plane polarized light at a fixed azimuth is made to be incident at any arbitrary angle of incidence. The reflected beam is analysed by means of the compensator and analyser. This method also uses the set-up indicated in Fig. 6(a).

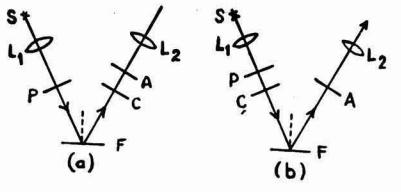

Fig. 6 — Ellipsometer set-up [S, source; L_1, collimating lens; P, polarizer; C, compensator; A, analyser; L_2, the lens system for observation; and F, the film surface. (a) Set-up using plane polarized light incident at the principal angle of incidence; and (b) set-up using elliptically polarized incident light]

3. Elliptically polarized light is made to be incident on the film in a third method. The beam is produced by means of a linear polarizer and a compensator. By changing the relative azimuth of these two the characteristics of the beam are varied until plane polarized light is obtained after reflection, and the characteristics are calculated from the positions of the polarizer, compensator and analyser. There is nothing much to choose between methods 2 and 3 except personal choice and preference. The set-up shown in Fig. 6(b) is used in this method.

4. There is another method which uses elliptically polarized light. In this, the characteristics of the incident beam and the angle of incidence are varied until the beam is circularly polarized. In this method the set-up shown in Fig. 6(b) is used. However, provision is made to rotate the analyser continuously. The light emerging from the analyser is focused on a phototube. The phototube output is fed to an oscilloscope. When the reflected beam is circularly polarized, a perfectly linear trace is obtained, as the intensity of the circularly polarized light is independent of analyser orientation. We have not come across any instance of this method being used practically. Apparently, this is a sophistication without any special advantages.

5. For use in regions of the spectrum where compensators are not available, the following method was devised. The beam after reflection at the film surface is made to retrace its path. The angle of incidence and the azimuth of the incident beam are varied until the beam on its return is polarized linearly in a direction normal to the original one.

Mention should also be made of the methods of Prishivalko[24] and Meyer *et al*[25]. They measured the intensity of the reflected light at various azimuths of the incident linearly polarized light rather than Δ and Ψ. Prishivalko determined the values of Stokes parameters from the measurements. He could determine the values of n and k only from this method. The same is the case with Meyer *et al* who, however, applied a method of least squares.

We will now describe the instrument designed and constructed by us in this laboratory for carrying out ellipsometric studies on thin films of various materials.

Description of the Instrument

The ellipsometer was designed and constructed by us around an Andhra Scientific Company research spectrometer reading up to 20″. The design was such that the instrument lends itself readily for adopting either of the two major methods described, viz the one in which (i) linearly polarized and (ii) elliptically polarized light is incident.

The conventional slit of the collimator was replaced by an iris diaphragm. The polarizer and analyser are 8 mm square ended Glan-Thomson prisms. These are housed in attachments to the arms of the spectrometer which allow them to be rotated through 360° about a central axis. The positions of the prisms can be read off on circular scales cut (in our workshops) on the attachments which can read up to 3″.

For compensation of the phase difference, use is made of a quarter wave plate which is fitted in an

aluminium housing which fits on either the polarizer or the analyser housing. The quarter wave plate position can be read on the same scale as that of the prism. Provision is made for moving either the prism or the quarter wave plate independently.

The main observation being the position of complete extinction, it is necessary to control the intensity of the light. An iris diaphragm is introduced for this purpose between the collimating lens and the polarizing prism. Its position is adjusted until the aperture of the polarizing prism is just filled by the collimated beam. It is also necessary to use polarizing prisms of sufficient aperture so that the inherent deviation of the emergent ray does not take it outside the field of view of the telescope. It is possible to overcome this difficulty by using a telescope having sufficient angular field of view. Perfect centring is obviously a necessity.

A special type of sample holder is designed for the ellipsometer which can hold samples of considerable thickness and blocks any light from entering from the rear surface. It is also possible to hold the samples (between rubber paddings in order to minimize strain effects) at various positions to study them. The whole of the instrument is enclosed in a closed cabin so that extraneous light does not enter while making measurements.

Measurements and Calculations

The quantities to be determined experimentally are the positions of the polarizer, analyser and the quarter wave plate when complete extinction is obtained at any particular angle of incidence. In each method either the polarizer or the analyser is fixed and the other adjusted along with the compensator. There are four pairs of positions at which extinction is obtained, since either of the components can be placed at a position differing by 180°. The mean of all the readings is taken.

Method using linearly polarized incident light — The polarizer is fixed at $\pi/4$ azimuth. This implies p and s components to be of equal intensity and the phase difference between them to be zero. The positions of quarter wave plate and analyser which give complete extinction are noted. Referring to Eqs (1) and (3), the quarter wave plate position gives ϕ and the analyser position gives $\pi/2+\chi$, all angles being positive when read anticlockwise looking into the beam. Then using Eqs (3), Δ and Ψ can be calculated.

Method using elliptically polarized incident light — In this method, any three arbitrary positions of the three components which give complete extinction are linked by the following expressions[26]:

$$\left.\begin{aligned}\tan\Delta &= \frac{T\sin\delta\sin 2(Q_0-P_0)}{\sin 2Q_0[\cos^2(Q_0-P_0)+T^2\sin^2(Q_0-P_0)] - T\cos 2Q_0\cos\delta\sin 2(Q_0-P_0)}\\ \tan\Psi &= \pm\tan A_0 \times\left[\frac{[\tan Q_0\cos(Q_0-P_0)-T\sin(Q_0-P_0)\cos\delta]^2+T^2\sin^2(Q_0-P_0)\sin^2\delta}{[\cos(Q_0-P_0)+T\tan Q_0\sin(Q_0-P_0)\cos\delta]^2+T^2\tan^2 Q_0\sin^2(Q_0-P_0)\sin^2\delta}\right]^{1/2}\end{aligned}\right\} \quad ...(38)$$

where P_0, Q_0 and A_0 specify the positions of the three components, δ is the phase difference introduced by the quarter wave plate and T the relative attenuation of p and s components introduced by it. Thus it is evident that an exact quarter wave plate is not essential and it is sufficient that the phase difference introduced by it is known exactly.

The equations given by (38) are considerably simplified when any one component is fixed at a convenient position. For example, with the polarizer remaining in zero azimuth we obtain the following expressions:

$$\left.\begin{aligned}\tan\Delta &= \frac{D}{(C-B+1)\cos^2 Q_0 - C\cos^2 Q_0}\\ \tan\Psi &= \tan A_0\tan Q_0 \times\left[\frac{(1-B)^2+D^2}{[1-B\tan^2 Q_0]^2+D^2\tan^4 Q_0}\right]^{1/2}\end{aligned}\right\} \quad ...(39)$$

where B, C and D are functions of δ and T. The more popular method is to fix the quarter wave plate at $\pi/4$ for which position the expressions

$$\left.\begin{aligned}\tan\Delta &= \sin\delta\tan(\pi/2-2P_0)\\ \cos 2L &= -\cos\delta\cos 2P_0\\ \tan\Psi &= \cot L\tan(-A_0)\end{aligned}\right\} \quad ... \quad ...(40)$$

The extinction positions may be observed with a photoelectronic arrangement. It is optional to have a half-shade adjustment. Readings of about the same accuracy can be obtained by taking the mean of two readings which give the same intensity level on either side of the extinction position. With some experience it is possible to determine the extinction settings quite accurately with the naked eye.

Alignment, Adjustments and Possible Errors

The preliminary step is to make the normal adjustments of the telescope and collimator and levelling the instrument.

The next step is the alignment of the prisms. This means that the scales are adjusted to read zero when the prisms are in zero azimuth with respect to the plane of incidence. As was mentioned all angles are measured from the plane of incidence, counterclockwise being taken as positive. As both the scales are facing the specimen, it is necessary to graduate the polarizer scale counterclockwise and the analyser scale clockwise.

The polarizer is placed in the housing with the analyser removed and adjusted to be at zero azimuth by observing, say, the reflection off a glass surface at the polarizing angle. The scale is adjusted to read zero when the prism is in this position. The analyser is now placed in position, put in the 'crossed' position with respect to the polarizer, and its scale is adjusted to read 90°. Finally the quarter wave plate is introduced, rotated until complete extinction is obtained and the reading is taken. This gives the position at which either the fast or slow axis is at zero azimuth; which it is to be determined in a separate experiment[27]. The reading which gives zero azimuth for fast axis is noted. Correct alignment is very critical for measurements on surfaces, though not as much for

measurements on thin films, as will be evident from the following discussion.

Errors

In the method random as well as systematic errors may arise. The chief sources of error are: (i) multiple reflections at the surfaces of the various components, and (ii) errors in the alignment of prisms. These errors carry into the derived quantities the relative phase shift and the relative amplitude variation and from then to the calculated values of the optical constants and thicknesses.

For an instrument such as the one described here as many as 6 parasite beams can be counted (Fig. 7). This number will increase with the introduction of additional components such as half-shades, etc. Even then account is not taken of the collimator and telescope lens elements.

This is the case if only one reflection is taken into account. The polarization characteristics of these parasite beams vary as the value of Δ varies from $\pi/2$ to π. These beams cause an error of the order of about 1° in Δ and about $\frac{1}{2}$° in Ψ throughout the range[5]. It is not possible to either eliminate the errors by manipulation of the instrument or to apply any exact correction by calculation. The only remedy, therefore, is to use components coated for antireflection. Errors in alignment are also serious but can be minimized by careful setting.

Any small errors in the angles of the prisms, etc, will cause deviations in the incident ray and it is essential that the accuracy of these angles is at least as much as that of collimation.

Half-shades, etc, which are used should be perfectly balanced since otherwise they might introduce some additional ellipticity in the beam. We have not used any in our set-up.

The error in Δ can be seen from expression (38) to be caused mainly by error in the relative settings of polarizer and compensator while in the case of error in Ψ analyser setting also plays an important part.

In calculating the optical constants of a surface, error in the determination of k mainly comes from errors in Ψ while any error in the determination of angle of incidence also plays a small part in the determination of n. However, an accuracy of 1′ should be sufficient for its determination. The following example will show the order of accuracy needed in the measurement of the angles. It was calculated that an error of $\pm 0{\cdot}05$° in the measurement of P_0, Q_0 and A_0 causes an error of ± 2° in Δ and $\pm 0{\cdot}05$° in Ψ and $\pm 0{\cdot}006$ in n and $\pm 0{\cdot}005$ in k. Thus it is evident that errors in measurement of angles carry by almost 10% into the values of n and k. As these are dependent on the values of P_0, Q_0 and A_0 the criticality of the correct alignment is seen.

However, when making measurements on thin films, it is the change in the values of Δ and Ψ that are caused by the film which is important. As such, the systematic errors which are present in the measurements taken both with the bare substrate and filmed surface do not matter much while taking the differences.

We have also to consider the effect of random errors which have a direct contribution, as also the indirect effect of the systematic errors which transmit through the values of the optical constants of the substrate. The latter, however, are second order effects. There seems to be no particular procedure for the elimination or compensation of the random errors, other than greater care in experimentation and control and maintenance of experimental conditions.

Typical Results

Silver films — In order to evaluate the performance of our instrument, we undertook to track the variation with angle of incidence, of the relative phase shift between the p and s components of a polarized light beam when reflected, at an evaporated silver surface. The silver surface was prepared by evaporation of 99·99% pure silver (Johnson & Matthey) wire on to a clean microscope slide at a pressure of 5×10^{-6} torr. The microscope slide was cleaned by treatment with tap water, acid, alcohol and distilled water in that order and finally heated by ionic bombardment for a final cleaning. The thickness of the film was about 800 Å.

Fig. 8 shows the curve obtained by us which agrees excellently with the theoretical curves. From the curve, the value of the principal angle was found to be 74·5° which agrees favourably with the value mentioned in the literature[28].

The thickness of some silver films on glass slides has been calculated using the approximation $d/\lambda \ll 1$ and substituting the values of n and k for silver in bulk form. The value of d/λ in our experiment was 0·132. We have used the D_1 and D_2 lines of

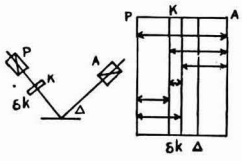

Fig. 7 — Multiple reflections in the ellipsometer [P, polarizer; K, compensator introducing a phase difference δk; F, film introducing a phase difference Δ; and A, analyser]

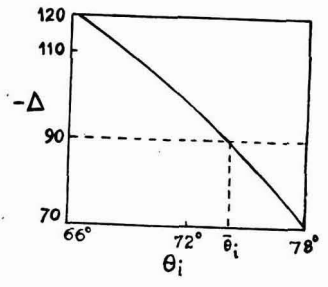

Fig. 8 — Variation of the phase difference Δ on reflection at a silver surface with angle of incidence [$\Delta = 90$° at angle of incidence = 74·5°]

sodium, the average wavelength being 5893 Å. The thickness values obtained by ellipsometry and by multiple beam interferometry are compared in Table 1.

The agreement of the values obtained ellipsometrically with those obtained by interferometry was found to be best when the angle of incidence used was 71°. This is about 3° less than the principal angle. This value, however, has to remain in the vertical part of the ellipticity versus angle of incidence curve (Fig. 9). This observation was made by Mertens *et al*[28] also. No reason for this is apparent.

Iron films — Two similar films of iron (more than 98% pure) were prepared on glass microscope slides. Conditions of preparation were similar to those for silver films.

One of the specimens was studied on the ellipsometer immediately after preparation. The values of n and k of the surfaces were computed. The other specimen was baked in air continuously for 5 hr at 200°C. The n and k values of this specimen were also computed. The colour of this specimen was brick red.

The first specimen was exposed to atmospheric action. The colour of the film which was originally black changed continuously during this time and was almost the same as the baked specimen after 14 days. However, the adhesion of the aged film was poor compared to the baked film. The n and k values for the aged film, determined at regular intervals, were found to approach the values of the baked film gradually. The results are shown in Table 2 and Fig. 10. The average levels of temperature and humidity during the period of study were 30°C and 70% respectively.

TABLE 1 — THICKNESS OF Ag FILMS AS MEASURED BY ELLIPSOMETRY AND INTERFEROMETRY

Film No.	Thickness (in Å) by	
	Ellipsometry	Interferometry
1	860	848
2	962	975
3	919	913

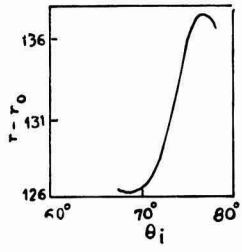

Fig. 9 — Variation of ellipticity of the reflected beam of light for a silver surface with angle of incidence [r_0 represents the ellipticity when reflected from the bare glass surface]

TABLE 2 — VARIATION, WITH AGEING, OF n AND k OF AN Fe FILM

Condition of the film	n	k
Immediately after deposition	2·77	1·08
After 5 days	1·009	0·36
After 10 days	0·7674	0·0146
After 14 days	0·7581	0·00124
After baking in air for 5 hr	0·7521	0·00111

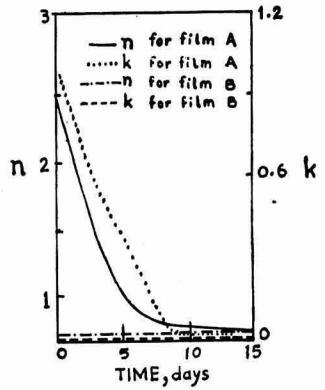

Fig. 10 — Curves showing the oxidation of film exposed to atmosphere [Film A was left exposed to the atmosphere and n and k of the surface were measured at regular intervals. Film B was baked immediately after deposition for 5 hr at a temperature of 200°C]

SUMMARY

A detailed review of the representation and analysis of polarized light leading to the theory of ellipsometry is given. The various methods of calculation of optical constants of thin films by ellipsometry are critically discussed. An ellipsometer designed and fabricated by the authors is described. The measurements, adjustments and calculations to be made in determining n and k are dealt with in some detail and the possible errors and ways of minimizing them are mentioned. Some typical results obtained with silver and iron films using the instrument are presented. The data are compared with data obtained using other methods. In the case of iron, the variations of n and k with oxidation of the thin film have been studied and the values found to approach those for the baked film.

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Determination of Effectiveness Factor of Porous Catalysts & Its Relationship with Other Reaction Parameters

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MASS transfer due to intraparticle diffusion in porous catalysts affects the concentration, temperature and pressure gradients. This pore diffusion effect is more pronounced under isothermal conditions. The yields of the desired product are severely limited by mass transport rates. The rate equation based on the apparent kinetics and the design of the chemical reactor are incomplete unless these factors are taken into account. This was recognized by several workers[1-7] and their studies led to quantitative assessment of the factors which determine the effectiveness of a porous catalyst. The effectiveness factor, η, is defined as the ratio of the actual reaction rate to that which would occur if the entire surface through the inside of the catalyst were exposed to the reactant of the same concentration and temperature as that existing at the outer surface of the catalyst.

To consider the effect of diffusion in a chemical reaction Thielie proposed a parameter

$$\phi_s = R\sqrt{\frac{k_v C_s^{m-1}}{D_{eff}}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots (1)$$

where ϕ_s is Thielie's parameter for spherical geometry; R, radius of sphere; k_v, intrinsic reaction rate constant per unit volume of the catalyst; C_s, concentration at the outer particle surface; D_{eff}, effective diffusion coefficient; and m, the reaction order.

Apart from Thielie's dimensionless parameter, one must consider the pore geometry of the catalyst system, the order of the chemical reaction and the thermal nature of the system, ie whether the system is isothermal or non-isothermal. Under isothermal and constant pressure conditions, the only effect would be the reduction in concentration within the pellet. When the heat of reaction is significant, the temperature increases for an exothermic reaction with penetration because of the thermal conductivity of the catalyst pellet. In such cases up to a certain value of Thielie's modulus, the value of the effectiveness factor increases and then falls. To take into consideration this effect, the heat generation function, β, is used and to take into consideration different reaction activation energies, the exponent, γ, in Arrhenius rate expression is used. In addition, one must consider reversible and irreversible processes. The heat generation function, β, is defined as

$$\beta = \frac{C_s(-\Delta H)D_{eff}}{\lambda T_s} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots (2)$$

where C_s is the concentration at the surface of the pellet; T_s, the surface temperature; ΔH, heat of reaction; and D_{eff}, the effective diffusion coefficient.

The exponent, Υ, in Arrhenius rate expression is defined as in the conventional use, viz

$$\Upsilon = \frac{E}{R_T} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3)$$

where E is the activation energy; R, the gas constant; and T, temperature.

If pore diffusion is predominant, the order of the magnitude of the activation energy and the thermal nature of the system will be in error, and hence the reaction rate constant and the design of the reactor itself will be wrong. The above discussion brings out the qualitative importance of the effectiveness factor.

First order kinetics and the spherical geometry of the pellets have been treated exhaustively in the literature, although other geometries and reaction orders can be treated similarly, mathematically. For this case, the most commonly required expressions are: (1) Thielie's modulus; (2) heat generation function; and (3) Arrhenius reaction rate function. A family of curves has been given for these three parameters for both isothermal and non-isothermal conditions.

Assuming isothermal conditions and representing the complicated diffusion phenomena by a single effective diffusion coefficient, Satterfield and Sherwood[8] derived the following equation for first order kinetics and spherical geometry:

$$\eta = \left[\frac{3}{\phi_s}\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s}\right] \quad \ldots \quad \ldots \quad \ldots \quad \ldots(4)$$

Since Thielie's modulus contains the undeterminable intrinsic reaction rate constant, k_v, this has to be transferred into an experimentally determinable parameter as follows:

$$\Phi = \phi_s^2\eta = \frac{R^2}{D_{eff}}\left(-\frac{1}{V_c}\cdot\frac{dn}{dt}\right)\frac{1}{C_s} \quad \ldots \quad \ldots \quad \ldots(5)$$

This is the practical form of the equation for effectiveness factor which could be used easily. A family of curves is available for various values of η and ϕ.

For other geometries and complicated reactions similar forms of equations are possible, although the analytical solutions of these equations are difficult.

In addition to the above equations, Wheeler's[3] expression for isothermal case is also useful, particularly when only one experimental value is available.

$$\phi \tanh \phi = \frac{a^2}{18D}\left[\frac{\text{Feed rate}}{C_a\,(\text{inlet})} \times \frac{1}{\rho_p V_g} \log_e \frac{1}{1-\alpha_c}\right] \quad \ldots(6)$$

Literature Survey

In addition to the above equations, many other investigators have contributed to the knowledge of effectiveness factor. Wacko and Smith[9,10] considered the bimodel pore size distributions for first order isothermal reactions. Weisz *et al*[6,11], Wicke *et al*[12,13] and others have contributed to the understanding of isothermal effectiveness factors. Schilson and Amundson[14] contributed to the knowledge of non-isothermal effectiveness factor. Tinkler and Pigford[15] studied the effect of heat generation in the case of a first order irreversible reaction inside a spherical pellet. They gave charts of η versus ϕ for exothermic and endothermic reactions. Tinkler and Metzner[16] considered the first order non-isothermal system for both spherical and slap geometries. They also obtained numerical solutions for the second order kinetics in a spherical geometry. Carberry[7] considered first and second order non-isothermal systems for slab geometry. In this case, they observed that heat effects are less important as the reaction order increases. Weisz and Hicks[4] gave a family of curves correlating the effectiveness factor with Φ $(=\phi^2\eta)$ for irreversible first order reaction in a sphere. They observed that at high values of ϕ, the effectiveness factor becomes inversely proportional to Thielie's modulus, as in the isothermal case. Peterson[17] reported a method of analysis which is applicable for high values of ϕ. Weisz and Prater[6] developed the following relationship between the activation energy and the effectiveness factor:

$$E_0/E = 2-\eta$$

where E_0 is the real activation energy; and E, the experimental activation energy. From this relationship it is possible to obtain the actual activation energy from a knowledge of effectiveness factor and experimental activation energy. Hougen and Watson[18] and Saleton and White[19] suggested a triangular method to obtain η from particle size data. Scott[20] has discussed the significance of effectiveness factor in the context of effective diffusivity for a transition region between Knudsen and bulk diffusion. Roberts and Satterfield[21] have given a generalized method of predicting the value of the catalyst effectiveness factor. They prepared charts using modified Thielie's modulus. They also considered a second order system. Gupta and Douglas[22] proposed a method whereby η can be calculated from the reaction rate without recourse to curve fitting and without the knowledge of effective diffusion coefficient, surface concentration and reaction rate constant. It is necessary to know the rates of reaction with different particle sizes.

Determination of Effectiveness Factor

In general, the effectiveness factor can be determined by any one of the following three methods: (1) using effective diffusion coefficient; (2) using different particle sizes; and (3) using some model of pore structure.

Method based on the use of effective diffusion coefficient — The effective diffusion coefficient can be determined experimentally using a special diffusion cell. Usually the data obtained in this way are for non-reacting conditions. With this, Eq (5) can be used to calculate the value of the effectiveness factor. Whenever the experimental value of the effective diffusion coefficient is not available, the following equations can be employed:

$$D_{eff} = (D_{12}\theta)/\tau$$

where D_{12} is the bulk diffusion coefficent; τ, the tortuosity factor, assumed to be equal to 2·0; and θ, the porosity. Alternatively, one can use the expression

$$\frac{1}{D_{eff}} = \frac{1}{D_{12}} + \frac{1}{D_k}$$

where D_k is the Knudsen diffusion coefficient defined as

$$D_k = 9700 r_e \sqrt{T/M} \quad \ldots \quad \ldots \quad \ldots(7)$$

where r_e is the average pore radius; and M, the molecular weight. The effective Knudsen diffusion coefficient is given by

$$D_{k,eff} = 19400 \ (\theta^2/\tau S_g \rho_p) \ \sqrt{T/M} \quad \ldots(8)$$

For large pore radius, the influence of Knudsen diffusion coefficient is negligible, and hence

$$D_{eff} = D_{12} \quad \ldots \quad \ldots \quad \ldots(9)$$

Method based on particle size variation — Experimentally, the effectiveness factor can be determined most accurately by calculating reaction rates for different catalyst particle sizes, under otherwise identical conditions. The effectiveness factor approaches unity when no increase in rate per unit quantity of the catalyst occurs on subdivision. Even when experimental data are available only for two particle sizes, the value of η may still be obtained without knowing independently the values of k_v or D_{eff}. The details of this procedure have been given by Satterfield and Sherwood[8]. When the ratio of rates per unit volume of catalyst with reference to two particle radii r_1 and r_2 is η_1/η_2, it can be shown that

$$\Upsilon_1/\Upsilon_2 = \phi_1/\phi_2$$

By assuming $\eta = 1$ for small particles, the value of η_{large} can be calculated. Employing trial and error procedure and with the help of η versus ϕ plots one can obtain the value of η_{small}.

An alternate triangle method is based on the fact that η_1/η_2 and ϕ_1/ϕ_2 form lines of fixed length on the ordinate and abscissa respectively on a logarithmic plot of η versus ϕ. The two lengths constitute a triangle which can be fitted to the curve to get the individual values.

Method based on models of pore structure — The value of the effectiveness factor can be determined by assuming certain models for pore structure. The most frequently assumed model is that in which the pore structure is represented by cylindrical pores of a uniform diameter randomly oriented, so that any plane will intersect the cylinders at an average angle of 45°. Thus, $D_{eff} = (D_{12}\theta)/2$. In this case, the tortuosity factor works out to 2·0. Actually the tortuosity factor may be found to be greater or less than 2·0.

The other model that is of importance is the random pore model due to Wacko and Smith[9]. In this, it is assumed that there are three paths for diffusion. One path is entirely through the macropores, another entirely through the micropores and the third one through both macropores and micropores in series. The total diffusion through a unit area of pellets is equal to the sum of these three contributions. Associated with each diffusional path will be a diffusivity multiplied by the appropriate area fraction available for each path. A probability concept is used to determine the area fractions. To use the model one must know pore size distribution, pore volume, surface area and the number of dead pores and the shape of pores. Because of the difficulty in knowing the last two parameters, the practical usefulness of this model is limited.

Whatever be the method of approach to obtain the value of η, the accuracy depends upon the accuracy of D_{eff}. Thus, experimental determination of D_{eff} is necessary to have meaningful values of effectiveness factor.

Physical Significance of Various Parameters

Generally, small values of ϕ (>2) indicate that the catalyst surface is almost completely available for the reaction. A high value of ϕ (<2) involves that the catalyst surface is only partially available for the reaction. A high value of ϕ (<2) also indicates a fast reaction.

When the value of the effective diffusion coefficient is large, the average pore radius is small and the intrinsic reaction rate constant is small. Therefore, the catalyst surface is completely available for the reaction. It indicates an effectiveness factor of unity. When the value of the effective diffusion coefficient is small, the average pore radius is large and the intrinsic reaction rate constant is large. Therefore, only a partial surface of the catalyst is available for the reaction. It indicates that the value of the effectiveness factor is less than unity.

It is important to note that the extent to which the diffusion effects within the pellet are significant is determined solely by the value of the diffusion modulus and not by the individual values of the effective diffusion coefficient, intrinsic reaction rate constant or the average pore radius.

When the value of ϕ is substantially less than unity (or $\phi_L = \frac{1}{3}$), the diffusion effects are relatively insignificant for first order reaction. This is also true to a certain extent for higher order reactions.

A low value of the effectiveness factor (η) does not automatically mean that diffusion is the controlling mechanism. If the mass transfer from the fluid to the outside surface were the rate controlling mechanism, the activation energy will be of the order of 1·0 kcal/g mole. Generally, the value of the activation energy for the diffusion mechanism is low (>1·0 kcal/g mole), whereas for the chemical reaction (vapour phase) it is high (<10·0 kcal/g mole).

When the catalytic activity varies with the particle size, it indicates that the catalyst is operating at a low effectiveness factor value. When the catalyst activity does not vary with the particle size, the entire surface of the catalyst is available for the reaction and the value of the effectiveness factor will be tending towards unity. The same general conclusion can be reached qualitatively if the activity is same for the fixed bed data and the fluidized bed data.

The following broad conclusions emerge from the above discussion: (1) when ϕ_L<1·0, it is unlikely that pore structure is causing decreased activity; and (2) when ϕ_L>1·0, it is likely that pore structure is influencing the yields of the desired product.

The parameter, β, represents the maximum temperature difference that could exist in the particle relative to the particle surface temperature $(T-T)_{max}/T_s$. This would occur if the concentration drops to essentially zero within the pellet.

For an exothermic reaction, β is positive and when $\beta = 0$ it indicates an isothermal reaction. When $\beta > 0$, the value of the effectiveness factor may exceed unity, since the increase in rate caused by the temperature rise towards the centre of the particle more than offsets the decrease in rate caused by the drop in concentration.

In a slow reaction, larger catalyst surface area is useful, but a highly active catalyst causes the reactant molecules to react before they can diffuse very far into the pellet. Thus, the value of the effectiveness factor is low in the case of very active catalysts. This explains why an expensive catalyst, such as platinum or palladium is sometimes prepared by depositing metals in a thin layer on the pellet surface. On the other hand, inactive catalysts in a slow reaction tend to have high value of effectiveness factor. For assessing the full significance of the effectiveness factor one must know the reaction velocity also.

Nomenclature

B_h = heat transfer coeff, g cal/sec cm² °C
C = conc (g moles/cm³); C_s, conc at outside particle surface; C_∞, conc at ∞ distance from the catalyst surface
D = coeff of molecular diffusion, cm²/sec
D_{12} = bulk diffusion coeff on a mixture of species 1 and 2, 1 diffusing into 2
D_k = Knudsen diffusion coeff
D_{eff} = effective diffusion coeff
E = activation energy (g cal/g mole)
ΔH = enthalpy change, g cal/g mole
k_v = intrinsic reaction rate constant
m = order of reaction
M = mol wt
dn/dt = rate of reaction, mole/sec
$(Nu)_h$ = Nusselt No.$= B_h R/\lambda_g$, where λ_g is the thermal conductivity of fluid
R = radius of sphere, cm
T = temp; T_∞, temp at infinite distance from the catalyst surface
V_c = catalyst vol
β = heat generation function
γ = exponent in Arrhenius reaction rate expression $= E/Rt$
η = effectiveness factor
θ = porosity
λ_g = thermal conductivity of fluid mixture
ϕ = Thielie's diffusion modulus

Summary

The concept and importance of effectiveness factor of porous catalysts in kinetic analysis have been discussed. The present status of the knowledge on effectiveness factor has been critically reviewed. The methods of determining it are presented and the physical significance of the various parameters has been discussed.

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Use of Surface Active Agents in the Isolation of Enzymes from Plant Tissues & in Their Assay

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IN spite of the extensive application of surface active agents in the study of enzymes, there exists no review on the subject. A monograph just published[1] deals extensively with the solubilization reactions by surface active agents, but only cursorily with their applications in enzymology. Although this review relates specifically to enzymes from plant tissues, the authors have made extensive use of data relating to animal tissue. However, the role of detergents in the study of enzymes from microorganisms is excluded. It is also not intended to deal with the application of detergents in the isolation of structural proteins and chlorophyll-protein complexes and of nucleic acids. The terms surface active agent, detergent and wetting agent are used synonymously.

Action on Enzyme Proteins

Surface active agents react in a variety of ways with proteins[2,3]. Generally, the ionic surface active agents are believed to act by combining with proteins, primarily through electrostatic forces. They may cause denaturation, precipitation and dispersion of proteins, or even catalysed hydrolysis of amide and peptide bonds. According to Putnam[3], the linkage through electrostatic forces is facilitated and the complex stabilized by factors of specific affinity arising from van der Waals' forces between nonpolar groups of the bound detergent ions. Nonionic compounds exert their effects by interactions involving van der Waals' forces or hydrogen bonding. A configurational change in the protein molecule is also a possibility. The studies of Jirgensons[4] and Imanishi *et al*[5] on a number of proteins, inclusive of bacterial α-amylase, showed that while the ionic detergents induced α-helix in the protein molecule, nonionic detergents failed to do so. Brewer and Spencer[6] found that yeast enolase, which behaves as a compact sphere in the native state, changes to an asymmetric rigid complex on treatment with sodium dodecyl sulphate.

The detergents may not have any action on enzyme activity, or they may inactivate or activate the enzyme.

Action on Substrate Molecules

The detergent may function as an ideal substrate for enzyme action[7]. Surfactants also aid in maintaining substrate and cofactor molecules, such as lipids, quinones, terpenoids and porphyrins, in emulsion or solution during enzyme assay or other determinations[8-11]. The stimulation by ionic surfactants of post-heparin lipase activity was attributed by Doizaki and Zieve[12] to the influence of these surfactants on the charges surrounding the substrate (olive oil) particles; lipolysis was more likely to occur if the charge was positive.

Nonionic versus Ionic Detergents

In general, nonionic detergents, because of the comparative weakness of their linkage with protein, exert less inhibitory effect on enzymes than ionic detergents. On the other hand, deoxycholate, in spite of its tendency to inhibit enzyme activity or render the enzymes unstable, remains unsurpassed as the detergent for 'solubilizing' microsomal enzymes.

Solubilization of Bound Enzymes

Structural Association as an Artifact

The process of cell rupture may result in an enzyme being attached as an artifact to cell wall or intracellular particles or even to colloidal material. One of the best studies made concerns the linkage of ribosomes with acidic groups to enzyme proteins with basic groups[13]. Examples are also known of the binding of enzymes to the 'structural proteins' of mitochondria[14]; such a binding may be expected also in the case of the 'structural proteins' of chloroplasts and microsomes. A recent development in enzyme biochemistry has been the attachment of enzymes *in vitro* to water-insoluble particles, not only by chemical methods, but also by physical methods[15].

In general, the order of activation achieved by detergents is only marginal when the particle association is an artifact. Thus, the order of activation on treatment of banana polyphenol oxidase with detergents was of the order of 50-100% (ref 16).

Enzymes Associated with Membranous Structures

Many cellular systems depend for their activity on the presence of membranes which function as semipermeable envelopes enclosing material which is different in composition from that of the exterior. The term 'membrane', as used in this review, connotes the classical triple layer structure, made up of lipid sandwiched between two protein layers, which manifests in electron micrographs as two closely facing electron opaque lines and which limits the passage of solutes. However, lipoprotein subunit models which are at variance with the classical bimolecular membrane concept have been proposed for chloroplast lamellae and mitochondrial membranes[17]. Enzymes in membranes are presumably bound to lipids and are resistant to solubilization, unless treatments such as detergent action are applied to remove the lipid or break the bonds assumed to be involved in the linkage of protein to lipid. These linkages are presumably through hydrogen bonds and van der Waals' forces.

Under conditions of low ionic strength and appropriate *p*H, surface active agents form stable micelles by an association of the hydrophobic

groups and cause a physical dispersion of water-insoluble material. All detergents can probably combine with lipoproteins; in addition, the synthetic ionic detergents may actually induce dissociation of lipoproteins. In general, the synthetic nonionic detergents are less effective than the ionic detergents, on weight basis, in solubilization, since stable electrostatic linkages are not involved[18].

Enzyme Enclosed in a Membranous Structure as True Solution

The activity of such membrane bound enzymes depends on the ease with which the substrate penetrates the membrane during assay. A rupture of the membrane by the action of surface active agent will readily release the enzyme, which was already in solution. Under these conditions, there is either a marked increase in the activity of an enzyme whose existence was demonstrable without special treatment or appearance *de novo* of enzymic activity. The enzyme is thought of as being latent under normal conditions.

Lysosome — The 'structure-linked latency' of enzymes[19,20] is best illustrated in the case of rat liver lysosomes. Sawant *et al*[21] reported that in these particulate fractions acid phosphatase (EC 3.1.3.2), arylsulphatase (EC 3.1.6.1) and ribonuclease (EC 2.7.7.16) were latent to the extent of 90-95%. That some activity can be demonstrated in lysosomes without special treatment probably shows that they are not entirely impermeable.

According to Novikoff[20], the lysosomes are characterized by a 'single' outer membrane. The membrane fraction contains 60-70% of the total protein of lysosomes. The entire phospholipid content of lysosomes is contained in the membrane, but it is doubtful whether any enzyme is structurally associated with this membrane. Verity *et al*[22] adduced experimental evidence to show that the cryptic activity of lysosomal hydrolases is associated with the presence of different enzyme-membrane bonds conferring structure-linked latency upon individual lysosomal enzymes.

Cytochemical and related evidences for the occurrence in plants of lysosome-like structures have been reviewed by Straus[23]. However, differential centrifugation studies on plant tissues by Corbett and Price[24] failed to support lysosomal association for acid phosphatase, or a latency for the enzyme solubilizable by techniques involving treatment with Triton X-100.

Microbody (peroxisome) — Catalase (EC 1.11.1.6) is truly latent in the microbodies (peroxisomes) isolated from liver tissue[19]. Evidence for the occurrence of peroxisomes in spinach leaves was recently reported[25]. These bodies had a single membrane envelope which got ruptured under the assay conditions. These workers, however, did not investigate the effect of detergents during the assay of the peroxisomal enzymes.

Glyoxysome — Breidenbach and Beevers[26] and Breidenbach *et al*[27] reported the isolation from castor bean endosperm of a class of cytosomes characterized by malate synthetase (EC 4.1.3.2) and isocitrate lyase (EC 4.1.3.1) activities and designated the particles as glyoxysomes. Since these particles contained also the major part of catalase and glycolate oxidase (EC 1.1.3.1), it is not clear whether the glyoxysomes and peroxisomes are distinct organelles or are identical. The particles isolated by the above workers by gradient density centrifugation were bounded by a single unit membrane and the stroma had a finely granular appearance. These particles were not subjected to any special treatment prior to enzyme assay. It has, therefore, to be assumed that the membranes were readily permeable to substrate, or were ruptured during the assay. Nevertheless, the use of detergents may be expected to reveal interesting aspects of the enzymic make-up of the glyoxysomes. Firenzuoli *et al*[28] studied the enzymes of the glyoxylate bypass in the soluble fraction of pine seedling homogenates prepared in a medium containing Tween 80. The detergent might have facilitated the release of the particle-bound enzyme, or, more likely, might have functioned by preventing the complexing of the enzyme with tissue phenolics.

A True Localization in Membranous Structures

Consequent on the action of the surface active agent, the membrane-bound enzyme is released either in true or in apparent solution. This may result in either a marked increase (suggesting a latency) or only a marginal increase in the enzymic activity. The release of the enzyme may be either because of the general solubilization of membrane protein, or it may be somewhat selective. Consequent on the action of the detergent, an enzyme may be activated, but may still remain particle bound.

Nucleus: Nuclear membrane — The nuclear envelope is made up of two membranes, the external one being essentially an extension of the endoplasmic reticulum. However, many of typical enzymes of the endoplasmic reticulum are absent in the nucleus. The permeability characteristics of the nuclear membrane are not properly understood; the isolated nuclei are permeable to certain enzyme proteins, but at the same time impermeable to low molecular substances. The nuclear membrane is extremely fragile and gets damaged on isolation in aqueous media. Detergents have found only limited application in the study of nuclear enzymes.

Intranuclear enzymes — The assay of the enzymes inside the nucleus and especially in the nucleoplasm, as in the case of NAD-pyrophosphorylase (EC 2.7.7.1), may not require the use of detergents, since the dilution occurring in the assay system may lead to rupture of the intact nucleus. Such membranous intranuclear structural elements as are known to contain associated enzyme activity may be expected to respond to detergent treatment, but there is apparently no systematic study conducted in this direction. Mild treatments such as dilute or concentrated salt solution have been satisfactory in solubilizing the particle-associated nuclear enzymes, viz RNA-polymerase. Some enzymes such as DNA-polymerase of chromosomes are actually extractable by water[29]. Nevertheless,

protein synthesis in the nucleolo-chromosomal complex has not been studied in cell-free systems. Unspecific ATPases (EC 3.6.1.3) are known to be tightly bound to DNA chromosomal complex.

The advances in the field of plant nuclei have not kept pace with those of animal nuclei. The nuclear envelope in the interphase cell of the maize root tip is a double membrane structure. There appears to be sufficient evidence that the nuclear membrane in the plant is actually a differentiation of the endoplasmic reticulum. Nucleolonematal structures are also likely to be present[30].

Chloroplast: Ultrastructure — The thylakoids, the structural units of the photosynthetic lamellar systems, are lipoproteinous double membranes closed in themselves, which are embedded either singly or in stacks in the stroma. According to Muhlethaler[31], the inter-grana region, the stroma, which was formerly believed to be homogeneous, is actually layered.

Outer membrane — The chloroplast is bounded by a double membrane. Since this membrane has not been isolated in a pure form and, therefore, could not be subjected to biochemical studies, no information as to the location of any enzymes in this membrane is available.

Sub-chloroplast fractions — The overall photosynthetic activity of sub-chloroplast preparations studied so far formed only a small proportion of the activity of the whole chloroplasts[32]. Detailed studies have been made on the action of Triton X-100 on chloroplasts. In high concentrations, it solubilizes the enzyme from the fraction, while in low concentrations it produces specific effects on the intermediate electron transport complexes[33]. It may function also as an uncoupling agent[34].

Intra-plastid enzymes — The chloroplast membrane is readily permeable to substrates[35]. Also, as isolated in aqueous media, the chloroplasts undergo considerable damage to the bounding membranes[36], as illustrated by the leaching out of ribulosediphosphate carboxydismutase[37] and fructose-diphosphatase (EC 3.1.3.11)[38]. It is well known that mere osmotic shock is sufficient to rupture the chloroplasts[39]. According to Menke[40], washing of chloroplasts several times results in preparations consisting exclusively of lamellar system. Nevertheless, it has been the usual practice to assay the enzymic activity of chloroplast preparations only after rupture by mechanical means or by the action of detergents. Friend and Mayer[41] and Friend and Acton[42] reported that treatment of sugar beet chloroplast suspension with deoxycholate doubled the rate of enzymatic oxidation of carotenoids. Brandon[43,44] conducted the enzyme assays in chloroplast fractions after treatment with Tween 40. Harel *et al*[45,46] employed Triton X-100 to extract catechol oxidase preferentially from chloroplasts and digitonin for the enzyme from mitochondria of apple.

According to Menke[40], ferredoxin is loosely bound to grana, but von Wettstein[47] considered it to be in the stroma. Zanobini *et al*[48] found that ferredoxin was extractable from conifer leaves only when Tween 80 was incorporated into the extraction medium. Extracts prepared without the detergent did not contain protein, which the authors attributed to the presence in the tissue of resins and tannins. Forti *et al*[49] reported that parsley leaves released cytochrome *f* into the 19000 *g* supernatant fraction in high yields only when Triton X-100 was incorporated into the extraction medium.

A more important application of detergents in the study of chloroplast has been in the isolation of chlorophyll-protein complexes. The finding that chlorophyllase activity was marked in the chloroplast-lipoprotein complex obtained by digitonin treatment of chloroplasts suggested that all the chlorophyllase may be present as a chlorophyll-lipoprotein complex[50]. Klein and Vishniac[51] obtained a 500-fold enriched chlorophyllase preparation in the form of a deoxycholate-chlorophyllase complex by extracting isobutanol-treated etiolated rye seedlings with sodium deoxycholate.

Mitochondrion: Distinctive structural features of plant mitochondria — By comparing the ultrastructure of mitochondria *in situ* in the cells of wheat roots with that after isolation by the usual techniques, Hodge *et al*[52] established that the isolated organelles had undergone some disruption in their internal structure. They suggested that the structural alteration undergone by the mitochondria may induce quantitative, though not qualitative, changes in enzymic activity.

Hackett[53] drew attention to certain fine structural features distinctive of plant mitochondria; the internal membranes of many plant mitochondria take the form of sinous tubules or microvilli. Bonner[54] pointed out that plant mitochondria cristae frequently connect with one another forming closed loops, a condition not seen in animal mitochondria. The presence of extensive mitochondrial membranes may account for the finding that structural modifications of isolated mitochondria cause pronounced stimulation of certain enzymic activities, in particular cytochrome oxidase[55] and NADH oxidase[56]. Animal mitochondria when intact are characteristically impermeable to external NADH. On the other hand, NADH can pass through the membranes of many plant mitochondria which are apparently intact as judged by their ability to exhibit respiratory control.

Use of Detergents in Enzyme Studies

Mitochondria

Localization of enzyme activities—Recently, detergents, particularly digitonin (which was first employed in mitochondrial study by Lehninger[57]), have been employed extensively in delineating the topography of enzymes in the mitochondria. Hoppel and Cooper[58] claimed that repetitive treatment with digitonin enabled the separate isolation of the 'outer' and 'inner' membranes of rat liver mitochondria. The outer membrane contained the entire rotenone-insensitive NADH-cytochrome *c* reductase (EC 1.6.2.1) activity, while the inner membrane contained rotenone-sensitive NADH-cytochrome *c* reductase, succinate dehydrogenase (EC 1.3.99.1), β-hydroxybutyrate dehydrogenase (EC 1.1.1.30), ATPase and the cytochromes and carried out oxidative phosphorylation. Malviya *et al*[59]

compared the ultrastructure and respiratory activity of submitochondrial particles obtained by ultrasonic and digitonin treatments of beef heart mitochondria. Many properties of the digitonin fragments were similar to those of mitochondria, while sonic fragments showed different behaviour.

Enzymes such as malate dehydrogenase, fumarase (EC 4.2.1.2), glutamate dehydrogenase (EC 1.4.1.2) and isocitrate dehydrogenase (EC 1.1.1.41) are believed to be localized in the matrix[60]. However, there is no direct evidence that such enzymes exist in a soluble form within the mitochondria. They may be released merely because they are easily discharged from some intramitochondrial structure.

Considerable caution has to be exercised in drawing positive conclusions as to enzyme localization in isolated membranes. The availability of acid phosphatase as marker for lysosomes has revealed that the outer mitochondrial membrane, as purified by density gradient centrifugation and found apparently homogeneous under the electron microscope, is contaminated with lysosomal membrane[61].

Detergents have not been employed so far for the localization of enzymes in plant mitochondria.

Enzyme exposure and solubilization — The kinetic studies of Tedeschi[62] established that whereas the semipermeable characteristics of the mitochondria (from animal tissue) did not reveal special features, as distinct from the usual membranes, the organelle was unique in that it could swell to 4-5 times in volume and 2- to 3-fold in apparent surface area without lysis or loss of internal solutes. Membrane barrier may, therefore, not be overcome during assays for enzymic activity using aliquots of isolated mitochondrial suspension. As an alternative to ultrasonic treatment, a number of workers have utilized detergents to disrupt plant mitochondria for assay of enzymic activity[63-68]. Some of the mitochondrial preparations of Yakoveleva *et al*[67] showed no glutamate dehydrogenase activity unless exposed to the action of (nonionic) detergent; this is probably the only reported instance of a completely latent plant mitochondrial enzymic activity.

Microsome

Ernster *et al*[69] consider that microsomes are small vesicles representative of the intact endoplasmic reticulum, with outer and inner surfaces of membrane surrounding a portion of the original solution of lumen. Such enzymes as are present in the lumen of the endoplasmic reticulum, or loosely bound *in vivo* to the membranous structure, may be expected to appear in the supernatant fraction on tissue homogenization and high speed centrifugation. Other enzymes are closely bound to the membranous structure of the microsomal fraction. An important test to establish true structural association of an enzyme with the microsomal membrane is to dissolve off the RNA particles with RNAase and determine whether the enzyme is still associated with the membranous residue. Another test consists in the solubilization of membrane bound enzymes, leaving the ribosomes intact.

Enzyme solubilization — In spite of the extensive advances made in this field, very few microsomal enzymes seem to have been purified thoroughly employing detergent treatment.

A number of enzymes are known to be associated with the microsomal fraction. With important exceptions, the microsomal enzymes are activated by digitonin treatment, the maximal activation achieved being about 3-fold. Gorlich and Heise[70] found that digitonin solubilized and activated bovine liver microsomal glucose-6-phosphatase (EC 3.1.3.9). Carruthers and Baumler[71] reported that synthetic detergents differ in their action on glucose-6-phosphatase and esterase activities of isolated mouse liver microsomes. All anionic and nonionic detergents tested effected a true solution of esterase, along with microsomal protein. However, some of these anionic and nonionic agents also activated glucose-6-phosphatase up to 2·3-fold, but the enzyme remained particle bound. The use of digitonin solubilized both the enzymes. Collipp *et al*[72] solubilized liver glucose-6-phosphatase by exposing the enzyme fraction to the action of Triton X-100; however, analysis of the active fraction from Sephadex columns revealed 38% lipid content. They concluded that the detergent had served merely to remove most of the RNA and to disperse the large lipoprotein colloidal particles into smaller ones.

Recent investigations have revealed interesting features of liver amylase. Most of the liver amylase (EC 3.2.1.1) which is present in a latent form gets activated on detergent treatment. Mordoh *et al*[73] presented evidence to show that the enzyme is localized in the microsomal fraction mostly in a latent form. Detergent treatment resulted generally in 4- to 6-fold activation, with occasional 25-fold activation. They claimed that by modifying the method of treatment with detergent, true solubilization of enzyme could be effected.

Enzyme localization — A certain measure of success has been achieved in the separation of membranous components of microsomes by detergent treatment, although less significant than in mitochondria. Ernster *et al*[69] found that when a microsomal fraction in 0·25*M* sucrose containing 0·024% deoxycholate was centrifuged, a loose reddish sediment overlay the ribosome-containing pellet. It was believed that the 'smooth surfaced' cytomembranes had dissolved preferentially leaving behind some of the 'rough' membranes. Supernatants, thus obtained, yielded a pellet when exhaustively recentrifuged after dilution with sucrose medium free of deoxycholate. Moule *et al*[74] found that the addition of extra deoxycholate may also sediment a pellet.

An enzyme located on the membrane with active site on the outer surface of microsome is more susceptible to the action of detergent than an enzyme located on the inner surface. Also, if an enzyme be multifunctional, with active groups distributed differently on the inner and outer surfaces, the externally situated activity will be less activated by detergent than an internally located activity[75,76].

Studies on microsomal enzymes in plant tissue have lagged far behind those in animal tissue.

Golgi Apparatus

Because of the highly membranous nature of the Golgi apparatus, the use of detergents may be expected to yield valuable information on the enzymes associated with these structures. Nevertheless, few studies have been conducted in this direction. Histochemical studies of Malite *et al*[77] suggested the location in part of plant acid phosphatase in dictyosomes. Recent evidences, reviewed by Beams and Kessel[78], show that a number of enzymes, phosphatases in particular, are associated with the Golgi apparatus of both animal and plant tissue.

Other Membranes and Membranous Structures

The cell membrane and intracellular connections — Electron microscopy has not established definitely whether the cell membrane is a single membrane or a double membrane with a clear space. The membrane is readily ruptured during isolation. If a gentle mechanical procedure is used to rupture the cells, plasma membrane fragments are recovered largely in the crude 'nuclear' fraction obtained on low speed centrifugation. These fractions are rich in certain enzymes, such as 5'-nucleotidase, which is used as the marker. Emmelot *et al*[79] subjected their plasma membrane fractions to deoxycholate treatment, which enhanced the activities of certain enzymes, such as arylesterase (EC 3.1.1.2).

Vacuolar membrane — The tonoplast appears as a single membrane and resembles the plasma membrane more than the membranes of any of the other inclusions or that of the nucleus[80]. There is considerable divergence of view as to whether a continuity exists between the endoplasmic reticulum and the tonoplast[30]. The membrane is fragile and gets ruptured during cell dispersion. There has been no study on detergent action in relation to enzyme activity in the isolated membranes.

Non-membranous Stuctures

Cell wall material — Whaley *et al*[80] reported evidence for the presence of reticulum membranes within primary walls. Elements of the endoplasmic reticulum extended to the cell surface and, occasionally, through the wall into neighbouring cells.

Lamport and Northcote[81] reported that at least 80% of the acid phosphatase activity of sycamore cells was associated with the cell wall fraction isolated by grinding with glass beads in a suspension medium of water. Kivilaan *et al*[82] isolated cell wall preparations in reasonably pure form from corn coleoptiles and found that the activities of ATPase, invertase (EC 3.2.1.26) and UDPG-pyrophosphorylase (EC 2.7.7.9) were comparable to those of the soluble protein fraction and that inorganic pyrophosphatase and α-glycerophosphatase activities were also demonstrable. Both the groups of workers did not employ detergents to test whether the attachment of the various enzymes was to any membranous component. Palmer[16] observed that the activity of the polyphenoloxidase of banana pulp was associated almost wholly with the cell debris fraction, but that the use of detergent in the isolation medium resulted in complete solubilization.

Starch granules — During photosynthesis starch deposits between the grana lamellae in the chloroplast and no membranous structure appears to be present around these starch particles. On the other hand, the storage form of starch is contained within amyloplasts. The starch is laid down as large grains, usually made up of a series of concentric layers successively deposited about a centre. The amyloplast membrane and accompanying stroma become greatly distended and finally become a thin pellicle enveloping the starch grain. Detergents do not seem to have been employed in a search for any membrane-associated enzymes in (storage) starch grains.

Ribosomes — The ribosome is not bounded by a membrane and it is to be anticipated that the enzymes associated with these particles will not be amenable to solubilization by the action of detergents. 'Latency' as applied to ribosomal enzymic activity is quite different from the structure-linked latency in the lysosomal enzymes[19,23]. Hsiano[83] employed sodium deoxycholate in the isolation medium to separate ribosomes from the roots of *Zea mays* seedlings; these particles had ribonuclease activity.

Latency of an Enzyme Apparently Unrelated to Membrane Enclosure or Binding

A special example of activation by detergent of a truly latent enzyme was provided by the studies of Kenten[84] on the polyphenol oxidase of broad-bean leaves. The starting material was the 8000 *g* supernatant of leaf extract in water, which had been dialysed, frozen and thawed and clarified in order to eliminate the possibility of chloroplast association or, in a less certain measure, mitochondrial association. The degree of activation achieved exceeded the activation of lysosomal enzymes reported by Sawant *et al*[21]. That changes in tertiary structure occurred was shown by Robb *et al*[85] and Swain *et al*[86].

Some Analytical Aspects Arising out of the Use of Surface Active Agents

Preparation of Stock Solutions

Since some of the solid detergents are comparatively insoluble, special care has to be exercised in the preparation of their solutions. Digitonin is available apparently in two forms; one of them is difficultly soluble in water. A satisfactory method of preparing digitonin solution has been referred to by Morton[87]. As a rule, detergent solutions should be neutralized before use, or should be prepared in buffer. Sodium dodecyl sulphate is nearly insoluble and precipitates slowly. It has been recommended that a concentrated standard be prepared at room temperature and this be diluted with cold buffer just before use[88]. Secondary changes likely to occur in stock solutions have also to be considered. Vernon and Shaw[33] observed that the molar absorptivity of Triton X-100 (around $1{\cdot}33 \times 10^3$ at 275·5 mμ in freshly diluted solutions)

slightly decreased on standing for a few days. Although Emasol 4130 was one of the most effective detergents in the solubilization of cytochrome oxidase, Orii and Okunuki[89] found this reagent unsuitable, since stored preparations led to spontaneous oxidation of ferrocytochrome *c*, due to the formation of peroxides. Tween 80 may be expected to suffer from the same disadvantage.

Exposure to Detergent Action

The effect observed will depend on the particular detergent used and its concentration[5,90], the *p*H of the medium (an anionic detergent is used at alkaline or neutral *p*H conditions and a cationic detergent at acidic or neutral conditions), the concentration of salt in the medium[91,92], the detergent to protein ratio[45,58], the period of contact[84,90] and whether there was a period of preincubation with detergent or whether the detergent was added during assay[75,76]. Successive treatments with different detergents may sometimes have to be employed. Hence, for the study of detergent action the reaction conditions will have to be carefully standardized for each particular enzyme and its source. Also, unless steps are taken to eliminate the detergent, its action may continue during the subsequent processing or treatment of enzyme.

Routine Use of Detergents in Phosphatase Assay Systems

Following the beneficial effect noticed by Tsuboi and Hudson[93] when nonionic detergents were incorporated in assays on acid phosphatase, which the authors ascribed to a protective effect against surface denaturation, it has been the practice in some laboratories to incorporate nonionic detergents routinely in acid phosphatase assays[94,95] and sometimes in alkaline phosphatase assays[96].

Particle Association and Detergent Stimulation

The stimulation of enzyme activity following detergent action cannot be taken as conclusive evidence for particle association of the enzyme. In studies on intracellular distribution of acid phosphatase in plant tissue, Corbett and Price[24] found that both the sedimentable and non-sedimentable fractions were stimulated, although the stimulation of the sedimentable fraction was usually greater.

When the action of a surface active agent on a complex mixture of enzymes is being tested, as in the determination of NADH-oxidase activity, the net effect observed is the resultant of the detergent effects on a number of constituent enzymes.

Interference with Enzyme Localization

Because of the action of detergents on the membranous structures in the cells, homogenates prepared in their presence cannot be used in enzyme localization studies. There is, however, an important exception. A separation between lysosomes and peroxisomes of liver is best effected by employing the tissue from animals injected with Triton WR-1339 (ref 97). Lysosomes with acid phosphatase activity are obtained in higher yields from rats injected with Triton than from normal rats[98]. Coffey and de Duve[99] obtained a lysosomal fraction with 50-fold enriched phosphatase activity, in relation to homogenate, by fractionating livers of rats injected with Triton WR-1339. Mahadevan and Tappel[100] claimed a 40-fold enrichment in the *o*-seryl-*N*-acetylgalactosaminide glycosidase activity of Triton WR-1339-filled lysosomes.

Secondary Changes Associated with Phospholipid Requirement

Some of the mitochondrial activities are intimately related to the content and steric arrangement of phospholipids. Since detergents rupture lipid-protein bonds and often effect solubilization, the enzyme activities may be inhibited in detergent-containing assay systems[14]. The same consideration applies also to the purification of membrane bound enzymes.

Interference by Phenolase Activation

If phenolases were to be 'activated'[84] or/and released from membranous structures[16,45], the oxidation of phenolics may be expected to be enhanced, leading to inactivation of desired enzymes or to interference in their assay[101]. Detergents may also lead to increased extraction of phenolics which, in turn, may interfere with the subsequent isolation of enzymes. At the same time, detergents may function by protecting enzymes from precipitation and/or inactivation by phenolics[102].

Secondary Shift in pH Optimum

A possible shift in *p*H optimum consequent on detergent action has to be separately ascertained. Wallach[103] showed that charged and uncharged surfactants shifted the *p*H optima (and substrate-specificity) of adipose tissue lipase. Stetten and Burnett[75] drew pointed attention to the changes in *p*H optima of phosphatase and phosphotransferase activity on detergent treatment. Collipp *et al*[72] could not confirm this observation. In case a shift occurs, comparison between the treated and untreated enzyme preparations at a constant *p*H will not be valid.

Interference during Enzyme Purification and Characterization

One of the advantages claimed for the various Tweens has been the ease with which they could be dialysed out[104]. Triton X-100, with a molecular weight in the neighbourhood of 625 (ref 33) may also be expected to be dialysable, but Harel *et al*[45,46] observed that it could not be 'adequately' removed by dialysis. Palmer[16] reported that the nonionic polyoxyethylated detergents 'Cutscum' and 'Igepal CO-630' could not be removed by dialysis.

Zittle *et al*[105] found that Tween 20 and lipid could ultimately be removed from preparations of acetylcholine esterase of red cell stroma by successive extraction with acetone, followed by *n*-butanol or ethanol. On the other hand, Palmer[16] pointed out that some detergents are actually precipitated by higher concentrations of acetone.

The use of gel filtration[106], or cellulose column fractionation[45,46], permits the removal of detergents used in enzyme extraction.

In the majority of cases, methods do not exist for the estimation of detergents in biological samples or enzyme preparations. Heron and Paton[107] suggested a colorimetric method which may have general application to nonionic detergents of the ethylene oxide class. Triton X-100 can be determined turbidimetrically by adding Na_2CO_3 in NaOH[108]. The availability of labelled detergents permits the detection and determination of minute amounts of detergent in enzyme preparations[108].

A surface active agent, when not eliminated at the outset, may interfere in enzyme purification. Deoxycholate has been found to lead to gel formation during enzyme activity enrichment[45,46]. In general, protein fractions precipitated by the addition of ammonium sulphate do not sediment well, or they float as a layer at the top during centrifugation.

An enzyme can be said to be soluble only when the protein is completely surrounded by water molecules. When the solubilization of an enzyme is only an instance of fine dispersion, the enzyme gets precipitated during some stages of purification[106] and the detergent may have to be employed for effecting a resolubilization[106,109]. Detergents may also have to be employed for the elution of enzyme from cellulose column[110], and in preventing sedimentation during dialysis[111].

The ionic surface active agent may be associated with the purified enzyme by electrostatic linkage, resulting in interference with physico-chemical studies. A detailed study of the binding of sodium dodecyl sulphate with various proteins has been made by Pitt-Rivers and Impiombato[112].

Artifact formation by changes in tertiary structure may be interpreted as the occurrence of isozymes[86].

Sodium dodecyl sulphate has been reported to remove copper from combination in ascorbate oxidase[113].

Occasionally, detergent treatment may elicit an enzymic activity different from that in untreated particles. Friend and Dicks[114] observed a doubling of the crocin oxidizing activity of sugar beet leaves following treatment with Triton X-100 and separation into extract and residue. The washed residual fraction of the treated mitochondria contained about 75% of the original activity and resembled the untreated mitochondria in its properties. The enzymic activity in the extract showed properties different from those of the residual fraction.

Interference in Enzyme Assay Systems

The presence of Triton X-100 has been reported to interfere in the development of orthophosphate colour[76,115]. That various Tweens also interfere by giving rise to opalescence has been shown earlier by us. This can be corrected by the addition of a pinch of charcoal, following acidification of the assay system with TCA.

Since the cytolytic action of detergent may be time-dependent, it is to be anticipated that membrane solubilization occurring during assay may affect the spectrophotometric determination of enzymic activity. An enzyme released into solution may react with detergent causing precipitation during assay, which again would affect the absorption measurements. Another complicating factor is the possible sedimentation, during assay, of particulate material on dilution of detergent-treated sample. It is essential to have a control included consisting of enzyme preparation and the surface active agent. One of the earliest detailed studies on changes in the turbidity of mitochondrial suspensions under the influence of detergents has been that of Witter and Mink[116].

Special care has to be exercised about the optical properties of the assay system if the enzyme assay is based on spectrophotometry in the ultraviolet region. Some detergents (Triton X-100, Cutscum) absorb powerfully in the ultraviolet region and the need for rigorous controls is apparent. Protein determination by spectrophotometry can also be interfered with[16].

Apart from any intrinsic absorption due to detergent, secondary changes in the absorption maximum and extinction coefficient of the desired component may occur. Ke and Clendenning[117] observed that sodium dodecyl sulphate (0·35%) or Tween 20 (1%) shifted the optical density of chloroplast pigments. The shift was observed also by Brown and Duranton[88] during their studies on the effect of sodium dodecyl sulphate on tobacco chloroplasts. Digitonin (0·085%) also caused a 50% increase in the light absorption[118]. Sauer and Park[119] made a critical study of the effect of dodecyl sulphate and Triton X-100 on the peak of absorption as well as optical density of chloroplast preparations.

General Conclusion

Reviewing the then existing methods of enzyme extraction from animal tissue, Morton[87] considered that the use of detergents was not desirable. However, the availability of newer types of detergents and a better understanding of the membranous ultrastructure of organelles have led to frequent use of detergents in the isolation and purification of enzymes from animal tissues. Detergent action has sometimes been claimed to yield more reliable data than other treatments. According to Ito and Sato[111], the use of detergents for solubilization yielded the undegraded form of cytochrome *b* 5 from liver microsomes, in contrast to the isolation of two spectrally identical, but structurally different, components when the solubilization was effected with proteases or lipases. Instances are known where detergent treatment was indispensable in the isolation of an enzyme[120], particularly from plant tissues. This is not surprising, since disintegration of plant cells is generally more difficult and because a number of enzymes tend to form artifact association with the cell wall debris fraction and also due to the fact that the presence of phenolics in plant cells facilitates particle association of enzymes.

Detergents have found more important applications in enzyme assays than in their isolation. There are several advantages in the use of detergents in preference to mechanical disruption, viz high pressure (' French press ') or ultrasonication, in the analysis of chloroplasts and mitochondria. In microsomal analysis, the use of detergents is

probably indispensable. Detergents constitute a valuable tool for the demonstration of structure-linked latency, as in the search for lysosomal structures in plant tissues.

The *in vivo* significance of the increased enzyme activity following detergent treatment of particles such as chloroplasts, mitochondria and microsomes cannot be assessed at present. It has been suggested that an enzyme latent *in vitro* may in reality be active in the membrane as existing *in vivo* and that the latency observed *in vitro* represents an isolation artifact[73]. On the other hand, Wilson[121] presented evidence to show that the particulate hexokinase of rat brain was interconvertible among soluble, particulate and latent (also particulate) forms by changes in the levels of common metabolites in assay systems. He proposed that hexokinase activity *in vivo* may be controlled by the relative distribution between the soluble and the particulate forms. The latency of enzymes in lysosomes, as existing *in vivo*, is beyond doubt. Even in this case, it is now held that organelles play a physiological role by aiding the digestion of a variety of substrates, derived from the extracellular environment by endocytic uptake or from the cell's own substance through autophagy. Lysosomes possess the requisite enzymes for the digestion of macromolecules[99,122].

Summary

The mechanism of the action of detergents on enzyme proteins has been considered briefly. The application of detergents in the solubilization of 'bound' enzymes and in enzyme assays has been dealt with. Several distinctive features arising out of the application of detergents in enzyme research have been stressed. The possible biological significance of enzyme latency as established *in vitro* by the use of detergents is indicated.

Acknowledgement

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REVIEWS

STATISTICAL MECHANICS by K. M. Khanna (Asia Publishing House, Bombay), 1968. Pp xii+283. Price Rs 18.00

The book under review is a welcome publication. The price of the book is reasonable and so it will be easily available to students and teachers in this country who often find it difficult to buy books on this subject published in other countries.

As the author has indicated, the book is the outcome of lectures on this subject that he has given to M.Sc. and research students. The choice of topics covered in the book is that of the author himself and is based on his research interests.

The connection of statistical mechanics with thermodynamics and the Maxwell-Boltzmann statistics have been covered only in one chapter. This part of the subject is of greater interest to a physical chemist and, therefore, in the opinion of the reviewer, the utility of the book is very much limited for a physical chemist.

From Chapter II onwards the emphasis is exclusively on quantum statistical mechanics, which is of interest mostly to physicists. A fuller appreciation of quantum statistics normally requires that the readers have been exposed to fairly advanced courses in quantum mechanics. In the majority of Indian universities the discussion of an assembly of interacting identical particles on the basis of the symmetry of wave functions is barely discussed. The discussion of such assemblies using the second quantization formalism is still much more advanced and is hardly touched upon in most M.Sc. courses. On account of this, M.Sc. students will find their preparation rather too inadequate to understand the major part of the book. They can, however, be helped in this task by their teacher if he is well versed in the use of these methods. The author has also indicated this by saying that a graduate level course in quantum mechanics is a prerequisite. Such graduate level courses as required for a full utilization of this book hardly exist at the M.Sc. level in most places except, maybe, in a few exceptions.

To be able to use the second quantization and Green's function method the readers must also have a good preparation in methods of mathematical physics without which they will find it hard to follow the steps given in the text for dealing with many-particle interacting systems.

The book can be used profitably by those who are in a position to follow the material given in it. For those who know the subject it will serve as a good reference book. The problems given in the book are a good feature, as a solution of these will enhance the understanding of the subject.

R. P. SINGH

EXCITONS, MAGNONS AND PHONONS IN MOLECULAR CRYSTALS, edited by A. B. Zahlam (Cambridge University Press, London), 1968. Pp xi+224. Price 70s

This conference proceedings is somewhat unusual in the manner in which the papers are presented. The keynote talks, as also the other papers, are reported in detail, so that the reader is not obliged to refer to other source material to see what is going on. One wishes that this approach towards reporting conference proceedings was emulated more extensively.

The papers have been divided into three sections: (1) Phonons — spectra and density of states; (2) Phonons in combination with electronic transitions; and (3) Excitons — coupling to phonon and radiation fields. The emphasis is on phenomena associated with these three aspects in molecular crystals, though many of the papers are quite general in their implications. Notable are the excellent review papers by D. S. McClure on excitons and magnons in antiferromagnetic crystals, by Max Wagner on investigation of lattice dynamics by means of vibronic spectra, and by P. Gosar and S. Choi on properties of narrow band and small polaron propagators.

The title of the book perhaps would mislead the reader in regard to the range of topics that he may expect in it. The experimental papers are few and are rather restricted in their scope, dealing with only a few properties of some organic molecular crystals such as far infrared absorption, Raman effect and spin-lattice relaxation. However, all the papers are readable and would be extremely useful to the workers who are starting to work in this field. Perhaps the advanced research workers would find the somewhat limited scope of experimental papers and also the disproportionate amount of space devoted to the review papers not very useful. But I would consider this aspect a particular merit of the book, which is an excellent introduction for one who wishes to get into the field and in its style of presentation somehow captures the atmosphere of the conference which must have been very informal and must have reflected the tremendous enthusiasm of the organizers in the American University of Beirut.

J. MAHANTY

PRACTICAL POLAROGRAPHY by J. Heyrovsky & P. Zuman (Academic Press Inc, London), 1968. Pp viii+237. Price 50*s*

The reviewer deems it a privilege to review the above book written by Prof Heyrovsky, the inventor of polarography. In fact the book was written by Dr Zuman one year after the death of Prof Heyrovsky and is based mainly on the second Czech edition of Heyrovsky's original book. Although an introductory text meant specially for undergraduate students at Charles University, Prague, it would serve well the purpose of postgraduate and research students. Nay, even persons working in industries and technicians can be benefited to a great deal by it.

The book has been divided into eight chapters, including the introduction (first chapter) which deals with the fundamental principles of polarography. In the second chapter, polarographic curves and their interpretation have been discussed, with special

reference to types of electrode processes at the dropping electrode as well as measurement and different types of polarographic limiting currents. Sufficient light has been thrown here on the significance and measurement of half-wave potentials. Chapter III deals with the use and application of polarography and some auxiliary electrical equipment. Here the reader is also made familiar with the precautions and the general problems in the handling of the apparatus. In Chapter IV some seventeen simple polarographic determinations, including those involving proteins, have been given elaborately, whereas in Chapter V more advanced procedures in the absence of air have been described for quite a few estimations. In both these chapters such examples have been chosen as will assist the beginner's approach to practical polarography. Nevertheless, some more general features characteristic of most applications of polarography have been discussed. In Chapter VI some selected examples of practical applications have been elaborated with a view that the main application of polarography in the analysis of metals and alloys is usually not the determination of the main component, but more often the determination of components present in the alloy as traces. The selection of the practical examples is indeed very careful and is such that it can be carried out with any type of available polarograph. Lastly, in Chapters VII and VIII respectively some important buffers and tables of half-wave potentials have been given which are of great value for the polarographists.

Although the book has been written by a Czechoslovakian, its English rendering is remarkable and there are no linguistic flaws. Its treatment is simple and lucid. The sequence of different topics chosen under different chapters is quite logical and coherent. The text has been made up to date by inclusion of the development of the polarographic technique during the last three decades in which it has advanced by leaps and bounds. However, instead of overemphasizing at places rather old aspects inconsistent with present-day practice, it would have been more advantageous to the beginners for whom the book is intended to include the mathematical details of some of important theoretical aspects which have been surprisingly excluded. But this omission is not serious.

The book is a befitting academic commemoration of Prof Heyrovsky and it will help many in opening new vistas where the powerful electrochemical tool of polarography can be applied.

S. N. SRIVASTAVA

PLANT DESIGN AND ECONOMICS FOR CHEMICAL ENGINEERS by Max. S. Peters & Klaus D. Timmerhaus (McGraw-Hill Book Co Inc, New York), 1968. Pp 850. Price $ 16.50

The authors, in this new edition, have treated the design and economic evaluation in an integrated manner offering extensive coverage on the subject matter. Considerable expansion of the earlier edition with a view to effecting improvements has been made in this edition by incorporating in detail topics like interest evaluation, profitability analysis and cost data for different types of chemical engineering equipment. Statistical analysis in design has been added as a new chapter. The text runs to 850 pages, nearly 340 pages more than the earlier edition.

The book is divided into sixteen chapters and is covered with a wide spectrum of related information. The subjects dealt with are process design development, general design considerations, cost estimation, interest and investment costs, taxes and insurance, depreciation, profitability, alternative investments and replacements, optimum design, cost and asset accounting, materials and fabrication selection, design report and statistical analysis in design. The rest of the three chapters cover extensively the design and costs of equipment related to the three major aspects of chemical engineering, viz materials transfer, heat transfer and mass transfer. The treatment of these subjects has been made in a clear and easy-to-grasp form explaining the underlying basic principles and citing typical illustrations with solution. Adequate number of cost data curves showing the purchased costs of the equipment of various duties and graphs for optimum design factors have been provided. Useful bibliography has been included at the end of each chapter and adequate references in connection with the design and cost of various equipment have also been provided.

Notes giving the additional information of process design strategy, such as linear programming, dynamic programming and computers solution for reactor design have also been appended which have rendered the book more useful. The inclusion of the sections on auxiliary and utility cost data and tables of physical properties and constants has made this volume a very valuable reference book.

The book is free from mistakes of minor or major nature and the printing and format are excellent and the illustrations superb. The book is written in a thorough and systematic style, with special emphasis on the economical and engineering principles involved in the design of chemical plants and equipment.

The book is considered to be a valuable addition to the chemical engineering publications and will undoubtedly be highly useful to the chemical engineers assigned the job of design, production, administration, research and development work in process industries and also sales. It will also be useful to chemical engineering undergraduates having introductory knowledge of chemical engineering.

A. K. CHAKRAVARTI

PUBLICATIONS RECEIVED

PREPARATIVE ORGANIC PHOTOCHEMISTRY by Alexander Schönberg, Günther Otto Schenk & Otto Albrecht Neumüler (Springer-Verlag, Berlin), 1968. Pp xxiii+608. Price $ 37.00

THE CHEMISTRY OF BIGUANIDES by F. Kurzer & E. D. Pitchfork (Springer-Verlag, Berlin), 1968. Pp 97 (375-472). Price $ 8.50

PHYSICAL PROPERTIES OF STEROID CONJUGATES by S. Bernstein, J. P. Dusza & J. P. Joseph (Springer-Verlag, Berlin), 1968. Pp xii+212. Price $ 12.00

ULTRASONICS THEORY AND APPLICATIONS by G. L Gooberman (The English University Press Ltd, London), 1968. Pp. xii+210. Price 45*s*

NOTES & NEWS

X-ray images of crystals using 'picturephone' camera tube

Studies at the Bell Telephone Laboratories using picturephone system have revealed a new application for the 'picturephone' camera tube, viz taking of X-ray images of crystals. In the experiment conducted, an X-ray beam was passed through a crystal and the scattered radiation was allowed to fall directly on to the target of the camera tube. The resulting video signal produced a diffraction image of the crystal on the screen of a cathode ray tube. A changing pattern results when the crystal is rotated. This technique allows instantaneous study of crystal orientation and will have value as a manufacturing technique.

The camera tube has also been used experimentally with X-rays to examine the internal structure of manufacturing defects in electronic components.

Recently developed for videotelephone service and slightly modified for X-ray imaging experiments, the new camera tube is an improvement on the standard X-ray vidicon tube. Compared with vidicon tube, the new tube has several times higher sensitivity and a much more uniform spectral response to X-rays. The tube is rugged and simple to use. When used in a closed circuit television system, the new camera tube has about 20 times the spectral resolution available from X-ray image intensifier tubes and is much less expensive. The present design is limited to the X-ray energy range 5000-20000 eV. With modifications, the tube can find application in medicine, biology and electron microscopy as well as in production line testing of small electronic components and crystal orientation [*Bell Lab. Rec.*, **16** (1968), 310].

Fast internal conversion electron spectrometer

A unique superconducting, internal conversion electron spectrometer has been built at the United States Atomic Energy Commission's Argonne National Laboratory for studying electron emissions from the nucleus of an atom, after it absorbs a slow moving neutron. Unlike the three existing electron spectrometers for this purpose located in different parts of the world, the new spectrometer detects two different types of nuclear emissions, gamma rays and electrons, simultaneously. Further, with the much greater counting rate of the solid state detector, the new instrument cuts down the experimental time considerably (a few hours versus a few weeks required earlier). In the new instrument the target is enclosed in a vacuum chamber to prevent the emitted electrons being captured by the air before detection. A superconducting magnet placed above the target focuses the electrons onto the detector. The gamma ray detector is placed below the target.

The energies and relative intensities of emitted gamma rays and electrons are measured after a neutron is captured by the nucleus of the target atom. The resulting changes in energy levels of the nucleus and nuclear spin are then calculated from the energy information. The new spectrometer allows the study of target elements with lower capture cross-sections, eg tantalum-182 and rhenium-186 and 188, which could not be studied with the earlier spectrometers [*Chem. Engng News*, **46** (48) (1968), 19].

A new type of halftone charge-controlled viewing storage tube

A new type of halftone charge-controlled viewing storage tube which uses the field-effect principle and requires no flood beam on storage mesh has been developed at the Thomas J. Watson Research Centre of the IBM Corporation, New York. Such tubes are potentially capable of high writing speeds (10^6 cm/sec) and very long viewing times. In addition, selected portions of stored patterns may be erased and information can be displayed without being stored.

In existing charge-controlled viewing storage tubes, a charge pattern is established by the writing beam on a storage mesh or phosphor screen. This pattern is then converted into a luminescent image by means of a separate flood beam. In the new storage tube developed, this conversion is accomplished in a manner similar to that employed in field-effect image storage panels, thus eliminating the need for either a flood beam or a storage mesh.

The inner surface of the glass face plate of the field-effect storage tube is provided with a set of fine transparent conducting strips interdigitally connected to an ac source. The surface is then coated in sequence with an electroluminescent phosphor layer, a semiconductor and an insulating film. In writing, a charge pattern is established on the surface of the insulator by the electron beam, thus producing a corresponding conductivity pattern in the adjacent semiconductor film by field-effect action. As in the case of field-effect image storage panels, a halftone luminescent image is generated in accordance with the conductivity variations. Observations made with the new type of tube have shown that stored traces have a brightness of 10 footlamberts and these traces can be viewed for long periods without any significant deterioration. It is also possible to have traces with a dark or a bright background [*Proc. IEEE*, **56** (1968), 1716].

Synthesis of methionine under simulated prebiotic conditions

Studies aimed at understanding the appearance of various classes of biomonomers under hypothetical conditions on primitive earth have accounted for most of the compounds, the notable exception being the sulphur-containing amino acids. The detection of methionine in the products of ultraviolet irradiation of an aqueous solution of ammonium thiocyanate has now been reported. An aqueous 0·1*M* solution of ammonium thiocyanate was irradiated for 3 hr with a submerged quartz ultraviolet lamp. The thiocyanate was labelled with ^{14}C and its radio-

purity was confirmed by paper chromatography and autoradiography. The reaction vessel was placed in an ice-water bath during irradiation. The product was hydrolysed in 6*N* hydrochloric acid for 16 hr in a sealed ampoule under nitrogen. A cloudiness formed in the irradiated product disappeared on hydrolysis. The hydrolysate on chromatographic examination showed positive presence of methionine. The yield of methionine was less than 1% [*Science, N.Y.*, **159** (1968), 1108].

Division of Tribophysics, CSIRO, Australia

The work of the Division of Tribophysics (study of friction) of the CSIRO, Australia, Melbourne, during the year 1967-68 was broadly concerned with the study of the behaviour of solids under stress, ie the mechanical properties such as strength and plasticity, and with adsorption and the study of the relationship between structure and properties of metallic crystalline surfaces, particularly the performance of such surfaces as catalysts. A notable achievement of the Division during the year was the generation of electron micrographs by a computer. Technical advice and assistance were provided to several industrial firms, government organizations, university departments, etc, in a wide range of subjects, eg lubrication, bearing materials, wear, electrolytic polishing, electronics, etc. This resulted in effectively relating the fundamental investigations obtained in the laboratory to practical applications and problems in industry.

Properties of solid surfaces — Results of an experimental study applying the 'field evaporation' technique to study the sequence of removal of atoms from around the (111) plane of defect-free tungsten crystals, observed at 77°K, showed a close correlation with the computer-simulated sequence based on a simple bounding criterion, ie on the total number of neighbours out as far as the sixth shell. The result coupled with those on the probability of evaporation of atoms from different surface sites led to the conclusion that bonding and protrusion play different roles in the process of image formation and of field evaporation.

From studies on the changes which Ag and Au films (of different thicknesses) prepared in ultra-high vacuum undergo when exposed to air at room temperature, many useful specific observations have been made. The studies indicated that exposure to air accelerates the processes which occur during deposition. Recrystallization proceeds in the direction of lower free surface and interfacial energy, but the main driving force appears to be the grain boundary energy. Adsorption accelerates recrystallization by increasing the surface mobility of Ag atoms.

Studies on adsorption comprised the correlation between the data of physical adsorption in the case of gases, their interpretation on the basis of a patch model of a heterogeneous surface, and surface structure as observed by electron microscopy. A redesign of the adsorption vessel led to improved accuracy in the measurement of pure gases and enabled the adsorption of a mixture of gases to be studied on a metal film in isolation. Thus, adsorption data for Kr and Xe on polycrystalline nickel films have been collected without break in vacuum conditions. In the case of chemisorption of C-14 formic acid, tracer studies of the adsorbed layer during formic acid catalysis have led to the proposal of a model involving the interaction of a chemisorbed formate ion with a more weakly adsorbed formic acid molecule.

In connection with the gas chromatographic studies on the effect of varying film orientation on the distribution of reaction products, viz isopropanol and propane, in the hydrogenation of acetone over Ni films, a valve has been developed to enable samples of the reaction products to be withdrawn from the reaction vessel and injected into the gas chromatograph for quantitative analysis.

Defects in crystals — Many investigations in this area were concerned with the nature and behaviour of defects which can be easily controlled by experimental conditions. Special attention was paid to behaviour on annealing of vacancies retained by quenching from high temperatures.

An outstanding achievement of the Division during the year was the generation and printing, by the computer, of a theoretical picture of an electron micrograph. This was done much in the same way as a photograph with different shades of grey being represented by dots of different sizes. The general characters of the photograph of the electron micrograph and the theoretical counterpart generated by the computer agree. The computer pictures can be produced in only 1 min. The programme developed is applicable to a wide range of defects observed in the electron microscope. It allows the computation of images of defect configurations consisting of up to 2 dislocations or 3 stacking faults, and the determination of Burgers vectors and the geometry of complex faulted configuration of dislocations and stacking faults where direct observation and resolution are not possible. The method proved an invaluable aid in the interpretation of experimental electron micrographs.

A new theory has been proposed to describe the process of formation of stacking fault tetrahedrons from triangular Frank loops when fcc metals are plastically deformed. It is based on considerations of the energy of the defect at various stages during the transformation, but differs from previous treatments of this problem in that it includes the kinetic energy associated with the moving dislocations. It has been shown that nearly all the kinetic energy of these dislocations is conserved and is available to help the dissociating defect surmount the potential energy barrier which occurs during the later stages of the process. Application of the new theory gave values of the stacking fault energy for Ag in good agreement with that obtained from measurements on extended threefold nodes.

Entomological Research in Australia

The annual report of the Division of Entomology, CSIRO, Australia, for the year 1966-67 (50 pages) records its main

activities and achievements in the fields of taxonomy, physiology and biochemistry, insect pathogens and insect-borne diseases, biological control of parasites, ecology, orchard, pasture and forest insects, flies, cattle tick, and insect pests of stored products.

In taxonomy, research was continued on all the major insect orders leading to progressive expansion and reorganization of the Australian national insect collection, with particular reference to Microlepidoptera, Coleoptera, Isoptera, Orthoptera, Odonota, and mites.

In physiology and biochemistry, investigations have been carried out on scent secretions of cockroaches, chitinase, lytic enzymes in insects, chemistry of cuticular components of blowfly pupae, water relations of insect cuticle, cuticular lipids of cockroach, *o*-diphenoloxidase in the larvae of *Lucilia caprina*, biochemistry of termites, ultrastructure of muscle and electron microscope studies of insect parts. Of especial interest is an apparatus constructed to measure the water loss from the insect body; adapted from an electromicrobalance, it enables the continuous precise recording of weight changes in a specimen maintained in a dry gas stream at controlled temperatures. Evidence has been obtained suggesting that sclerotization and melanization of the insect cuticle are independent processes. The volatile secretions of soldier termites have been found to function as alarm pheromone which in one species is limonene, and in the other terpinolene.

In the field of insect pathogens and insect-borne diseases, studies were made on the growth of arbovirus in mosquito cells, the susceptibility of the cloned cells to insect viruses, AV virus, growth factors in insect haemolymph, granulosis virus of potato tuber moth, and milky disease.

Biological control of potato moth, green vegetable bug, white wax scale, purple scale, circular black scale, skeleton weed, lantana, and St John's wort has been investigated.

Ecological research has centred round population ecology. Using laboratory and field data on the population dynamics of the cabbage aphid, a deterministic mathematical model has been constructed to simulate the ecological events and processes involved in growth of aphid populations on crops. The model has been found to reveal the existence of processes which had remained unnoticed in field studies. The population models will help predicting the consequences of manipulating populations in programmes of pest management.

Among the orchard insects codling moth, light brown apple moth, fruit flies and scale insects were the subjects of investigation. Data on codling moth will help construction of a general predictive model of population events that will serve in the experimental planning and evaluation of control strategies. The fruit fly studies using radioactive larvae in selected areas have confirmed the importance of predators like ants in the soil on the survival of mature larvae, pupae and newly emerged adults. An examination of environmental stimuli and neuroendocrine systems has indicated that ovarian maturation is faster where females have access to maturing fruit; a chemo-tactile response is possibly involved—the chemical factor being an alcohol derivative present in the waxy cuticle of maturing apples and other fruits.

Studies on pasture insects include clover seed moth, pasture scarabs, artificial populations, adult activity, food preference studies of larvae, pasture insect studies, lucerne flea and red-legged earth mite.

Locusts have been studied from the standpoint of ecology. Outbreaks depend on the amount of rain and its frequency. The frequency of rain above a minimum amount influences the timing of life-cycle events and also determines the conditions essential for survival of young stages. It is, therefore, the ultimate factor which determines population increase. Considerable emphasis has been placed on movement and dispersal studies. Under dry conditions when the quality of food plants appears to be nutritionally inadequate to permit sexual activity, dispersal occurs in populations at all levels of density, but under favourable conditions for reproduction, low density populations are sedentary, and high density populations are mobile, resulting into mass flights.

Forest insects studied comprise Christmas beetles, jarrah leaf miner, psyllids, phasmatids, termites, chrysomelids.

The study on flies is based on sheep blowfly, bushfly, buffalo fly and the housefly. Investigations into group oviposition by the sheep blowfly have shown that females are stimulated (by pheromones?) to lay eggs adjacent to already oviposing females. Physiological investigation of thirst in the sheep blowfly has conclusively demonstrated that chloride ion concentration in blood is the dominant factor in determining the insect responsiveness to water.

Acarological investigations include breeding, tick resistance in different breeds of cattle, tick resistance and nutritional state of cattle, tick reproduction and survival, population dynamics, growth of ticks on cattle, reproductive potential of cattle ticks, tick feeding and host resistance, tick haemolymph and egg proteins, tick lipids and cuticular waxes, tick resistance to acaricides, mechanism of tick resistance, tick cholinesterase and organophosphorus resistance, inheritance of OP resistance, synergism of acaricides against ticks, control of various strains of ticks, organotins for tick control, glutathione in cattle tick eggs, organophosphorus resistance in sheep blowflies.

The research project on insect pests of stored products embraces the study of effect of disturbance on development, airtight storage of grain, aeration of grain and larder beetle. Some ingress of oxygen does take place even in airtight storage of grain. Attempts are being made to devise methods to make this oxygen unavailable to grain insect population.

SUPPLEMENT

to

Glossary of Indian Medicinal Plants

by

R. N. Chopra, I. C. Chopra & B. S. Varma

In the year 1956, the Council of Scientific & Industrial Research, New Delhi published a Glossary of Indian Medicinal Plants with a view to presenting concise information regarding their properties, uses and important constituents. Over 2600 species, belonging to about 1350 plant genera, have been dealt with. The information is given under the botanical names of the plants, which are arranged in their alphabetical sequence; trade and vernacular names are also mentioned. The Glossary gives distribution of the plants, diseases for which the particular plant is used, and the active principles. Adequate literature references to the sources of information are also provided. The book ends with two comprehensive indexes: one pertaining to the vernacular and trade names, and the other to the chemical constituents.

In order to bring the Glossary up to date, this Supplement has been brought out. It follows the style of the Glossary and covers all relevant information published during the period 1955-64. The Supplement provides additional information on over 700 species already mentioned in the Glossary, and includes about 380 new species. Indexes covering additional vernacular and trade names and chemical constituents have been provided. The Supplement, like the original Glossary, will be useful not only to the practitioners of indigenous system of medicine, but also to all others who are interested in drugs of vegetable origin and common bazaar medicines.

Pages xii+119, Royal 8vo **Price Rs 14.00; Sh. 28; $ 4.50**

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