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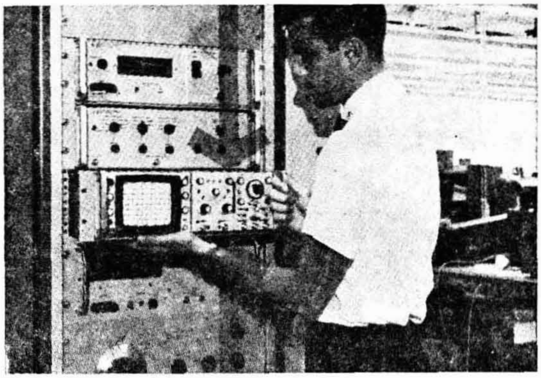

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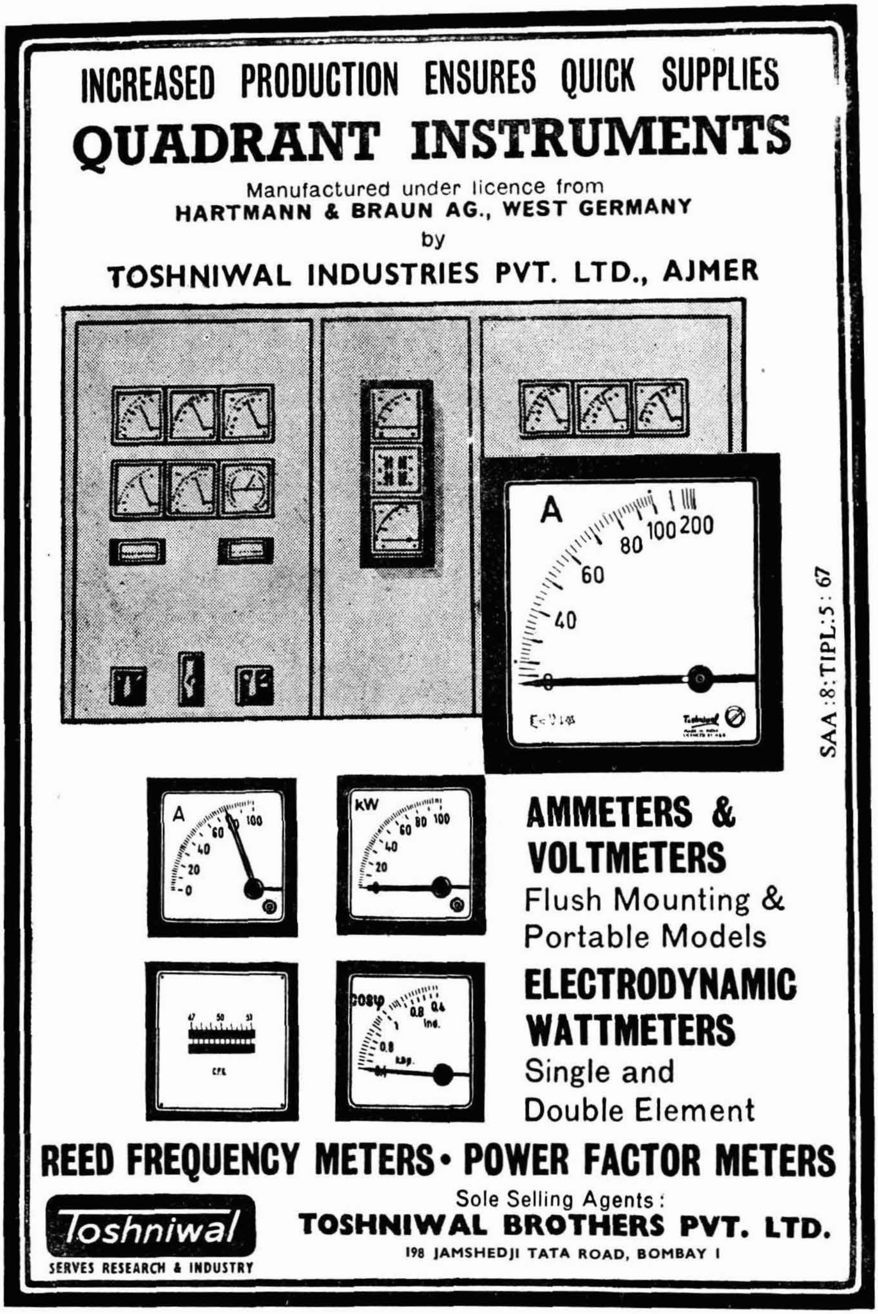

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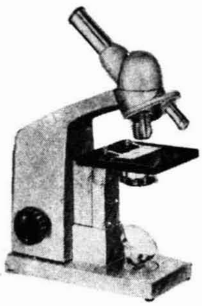

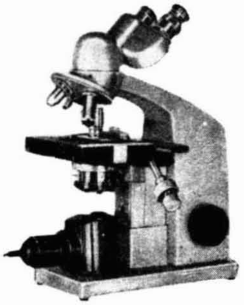

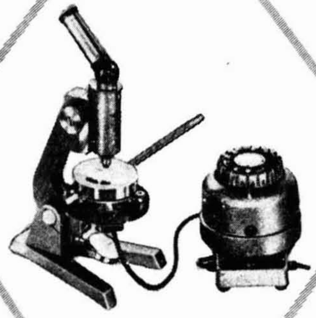

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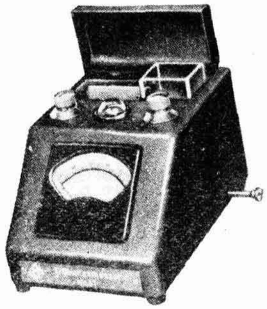

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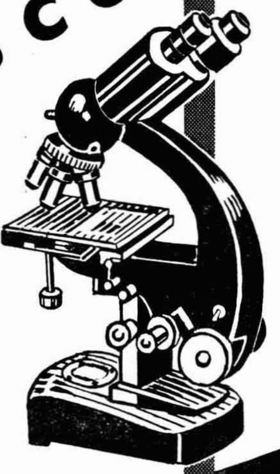

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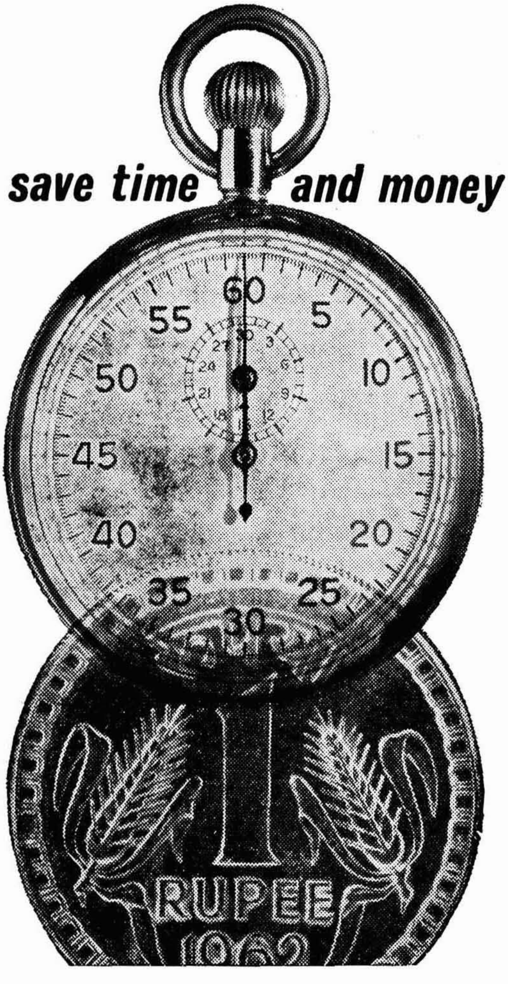
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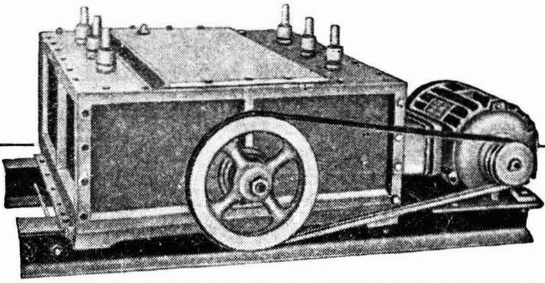

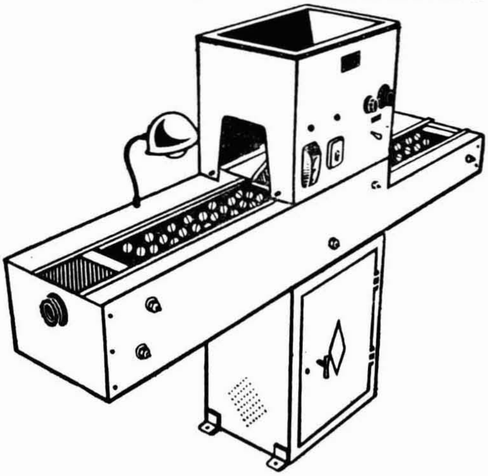

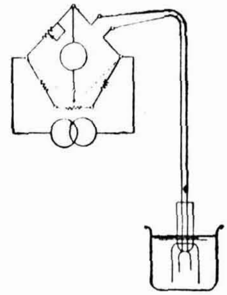

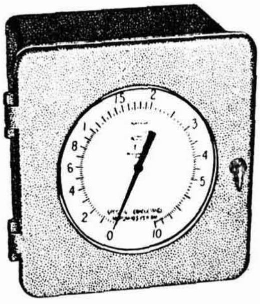

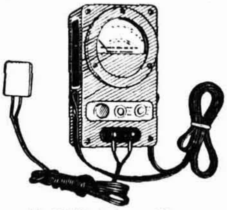

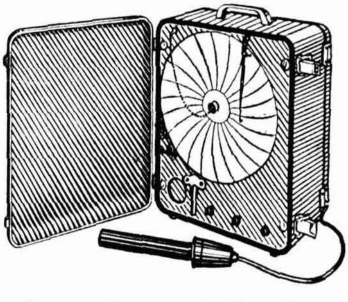

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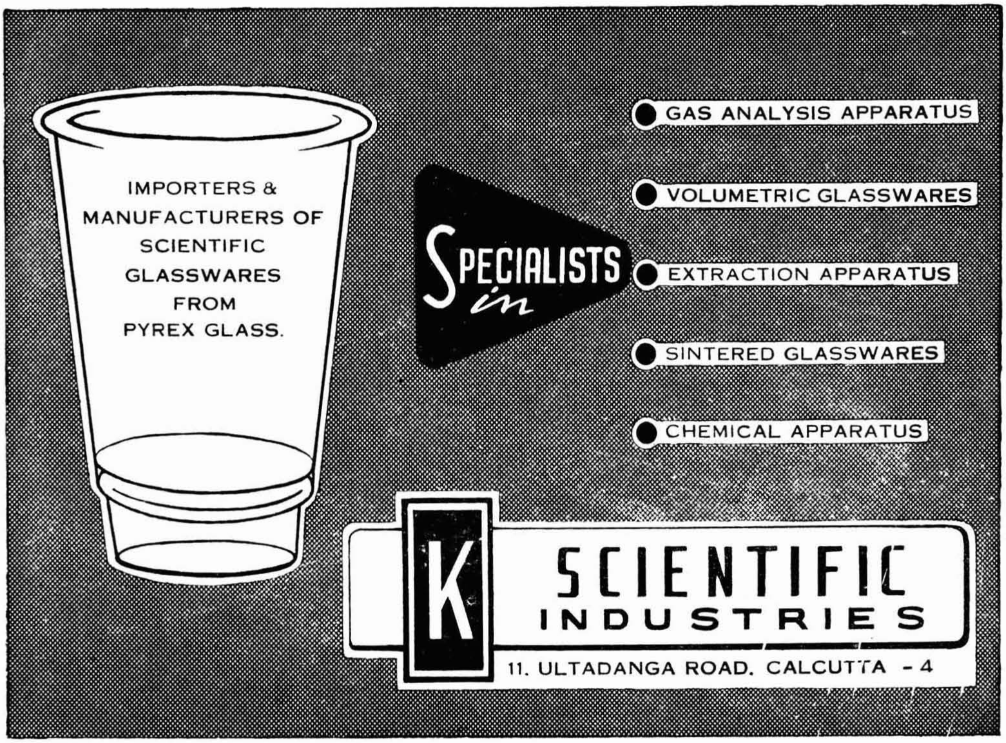

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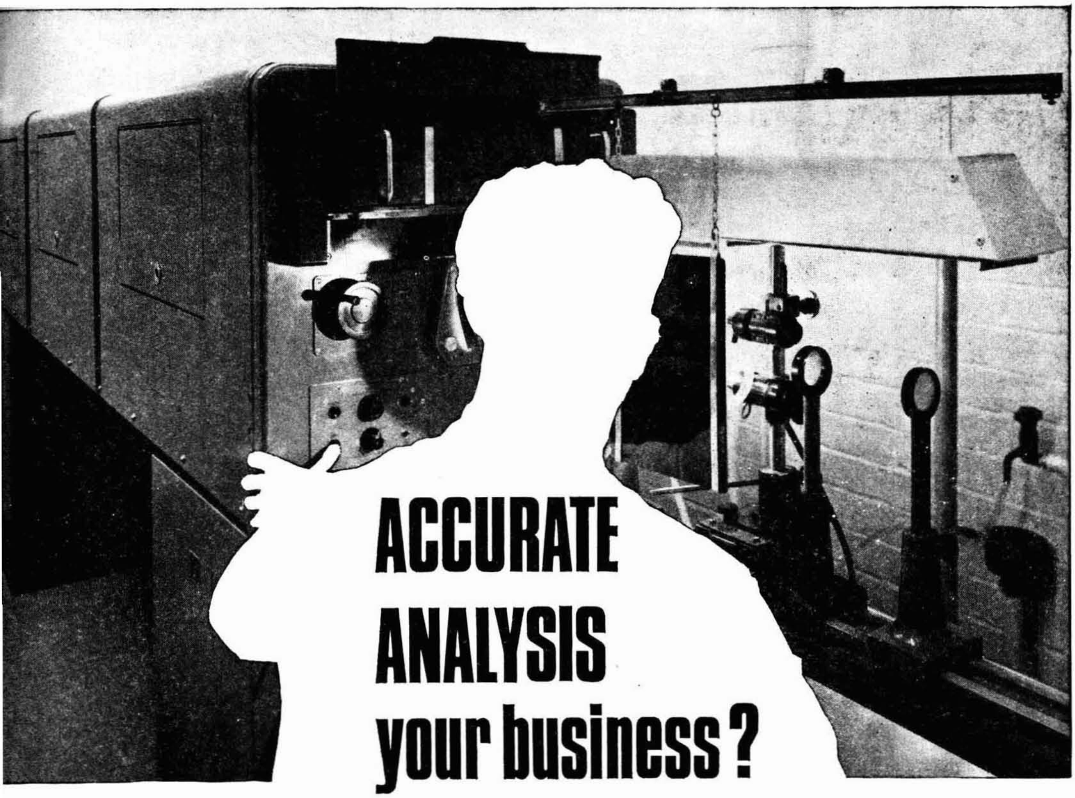
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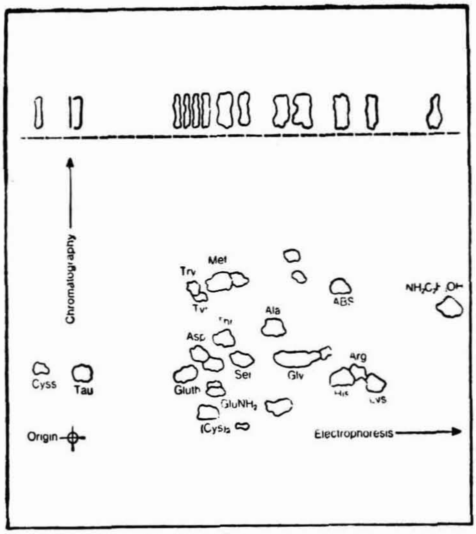
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Research Utilization*

IN a discussion of general appraisal of utilization of results of research carried out in research laboratories, the problem has to be looked at from two angles — utilization of results obtained in fields related to the needs of the country and results of basic research which may form the basis of new developments not anticipated at the time of undertaking research, but we may confine ourselves in this discussion to the first category. Obviously, the first thing is to determine the country's needs. Activities of the research laboratories have to be geared to these needs; otherwise one cannot expect the results flowing out of the laboratories to be utilized. Let us, therefore, first find answers to the question, " What are our needs ? "

In a developing country, the first task is to develop the resources, acquire the skills and produce the means for this purpose. For developing the skills, we have to develop technological competence or capability. I lay very great stress on our achieving technological competence. We are training a large number of scientists and engineers in our educational institutions. This basic human material has to be developed into necessary technological capability and competence in order to be useful for a self-generating economy.

I would like to mention here a related problem. For technological growth, scientists and engineers alone are not enough. We need a large body of technicians. I doubt whether we have paid enough attention to the training of technicians. For a proper utilization of scientists' and technologists' work, we need good technicians. The problem is not merely of training, it is also a social problem. Society has not, by and large, given the technician the status he deserves by virtue of his contribution to economic progress.

Authentic information on resources of raw materials, power, etc., and their proper evaluation is one of the first essential things. Plenty of natural resources may be available in a country, but if the people are not able to use them efficiently and effectively, they will continue to be poor. It is here that science and technology play a vital role. Not only science and technology are needed to discover and assess the sources but also for their efficient and expeditious exploitation. Natural resources, as they exist, may not be directly usable in industrial growth; they have to be beneficiated and technology has to be used for this purpose.

The third most important need is the bringing together of the human material, i.e. a well-developed corps of scientists and engineers, and the natural resources. With the help of capital and the interaction of these two resources, wealth is created for the nation's good.

Flowing from this is the fourth need of the country, namely the development of indigenous sources of technology. Much of India's present industrial growth, which is by no means small, is based on reliance on foreign sources of technology. There is nothing basically wrong about it, but we should be aware of its implications. Technology should be imported only when suitable local technology is not available. In developing countries like India, time is the essence. Therefore, if a technology can be purchased from others without compromising national interests and crippling local efforts, there is no reason to take a doctrinaire view. It reduces the time factor for the development of such technology anew. In the present context of world development, complete technological independence is unthinkable. India can also soon attain a position of interdependence; that is to say, apart from borrowing technology from abroad when needed, we should also be in a position to lend technology; otherwise in the long run we will be relegated to an inferior position in the world.

There is the need for substitution of indigenous material for imported ones. Once we build up the competence which I have described, this should not be difficult. At present, particularly because many of our industries are based on foreign technology, our plant and machinery may be designed to handle certain types of materials which are used in the countries of their origin, and we have to sometimes import things produced in the country. This cannot continue and this became apparent when during emergency we were faced with the situation of being cut off from foreign supplies.

Import substitution is a negative virtue. I think we should psychologically turn ourselves to export, and export product development should receive attention. Without developing our capacity to export, not raw materials but processed goods, we will never be able to become a modern nation in a position to pay for our imports.

One related problem, particularly in the context of our present policy of importing technology from abroad, needs special mention, namely adaptation. This is essential both from the point of view of the environment in which we live and in terms of our raw materials. Labour is another factor. We have

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*Address delivered by Dr Atma Ram, Director-General, Scientific & Industrial Research, at the Seminar on Science in India's Basic Problems, New Delhi, 12 August 1967.

to think in terms of the large population of over 500 million people. Wholesale transference of foreign technology to Indian conditions may be unsuitable. Capital-intensive technology of the advanced nations may have to be replaced by labour-intensive methods. Attention should, therefore, be paid to what is sometimes called 'intermediate technology or appropriate technology'. Non-automatic technology is not necessarily primitive technology.

Having analysed some of the needs, let us now look into the working of our research institutions from the point of view of research utilization. As I said, unless our institutions are geared to our needs, utilization of the results flowing from research will be remote. Let me take up the needs which I have mentioned and indicate to what extent we have satisfied them and what remains to be done.

In my opinion, the training of scientists has to be much more production-oriented. While both technical education and industrialization have made rapid progress, one has not substantially acted upon the other. For best results, one should energize the other. It is in this way that we will be able to develop necessary technological competence. To some extent, the technological research laboratories in India have helped scientists and engineers to develop this competence by working on applied problems and on pilot plants and on the utilization of results in industrial production. During the last few years industry has also developed considerable ability to innovate. Design and engineering of processes is also being done. In this way, certain amount of technological capability has developed. Utilization of research results from research laboratories in industrial scale needs several steps, such as pilot plant, development, design, fabrication and erection of plant and equipment, production and marketing. It is these several stages that go to build progress in this respect; there is still a lot more to be done. But unless we develop this capability, utilization of research results from the research laboratory will be difficult. There are cases where the knowledge of operations for a certain manufacture may have been developed, but the means of practising them, i.e. the machines and implements, may not be available in the country, with the result that results of research remain unutilized.

In regard to natural resources development, we have done fairly well. We have scientific surveys which have given us the basic understanding of our resources. We may have to put in a lot more effort in discovering new geological and mineralogical resources. As far as the oceans around us are concerned, we have just started. In the exploitation of the resources we have to employ scientists, technologists and engineers. Many of our laboratories have made some significant contribution in the beneficiation of resources. For example, the work of the Central Fuel Research Institute in regard to the survey of coal resources and the work they have done on washing and blending of coals have been of immense benefit. Such work may not look spectacular, but is of absolute basic nature. I would say the money value of such work is actually immeasurable. Similarly, the surveys conducted and beneficiation studies carried out on ores and minerals by the National Metallurgical Laboratory and the Central Glass & Ceramic Research Institute have been exceedingly valuable in industry. Similar work has been carried out by many of our laboratories in relation to the materials they are concerned with, such as the Building Research Institute, Road Research Institute and the Leather Research Institute. In my opinion, the work of the national laboratories in this respect has been truly commendable. The great advantage of such work is that results are available easily to all those who are interested. Government, public and private sector organizations have freely drawn upon these results and have used them.

My personal views on the development of indigenous technology and on the borrowing of technology are well known. I had occasion to mention them at the Bose Memorial Lecture at Calcutta some time back. There is nothing basically wrong for a developing country like India to benefit from all the advances that have taken place abroad in the field of technology. But, as I said, it is harmful to borrow to continue borrowing. We should take appropriate steps to see that once we borrow a technology, further development in that technology should be made within the country. Japan made a great success of this method and I do not see why we should not. There are many ways of doing this. One way is that every large industrial establishment which is brought into being by importing know-how should have attached to it a research and development laboratory which should be made responsible for the future growth of the industrial establishment. In other cases, an existing laboratory in India may be selected and associated with the industrial firm, so that it has the full responsibility for dealing with all the technological problems of the firm and its future growth and development. By this means, the programme of work of the laboratory will be made purposeful and at the same time the industrial establishment will also be benefited. Utilization of research will not be a difficult problem.

Import substitution has come to the forefront during the last few years. Here is another area where some of our laboratories have done some fine work. During the short time at my disposal, I do not want to list out the achievements in this respect. I have had some personal experience in this field. It has not always been a very happy experience. In some cases, due to various reasons, valuable results were not utilized. The government have recently taken a number of steps to encourage import substitution. The announcement of awarding prizes and other incentives to those who have worked in this area is welcome. If our laboratories are to be effective in the field of import substitution, it is necessary for government, industry and the laboratories to sit together and identify the specific problems and tackle them and use the results expeditiously. Only by such an arrangement one can ensure that the results of researches carried out are fully utilized. Nothing is more frustrating to a research worker than to see his/her even well-established results remaining unutilized.

Export product development is relatively new. But in the long run it is necessary for research laboratories to devote some attention in this direction.

It will be necessary to identify the special areas in which India can enjoy economic advantages over other countries and take up such items for development from the point of view of export. This will ensure efficient research utilization.

As I have always held, in a developing country like India, adaptation research is of particular significance. When we import technology, we should consider it desirable to associate an Indian research laboratory right from the beginning so that problems of adaptation may be dealt with. When technology is transplanted in different conditions and environments, there are always problems of various types. These have to be dealt with. It is not desirable to completely depend upon the principles for dealing with all types of problems. By proper association, Indian scientists and technologists will also be able to get much intimate knowledge of the technology, the plant and equipment. In each case, a team could become a part and parcel of the factory and undertake full responsibility for the further development and growth of the technology within the country. Japan has successfully adapted this method and I think we should learn to use this method in our situation. Such a close association of our research laboratories in the process of industrialization will ensure proper utilization of research carried out in the laboratories.

Industrial management has, in my opinion, now become a technology by itself. The utilization of results depends very much on the management organization of a firm. The extent of receptiveness of a firm to innovation will depend very largely on the effectiveness of the appraisal of results by the technical component of management. This needs highly competent managers with adequate technical understanding and they can make a great impact in this direction.

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PETROLEUM industry is often spoken of as a 'science-oriented' or 'science-based' industry. It is also most conscious of the end uses of products and user reactions. While this is broadly true of any chemical industry, the petroleum exploration, refining and petrochemical industries can claim to have a deeper awareness of the need to apply basic scientific principles in their development. In its turn, the whole spectrum of petroleum industry, from exploration and exploitation of oilfields, through refinery operations and processes, and marketing and utilization of products, has led to many fundamental scientific developments. This industry has also led to the birth of many new managerial, operational, economic and administrative concepts. The rapid growth of petroleum sciences, technology and engineering and their broad interdisciplinary base have necessitated creation of a forum for exchange of thoughts and experiences so that costly mistakes could be avoided and constant improvement in product quality and performance could be achieved by the interaction of fresh brains with up-to-date experiences. This common desire has given birth to the creation of an international and non-official organization called World Petroleum Congress (WPC).

The phenomenal growth of the congress, held quadriennially, and the involvement of scientists, engineers and technologists all over the world in its development and working can be understood from Table 1.

The Seventh World Petroleum Congress held in Mexico City during 2-8 April 1967 had two special features. Firstly, there was no equipment exhibition, which was an important, yet somewhat distracting, feature of the Sixth Congress at Frankfurt, Germany, in 1963; secondly, the congress was wholly devoted to scientific and technical activities, namely sessions and technical tours. The President of the Permanent Council of the Congress, Mr R. Navarre, who is also the President of the French Petroleum Institute, asked the delegates to "strictly adhere to this rule", of confining only to scientific matters and not drift to business aspects. The distribution of papers among different subjects, technical sessions and panel discussions is given in Table 2.

TABLE 1 — PROGRESS OF WORLD PETROLEUM CONGRESS

Year	Venue of congress	No. of delegates	No. of participating nations	Papers (sessions)
1933	London	1250	23	244
1937	Paris	1630	33	392 (70)
1951	The Hague	2118	40	289
1955	Rome	3250	50	250
1959	New York	4410	53	278 (93)
1963	Frankfurt	7000	65	250
1967	Mexico	3500*	80	435 (74)

*(i) Excluding accompanying lady delegates. (ii) USA, 1075; France, 348; UK, 160; Germany, 145; USSR, 101; Japan, 90; and India, 10.

TABLE 2 — SUBJECT-WISE DISTRIBUTION

	No. of sessions		No. of papers			
	PD	Technical sessions	RP	PD	Sessions	Total
Exploration, drilling, production	12	7	7	110	28	145
Refining, chemistry and analysis	5	2	2	28	9	39
Application of petroleum products	7	2	1	44	7	52
Petrochemicals	5	2	2	37	9	48
Engineering, materials, services, transport, economics, etc.	7	2	4	54	8	66
New sources (tar sands, oil shales)	2	—	—	18	—	18
New applications — border fields	4	1	—	24	4	28
	42	16	16	315	65	396

Extra papers presented later (approximately 10%) = Total 435
RP = review papers; PD = panel discussions

Philosophy of the Congress

'Petroleum for Welfare of Mankind' was the main theme for the congress. 'Science is Unity' was the theme elaborated by the President of the Seventh Congress, Mr Jesus Reyes Heroles, the Director-General of the Petroleos Mexicanos. He emphasized on fight against poverty, quoting the International Labour Organization, that "Poverty in any one place constitutes a danger everywhere". He pleaded for the use of science to eradicate poverty. Mr Navarre emphasized the need for a free exchange of 'know-how' as well as 'know-why' of things between participants. He hoped that the proceedings of the congress would constitute a "complete and firm working instrument of consultation and, long after the congress is over, they would continue to promote fruitful relationships between colleagues".

The President of Mexico, who inaugurated the congress, emphasized that scientific progress must be joined with liberty and justice to form a real base for peace in the world.

Organization

Such large conferences have many organizational problems. Technical sessions were held daily, simultaneously in 8 auditoria, 7 of them at one place called the National Medical Centre, and one in the University Science Faculty, about 7 miles away. Delegates had to choose the sessions they had to attend and move from room to room at the proper time. As was done by many countries, it is essential to depute adequate number of delegates to cover each aspect of the industry. In the official Indian delegation of seven members, since this author was alone in dealing with refining, products application, petrochemistry and some new developments, it was extremely trying to make a selection of preferred papers and sessions. Sometimes parts of the sessions had to be selected to cover interesting papers. The sessions were held continuously from 9 a.m. to 2 p.m., or sometimes till 3.30 p.m., without any lunch break.

In this review, reference will be made only to the salient features of some of the important papers and emerging trends, and that too will be restricted to the fields of refining, petrochemicals and product development and application.

Review Papers

The first day began with a review paper[1] presented by Dr C. L. Thomas (Sun Oil Co., USA). Since almost every conversion process in petroleum refining involves organic chemical reactions, mostly involving carbonium ion type, this formed the major part of the review paper. After explaining the basic concepts behind the formation of carbonium ions and Markownikoff's rule explaining their behaviour, the author reviewed the general reactions of alkyl carbonium ions, with particular reference to polymerization, alkylation of iso-paraffins, catalytic cracking, hydrocracking and catalytic reforming processes. The authors discussed the product composition and yields of alkylates and polymeric products in the light of the reaction mechanisms. The role of bi-functional catalysts in hydrocracking, the poisoning of such catalysts by nitrogen bases through neutralization of acidic components of the catalyst, thereby reducing the activity, the hydrocarbon distribution in different fractions and the need for subsequent secondary processing (e.g. more of naphthenes in the 100-200°C. gasoline fraction required reforming to increase octane number) and other aspects of product quality were discussed.

The chemistry of free radicals involved in the deterioration and stabilization of petroleum products while stored or under the wide variety of conditions of use was then reviewed. The phenomena of autoxidation of hydrocarbons, catalysed by light, heat and traces of metal impurities and photo-oxidation were discussed. The performance of inhibitors in gasoline and naphtha and motor oils were reviewed. The authors referred to the role of nitrogen compounds as inhibitor antagonists, and felt that the presence or otherwise of natural inhibitors and antagonists is yet to be demonstrated. This is an interesting research project.

The next review paper discussing trends in petroleum refining catalysis was by Dr Frank G. Ciapetta[2] (W.G. Grace & Co., Davison Chemical Division, USA). After an exhaustive and critical review of the trends in the growth of demand in petroleum products in different regions of the world, Dr Ciapetta concluded that almost every country will have a refinery by 1968 and that over 9 million barrels per day (b.p.d.) will be the estimated increase in catalytic processing capacity all over the world from 1965 to 1975. Of this, over 5 million b.p.d. are accounted by hydrogen processing and over 3 million b.p.d. by new catalytic reforming capacity. He anticipated that the technology of catalytic process techniques is likely to undergo many changes, particularly due to the use of the new zeolite catalysts introduced in 1962, which have offered many advantages, such as high conversion efficiency and activity, high throughput rates and high gasoline yields at the same conversion levels. The use of these catalysts, however, necessitated many changes in reactor design, leading to smaller regenerators and smaller gas compressor capacity.

Hydrogen processing is expected to record phenomenal increases, particularly in the western world, due to increasing stringency in anti-pollution laws. Although the application of hydrogen processing was known to petroleum technologists for a long time, it did not become an economic feasibility until byproduct hydrogen was available from large-scale expansion of catalytic reforming plants. The development in recent years of cheap processes and plants for production of hydrogen has accelerated the growth of hydrogen processing. Hydrotreating is expected to be almost a service operation as a finishing process to reduce sulphur content to meet the social laws. Hydrocracking is gaining considerable ground due to the wide degree of flexibility that it offers both in product pattern as well as in feedstock selection. Among the new developments in catalyst systems mentioned by the author, increasing use of molecular sieves, with sodium replaced by other metal ions, such as calcium and magnesium, resulting in high isomerization activity useful in the hydrocracking process, and the use in refining processes of transition metal organic complexes, which are already important in petrochemical processes, have been indicated.

Another review paper of importance to chemical engineers was presented by Prof. M. R. Fenske[3] (Pennsylvania State University, USA). Emphasizing the fact that petroleum industry is characterized by rapid application of new technology and consequent high rate of obsolescence, the paper pointed to the need for extensive and reliable engineering data in the form of readily applicable correlations, which are the major tools of a design engineer. This requires not only selection of accurate data after screening adequately large volume of information sources, but also development of suitable correlations. After reviewing the available correlations of different properties of hydrocarbons and their mixtures, the authors caution regarding the reliability of correlations claimed in different published papers. A variety of available correlations have already created selection problems for the engineer. The Pennsylvania State University has undertaken an extensive review on evaluation of correlations of physical and thermodynamic data on hydrocarbons. Using more than 10000 data points from over 100 sources for hydrocarbon mixtures, the study has evaluated about 20 correlations for compressibility factors and vapour-liquid equilibrium K factors. Similarly, from another 10000 data points on pure hydrocarbons from over 500 sources, about 20 correlations were evaluated for basic properties, like vapour pressure, enthalpy, etc. The authors pointed out the urgent need for additional data for mixture enthalpies and mixture critical properties. There is also scope for very profitable research in the development of significant correlations before new data are measured for vapour-liquid equilibria. They also suggest that until authors of publications of correlations provide more realistic quotations, extensive independent evaluations with reliable data are necessary.

It is not possible to review the many other important review papers presented by authorities in the field. It is, however, worth noting that subjects such as 'Application of hydrodynamics to oil exploration', 'Recent advances in formation evaluation', 'Progress in drilling, production and transportation', 'Purity and structural requirements for petrochemical raw materials', 'Impacts of recent scientific progress on evolution of petroleum techniques', and 'Developments in combustion theory related to petroleum, formed subjects of other review papers.

Panel Discussions

In the panel discussion on 'Advances in conversion processes in refining', presided over by Dr Alex Voorhies, advances in catalytic cracking, catalytic reforming, hydrocracking, alkylation and isomerization were discussed in 6 papers. In the field of catalytic cracking, fluid bed and moving bed, two authors[4,5] referred to the growing application of zeolite catalysts. Presently, in the USA nearly 65 per cent of the total cracking capacity has changed over to zeolites. The zeolites are dispersed in small concentration over conventional silica-alumina catalysts. Advances have been made particularly regarding application of higher pressures, accurate heat balances, riser cracking, liquid recycle, feed and catalyst treating and application of computer control systems. Due to the use of zeolite catalysts, measures to reduce catalyst attrition and metal erosion, particularly in the moving bed systems, have received attention in recent years. The paper on hydrocracking, presented by J. W. Scott[6] (Chevron Research Co., USA), reviewed the growing importance of the process which was facilitated by the development of new hydrocracking catalysts and better metallurgy and technology. There has been a reduction in the cost of hydrocracking plants by more than 20 per cent since the last congress. Integration of hydrocracking and petrochemical operations is becoming increasingly important. Many refineries are resorting to residium hydroprocessing. It is clear that full advantage is being taken of the versatility of the hydrocracking for processing varieties of feedstocks to produce desired products. For example, it can be used to produce maximum gasoline as is practised in the USA, or maximum middle distillates or low sulphur fuel oils as is practised in European continent. In fact, it is becoming increasingly clear that hydrocracking will be considered in future, not merely as a refinery process step to produce fuels in the desired pattern, but also as a preparative process step to produce petrochemical intermediates. Hydrocracking may, thus, prove to be an important connecting link between the refiner and the petrochemical manufacturer, thereby facilitating diversification in industry.

Dr V. Haensel[7] (Universal Oil Products Co., USA) made an excellent review of the advances in catalytic reforming with reference to the catalyst mechanisms and product quality. Dr P. van't Spijker[8] (Netherlands) reviewed advances in alkylation and pointed out that the sulphuric acid and hydrofluoric acid alkylation processes, which are essentially dissimilar, are able to compete economically. During discussion, it was indicated that more research in mixing operation might show better economics of sulphuric acid process. It was considered desirable to establish the likely maximum yield and then undertake researches on improvement of mixing operation. While reviewing isomerization[9] it was stated that isomerization of pentane is gaining importance for production of high octane gasoline free of lead.

The fact that a separate panel discussion was devoted for hydrotreating processes under the chairmanship of Dr Hoog indicates the importance of hydrogen processing. Seven papers were presented in this discussion, covering hydrodesulphurization of distillates and residual fractions, hydrotreating of catcracker feedstocks and lubricating oils and hydrogenation of aromatic feedstocks. Although hydrodesulphurization has been in use for more than a decade, it has gained considerable importance in recent years as an essential process step to improve the quality of petroleum products. As stated earlier, its value as finishing operation to improve the quality of product or to prepare a feedstock for better processing is being fully utilized by refiners. Incidentally, the hydrodesulphurization and hydrocracking steps have together enabled sulphur recovery as well. It was brought out during discussion on hydrodesulphurization processes that removal of metals from the feed would help this process. Up to 100-200 p.p.m. of vanadium in propane deasphalted feed is better than pentane deasphalted feed for this process. Hydrofinishing of lubricating oils and waxes is also gaining considerable importance, although differences of opinion exist with regard to oxidation stability characteristics of the hydrofinished lube oils.

Advances in hydrogenation of aromatics were discussed by Dr La Page[10] (French Petroleum Institute). The paper refers to work on improvement of smoke point of kerosenes and diesel index of diesel fuels by hydrogenation of armcmatic constituents. Improved catalysts have facilitated the use of lower temperatures and practically no cracking. During discussion on this paper, the author of this review presented a correlation developed for hydrogenation of aromatic kerosenes based on the work done at the Indian Institute of Petroleum, Dehra Dun.

Production of olefines for manufacture of petrochemicals formed the subject of a separate panel discussion, presided over by Dr J. Fouchier (France). Dr Yarze[11] (M.W. Kellog Co., USA) described a unique pilot testing unit for production of ethylene which enables translation of pilot plant data to commercial scale, with great confidence. Dr Kunugi *et al.*[12] (Tokyo University, Japan) described selective pyrolysis of hydrocarbons in the presence of hydrogen, which increased yields of ethylene of about 40 per cent by weight compared to about 20 per cent by weight with steam cracking. Methane and ethane yields also increased. Submerged flame process for acetylene and ethylene production was discussed by Dr Kröper[13] (BASF, Germany). Isomerization of propylene to ethylene and butadiene was discussed by Dr P. H. Johnson[14] (Philips Petroleum Co., USA). Not much detail was given in this paper and the author stated during discussion that he was not permitted to disclose details of plant operating conditions and mechanism. It was, however, stated that the mechanism of propylene isomerization does not involve carbonium ion reaction.

Another very interesting subject, viz. 'New contribution of petroleum to agriculture', was covered by 6 papers in a separate panel discussion. The general theme of the papers refers to a variety of subjects, such as carbon dioxide enrichment in greenhouse atmospheres, flame cultivation in agriculture, progress with bituminous mulches in agriculture, role of petroleum oils in the effective and safe application of pesticides, large-scale production and distribution of ammonia for the Mexican soil, and mass utilization of carbon dioxide from combustion gases for production of food algae. Madame Clement[15] (French Petroleum Institute) presented an excellent paper on the production of algae. It was stated that up to 45 tons of dry algae per hectare can be produced. During discussion, attention was drawn to the rapid rise in the world population and food shortage in the developing countries. In the developed countries, arable acrage is going down rapidly. For instance, in Japan, the drop in arable acrage during the past 40 years was 13 per cent; the rate of loss in the USA is about 1 million acres/year at present. The answer is stated to lie in increasing food production per acre through intensive irrigation, application of fertilizers and other techniques.

'New concepts and techniques in oxidation of hydrocarbons' formed the subject of a separate panel discussion, comprising 10 papers. Liquid phase oxidation of hydrocarbons, rate of autoxidation, ozonolysis of olefines, production of resorcinol by the oxidation of *m*-di-isopropyl benzene, oxidation process for the production of vinyl acetate from ethylene, production of lower fatty acids, liquid phase air oxidation of light naphthenic naphtha, epoxidation of olefines and selective oxidation of cyclohexane were the subjects discussed in this panel.

Interestingly, in another panel discussion on 'Petroleum and microbiology', two papers were presented on microbiological oxidation of aromatic hydrocarbons by controlled microbial action. Dr Tsuru (Tokyo University) conducted oxidation studies of hydrocarbons using yeasts (*Candida rugosa*) isolated from jet fuels. Cultures grown on glucose and kerosene were also used.

In the same panel, the role of microorganisms in transformation and destruction of oil deposits and control of microbial growth in storage and utilization of petroleum fuels were discussed. The importance of microbial growth during storage of petroleum fuels with regard to corrosion and deterioration of product quality was considered in detail. Synthesis of proteins from petroleum hydrocarbons was discussed in 3 papers in this panel. Papers were presented by Dr A. Champagnat[16] of BP (France). Dr B. Laine[17] (France) and Prof. S. V. Tchepigo[18] (USSR) reviewed developments on this subject in their respective countries. The work done at the Regional Research Laboratory, Jorhat, and the Indian Institute of Petroleum, Dehra Dun, and the collaborative programme with the French Petroleum Institute formulated in this regard in India on the preparation of proteins from petroleum hydrocarbons was presented by the author of this review. The problems involved in purification of the protein concentrates, their nutritional value and their possible toxicity were discussed. Considerable progress appears to have been made since the last congress in developing the project on preparation of proteins from petroleum feedstocks. Several pilot plants have been claimed to be in operation in France as well as USSR.

Additives have long been known to form an important part of the petroleum industry. Their contribution to the improvement of performance of petroleum products formed the subject of a separate panel discussion, where 8 papers were discussed. The trends in performance requirements and lubricant additives, additives for gasoline, diesel and jet fuels, comparative study of tetra-ethyl and tetra-methyl lead additives, additives to improve the stability of middle distillates, and additive structure and its effect on solubilizing action and performance of lube oils were discussed by the authors. It was revealing that the problems faced in advanced countries with better cleanliness and public health and traffic consciousness are similar, for entirely different set of reasons, to the problems faced in engine performance in developing countries such as India, with poor roads and traffic conditions. In both cases, the severity of operation of the engine increases, demanding improved additives. For example, it was most interesting to hear that in the western countries, the load on vehicles due to air pollution has increased significantly, although there is less dust due to paved roads. The discussion on these papers revealed the depth to which scientists and engineers are considering the problem of vehicle performance with changing social habits and environments.

The foregoing review has covered only a few of the panel discussions and review papers that the present reviewer could personally attend. It would be impossible to cover all the 42 panel discussions and other papers. Some of the panel discussions were exclusively devoted to subjects, such as origin of oil and gas, new geophysical developments and methods, new methods of secondary recovery, rock mechanics in oilfield geology, drilling and production, new concepts and techniques for hydrogen production and oil gasification, development of industrial burning equipments, quality requirements and use of fuels in internal combustion engines, corrosion, new uses of petroleum, etc. It is interesting to note that two panel discussions were exclusively devoted to new sources of liquid fuels, viz. occurrence and prospects of tar sands and oil shales. Operational research in petroleum industry, instrumentation, analytical techniques, separation processes, scientific and technical aspects of air and water services, and polymerization are the subjects of some of the panel discussions which show the broad spectrum of disciplines that are entering the field of petroleum science and technology. It would indeed require a Herculean effort to keep pace with such rate of progress. It would require a well-organized and collaborative effort in a country like India to benefit from progress in a field of this type.

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Dependence of Strontium-90 in Milk on Its Concentrations in Air & Surface Deposition

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A NUMBER of relations have been used in the past to determine how far the levels of Sr-90 in milk are dependent on its cumulative deposition and its rate of fallout. If such a relation can be applied to a particular area, approximate levels in milk in that area can be predicted. Russel[1] suggested a relation of the type $C = bD_p + dD_t$, where C is concentration of Sr-90 in plant or in milk and D_p and D_t are the deposition of Sr-90 during the life of the plant and the cumulative deposition respectively; b and d are constants to be determined from the data. He found that not more than 20 per cent of Sr-90 in 1958 milk could be accounted for by uptake by grass through the soil. Further studies by Russel[2] using similar relations showed that Sr-90 in milk from cumulative deposition increased to 53 per cent in 1961 and again dropped to 20 and 25 per cent respectively in 1963 and 1964. Kulp's[3] investigations showed that the fallout rate dependence of Sr-90 in milk dropped from 60 per cent in 1957 to 16 per cent in 1961.

The broad relationship between the fallout rate and cumulative deposition of Sr-90 on one hand and the milk concentration of Sr-90 on the other have also been described in the First Report of the United Nations Scientific Committee on the Effects of Atomic Radiation[4] published in 1958. More data became available, since the publication of that report, from Argentina, Australia, Canada, Denmark, Germany, Japan, New Zealand, the United Kingdom and the United States and, in the light of these data, the Committee found[5] that the averages of the 'rate' and 'soil' factors for milk fall within the range of 0·8-1·0 and 0·2-0·3 respectively. The terms 'rate' and 'soil' factors refer to the values of constants b and d of the equation $C=bD_p+dD_t$. In Eqs. (1) and (2), given later for Bombay data, the constants b and c are representative of rate factor and constant d of soil factor. However, application of these values to the data given for Bombay did not give satisfactory results. Hence it was felt that for places like Bombay located in tropical regions it is necessary to relate the levels of Sr-90 in milk to air concentrations, in addition to deposition rate and cumulative deposition of Sr-90.

The present analysis shows that the two component systems described in the 1958 report of the UN Scientific Committee on the Effects of Atomic Radiation may be valid for the rainy season when the scavenging mechanism is available for accelerated deposition of Sr-90. For the dry deposition periods it is necessary to take into account the air concentrations in correlating milk levels to the rate of fallout and cumulative deposition. The milk samples are obtained from Bombay's major milk supply scheme at Aarey, situated 30 km. north of Bombay and having climatic conditions similar to Bombay. It has an annual rainfall of about 180-210 cm. during the south-west monsoon from June to September, when about 90-95 per cent of the annual rainfall takes place. It has temperate climate with maximum temperature of 33°C. in May and minimum of about 18°C. in January. The colony is located in a hilly area and many of the pastures of the colony are maintained on sloping regions. The pastures are maintained throughout the year and the cattles are fed on the paragrass from these pastures, the average feed being about 11 kg. per day per cattle. Eight kg. of hay is given per day per cattle. However, in rainy season (July to November) 3-4 kg. of jungle green grass from nearby areas is fed to the cattle every day and the quota of hay is correspondingly reduced. In addition, 5·5 kg. of concentrate mixtures consisting of oilcakes, wheat brans, etc., are given to cattle every day. These considerations led to the classification of the data in two periods as rainy season period and dry deposition months, as explained later.

For Sr-90 analysis, 10-20 litres of milk are collected every month. The samples are ashed before the separation of Sr-90. Measurement procedure and the results of measurement are described elsewhere[6,7].

When the levels of Sr-90 in milk are plotted against cumulative deposition at Bombay, it is found that the effective delay period between the deposition of activity and its appearance in milk was one to two months. Therefore, in correlating the Sr-90 levels in milk with the Sr-90 deposition rate, we have taken effective fallout rate as the arithmetic mean of the deposition during the month of milk production and the deposition during the preceding two months. In some of the reports, where this type of correlation is tried, the effective period of contamination is taken as three months for any crop or vegetation[8,9]. Anderson *et al.*[9] found that the deposition of Sr-90 in the month preceding milk production plays an important role in rate dependent component of Sr-90 activity in milk and smaller contributions are made by deposition during the month of milk production and second previous month. When the levels of Sr-90 in milk are plotted against this effective rate of Sr-90 fallout, it is found that there is no positive correlation between the levels of Sr-90 in milk and fallout rate for dry deposition months, where fallout in dry months is only 1-3 per cent per month of the annual total. But the levels in milk indicate a positive correlation to the average Sr-90 concentrations in air for the month of milk production and the preceding month. Hence, in developing the equation for dry fallout months, average Sr-90 levels in air for two months are taken as effective Sr-90 rate of fallout.

In developing the equation for rainy season, for which again half the days are likely to be dry days, the levels are related to the effective average fallout deposition rate for three months, effective Sr-90 levels in air for two months and the cumulative deposition. Thus if X_1 denotes the Sr-90 level in milk in μμC. per gram of calcium, X_2 the average deposition rate for three months (in μC./km.$^2\times10^{-2}$), X_3 the average Sr-90 concentration in air for two months (in 10^{-15} curies per cubic metre) and X_4 the level of cumulative deposition at the beginning of the month of milk production (in mC./km.^{2}), we get the following equations:

for dry fallout months : $X_1=cX_3+dX_4$ ...(1)

for rainy season months: $X_1=bX_2+cX_3+dX_4$ ...(2)

The constants of Eqs. (1) and (2) are found by the method of multiple regression equation assumed to take the linear form[10]. The regression system is restricted to pass through the origin, since when the values of X_2, X_3 and X_4 are all zero, value of X_1 should be zero.

The levels of Sr-90 in air are determined from air filter samples collected at Bombay. Monthly data for Sr-90 deposition is obtained by analysis of monthly samples collected in high-walled stainless steel pots. Cumulative deposition levels of Sr-90 are calculated by assuming level of 2·8 mC. per km.^{2} by the end of August 1956 (ref. 11). The monthly Sr-90 deposition values are then added to this to get the cumulative deposition of Sr-90. Cumulative deposition levels are corrected for decay and then multiplied by 0·7 to account for leaching effect and Sr-90 lost by runoff. The factor 0·7 is taken for average soil, as suggested by Kulp *et al.*[12]. This then gives the level of Sr-90 in upper 2 in. of soil which is available for uptake by pastures. Thus all the values necessary for getting the constants *b*, *c* and *d* of Eqs. (1) and (2) are available.

All the data are divided into two periods for reasons given earlier. Dry deposition season is taken as the period starting from December and ending in May of the following year while rainy season deposition as that starting from June and ending in November.

From regression analysis it was found that for the dry deposition period (December to May), $X_1=0{\cdot}156X_3+0{\cdot}2X_4$ with standard error of estimate $\bar{S}=2{\cdot}86$ S.U. and coefficient of multiple determination $\bar{R}^2=0{\cdot}834$; and for the rainy season (June to November), $X_1=0{\cdot}308X_2+0{\cdot}023X_3+0{\cdot}346X_4$ with standard error of estimate $\bar{S}=4{\cdot}10$ S.U. and coefficient of multiple determination $\bar{R}^2=0{\cdot}832$. Units of net regression coefficients, i.e. constants *b*, *c* and *d* in Eqs. (1) and (2) are: $b=0{\cdot}308\times$S.U./(μC./km.$^2\times10^{-2}$), $c=0{\cdot}156$ or $0{\cdot}023\times$S.U./(10^{-15}C./m.^{3}), and $d=0{\cdot}20$ or $0{\cdot}346\times$S.U./(mC./km.^{2}).

The average rate dependence for each six-monthly period for the years 1958-65 is given in Table 1. Table 2 gives the contributions from these factors obtained by using six-monthly average data for X_2, X_3 and X_4. The average values of X_2, X_3 and X_4 used for calculations are also included in Table 2.

Discussion

Monthly surface deposition used in correlation analysis, usually measured by collection on flat surfaces of known area, is not likely to give a true picture of activity trapped by vegetation from

TABLE 1 — RATE DEPENDENCE OF Sr-90 IN MILK FOR DIFFERENT YEARS

Period	1958	1959	1960	1961	1962	1963	1964	1965
January to May and December of previous year	62·8	68·5	30·7	14·3	37·0	58·0	62·1	25·7
June to November	48·5	38·4	31·2	21·9	34·3	50·6	33·0	14·6

TABLE 2 — COMPARISON OF CALCULATED AND ACTUALLY OBSERVED VALUES OF Sr-90 IN MILK

Equation for the rainy season: $X_1 = 0{\cdot}308X_2+0{\cdot}023X_3+0{\cdot}346X_4$; standard error of determination $\bar{S} = 4{\cdot}1$ S.U.

Equation for the dry season: $X_1 = 0{\cdot}156X_3+0{\cdot}20X_4$; standard error of determination $S = 2{\cdot}86$ S.U.

Period	X_2 µC./km.$^2\times10^{-2}$	X_3 10^{-15}C./m.^{3}	X_4 mC./km.^{2}	Contributions in S.U. from			Calculated S.U. X_1	Observed S.U. X_1
				X_2	X_3	X_4		
Jan. 1958-May 1958	—	6·32	2·93	—	0·990	0·586	1·576	1·560
June 1958-Nov. 1958	4·83	4·50	4·85	1·485	0·104	1·680	3·269	2·730
Dec. 1958-May 1959	—	13·83	5·00	—	2·165	1·000	3·165	4·730
June 1959-Nov. 1959	4·47	3·90	6·84	1·370	0·090	2·370	3·830	4·970
Dec. 1959-May 1960	—	4·00	7·01	—	0·624	1·402	2·026	2·950
June 1960-Nov. 1960	3·99	0·92	8·00	1·225	0·021	2·770	4·016	2·500
Dec. 1960-May 1961	—	1·73	8·10	—	0·270	1·620	1·890	0·600
June 1961-Nov. 1961	2·81	1·85	9·31	0·864	0·043	3·230	4·137	1·000
Dec. 1961-May 1962	—	7·20	9·50	—	1·120	1·900	3·020	1·700
June 1962-Nov. 1962	6·04	13·50	12·00	1·860	0·310	4·160	6·330	2·700
Dec. 1962-May 1963	—	22·56	12·80	—	3·530	2·560	6·090	3·450
June 1963-Nov. 1963	21·59	21·30	20·20	6·640	0·490	7·000	14·130	12·550
Dec. 1963-May 1964	—	48·40	23·00	—	7·560	4·600	12·160	15·000
June 1964-Nov. 1964	13·67	9·21	26·8	4·210	0·210	9·300	13·720	16·400
Dec. 1964-May 1965	—	12·80	28·9	—	2·000	5·780	7·780	6·400
June 1965-Nov. 1965	5·45	6·30	31·0	1·675	0·145	10·700	12·500	10·500

airborne Sr-90. This applies for eight dry months in a place like Bombay where there is no mechanism like dew, snow or rainfall giving rise to the deposition of Sr-90. The airborne activity, however, takes part in contaminating milk because it is trapped by vegetation when it comes in contact with leaves. The activity so deposited on leaves is roughly proportional to the area of leaves and radioactive content of the air. It is also a function of surface characteristics of the foliage. Eddy currents and Brownian movements bring the particles in contact with the surface where they stick by impaction. For this reason, it seems necessary to correlate Sr-90 levels in milk to Sr-90 air concentrations for areas having similar climatic conditions as Bombay. The method of regression analysis gives positive values for net regression coefficient c for concentration in air in both the equations; however, the effect of air concentrations is negligibly small for rainy season. This explains the dependence of Sr-90 in milk also on Sr-90 content of air, especially in dry season.

Since very small amount of Sr-90 is deposited monthly in dry season (1-3 per cent of the annual deposition of Sr-90), it is difficult to have any significant changes in milk levels of Sr-90 by small variations in monthly deposition of Sr-90. The plot of levels in milk and monthly deposition for dry season does not indicate any dependence of the level in milk on monthly deposition. Hence the relation is arrived at by assuming equation of the type $X_1 = cX_3+dX_4$ and the net regression coefficients c and d are determined by regression analysis.

In the UK[1,2,9] the correlation is obtained between the deposition of Sr-90 during the life of the plant, the cumulative deposition of Sr-90 and Sr-90 levels in milk. Non-inclusion of air concentrations in such studies will not affect the correlation to a great extent because in the UK more or less uniform distribution of precipitation throughout the year results in the deposition of Sr-90 on ground. In winter, in addition, dew, fog and snowfall also give rise to the deposition of Sr-90. This is partially true for Bombay also for the rainy season period (June to November) when the monsoon rains accelerate deposition of Sr-90. It can be seen from Table 2 that air concentrations for this period of the year are responsible for less than 2·44 per cent of the levels of Sr-90 in milk on the average.

When these equations are applied to six-monthly data, taking average values of X_1, X_2, X_3 and X_4, the calculated values of Sr-90 in milk are found to be within the limits specified by the standard error of determination (Table 2). Calculated values are, however, much higher for the year 1961 when compared to the observed values. This may be partly due to depletion of soil reservoir of Sr-90 by redistribution of the activity with time[13]. Also, the feed, other than paragrass, given to the cattle might have been from places of different fallout origins. It may be noted that when the Sr-90 levels in milk are rising, the calculated values are lower than the observed ones, and when the levels are falling, the calculated levels in milk are higher than those actually observed. Thus the actual data indicates a positive bias of the current fallout rate on the results than given by the above equations. The equations indicate a positive bias of cumulative deposition on the results. However, differences can be attributed to supplementary feeding, different soil conditions, runoff and the effects of climatic factors both on the retention of direct contamination by plants and on absorption from soil. Such variations are likely to be greatest when small areas are considered as is done here[14].

Considerable variations from the predicted values can occur under variable conditions in any one month. If, however, these variables are averaged out by considering the average values of X_1, X_2, X_3 and X_4 for six months, the equations give fairly good agreement between the predicted and observed values to within 30 per cent for the data except for 1961. Predicted levels cannot closely agree with the observed levels because the equations are not arrived at from the data based on strictly controlled conditions. These equations can only serve as guide for the prediction of general trends of Sr-90 levels in milk.

Summary

Regression analysis has been carried out to find the dependence of Sr-90 content of milk on its concentration in air, its monthly rate of deposition, and cumulative deposition in soil at Bombay. This analysis shows that the dependence of Sr-90 in milk on its concentration in air is also important, especially in areas like Bombay where the major deposition on the ground takes place only during four months of the rainy season. The collection in the dry season on the foliage is mainly by impaction of airborne Sr-90. A comparison has been made between the measured levels of Sr-90 in milk and levels calculated from concentration in air, monthly deposition and cumulative deposition using net regression coefficients obtained from the data for eight years. Good agreement is obtained when the year is divided in two parts, viz. the dry months from December to May and rainy period from June to November; and average concentrations for these periods are used for the calculation of Sr-90 in milk from regression equations. The values so estimated agreed to within 30 per cent with the values measured experimentally.

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The Use of Stark Effect for Identification of Rotational Transitions & Determination of Dipole Moments

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THE presence of a molecular electric dipole moment is the most important criterion for the existence of a pure rotational spectrum and the intensities of the transitions are closely related to its magnitude. In addition, when an external electric field is applied to a polar gas, it interacts with the electric dipole, causing a splitting of the rotational energy level, which results in the appearance of fine structure in the rotational spectrum. This is known as the Stark effect.

Stark effects on molecular spectra are easily observed with the techniques of microwave spectroscopy and have proved useful in detecting molecular absorption lines, in identifying transitions, and in measuring molecular dipole moments. The allowed transitions in a uniform applied field correspond with $\Delta M=0$ (π Stark effect) or with $\Delta M=\pm 1$ (σ Stark effect) if the electric vectors of the Stark field and of the exciting electromagnetic field are parallel or perpendicular respectively. For transitions in which the electric vector of radiation is perpendicular to the electric field, the Stark pattern is moderately more complex than in the case in which the two electric fields are parallel, and is generally not employed. The spectrographs using Stark modulation technique, which are generally employed to study the rotational spectra of gases in the microwave region, have been discussed by many authors[1-7].

Theory

The relative directions of the dipole moment and of the angular momentum vector must be taken into account in considering the molecular Stark effect. Thus, in linear molecules the dipole moment is perpendicular to J, the total angular momentum of rotation, provided that the molecule is in a $^1\Sigma$ electronic state. Most of the stable molecules are normally in such a state, since their electrons are fully paired. In symmetric top molecules, the dipole moment is necessarily directed along the figure axis (except in the case of accidental symmetry) and, hence, their dipole moments may have components parallel to the angular momentum (except when $K=0$) and thus components which are fixed in direction rather than rotating. If the dipole μ is perpendicular to the direction of angular momentum, the splitting of the rotational levels by an electric field depends on the square of the field intensity E, giving what is known as a 'second-order' Stark effect, while if μ has a component along the direction of angular momentum, the splitting is directly proportional to E, i.e. a 'first-order' Stark effect.

Semi-classical Approach

First-order Stark Effects

This is the most important for symmetric tops. In such molecules the dipole moment μ has an electric dipole component μ_J in the direction of J, of magnitude

$$\mu_J = \frac{\mu K}{\sqrt{J(J+1)}} \qquad \ldots(1)$$

If now an electric field E is applied, this moment μ_J will interact with it and the energy of interaction is given by

$$\Delta W_1 = -\mu_J E \cos\theta \qquad \ldots(2)$$

where θ is the angle between J and the direction of E. The projection of J on a fixed direction, such as that established by the direction of E, is always an integer M, the magnetic quantum number. Therefore,

$$\cos\theta = \frac{M}{\sqrt{J(J+1)}}$$

and

$$\Delta W_1 = -\frac{\mu EMK}{J(J+1)} \qquad \ldots(3)$$

Thus each level is split by the field into $(2J+1)$ components unless $K=0$. The first-order Stark effect characteristic of symmetric tops is more generally characteristic of a system with degenerate levels. In the absence of an external field, no system can have a dipole moment fixed in direction unless it is in a degenerate energy level. Symmetric tops can have a dipole moment of this type because of the degeneracy of the $+K$ and $-K$ levels, and this moment interacts with the electric field.

Second-order Stark Effects

Other types of molecules, in general, have no component of the electric dipole which has a fixed direction in space in the absence of an electric field, i.e. have no degeneracy of this type, and hence the first-order Stark effect does not occur in the molecules other than symmetric molecules. The interaction of the applied field with the rotating dipole moment now produces a polarization of the molecule so that there is a net electric dipole, averaged over the motion, along the direction of the field. The Stark effect is then due to the interaction of the field with this net dipole, and is proportional to the square of the field strength. It is useful to consider two limiting cases, for which J is perpendicular and parallel to E respectively.

Considering first a rotating linear molecule with angular momentum perpendicular to the electric field, it can be shown that the dipole is oriented away from the field more often than with it, so that, on the average, the dipole is directed oppositely to the field (contrary to what would be expected if there were no rotation). The energy of interaction ΔW_2 is then[8,9]

$$\Delta W_2 \propto \frac{(\mu E)^2}{hBJ(J+1)} \qquad \ldots(4)$$

thus giving a second-order effect. Here B is the rotational quantum number.

In the other case, if a linear molecule rotates with its angular momentum parallel or antiparallel to the electric field, then the rotating dipole is slightly twisted in the direction of the field, and the energy is decreased by an amount again proportional to

$$\frac{(\mu E)^2}{hBJ(J+1)}$$

Quantum Mechanical Calculation of Stark Energy for Static Fields

Stark Effect for Two Nearby Levels

The intensity of the absorption or emission depends on the quantities $\int^{\tau}\Psi_i^{*}\mu_z\Psi_j d\tau$, called dipole moment matrix elements, where Ψ_i and Ψ_j are the wavefunctions of the two states associated with the transition, and μ_z is the component of the dipole moment along the direction of z. The matrix element is usually written $(\Psi_i|\mu_z|\Psi_j)$. There is no transition if the corresponding matrix element is zero. The two states are thus linked by the dipole moment for transitions between them. When a static (or near static) electric field is applied, the electric field interacts with the dipole moment, and if the appropriate matrix elements are non-vanishing, then there is an interaction between pairs of levels, which are thereby put ‘in contact’ with one another. The energy levels are split due to this interaction. However, this splitting is small compared to the basic rotational energies. This constitutes the molecular Stark effect, and the applied field is described as ‘perturbing’ the zero field energy levels.

Let us assume that a system has two energy states only, with wavefunctions Ψ_1^0, Ψ_2^0 and corresponding energy values W_1^0, W_2^0 respectively, in the absence of an electric field. The energy of interaction of the electric dipole μ of this system with a field E at an angle θ to the dipole is $-\mu E\cos\theta$. The mean interaction depends on the magnitude of the quantity $-\mu E\int\Psi_1^0\cos\theta\,\Psi_2^0 d\tau$ which is the matrix element $(\Psi_1^0|\mu_z|\Psi^0)$. The wavefunctions after application of the field E may be written as

$$\left.\begin{aligned}\Psi_1 &= a\Psi_1^0+b\Psi_2^0\\ \Psi_2 &= -\,b\Psi_1^0+a\Psi_2^0\end{aligned}\right\} \qquad \ldots(5)$$

The coefficients a, b in the present case are determined by the perturbation function[10] and satisfy the normalization condition

$$a^2+b^2=1 \qquad \ldots(6)$$

The matrix element due to perturbing interaction $-\mu E\cos\theta$ which connects the two states is

$$\left.\begin{aligned}-\mu_{12}E &= -\mu E\int\Psi_1^0\cos\theta\,\Psi_2^0 d\tau\\ d\tau &= \sin\theta\, d\theta d\phi\end{aligned}\right\} \qquad \ldots(7)$$

The energies, when a perturbing field is applied, corresponding with Ψ_1 and Ψ_2 may be obtained by a standard method of quantum mechanics[10] and are given by

$$W = \frac{W_1^0+W_2^0}{2} \pm \left[\left(\frac{W_1^0-W_2^0}{2}\right)^2+\mu_{12}^2E^2\right]^{\frac{1}{2}} \qquad \ldots(8)$$

where we assume $W_1^0 > W^0$.

For a small perturbation, with

$$\mu_{12}E \ll \frac{W_1^0-W_2^0}{2}$$

Eq. (8) may be expanded to give

$$W_1 = W_1^0+\frac{\mu_{12}^2E^2}{W_1^0-W_2^0}+\ldots \qquad \ldots(9a)$$

$$W_2 = W_2^0-\frac{\mu_{12}^2E^2}{W_1^0-W_2^0}+\ldots \qquad \ldots(9b)$$

This gives Stark energy dependent on E^2 which is typical of a second-order Stark effect. It is interesting to note here that the effect of the field is to cause an increase in the separation of the levels, i.e. coupling the levels by an electric field causes them to repel one another.

If the perturbation is large or if the levels W_1^0, W_2^0 are very close to each other, so that

$$\mu_{12}E \gg \frac{W_1^0-W_2^0}{2}$$

Eq. (8) may be expanded to give

$$W_1 = \frac{W_1^0+W_2^0}{2}+\mu_{12}E \qquad \ldots(10)$$

$$W_2 = \frac{W_1^0+W_2^0}{2}-\mu_{12}E \qquad \ldots(11)$$

In this approximation, the Stark effect appears linearly dependent on E which is typical of first-order Stark effect. For a given $\mu_{12}E$, therefore, the order observed depends only on the separation of the levels. This is just the approximation which holds for the symmetric molecule with doubly degenerate levels, since in this case $W_1^0-W_2^0=0$. For rather close (zero field) levels, Eq. (8) shows that it is sometimes possible to observe a smooth transition from a ‘second-order’ to a ‘first-order’ type of Stark effect as the field E is increased. Usually, this intermediate type of Stark effect for a pair of almost degenerate levels occurs for slightly asymmetric top molecules and linear molecules in excited bending vibration states and will be discussed in detail later on.

The above treatment can readily be extended to systems with more than two energy levels. Any particular level i will interact, via the field, with all other levels j for which the matrix elements $|\mu_{ij}|$ are non-vanishing. If W_i is the energy of the undisturbed state and W_j is the energy of any other state unperturbed by the electric field and μ_{ij} is the z-component of the dipole moment matrix element between the two states, then in the extreme cases:

Second-order energy shift:

$$\Delta W_{2(i)} = \sum_j \frac{|\mu_{ij}|^2E^2}{W_i - W_j} \quad (i \neq j) \qquad \ldots(12)$$

First-order energy shift:

$$\Delta W_{1(i)} = \sum_j |\mu_{ij}|E \quad (i \neq j) \qquad \ldots(13)$$

These equations are very important for evaluating Stark energies in particular cases where the matrix elements $|\mu_{ij}|$ are known.

Diatomic and Linear Molecules

If the electric field E is in the z-direction, then only the component of the dipole moment matrix element of the two states Ψ_i, Ψ_j associated with the z-direction is significant and is

$$(\Psi_i|\mu_z|\Psi_j) = \mu\int \Psi_i \cos\theta\, \Psi_j d\tau \quad (i \neq j) \quad \ldots(14)$$

where θ is the angle between the dipole and the field E. It can easily be shown[3,8,9,11] that only the matrix elements of this type for states with J differing by unity, and M remaining unchanged, are non-vanishing. Therefore, only levels of different J, and the same M, interact with each other through these matrix elements and because these differ widely from each other in energy, the change in energy level due to imposition of a Stark field will be small and second order, following Eq. (12).

For the state $\Psi_{J,M}$ linked with states $\Psi_{J+1,M}$ and $\Psi_{J-1,M}$ the matrix element can be written as[9]

$$(J, M|\mu_z|J+1, M) = \mu\left[\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)}\right]^{\frac{1}{2}} \quad \ldots(15)$$

$$(J, M|\mu_z|J-1, M) = \mu\left[\frac{J^2 - M^2}{(2J-1)(2J+1)}\right]^{\frac{1}{2}} \quad \ldots(16)$$

The energy differences between the unperturbed levels are

$$\left.\begin{aligned} W_{J,M} - W_{J+1,M} &= -2Bh(J+1) \\ W_{J,M} - W_{J-1,M} &= 2BhJ \end{aligned}\right\} \quad \ldots(17)$$

The substitution of Eqs. (15), (16) and (17) in Eq. (12) yields

$$\Delta W_2 = \frac{\mu^2E^2[J(J+1) - 3M^2]}{2hBJ(J+1)(2J-1)(2J+3)} \quad \ldots(18)$$

The level is, therefore, split into $(J+1)$ subsidiary levels of different $|M|$. Thus the imposition of an electric field results in the splitting of the transition $J \rightarrow J+1$ into a number of components due to the splitting of the individual levels corresponding to Eq. (18). If the applied electric field is parallel to the electric vector of the microwave radiation, then only the transitions with $\Delta M = 0$ can occur and if these fields are perpendicular to each other, then transitions with $\Delta M = \pm 1$ occur[12]. However, as pointed out earlier, the usual designs of Stark modulation spectrographs are such that only $\Delta M = 0$ transitions take place.

Applying the selection rules $\Delta J = \pm 1$ and $\Delta M = 0$, one can easily get the following expression for the difference of frequency $\Delta\nu$ between the line in the presence of an electric field and the zero field line (ν_0):

$$\Delta\nu = \frac{2\mu^2E^2[3M^2(8J^2+16J+5) - 4J(J+1)^2(J+2)]}{h^2\nu_0 J(J+2)(2J-1)(2J+1)(2J+3)(2J+5)} \quad \ldots(19)$$

where J is for the lower rotational level. However, in the special case where $J = 0$ the above expressions simplify to

$$(\Delta W_2)_{J=0} = -\frac{\mu^2E^2}{6hB} \quad \ldots(20)$$

and

$$(\Delta\nu)_{J=0} = \frac{8\mu^2E^2}{15h^2\nu_0} \quad \ldots(21)$$

For ν_0 and $\Delta\nu$ in megacycles, μ in Debye units and E in V./cm., the factor $2/h^2$ and $8/15h^2$ in Eqs. (19) and (21) are to be replaced by 0·5065 and 0·1351 respectively.

Second-order Stark energies are seen from Eq. (18) to be independent of the sign of M. Before Stark splitting, there were $(2J+1)$ different degenerate levels for each value of J corresponding to the different values of M. Second-order Stark effects depend on M^2 so that the levels are separated into pairs of degenerate levels ($\pm M$) except for $M = 0$, which is non-degenerate. Thus there are $(J+1)$ Stark components of a completely resolved spectral line, where J is the smaller of the two values of J involved in the transition.

Still higher order perturbation terms (fourth-order terms since third-order terms are zero) have been included in the Stark energy of a linear molecule[13,14], but in most cases are very small usually considerably less than 1 per cent. There is still a set of conditions under which linear molecules can show a first-order Stark effect. This occurs when they are in excited states of degenerate bending vibrations, provided $|l|$, the internal angular momentum, is not zero. For a linear molecule, the Stark effect of excited stretching vibrational states may be treated in the same way as for the ground state. In a bending vibration, however, the molecule is very nearly a symmetric top. The total angular momentum J is then not perpendicular to the line of centres of the molecule, but has a projection **1** ($= lh/2\pi$) along it. There is correspondingly a component of the dipole moment along the direction of J, and hence the doubly degenerate levels (or nearly so), if l-type doubling is taken into account, show a first-order Stark effect. Strandberg *et al.*[15] have studied the OCSe molecule and have shown that the Stark effect is quadratic for low fields (asymmetric top approximation) and linear for high fields (symmetric top approximation). It is interesting to note that the Stark components of the two l-type doublets approach each other as the field is increased and intersect at a field given by[15]

$$E = \frac{hJ(J+1)(J+2)}{4\mu M}\Delta\nu' \quad \ldots(22)$$

where $\Delta\nu'$ is the absorption frequency difference of the unperturbed l-doublet. This gives a convenient means of measuring the dipole moment for l-type doublets.

Symmetric Top Molecules

The rotational levels of symmetric top molecules are characterized by the twofold degeneracy, corresponding with values of $\pm K$ for given J apart from levels with $K = 0$. The dipole moment lies in the direction of the figure axis of the molecule and hence only the z-components of the dipole moment matrix elements, lying along the field direction, are to be considered. For symmetric molecule wavefunction with rotational quantum number J, K, M, there will be a first-order change in the energies of the levels given by Eq. (13). The corresponding first-order splitting ΔW_1 of the Jth energy level is, therefore,

$$\Delta W_1 = -\frac{\mu EKM}{J(J+1)} \qquad \ldots(23)$$

which is identical with Eq. (3) and vanishes for linear molecules when $K = 0$.

Transitions may occur with selection rules $\Delta J = \pm 1$ and $\Delta K = 0$ and $\Delta M = 0, \pm 1$. For a transition $J \rightarrow J+1$ with the microwave electric vector parallel to the Stark field E, as is the usual experimental case, selection rules are $\Delta K = 0$, $\Delta M = 0$. These conditions yield the frequency displacements from unperturbed rotational line frequency ν_0 as

$$\Delta\nu = \frac{2\mu EKM}{hJ(J+1)(J+2)} \qquad \ldots(24)$$

For ν and $\Delta\nu$ in megacycles, μ in Debye units (1 Debye $= 10^{-18}$ e.s.u. cm.) and E in V./cm., the factor $2/h$ is to be replaced by 1·0064. The first-order Stark effect, when present, removes the degeneracy of the energy levels completely and each level is split by the field into $(2J+1)$ components giving rise to $(2J+1)$ Stark components to a completely resolved spectral line where J corresponds to the lower rotational level.

The above first-order Stark effect has been derived on the assumption that μ is independent of the electric field. Actually, the field perturbs the rotational motion, giving rise to an additional component of the dipole moment proportional to the electric field. The next approximation or second-order perturbation theory considers the small changes in the molecular wavefunction due to the field and the resulting energy, ΔW_2, which is affected only by the two neighbouring states $J' = J+1$ and $J' = J-1$ may be written with the help of Eq. (12) as[16,17]

$$\Delta W_2 = \frac{\mu^2 E^2}{2hB}\left[\frac{\{(J^2-K^2)(J^2-M^2)\}}{J^3(2J-1)(2J+1)} - \frac{\{(J+1)^2-K^2\}\{(J+1)^2-M^2\}}{(J+1)^3(2J+1)(2J+3)}\right] \qquad \ldots(25)$$

The second-order energy is usually so much smaller than the first-order given by Eq. (23) that, in general, the second-order effect is completely negligible as compared to the first-order effect unless $K = 0$, so that the first-order energy is zero.

Furthermore, a linear molecule is equivalent to a $K = 0$ level of a symmetric molecule. The Stark effect of the inversion doubling of ammonia is a special case. Although NH_3 is a symmetric molecule, its dipole moment is only 'semi-permanent' because of inversion splitting. Hence, it possesses a second-order splitting[18,19].

Asymmetric Top Molecules

The evaluation of the theoretical Stark perturbation for asymmetric top molecules is arduous. Asymmetric top levels do not show K-type degeneracy, and, therefore, tend to show second-order Stark effects unless a rotational level is accidentally close to another, or if the asymmetry parameter is small. For the usual case, where near degeneracies do not occur, the Stark energy has the form of Eq. (12) which involves the sum of a number of terms containing matrix elements between rotational states. Golden and Wilson[20] have evaluated the Stark effect arising from the interaction of a uniform electric field with a permanent electric dipole that is arbitrarily oriented within a rigid asymmetric rotor, and with a dipole induced in the rotor by the field, by perturbation methods. For cases where the Stark splitting is small compared with the separation of the unperturbed energy level from its nearest neighbour (non-degenerate case), they derive the expression

$$(\Delta W_2)_{J_\tau M} = \sum_{g=a,b,c} \frac{2\mu_g^2 E^2}{(A+C)h}[A_{J_\tau}(\mathrm{K},\alpha) + M^2 B_{J_\tau}(\mathrm{K},\alpha)] \qquad \ldots(26)$$

Here g refers to the molecule-fixed principal axes of inertia a, b, c and μ_g are the components of the permanent dipole moment along the principal axes. $(\Delta W_2)_{J_\tau M}$ is the corresponding total second-order energy shift for the M component of the J_τ energy level, and K and α are asymmetry parameters of the molecule given by

$$\mathrm{K} = \frac{2B-A-C}{A-C} \text{ and } \alpha = \frac{A-C}{A+C} \qquad \ldots(27)$$

in terms of the three rotational constants of the molecule. Values of A_{J_τ} and B_{J_τ} have been tabulated[20] for $J = 0, 1, 2$. When the microwave electric field is parallel to the Stark field, the selection rules are $\Delta M = 0$ and $\Delta J = 0, \pm 1$. There are $(J+1)$ Stark components of a completely resolved spectral line, where J is the smaller of the two J's involved in the transition.

Golden and Wilson have also shown that Eq. (26) can be put in a more general form utilizing the tabulated line strengths[21] $S_{J_\tau, J'_{\tau'}}$ between levels whose unperturbed energy differences are $W^\circ_{J_\tau}$ and $W^\circ_{J'_{\tau'}}$, where $J' = J-1$ or $J+1$. The resulting relation is

$$(\Delta W_2)_{J_\tau M} = \sum_{g=a,b,c} \frac{\mu_g^2 E^2}{(2J+1)} \sum_{\tau'}{}' \left[\frac{J^2-M^2}{J(2J-1)} \cdot \frac{S_{J_\tau, (J-1)_{\tau'}}}{W^\circ_{J_\tau} - W^\circ_{(J-1)_{\tau'}}} + \frac{M^2}{J(J+1)} \cdot \frac{S_{J_\tau, J_{\tau'}}}{W^\circ_{J_\tau} - W^\circ_{J_{\tau'}}} + \frac{(J+1)^2-M^2}{(J+1)(2J+3)} \cdot \frac{S_{J_\tau, (J+1)_{\tau'}}}{W^\circ_{J_\tau} - W^\circ_{(J+1)_{\tau'}}}\right] \qquad \ldots(28)$$

The summation Σ' is over all states except J_τ. The prime over the summation indicates that the summation is to extend only over those values of $J'_{\tau'}$ for which $W^\circ_{J'_{\tau'}}$ is not near $W^\circ_{J_\tau}$. The energy difference may be the observed spectroscopic value or where these are not available, may be computed from the energy level tables of King *et al.*[22].

The Stark shifts for asymmetric top molecules may be written in a more general and simplified form as

$$(\Delta W_2)_{J_\tau M} = (A'+B'M^2)E^2 \qquad \ldots(29)$$

where A' and B' are characteristics of a particular level and have been computed (however, differing by certain factors) for all levels with $J = 0$, 1 and 2 (ref. 20). However, the Stark effect may be calculated[21] for levels with J as large as 12 by inserting values of line strengths into Eq. (28).

It is interesting to consider two special cases. The first is that many asymmetric tops differ only slightly from symmetric ones and, consequently, the levels for a given J are grouped in rather close pairs except the one tending to $K = 0$. Thus the transition from a second-order effect at low fields (12) to a first-order effect at high fields (13) is often found. The second case is somewhat similar — accidental near degeneracies occur with many asymmetric tops because of the large spread of the energy levels for given J when the asymmetry is large. Consequently, the second- to first-order transition will occur in such cases with increasing fields. This phenomenon can be of use in the approximate location of levels. In their paper[20] Golden and Wilson have pointed out the possibilities of accidental degeneracy of levels of asymmetric tops (even for low J values) and analysed this case in detail. Here a linear Stark effect may appear giving rise to $(2J+1)$ component lines. Also transitions with $|\Delta J| > 1$ become possible.

Stark Effect When Hyperfine Structure is Present

If the levels are associated with hyperfine structure produced by the nuclear electric quadrupole, which occurs very frequently, then resulting pattern of levels is often difficult to represent by simple formulae. When hyperfine structure is present due to a nucleus of spin I, the total angular momentum of a molecule is given by the quantum number $F = J+I,\ J+I-1, \ldots |J-I|$ rather than by J. The projection of the angular momentum on some chosen direction is $M_F = F,\ F-1, \ldots -F$. Thus the number of Stark components depends on F rather than J, and it is quite obvious that the energies of the Stark components will be different from the case with no hyperfine structure discussed earlier.

The Hamiltonian for a rotor in an external field having quadrupole coupling is

$$H = H^{(0)}+H_Q+H_E \qquad \ldots(30)$$

where $H^{(0)}$ is the Hamiltonian for the unperturbed rotor, H_Q is the quadrupole coupling Hamiltonian and H_E the energy in the electric field $-\mu E \cos\theta$ where θ is the angle between μ and E. It is convenient to divide the problem into three parts — the weak field, strong field and intermediate field.

Weak Electric Fields

In the weak-field case, the electric field is so small that the Stark energy is considerably less than the interaction between the nucleus and the molecule, i.e. the hyperfine energy. Hence, the electric field sees only the resultant angular momentum F, which is produced by the coupling of the molecular rotation J to the nuclear spin I. The molecular wavefunctions and the hyperfine structure are only very slightly perturbed by the electric field. In this case F, M_F, J, K and I are good quantum numbers but M is not. Each hyperfine line is then split by the Stark effect into various components according to the values of M_F and this splitting is small compared with the hyperfine splitting. In the weak-field case, the hyperfine structure is unperturbed and the Stark splitting can be calculated by essentially the same methods used for the case of no hyperfine structure. Both first- and second-order (linear and quadratic) Stark effects occur. If the Stark effect is first order (symmetric top) each F level is split into $(2F+1)$ different levels, while if it is second order the splitting is into $(F+1)$ levels of which those with $F \neq 0$ are doubly degenerate.

The first-order Stark perturbation energy is given by[23,24]

$$\Delta W_1 = -\frac{\mu EKM_F[F(F+1)+J(J+1)-I(I+1)]}{2J(J+1)F(F+1)} \qquad \ldots(31)$$

It should be noted that the Stark energy is proportional to K, so that no linear Stark effect occurs when $K = 0$. In addition, when $F = I+J = M_F$, Eq. (31) becomes

$$\Delta W_1 = -\frac{\mu EK}{(J+1)}$$

which is identical with what would be obtained if $J = M_J(M)$ and no hyperfine structure were present. For all other cases, however, the Stark effect is modified by the presence of the hyperfine structure.

A much more elaborate calculation is required for the second-order Stark effects, which occur for all other types of the molecules, and for symmetric tops when $K = 0$. Second-order Stark effects may be calculated, in general, by expanding the wavefunction with hyperfine structure in terms of the rotational wavefunctions which would occur if no hyperfine structure were present. For the general asymmetric top without degeneracy and without hyperfine structure, second-order Stark effects are of the form shown in Eq. (29).

When, as is usually the case, the rotational energy levels are widely spaced as compared with the hyperfine splitting of these levels, one can obtain the weak-field solution by replacing $M_J^2(M^2)$ in Eq. (29) by its quantum mechanical average in the $FJIM_F$ representation. This average is given by[25,26]

$$\overline{M_J^2} = \frac{[3M_F^2-F(F+1)][3D(D-1)-4F(F+1)J(J+1)]}{6F(F+1)(2F-1)(2F+3)} + \frac{J(J+1)}{3} \qquad \ldots(32)$$

where

$$D = F(F+1)+J(J+1)-I(I+1)$$

Thus the weak-field Stark effect for an asymmetric rotor with hyperfine structure can be expressed in terms of the Stark effect coefficients A' and B' for the case with no hyperfine structure. Second-order Stark effects can then be shown to be[25,26]

$$(\Delta W_2)_{J_\tau,F} = A'E^2+B' \times\left[\frac{[3M_F^2-F(F+1)][3D(D-1)-4F(F+1)J(J+1)]}{6F(F+1)(2F-1)(2F+3)} +\frac{J(J+1)}{3}\right]E^2 \quad \ldots(33)$$

One important case $F=(J+1)$, $M_F=F$ is simple. Here the Stark splitting is not affected by the quadrupole coupling. Since it is generally possible to observe $\Delta J=0$ transitions for asymmetric rotors, it is possible to select transitions for which $F=J+I$, $M_F=F$ for both levels of the transition. For such transitions the observed frequency shifts in the presence of an electric field are not affected by the quadrupole coupling, so that dipole moments may be computed directly from Eqs. (26), (28) or (29). Eq. (33) can be applied to a linear molecule (or symmetric top with $K=0$), for which it reduces to an expression given by Fano[26]

$$(\Delta W_2)_J = -\frac{\mu^2E^2}{hB}\times \frac{[3M_F^2-F(F+1)][3D(D-1)-4F(F+1)J(J+1)]}{2J(J+1)(2J-1)(2J+3)2F(F+1)(2F-1)(2F+3)} \quad \ldots(34)$$

Strong Electric Fields

In the strong electric field case, $|\mu E| \gg eQq$ the Stark energy is much larger than the hyperfine energy. The molecule is precessed so violently by the electric field that the nuclear orientation cannot follow the motion and nuclear spin I and angular momentum J are uncoupled and precess separately about the field direction. F is no longer a good quantum number and the appropriate quantum numbers are J, K, I, M_J and M_I. This gives the same Stark splittings of the basic rotational transitions as for a molecule without hyperfine structure. Each of these Stark components now shows a hyperfine structure due to the coupling of the nuclear quadrupole moment to the applied field. If the electric field is made very large, the Stark energy may be larger than the separation between the rotational levels and in this case J is no longer a good quantum number. However, we will study only the cases in which the Stark energy is large compared with the hyperfine energy but small compared with the rotational energy, since these are the common conditions.

In the case of a symmetric top with quadrupolar nucleus on the figure axis, the hyperfine energy due to a nuclear quadrupole moment is given in the strong-field case and where $|M_J| \neq 1$ by[8,27]

$$W_Q = \frac{eQq}{4I(2I-1)(2J-1)(2J+3)}\left[\frac{3K^2}{J(J+1)}-1\right] \times[3M_I^2-I(I+1)][3M_J^2-J(J+1)] \quad \ldots(35)$$

In the strong field, solution when $|M_J|=1$ cannot always be obtained by the above method, although it can when $|M_J|=1$ if $M_J=1$ and $M_J+M_I=I$ or $I+1$. In general, when $M_J=1$ and $M_J+M_I=1$ the energy must be obtained from the solution of the appropriate secular equation which has been given by Low and Townes[23].

The Stark effect in quadrupole hyperfine structure for a linear molecule is quite similar to that for a symmetric top and the formula for a linear molecule is obtained by putting $K=0$ in the above expression. This formula does not hold good for the case of $|M_J|=1$ for which, in general, more elaborate calculations are necessary[23,26].

In the case of asymmetric rotors, the quadrupole interaction is treated as perturbation on the Stark levels with the latter obtained as for molecules without hyperfine structure[25,28]. The quadrupole perturbation to be added to Stark levels is

$$W(Q)=eQ\left\langle\frac{\partial^2V}{\partial Z^2}\right\rangle_{\text{av.}}\frac{[3M_I^2-I(I+1)][3M_J^2-J(J+1)]}{8J(2J-1)I(2I-1)} \quad \ldots(36)$$

where the values of $\left\langle\frac{\partial^2V}{\partial Z^2}\right\rangle_{\text{av.}}$ have been expressed in different forms and can be conveniently obtained from the existing tables[3,29-31].

Intermediate Electric Fields

The intermediate electric field case occurs when Stark and hyperfine energies are comparable in magnitude ($H_E \approx H_Q \ll H^{(0)}$) and is generally very complicated. The appropriate expressions can, however, be evaluated and have been applied successfully to molecules in which changes from the 'low' to 'high' field cases are observed[23,25,26,32,33].

Stark Effects in the Presence of Hyperfine Structure due to Two Nuclei

Stark effects, when two nuclei produce hyperfine structure, obey very complicated relations. However, for strong fields, the hyperfine energy is just the sum of that which would be due to each nucleus individually [$W(Q)_{\text{total}}=W(Q_1)+W(Q_2)$ if two nuclei have quadrupole moments Q_1 and Q_2] and so this case is rather simple. For weak and intermediate fields, in general, more elaborate calculations are necessary[34-37].

Intensities

Relative intensities of Stark components in the presence of hyperfine structure are analogous under weak- or strong-field conditions to what are obtained without hyperfine effects.

In the weak-field case the relative intensities are

$$I\propto M_F^2 \text{ for } \Delta F=0 \text{ and } \Delta M_F=0 \quad \ldots(37)$$

$$I\propto[(F+1)^2-M_J^2] \text{ for } \Delta F=\pm1 \text{ and } \Delta M_F=0 \quad \ldots(38)$$

where F is the smaller value involved in the transition.

In the strong-field case, the relative intensities of each Stark component are the same as without hyperfine structure, or

$$I\propto M_J^2 \text{ for } \Delta J=0 \text{ and } \Delta M_J=0 \quad \ldots(39)$$

$$I \propto [(J+1)^2 - M_J^2] \text{ for } \Delta J = \pm 1 \text{ and } \Delta M_J = 0 \quad \ldots(40)$$

Each of these Stark components is split into hyperfine components corresponding to different M_I, and which, for a given Stark component, all have the same intensity except that for $M_I = 0$ which has half the intensity of the other lines. The intensities for the intermediate fields can be approximated by extrapolation from the strong- to weak-field case.

Identification of Transitions

The most valuable use of the Stark effect lines is the identification of rotational transitions from the number and relative intensities of the Stark components. We will discuss here only those transitions in which the electric vector of radiation is parallel to the electric field and which are normally the ones observable in usual Stark modulation spectrographs. For these transitions the $\Delta M = 0$, the following formulation has been developed for the frequency displacement of each component, measured relative to the position of the unsplit line, and the relative intensities of the Stark components[20].

Formulae for Transition Frequencies

If $\Delta M = 0$, the value of M must be no larger than the smallest J value involved in the transition. Hence, a count of number of components (different values of M^2) gives quite directly the value of the lowest J involved in the transition.

Case (a) for non-degenerate case (second-order Stark effect), the frequency displacement of each component is given by

$$\Delta\nu_M = (A'' + B''M^2)E^2 \quad \ldots(41)$$

Case (b) for degenerate case (first-order Stark effect) when $|\Delta J| = 0$, the frequency displacement of each component is given by

$$\Delta\nu_M = \pm F''|M|E \quad \ldots(42)$$

Case (c) and for degenerate case when $|\Delta J| = 1$,

$$\Delta\nu_M = \pm[G''\{(J+1)^2 - M^2\}^{\frac{1}{2}}]E \quad \ldots(43)$$

where A'', B'', F'' and G'' are coefficients that are independent of M. A spectral line under the influence of an electric field exhibits significant differences in appearance according to whether case (a), (b) or (c) applies.

Since $|M| \leqslant J$, a completely resolved spectral line will have $(J+1)$ components for non-degenerate case and $(2J+1)$ components for degenerate case where J is the smaller of the two J's involved in the transition. However, in case $\Delta J = 0$, the component $M = 0$ is missing entirely and other low values of M may be rather weak (since in this case intensity decreases rapidly with M^2). If complete resolution is not attained, it is nevertheless possible to determine the $|M|$ value of certain of the resolved component. From this information a good estimate of $|M|_{\text{max.}}$ may usually be made, with the result that the smaller of the two J's involved is determined. How this may be accomplished depends upon which of Eqs. (41), (42) and (43) is applicable.

Case (a): The successive components, when resolved, must differ in their values of M. For two such components, therefore,

$$\begin{aligned} \Delta\nu_M - \Delta\nu_{M\pm1} &= B''E^2[M^2 - (M\pm1)^2] \\ &= \mp B''E^2(2M\pm1) \quad \ldots(44) \end{aligned}$$

If there are at least three components, then ordering the components so that M corresponds to one extreme, $M\pm1$ to the intermediate and $M\pm2$ the other extreme, one obtains

$$r = \frac{\Delta\nu_M - \Delta\nu_{M\pm1}}{\Delta\nu_{M\pm1} - \Delta\nu_{M\pm2}} = \frac{2M\pm1}{2M\pm3} \quad \ldots(45)$$

solving

$$M = \pm\left(\frac{3r-1}{2-2r}\right) \quad \ldots(46)$$

The consistency of the solution may be determined by evaluating $B''E^2$ and then determining the frequency displacement of the component corresponding to some other value of M and comparing with observations. Sometimes Eq. (46) does not lead to an integral value of M (particularly if M is very large) due to experimental errors. In such a case certain limits are imposed upon the smaller J involved in the transition.

Case (b): For this degenerate case one may observe that

$$(\Delta\nu_M) - (\Delta\nu_{M\pm1}) = \pm F''E \quad \ldots(47)$$

so that

$$M = \pm\frac{\Delta\nu_M}{\Delta\nu_M - \Delta\nu_{M\pm1}} \quad \ldots(48)$$

As under case (a), consistency is established by comparing the frequency displacement computed from another value of M with the observed spectrum.

Case (c): For this case one readily obtains

$$(\Delta\nu_M)^2 - (\Delta\nu_{M\pm1})^2 = \pm G''^2E^2(2M\pm1) \quad \ldots(49)$$

Proceeding as in case (a)

$$s = \frac{(\Delta\nu_M)^2 - (\Delta\nu_{M\pm1})^2}{(\Delta\nu_{M\pm1})^2 - (\Delta\nu_{M\pm2})^2} = \frac{2M\pm1}{2M\pm3} \quad \ldots(50)$$

solving

$$M = \pm\left(\frac{3s-1}{2-2s}\right) \quad \ldots(51)$$

Formulae for Transition Intensities

The dependence of relative intensities upon the quantum number M usually facilitates the analysis. The relative intensities of the Stark components, for $\Delta M = 0$, are given by[38,39]:

Case 1: For $\Delta J = 0$ (Q-type transitions) the relative intensities are proportional to M^2

$$I \propto M^2 \quad \ldots(52)$$

i.e. the intensities become greater for larger M, as do also the displacements from the no field line. From Eq. (52) it is evident that the component for which $M = 0$ has a vanishing line strength. Hence, under conditions of complete resolution only J Stark components will be observed for case (a) (non-degenerate case) and $2J$ Stark components for cases (b) and (c) (degenerate case) above. From the above discussion one can easily get the relation for $\Delta J = 0$

$$M = \pm \frac{(I_M/I_{M\pm1})^{\frac{1}{2}}}{1-(I_M/I_{M\pm1})^{\frac{1}{2}}} \qquad \ldots(53)$$

Case 2: For $\Delta J = \pm 1$ (R- or P-type transitions) the relative intensities of the Stark components are proportional to $(J+1)^2-M^2$ ($\Delta J = +1$) and J^2-M^2 ($\Delta J = -1$) respectively

$$I \propto [(J+1)^2-M^2] \qquad \ldots(54)$$

where J is the smaller of the two J's involved in the transition. In this case no component has zero intensity. The smallest M values have the largest intensity. It can be shown that

$$M = \pm\left(\frac{3t-1}{2-2t}\right) \qquad \ldots(55)$$

where

$$t = \left(\frac{I_M - I_{M\pm1}}{I_{M\pm1} - I_{M\pm2}}\right) \qquad \ldots(56)$$

However, a factor of $\frac{1}{2}$ must be applied to those transitions for which $M = 0$.

Thus examination of Stark components allows a rather direct determination of M and thus the lowest J value involved in the transition and of whether or not J changes. In practice, the formulae involving frequency displacements yield somewhat better results since the frequency can be measured more accurately. Eqs. (53) and (55) may then be used to check the results so obtained. Moreover, the frequency displacements and relative intensities measurements give two entirely different kinds of information about the transition giving rise to the spectral line under observation. The frequency displacement measurements give information dealing with the degeneracies among the symmetric rotor levels and information leading to a determination of the quantum number J corresponding to the lower energy level. The relative intensity measurements give more pertinent information pertaining to the transition itself (i.e. whether $\Delta J = 0$ or $\Delta J = \pm 1$).

The spectrum of an asymmetric top molecule is, in general, quite complicated and one of the most difficult and also the most important stage in the analysis of the spectrum is the identification of the transitions. The information given by the Stark effect is a very valuable guide in making an assignment in this case too. However, in the case of asymmetric top molecules, it is simpler to establish an assignment on the Q-branch transition than on the R- or P-branch by its Stark pattern because a Q-branch transition is given by

$$\nu = \left(\frac{A-C}{2}\right)\Delta E(\mathrm{K}) \qquad \ldots(57)$$

and, thus, this formula has only two parameters $(A-C)/2$ and K while a R- or P-branch transition involves three parameters. A Q-branch transition can often be distinguished from the R- or P-branch transitions, as discussed above, even if it is not resolvable. Further, some idea of the transition's J value can be obtained even though it cannot be fully resolved. In general, a Q-branch Stark effect has the following characteristics.

As one increases the electric field strength, the Stark lobe maximizes in height and then at higher fields begins to flatten out. By comparing the size of the maximum Stark lobe height to the height of the parent line, it is possible to order the Q-branch transition in J. The larger the ratio of the maximum Stark lobe height to the line height the lower the J.

An excellent method of counting Stark components can be used with the help of a recorder. The klystron frequency is fixed at the point where the Stark lobe, under the influence of the electric field, just begins to break up. Then by recording the trace obtained when the Stark voltage is turned up the number of lobes can be given a minimum assignment in J.

Other Methods

Since the spectrum of an asymmetric top is quite complicated, all possible auxiliary information should be utilized in making an analysis. A major help is the Stark effect. However, other methods are also used for establishing an assignment.

The usual method of establishing a Q-branch assignment is to guess an assignment and then check it by plotting $(A-C)$ versus K (ref. 40). In a Q-branch transition the difference in energy of the two levels depends only on the two parameters $(A-C)$ and K. It is possible, therefore, to plot for each observed transition (in general, one has a rough idea of the structure of the molecule one is studying and can tell which Q-branch transition will be observable and in which region) the value of $(A-C)$ calculated as a function of K and lines correctly assigned should all intersect at the correct values of these two quantities. This assignment can later be confirmed by the quantitative Stark effect measurements. The frequencies of all transitions with $\Delta J = 0$ may then be predicted from these values of $(A-C)$ and K, and assignments made for all further observed lines of this type. The precise values of $(A-C)$ and K may be determined from an enlarged plot of the transitions of low J values of the region of intersection. It is interesting to note here that the transitions with higher rotational energies would be expected to have their moments of inertia altered by centrifugal distortion and due to the presence of centrifugal distortions the curves do not intersect at quite the same point. For practical purposes, however, these distortions can be neglected. Once $(A-C)$ and K are thus established, identification of any low J, P- or R-branch transition yields $(A+C)$ and hence all the term values. However, this technique is very time consuming and a much shorter method has been given by Tabor[41] for accomplishing the same result.

Suppose one has two Q-branch transitions ν_1 and ν_2. They can be written

$$\left.\begin{aligned} \log \nu_1 &= \log\left(\frac{A-C}{2}\right) + \log\,[\Delta E(\mathrm{K})]_1 \\ \log \nu_2 &= \log\left(\frac{A-C}{2}\right) + \log\,[\Delta E(\mathrm{K})]_2 \end{aligned}\right\} \qquad \ldots(58)$$

By subtracting one from the other

$$\log \nu_1 - \log \nu_2 = \log\,[\Delta E(\mathrm{K})]_1 - \log\,[\Delta E(\mathrm{K})]_2 \ldots(59)$$

Eq. (59) shows that if one makes a plot of log [ΔE(K)] versus K then the assignment can be obtained by finding the point where the vertical {log [ΔE(K)] axis} distance between the curves is equal to {log ν_1—log ν_2}. The K value is then given by the horizontal (K-axis) distance. If one can roughly guess the assignments, then a log [ΔE(K)] versus K plot can be made over a suitable range. It is to be noted that no knowledge of the actual frequencies is involved in such a plot. The time saved in this technique over the other techniques is huge. However, a better and convenient method of using this technique is to plot log [ΔE(K)] versus K for a number of transitions. The measured frequencies are marked off on a strip of paper using the same vertical scale. The strip of the paper is moved about on the graph, always keeping the strip parallel to the vertical axis of the graph, until the marks on the strip of paper line up with the curves on the graph. The distance on horizontal axis for this point is then the actual K value.

If one has a molecule with strong lines and clear Stark effect then probably the best would be to study the Stark effect quantitatively and establish the assignment. If, on the other hand, one is studying a molecule, which has weak lines and poor Stark effect, then the best technique would be to measure as many lines as possible that seem to have correct qualitative Stark effect and intensity and then to establish the assignment on log [ΔE(K)] versus K plot.

Determination of Molecular Dipole Moments

In addition to aiding in identification of transitions and providing a good means of modulating microwave lines for detection, the Stark effect affords a very accurate and convenient means of measuring molecular dipole moments since its size depends on the product of the dipole moment and the electric field strength. The determination of molecular electric dipole moments from a study in the microwave region, of the splitting of rotational energy levels by an electric field, has a number of advantages over the other methods. First of all, the moment is determined for a certain vibrational and rotational state and is not the average over all states as is done by other techniques. The variation of charge distribution and molecular shape with vibrational and centrifugal distortion may, therefore, be studied. The chemical purity of the sample is no longer any important requirement. Actually, since the sample is examined as a dilute gas and the rotational transitions of different substances are quite easily observed and resolved, 'impurities' may be more abundant than the sample and the molecule of interest may be decomposing at a fairly rapid rate without seriously inconveniencing the microwave measurements. Microwave measurements are made at a pressure of approx. 0·01-0·001 mm. of mercury and many substances (even a larger variety of involatile substances) may be studied in the vapour state which by other methods would have to be examined in solution, with the consequent complication of solvent effects. The microwave method has special advantages for molecules having small dipole moments, since in these cases the fractional accuracy remains the same, i.e. one per cent or less. The dipole moments as small as 0·1 Debye can be measured with the same accuracy as larger ones by this method, while large uncertainties arise when small dipole moments are measured from the temperature dependence of the dielectric constant.

If the electric field E (which must be a uniform field) is known and the transition is identified, then the molecular dipole moment μ may be determined by measuring $\Delta\nu$, the magnitude of the changes in frequency due to the Stark effect. However, transitions from which the dipole moment is to be estimated should be possibly those with fairly straightforward and large Stark effects. They should be as near pure first or second order as possible, and with the minimum of complication from hyperfine interactions. An appropriate one of the various expressions, applicable to different types of the molecules, developed earlier, is, however, needed to connect the measured Stark shift, $\Delta\nu$, with the quantity μE. For molecular dipole moment determinations the Stark shift of a particular transition is measured for several different field strengths. If this Stark shift is plotted against E^2 (for linear or asymmetric molecules) or E (for symmetric molecules), a straight line is obtained whose slope gives the coefficient of E^2 or E accordingly and hence gives the value of μ.

In the case of linear molecules the Stark shift, $\Delta\nu$, is linearly proportional to E^2. The Stark shift is measured for several different field strengths and when plotted against E^2 gives a straight line whose slope gives the coefficient of E^2 in Eq. (19) from which the value of μ can be computed easily.

The case of a symmetric molecule without hyperfine structure is very simple. When $K \neq 0$, Eq. (24) may be used. The Stark shift is linearly proportional to E as long as the Stark displacement is not very large, so that the second-order terms in E^2 are negligible. The plot of $\Delta\nu$ against E is a straight line whose slope gives the coefficient of E in Eq. (24). However, if $K = 0$, then the Stark shift is proportional to E^2 and when $\Delta\nu$ is plotted against E^2 a straight line is obtained whose slope gives the coefficient of E^2 in Eq. (19). In case hyperfine structure is present, similar measurements are made, but interpretation of Stark shifts is to be made from the expressions taking into account the hyperfine structure.

The dipole moments of asymmetric molecules can also be determined with the help of Stark effect. If the molecule has sufficient symmetry so that the direction of the dipole moment can be assumed along one of the principal axes, calculation of the coefficient of μ^2E^2 is made from Eq. (28) and μ is easily evaluated. In the case of asymmetric molecules for which the dipole moment does not lie along one of the principal axes of the molecule and the direction of the dipole moment is not known, the Stark interactions are rather more complicated than for other molecules. In this case, the stark shifts of a sufficient number of lines (arising from a-, b- and c-type transitions) are measured and the several measured coefficients of

E^2 are used to evaluate the various components of μ along principal axes, and from these the total dipole moment is computed. This case is not common, but when it occurs, the direction of the dipole moment in the molecule may be established from the Stark measurements while other techniques usually measure the magnitude only.

Molecular dipole moment determinations involve the measurements of the electric field strengths and frequency shifts of spectral line components, and it is desirable to measure these two parameters to within the same degree of precision. In order to measure the splitting, $\Delta\nu$, accurately, it is necessary to ensure that the Stark components are sharp. Their width will always be increased compared with no field line, because of the lack of uniformity of the electric field and is usually more marked at high field strengths. Hence, the field is kept as uniform as possible by careful design[42], and its magnitude may be obtained by calibration with a substance whose dipole moment is known accurately. Usually carbonyl sulphide (OCS) is used as a calibrant (μ in the vibrational ground state $= 0{\cdot}7124 \pm 0{\cdot}0002$ Debye units[42]) since its $J = 1 \rightarrow 2$ transition is very intense and shows two clear second-order Stark components.

Summary

The existing theories for the Stark splitting of the microwave rotational lines due to the application of an external electric field have been reviewed. The method of determining the dipole moment of a molecule from the observed splitting is illustrated with suitable examples. The use of Stark effect in the identification of rotational transitions is explained and other methods for this are also discussed in some detail.

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The Structure & Stereochemistry of the Diterpenoid Enmein*

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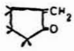
ENMEIN is the main bitter principle of the leaves of *Isodon trichocarpus* Kudo and *I. japonicus* Hara (Fam. Labiatae), both of which are morphologically very similar except for the colour of flowers, and is a common household medicine in Japan for gastrointestinal disorders.

Japanese name of this plant medicine is 'enmei-so' which means that the drug is effective for prolongation of one's life. Isolation of enmein from this plant material was reported in 1958 independently and simultaneously by three research groups at the universities in Kanazawa, Kyoto and Osaka respectively, and the name enmein came from the Japanese name of this plant medicine[1-3].

Earlier Investigations on the Structure of Enmein

The structural investigation of enmein was carried out first in competition by these three groups. The molecular formula, $C_{20}H_{26}O_6$, indicated that the compound must belong to a diterpenoid. The infrared spectrum indicated the presence of a hydroxyl, a carbonyl and an exocyclic methylene group in enmein. The ultraviolet spectrum showed an absorption at 232·5 mμ indicating the presence of an α,β-unsaturated carbonyl in the molecule. The group at the Kyoto University suggested in 1960 the partial structure (I) for enmein based on the above spectral properties[4]. The presence of an exocyclic methylene group in enmein was proved by ozonolysis which gave formaldehyde[2]. In 1961, Kanatomo[5] at the Kanazawa University undertook the baryta distillation of enmein employing a large amount of the material, and isolated a hydrocarbon, $C_{16}H_{24}$, which has been shown by degradative and synthetic methods to have the structure (II). He also carried out the selenium dehydrogenation of the lithium-aluminium hydride reduction product of enmein and isolated retene (III) in minute amounts[6]. On the basis of these findings, he suggested that enmein might have the skeleton of phyllocladene[6] (IV).

On the other hand, the research group at the Osaka City University reported that enmein contained a hemiacetal moiety, and a 1,3-dihydroxycyclohexane ring, and added that one of the hydroxyl groups took part in forming a lactone ring. Combination of their own findings with those so far published led them to propose the structure (V) for enmein[7]. However, some parts in this structure seemed to merit reinvestigation. For instance, while the hemiacetal ring in this structure (V) is seven-membered, bisdehydrodihydroenmein, an oxidation product of dihydroenmein, exhibited an IR absorption at 1770 cm.$^{-1}$ which should be assigned to a five-membered lactone.



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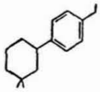

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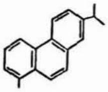

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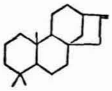

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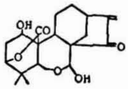
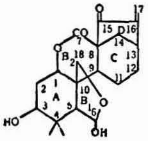


V



VI

Structure of Enmein

During the fifth national symposium on the chemistry of natural products held at Sendai in 1961, all the members of various research groups engaged in research on the elucidation of the structure of enmein decided to continue the investigations as a joint project. After a few years the cooperative efforts led to the structure (VI) for enmein[8,9]. Essential part of the chemical evidence secured in the course of the joint work can be summarized as follows:

(1) Chromic acid oxidation of dihydroenmein (VII) in acetic acid afforded bisdehydrodihydroenmein (VIII) which exhibited two new carbonyl bands in the IR spectrum along with those of the starting material. One of the new carbonyl absorptions at 1770 cm.$^{-1}$ indicated the presence of a γ-lactone moiety in this oxidation product. The *gem*-dimethyl signals in the NMR spectrum of dihydroenmein (VII) was shifted to the lower field (τ 8·61 and 8·56) on oxidation to bisdehydrodihydroenmein (VIII), showing that the *gem*-dimethyl group was adjacent to the hydroxyl group in the six-membered ring of dihydroenmein (VII).

(2) Hydrolysis of bisdehydrodihydroenmein (VIII) in very dilute alkaline solution resulted in cleavage of one lactone ring followed by β-elimination of the elements of water, giving a carboxylic acid (IX) containing an α,β-unsaturated ketonic function. This part of the structure was proved by the NMR spectrum which exhibited two olefinic protons of an AB-type quartet at τ 3·24 and 3·92. The carboxyl group in this compound could readily be decarboxylated, showing that this is in a β-position to a carbonyl group.

(3) Treatment of dihydroenmein (VII) in ethanol or methanol with hydrochloric acid gave the ethyl (X) or the corresponding methyl ether. These ethers easily reverted to dihydroenmein (VII) on heating with aqueous acid. It is obvious that the

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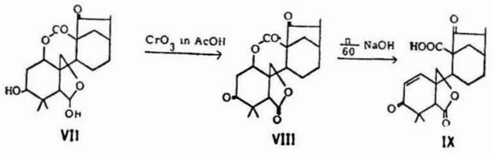
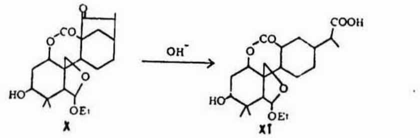
ethers are acetals and accordingly dihydroenmein (VII) contains a hemiacetal moiety. Alkaline treatment of the acetal (X) gave a carboxylic acid (XI) (reversal of the Dieckmann reaction) which no more contained the five-membered ketone. This experimental result confirmed the above assumption that the lactone carbonyl is in a β-position to the five-membered ketone in (VII). These findings and additional evidence[8,9] led us to propose the now accepted formula (VI) for enmein. There remained, however, some uncertainties concerning this structure. Especially, the skeleton of this diterpenoid was preferable to be established more conclusively.

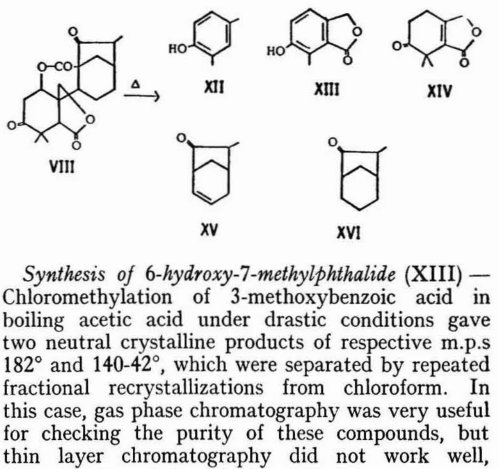




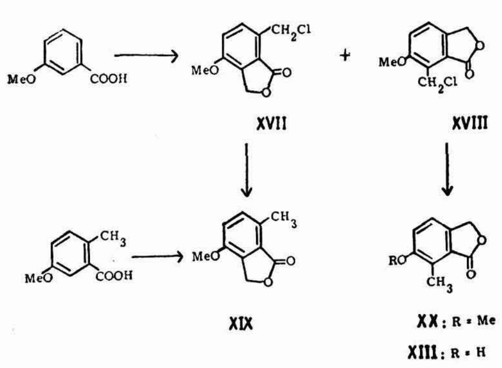
Thermal Decomposition of Bisdehydrodihydroenmein

To obtain a convincing clue for the skeletal structure of enmein, we have carried out thermal decomposition of bisdehydrodihydroenmein (VIII) which has obviously the same skeleton as enmein (VI) by applying the procedure used by Ruzicka *et al.*[10] for elucidating the structure of triterpenoids. On heating bisdehydrodihydroenmein in a sealed tube under reduced pressure at 350-60°, neutral, phenolic and acidic fractions were obtained. Of these, the oily phenolic product was easily characterized as the crystalline 3,5-dinitrobenzoate and shown to be 2,4-xylenol (XII). Crystallization of the acidic fraction gave a compound, $C_9H_8O_3$, m.p. 260-65°, which showed in the IR spectrum a hydroxyl band at 3240 cm.$^{-1}$ and a carbonyl band at 1720 cm.$^{-1}$, indicating the presence of a five-membered lactone of a phthalide type. The presence of a hydroxyl group was also supported by the NMR spectrum of this compound which showed a decrease of one proton by H-D exchange with deuterium oxide. In addition, the NMR spectrum showed a signal due to one methyl group attached to a benzene ring at τ 7·15. These facts and the isolation of 2,4-xylenol (XII) led us to assign the structure (XIII) to this compound.

Next, the neutral fraction was separated into two portions by column chromatography in ether on alumina. The first eluate contained two compounds as revealed by gas phase chromatography and gave two 2,4-dinitrophenylhydrazones, the molecular formulae of which differed only by two hydrogen atoms. Hydrogenation of this oily mixture gave a pure compound which was identical with one of the above compounds as shown by gas chromatography. The infrared spectrum of this oil showed a carbonyl band of a five-membered ring ketone at 1730 cm.$^{-1}$ and the NMR spectrum exhibited a signal for a secondary methyl at τ 8·85. From the above data and high possibility that enmein would have a skeleton related to phyllocladene, we proposed the structure (XVI) for this oily ketone. The semicarbazone of the ketone had m.p. 193-97° and $[\alpha]_D$ +106·5°. The second eluate gave a compound which had an empirical formula, $C_{10}H_{12}O_3$, and showed in the UV spectrum an absorption maximum at 215 mμ (ϵ 9600) and in the IR spectrum two carbonyl bands at 1753 and 1715 cm.$^{-1}$ and a weak band at 1678 cm.$^{-1}$ which was assigned to a double bond. Therefore, this compound must contain one α,β-unsaturated γ-lactone group and one strain-free ketonic group, which may be in a six-membered ring. NMR spectrum of this compound showed no signal due to olefinic protons but a singlet for a *gem*-dimethyl group at τ 8·59 and a singlet for two protons on the carbon bearing a lactonized hydroxyl function at τ 5·24. This compound was optically inactive. From the above data and the isolation of 2,4-xylenol (XII) and the phenolic phthalide (XIII) from the pyrolysis product, it was concluded that this compound should have the structure (XIV). Thus, we were able to assign the structures to all the compounds obtained by pyrolysis of bisdehydrodihydroenmein. In confirmation of the structures thus proposed, we have now synthesized compounds (XIII), (XIV) and (XVI) as follows.



Synthesis of 6-hydroxy-7-methylphthalide (XIII) — Chloromethylation of 3-methoxybenzoic acid in boiling acetic acid under drastic conditions gave two neutral crystalline products of respective m.p.s 182° and 140-42°, which were separated by repeated fractional recrystallizations from chloroform. In this case, gas phase chromatography was very useful for checking the purity of these compounds, but thin layer chromatography did not work well, since it showed invariably only one spot, even though we tried a variety of adsorbents and solvents for this purpose. Two crystalline products, thus obtained, had the same empirical formula, $C_{10}H_9O_3Cl$, and were isomeric. The product of m.p. 182° showed a carbonyl band at 1755 cm.$^{-1}$ and that of m.p. 140-42° exhibited an IR absorption at 1760 cm.$^{-1}$, indicating that both have a conjugated five-membered lactone ring. NMR spectra of both the compounds showed an AB-type quartet for two aromatic protons at low field, suggesting that each compound had *ortho*-hydrogens in the benzene ring. The assignment of the structures rested on the difference in chemical shift of the protons of the chloromethyl group. Since the protons of the chloromethyl group in (XVIII) are located between two oxygen functions, the chemical shift of the protons should be at the lower field than the same type of protons in (XVII) due to a deshielding effect by these functions. The compound of m.p. 182° showed a singlet at τ 4·86, while that of m.p. 140-42° exhibited a signal at τ 4·94. Based on this finding, structure (XVIII) was assigned to the compound of m.p. 182°. Furthermore, chemical evidence for this structure was provided by catalytic hydrogenolysis of both compounds. By this procedure the compound of m.p. 140-42° gave compound (XIX), identical with the one prepared unequivocally from 5-methoxy-2-methylbenzoic acid, while the compound of m.p. 182° gave the desired compound (XX), which was treated with hydriodic acid to give (XIII), identical in all respects with that obtained by pyrolysis of bisdehydrodihydroenmein.



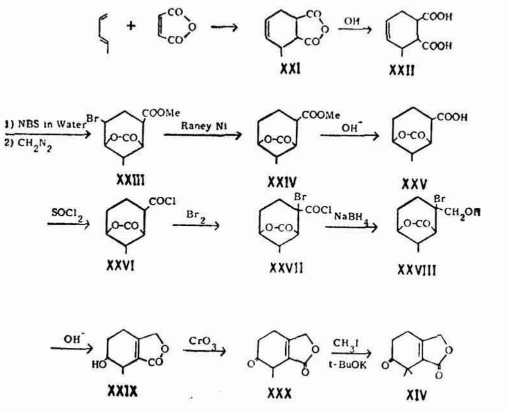


Chart 1 — Reactions describing the synthesis of keto-lactone (XIV)

Synthesis of the keto-lactone (XIV) — The synthesis was accomplished in two ways. In both the cases the Diels-Alder reaction was employed at the starting point. In the first method (Chart 1), the lactone-carboxylic acid (XXV) was obtained by the literature[11] method. Thus condensation of maleic anhydride and 1,3-pentadiene gave the tetrahydrophthalic anhydride (XXI) which was hydrolysed to the corresponding dibasic acid (XXII). The acid was treated with N-bromosuccinimide (NBS) in an aqueous solution and then with diazomethane to give the bromo-lactone-ester (XXIII) which was converted into the lactone-ester (XXIV) by reduction with Raney nickel. Hydrolysis of the ester group in (XXIV) and treatment of the resulting acid (XXV) with thionyl chloride gave the acid chloride (XXVI) which was brominated with bromine in thionyl chloride to give compound (XXVII) which was reduced with sodium borohydride to yield the lactone-bromohydrin (XXVIII). Treatment of bromohydrin (XXVIII) with aqueous sodium hydroxide followed by acidification gave the hydroxy-lactone (XXIX) which showed an UV absorption maximum at 215 mμ, IR absorptions at 3400 (OH) and 1745 cm.$^{-1}$ (α,β-unsaturated γ-lactone), and NMR signal due to a secondary methyl at τ 8·80 having a coupling constant of 7 cps. Since the Bredt rule precludes the possibility of an alternative lactone formation, this hydroxy-lactone must have structure (XXIX). Chromic acid oxidation of (XXIX) gave the keto-lactone (XXX) which showed two carbonyl bands at 1753 (α,β-unsaturated γ-lactone) and 1720 cm.$^{-1}$ (six-membered ring ketone) in the IR spectrum. C-methylation of the keto-lactone (XXX) with potassium *t*-butoxide and methyl iodide afforded a crystalline compound, m.p. 95-98°, which was identical with (XIV), one of the pyrolysis products of bisdehydrodihydroenmein, in m.m.p., UV, IR, and mass spectra, and thin layer and gas phase chromatographies.

In the second method (Chart 2), cyclohexadienedicarboxylate (XXXI), obtained from butadiene and dimethyl acetylenedicarboxylate, was converted into the acid anhydride (XXXII) with anhydrous formic acid and reduced with a calculated amount of lithium-aluminium hydride with cooling in an ice-bath to give the dihydrophthalide (XXXIII) in 50 per cent yield along with the starting material (XXXII), the lactol (XXXIV) and the glycol (XXXV) which were separated by chromatography on silica gel. The starting material was eluted first, then the dihydrophthalide, next the lactol and finally the glycol. The dihydrophthalide (XXXIII) showed a UV absorption at 225 mμ and IR absorptions at 1750 (α,β-unsaturated γ-lactone), 1698 (conjugated double bond) and 1640 cm.$^{-1}$ (isolated double bond). NMR spectrum exhibited a broad singlet for two olefinic protons at τ 4·12 and a broad singlet for two protons on the carbon bearing oxygen at τ 5·22. After confirming the structure by these data, the dihydrophthalide (XXXIII) was treated with NBS as in the first method, to give the bromohydrin (XXXVI). There are two possibilities concerning the positions of the bromine and the hydroxyl group in this compound, and the structure had to be established before the subsequent reaction was undertaken. For this purpose, we oxidized the bromohydrin (XXXVI) with chromic acid-pyridine complex to give a phenolic phthalide (XXXVII). Methylation

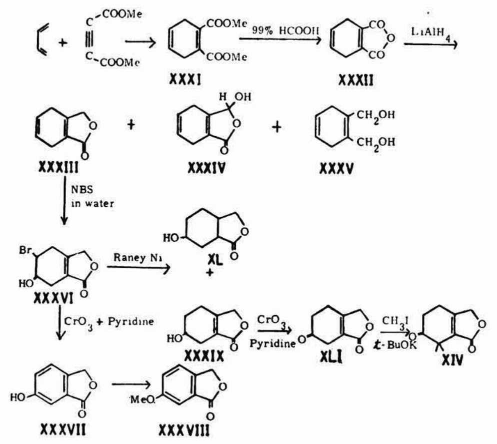


Chart 2 — Alternate scheme for the synthesis of keto-lactone (XIV)

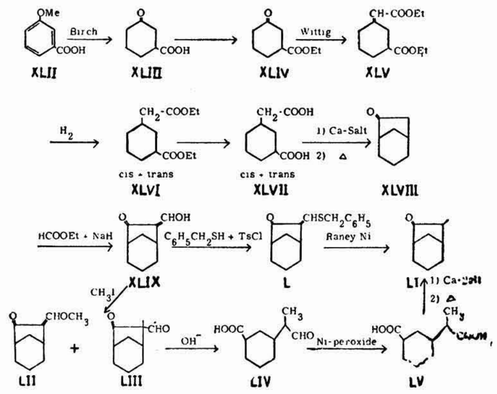


Chart 3 — Synthesis of the racemic compound of 6-methyl-7-oxobicyclo [3.2.1] octane (LI)

of this gave 6-methoxyphthalide (XXXVIII) which was identical with an authentic sample. Thus the structure of the bromohydrin (XXXVI) was established. The isomeric bromohydrin was not isolated from the reaction mixture of (XXXIII) with NBS.

In the next step, the bromohydrin (XXXVI) was treated with Raney nickel to give a mixture which was separated into two compounds by chromatography on silica gel. One of them was compound (XXXIX) (yield 15 per cent) that we expected and was shown to contain a double bond. The other compound (XL) contained no double bond. The hydroxyl group in (XXXIX) was easily oxidized to the corresponding keto-lactone (XLI) which was subjected to C-methylation to yield the identical end product (XIV).

Synthesis of 6-methyl-7-oxobicyclo [3.2.1] *octane* (LI) — Although the compound (XVI) isolated from pyrolysis of bisdehydrodihydroenmein was optically active, the corresponding racemic compound (LI) was prepared as a model compound (Chart 3).

m-Methoxybenzoic acid (XLII) was converted into ethyl cyclohexanone-3-carboxylate (XLIV) in good yield by Birch reduction followed by hydrogenation and esterification. The keto-ester (XLIV) was treated with ethoxycarbonylmethyldiethylphosphonate in the presence of sodium hydride employing the modified Wittig reaction to give the cyclohexylideneacetate (XLV). Hydrogenation of the diester (XLV) afforded a mixture (XLVI) consisting of *cis*- and *trans*-isomers with regard to COOEt and CH$_2$COOEt groups in the ratio of 13 to 10 as calculated from the integration of the peaks on gas phase chromatogram. However, separation of this mixture was not successful. The separation could be achieved by the hydrolysis of the diesters (XLVI) into the corresponding acids (XLVII) which were separated by fractional crystallization. The melting points of these acids were in good agreement with those reported in literature[12]. It was first thought that only *cis*-diacid would be cyclized to the bicyclooctanone (XLVIII), while the *trans*-isomer would be recovered unchanged on attempted pyrolytic cyclization of its calcium salt. In fact, the *cis*-diacid gave the bicyclooctanone (XLVIII) in good yield. But we found that the *trans*-isomer could also undergo cyclization, probably after epimerization of the carboxyl group. Therefore, we could use the mixture of *cis*- and *trans*-isomers in pyrolytic cyclization. Introduction of a methyl group to the carbon adjacent to the carbonyl in (XLVIII) was accomplished in two ways. (i) Treatment of (XLVIII) with ethyl formate in the presence of sodium hydride gave the formyl derivative (XLIX), which was converted into its thioether (L) using benzylmercaptan and tosyl chloride. Hydrogenolytic desulphurization of (L) with Raney nickel gave a very volatile compound (LI) which was characterized through its semicarbazone. The IR spectrum of this semicarbazone in chloroform was superimposable upon that of the pyrolysis product (XVI) of bisdehydrodihydroenmein. (ii) An alternative pathway to the same compound (LI) was worked out as follows: Treatment of the formyl compound (XLIX) with methyl iodide and alkali gave both the O-methyl (LII) and the C-methyl (LIII) derivatives which were separated by shaking with an alkaline solution after saponification of the enol ether (LII) with hydrochloric acid. In order to remove the formyl group from (LIII), it was treated with a concentrated alkaline solution. By this procedure, however, the five-membered ring was cleaved, giving the aldehyde acid (LIV). Hydrolysis of the keto-aldehyde (LIII) with hydrochloric acid in place of alkali gave the same compound as above, as a result of reversal of the Claisen type condensation. The aldehyde acid (LIV) was oxidized with nickel peroxide to the diacid (LV) which was on pyrolysis of its calcium salt easily cyclized to give the bicyclooctanone (LI), identical in all respects with the sample obtained by the first method.

Synthesis of optically active (LI) — The synthesis of the optically active form of the above bicyclooctanone (LI) (Chart 4) was achieved starting from (—)-3-oxocyclohexanecarboxylic acid (LVII) which was obtained by resolution of (LVI) through the brucine salt. The ORD curve (Fig. 1a) of the

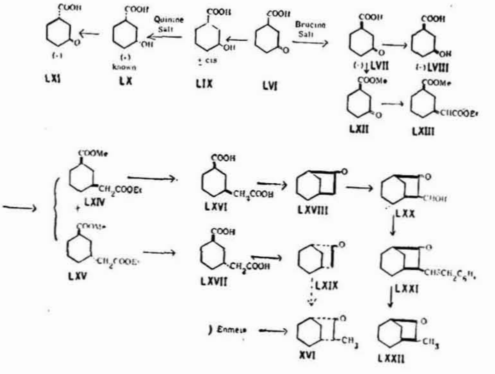


Chart 4 — Synthesis of optically active bicyclooctanone (LXXII)

acid (LVII) had a positive Cotton effect and according to the octant rule this acid should have the absolute configuration as represented by formula (LVII). This deduction was confirmed chemically as follows.

The (−)-3-oxocyclohexanecarboxylic acid (LVII) was hydrogenated to give a mixture of *cis*- and *trans*-hydroxy acids. Fractional crystallization of the mixture from chloroform gave (−)-*cis*-3-hydroxycyclohexanecarboxylic acid (LVIII), m.p. 133-34°, $[\alpha]_D$ −8·98° in good agreement with the data reported in literature[13]. On the other hand, catalytic hydrogenation of the racemic 3-oxocyclohexanecarboxylic acid (LVI) over Adams catalyst, separation of the resulting mixture of *cis*- and *trans*-3-hydroxycyclohexanecarboxylic acids by fractional crystallization from chloroform, and resolution of the *cis*-hydroxy acid (LIX) through the quinine salt afforded (+)-*cis*-3-hydroxy acid (LX) whose absolute configuration has been firmly established[14,15]. The (+)-hydroxy acid (LX) and the (−)-hydroxy acid (LVIII) which we obtained from (−)-keto acid (LVII) were identical in all respects except for the sign of the optical rotation, and the ORD curves of the two acids (LVIII and LX) exhibited antipodal plain curves, as expected. Oxidation of the (+)-hydroxy acid (LX) gave (+)-keto acid (LXI) which showed a negative Cotton effect (Fig. 1b). There is no doubt, therefore, that the (−)-keto acid (LVII) has the absolute configuration as predicted.

The (−)-keto acid (LVII) was esterified and the ester (LXII) subjected to the Wittig reaction. The double bond in the resulting diester (LXIII) was hydrogenated to give a mixture of *cis*- (LXIV) and *trans*- (LXV) isomers. The mixture was hydrolysed and the resulting acids separated into *cis*- (LXVI) and *trans*- (LXVII) isomers by fractional crystallization. Differentiation between *cis*- and *trans*-acids was achieved by comparison of the retention times of the respective esters (LXIV and LXV) on gas chromatogram with those of the racemic esters whose configurations are known. Cyclization of the (−)-*cis*-dicarboxylic acid (LXVI) in the usual manner gave 7-oxobicyclo [3.2.1] octane (LXVIII), which was characterized as its semicarbazone, m.p. 188-89°, $[\alpha]_D$ −31·6°. On the other hand, when somewhat crude (−)-*trans*-dicarboxylic acid (LXVII) was used, enantiomeric 7-oxobicyclo [3.2.1] octane (LXIX) was obtained; semicarbazone m.p. 183-85°, $[\alpha]_D$ + 7·4°. The ORD curves of this pair of bicyclooctanones are shown in Figs. 2a and 2b. The curves are approximately mirror images of one another. It may be worth while noting that if a mixture of equivalent amounts of *cis*- (LXVI) and *trans*- (LXVII) acids was used for the cyclization, the racemic modification (XLVIII) of the bicyclooctanone was obtained.

In view of this result, it is almost certain that the *trans*-diacid (LXVII) can cyclize only after epimerization of the carboxyl group attached to the cyclohexane ring. As we could not secure a sufficient amount of (−)-*trans*-dicarboxylic acid (LXVII) to proceed to the end product, we continued our synthetic work using 7-oxobicyclooctane (LXVIII) derived from (−)-*cis*-dicarboxylic acid (LXVI). Treatment of the octanone (LXVIII) with ethyl formate gave the formyl derivative (LXX), which was then converted into the thioether (LXXI). The thioether (LXXI) was then treated with Raney nickel to give the end product, 6-methyl-7-oxobicyclo [3.2.1] octane (LXXII) which was characterized as its semicarbazone, m.p. 195-97°, $[\alpha]_D$ −100°. Comparison of (LXXII) with the compound (XVI) from natural sources established that they are enantiomeric. Since the absolute configuration of the synthetic compound has been established, the bicyclooctanone ring of enmein is represented by formula (XVI). This

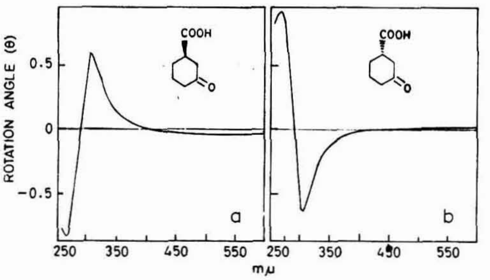


Fig. 1 — (a) Optical rotatory dispersion curve of (−)-oxocyclohexanecarboxylic acid (LVII) and (b) of its enantiomer (+)-keto acid (LXI) showing negative Cotton effect

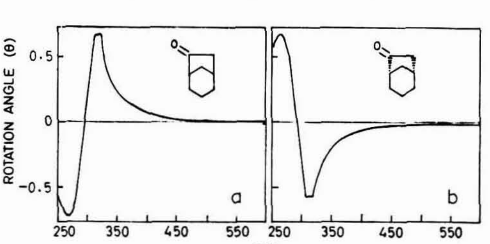
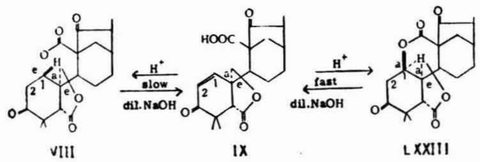


Fig. 2 — (a) Optical rotatory dispersion curve of 7-oxobicyclo [3.2.1] octane (LXVIII) and (b) of its enantiomer (LXIX)



conclusion is in accord with that deduced from the ORD curve of enmein[9].

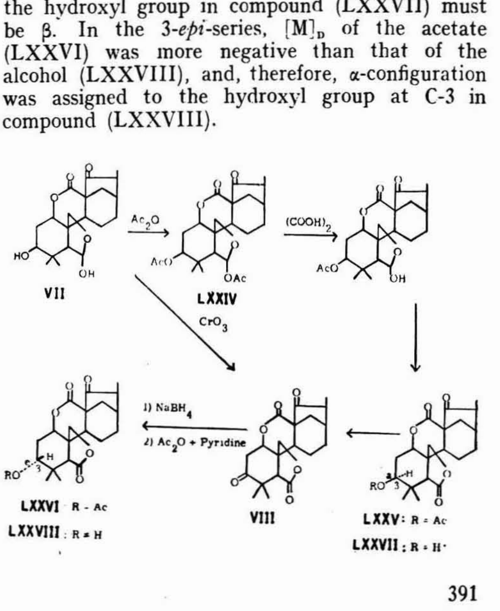
Thus, we have conclusively established the structures and stereochemistry of all the compounds isolated from the pyrolysis of bisdehydrodihydroenmein. From a study of these and a vast body of evidence mentioned earlier, we now are able to deduce the complete structure of enmein on a more convincing basis as represented by formula (VI).

Stereochemistry and Absolute Configuration of Enmein

With the establishment of the structure of enmein by degradative and synthetic methods, we now wish to discuss the stereochemistry and absolute configuration of this diterpenoid.

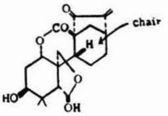
The configuration at C-1 in enmein has been established by interpretation of the NMR spectra of bisdehydrodihydroenmein (VIII) and isobisdehydrodihydroenmein (LXXIII), the latter of which was obtained by the action of acids on the α,β-unsaturated keto acid (IX). When acetic acid alone was used for lactonization of the compound (IX), *iso*-compound (LXXIII) was the sole product, while a mixture of hydrochloric acid, sulphuric acid, or hydriodic acid and acetic acid gave an equilibrium mixture of (VIII) and (LXXIII) in a ratio depending on experimental conditions. Not only the compound (VIII) but also (LXXIII) reverted to the unsaturated keto acid (IX) on treatment with dilute sodium hydroxide. It is, thus, clear that (VIII) and (LXXIII) are stereoisomers with respect to the configuration at C-1. It is accepted as a general rule[16] that in a cyclohexane ring of the chair form, the axial hydrogen gives a signal at higher field than the equatorial hydrogen and that the coupling constants between the axial and equatorial hydrogens and between the equatorial and equatorial hydrogens are nearly equal but are always far smaller than that between the axial and axial hydrogens. NMR spectrum of bisdehydrodihydroenmein exhibited a quartet for a proton attached to C-1 at τ 4·75 and its J_{AX} was about two times as large as J_{BX}. These values indicated that this hydrogen was in the axial orientation and accordingly the C-1—O bond was equatorial. On the other hand, the NMR spectrum of isobisdehydrodihydroenmein showed a quartet due to the proton at C-1 at τ 4·73 and the J_{AX} and J_{BX} values were nearly equal and relatively small. Therefore, this hydrogen is equatorial and the C-1—O bond in this compound (LXXIII) was in the axial orientation. From these results it has become certain that the C-1—O bond is attached to the cyclohexane ring of enmein in the equatorial orientation. Since axial-axial ring juncture is not possible, the C-10—C-9 bond which connects rings A and C in enmein must be equatorial in respect to ring A and consequently the C-10—C-18 bond is in the axial conformation and the C-5—C-6 bond is equatorial. Thus rings A and B_1 are *cis*-fused.

Next the conformation of the hydroxyl group at C-3 was established. For this purpose dehydrodihydroenmein 3-acetate (LXXV) and epidehydrodihydroenmein 3-acetate (LXXVI) which are epimeric with respect to the acetoxyl group at C-3 were prepared. The compound (LXXV) was obtained by partial hydrolysis of diacetyldihydroenmein (LXXIV) with oxalic acid followed by chromic acid oxidation in acetic acid. The compound (LXXVI) was obtained by sodium borohydride reduction of bisdehydrodihydroenmein (VIII) followed by acetylation. Since, in general, sodium borohydride reduction of a ring ketone gives rise to an alcohol with equatorial conformation, the acetoxyl group in the *epi*-compound (LXXVI) was assumed to be equatorial. In confirmation, the NMR spectrum of the *epi*-compound (LXXVI) showed a quartet for the axial hydrogen at C-3 at τ 5·43 with large coupling constants of $J_{AX} = 5·6$ cps and $J_{BX} = 11·5$ cps. In contrast, dehydrodihydroenmein 3-acetate (LXXV) showed a quartet at τ 4·99 with $J_{AX} = J_{BX} = 2·7$ cps for the equatorial proton at C-3. The acetoxyl group at C-3 in compound (LXXV) must, therefore, take an axial conformation. It follows that the hydroxyl group attached to C-3 in enmein is axial. For the assignment of the absolute configuration of this hydroxyl group, the Klein-Stokes rotation rule[17] was applied. According to this rule, the molecular rotation of the acetate must be more positive than that of the alcohol in enmein derivatives if the hydroxyl group has β-configuration and vice versa. Since $[M]_D$ of dehydrodihydroenmein acetate (LXXV) was more positive by 64·05° than that of the alcohol (LXXVII), the configuration of the hydroxyl group in compound (LXXVII) must be β. In the 3-*epi*-series, $[M]_D$ of the acetate (LXXVI) was more negative than that of the alcohol (LXXVIII), and, therefore, α-configuration was assigned to the hydroxyl group at C-3 in compound (LXXVIII).

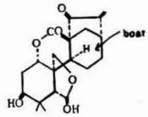


That the hemiacetal hydroxyl group at C-6 is *cis* to hydrogen at C-5 and β-oriented was established by a study of the NMR spectra of enmein and its derivatives. The NMR spectra showed invariably very small coupling constants of the hydrogen atoms at C-6 and C-5. This fact suggested that the dihedral angle of these hydrogens was approximately 90°. In order to take such a dihedral angle, the hydrogen at C-6 must be located *trans* to the hydrogen at C-5 and accordingly the hydroxyl group at C-6 is *cis* to the hydrogen at C-5 and β-oriented. This assumption was supported by the fact that pyrolysis of dihydroenmeindiacetate (LXXIV) gave a vinyl ether as a result of a *cis*-elimination of the elements of acetic acid.

Thus the stereochemistry and the absolute configuration in the moieties of rings A and B_1 in enmein have been elucidated, as represented by the formula (LXXIX) or (LXXX). Since we have already established the absolute configuration of ring D by a synthesis of optically active bicyclooctanone (LXXII) which was enantiomeric with the compound (XVI) from natural sources, the problem remained to be elucidated was concerned with the configuration of the hydrogen atom attached to C-9. The Dreiding model showed that the C-9—C-10 bond must be equatorial in respect not only to ring A but also to ring C. Otherwise the model cannot be constructed due to non-bonded interactions of the atoms on rings A, B_1 and B_2 and rings C and D. Summarizing the above findings two stereochemical structures (LXXIX and LXXX) are now possible for enmein, depending on the boat or the chair form of ring D. However, a choice between these two configurations could not be made until the X-ray crystallographic analysis of a dihydroenmein derivative had been accomplished by Iitaka and Natsume[18] who established that the stereochemistry of enmein was represented by the formulation (LXXIX) or its enantiomer. The absolute configuration of enmein can now be formulated as (LXXIX) based on the evidence presented.



LXXX



LXXIX

It may be noteworthy that very recently two research groups[19,20] in our country have succeeded in the conversion of enmein into (—)-kaurane whose structure and absolute configuration had been firmly established. This conversion constitutes a confirmative chemical evidence for the structure and configuration of enmein and involves a reversal of a probable biogenetic pathway to enmein from a diterpene hydrocarbon, (—)-kaurene.

Summary

The structure and stereochemistery of diterpenoid enmein, a bitter principle of the leaves of *I. trichocarpus* Kudo and *I. japonicus* Hara, and of all the compounds isolated from the pyrolysis of bisdehydrodihydroenmein are discussed. Synthesis of the major products of degradation of bisdehydrodihydroenmein are also described.

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Thermal Decarboxylation*

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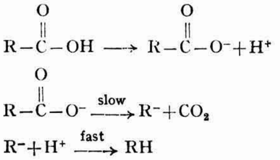
THERMAL decarboxylation has proved to be very useful in both degradative as well as synthetic procedures in organic chemistry. Brown[1] reviewed this subject in 1951 but a lot of information has accumulated since then. Physical chemists have over a number of years used the example of unimolecular decarboxylation of organic acids to illustrate the fundamentals of chemical kinetics. It has, however, been established now that decarboxylation could take place via a bimolecular electrophilic substitution mechanism as well. These two mechanisms, unimolecular and bimolecular, have been called S_E1 and S_E2 after the terminologies of Hughes and Ingold.

Unimolecular Thermal Decarboxylation

There are three possibilities by which organic acids may decarboxylate by a unimolecular electrophilic substitution (S_E1) mechanism. These are: (1) the acid may decarboxylate as its anion; (2) the acid molecule may decarboxylate as such; and (3) the acid may decarboxylate in zwitterionic form.

According to Brown[1] these possibilities are consistent with the following positions of a proton:

(a) Attachment of the proton to the solvent, decarboxylation proceeding in anionic form.

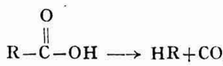


$$R-\overset{\overset{\Large O}{\|}}{C}-OH \longrightarrow R-\overset{\overset{\Large O}{\|}}{C}-O^- + H^+$$

$$R-\overset{\overset{\Large O}{\|}}{C}-O^- \xrightarrow{\text{slow}} R^- + CO_2$$

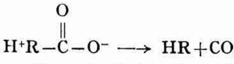
$$R^- + H^+ \xrightarrow{\text{fast}} RH$$

(b) Attachment of the proton to carboxyl oxygen atom, decarboxylation of the acid molecule taking place as such.



$$R-\overset{\overset{\Large O}{\|}}{C}-OH \longrightarrow HR + CO_2$$

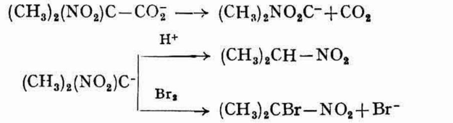
(c) Attachment of the proton to R, decarboxylation taking place via a zwitterion.



$$H^+R-\overset{\overset{\Large O}{\|}}{C}-O^- \longrightarrow HR + CO_2$$

Besides these three individual modes of decarboxylation, the rate data of decarboxylation of an acid may be explained in terms of more than one term involving the concentrations of anion, zwitterion or the undissociated molecule.

The decarboxylation of nitroacetic acid and α-nitro-isobutyric acid has been shown by Pedersen[2] to provide convincing evidence for unimolecular (S_E1) mechanism. Both processes are first order with respect to the anion of the acid and the addition of bromine has no effect on the rate of decomposition of the anions even though the nature of the products is completely changed as shown by the following example:

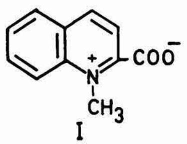


$$(CH_3)_2(NO_2)C-CO_2^- \longrightarrow (CH_3)_2NO_2C^- + CO_2$$

$$(CH_3)_2(NO_2)C^- \begin{cases} \xrightarrow{H^+} (CH_3)_2CH-NO_2 \\ \xrightarrow{Br_2} (CH_3)_2CBr-NO_2 + Br^- \end{cases}$$

This is further substantiated by the fact that 2-nitropropane does not brominate under the conditions of the reaction. Other acids which decarboxylate in an analogous manner are phenyl propiolic acid, 2,4,6-trinitrobenzoic acid, trihaloacetic acids[3,4] and cyanoacetic acid[5]. In these cases, the substituents have very strong electron withdrawing power which helps in the formation of a carbanion.

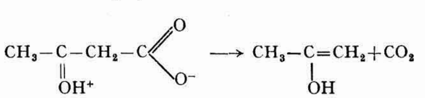
Brown and Hammick[6] showed that the decarboxylation of quinaldic acid proceeds via a zwitterion. The anion in this case is stable and the rate of decarboxylation is proportional to the concentration of the zwitterion and not to the free acid. This view is supported by the fact that the methylbetaine (I) of the acid decomposes very readily.



I

Several other acids, viz. α-methyl, α-2-pyridyl butyric acid[1], 4-pyridyl acetic acid[1], thiazole-2-carboxylic acid[1], 2-thiazolyl acetic acid[1], anthranilic acid[7], pyrazine pyridine dicarboxylic acid[8], and a few other N-substituted carboxylic acids[9] also decarboxylate through zwitterions.

For some acids, the rates of decarboxylation via anion and zwitterion are comparable. β-Keto acids could be placed in this class. The relative rates of decomposition of the anions and of the undissociated acids for several β-keto acids have been measured[1]. Since α,α-dimethyl acetoacetic acid which cannot exist in an enolic form is readily decarboxylated, Pedersen[2] believed that the keto forms of β-keto acids are unstable and, therefore, probably decarboxylate as zwitterions (II).



$$CH_3-\underset{\underset{OH^+}{\|}}{C}-CH_2-C\!\begin{smallmatrix}\nearrow O\\ \searrow O^-\end{smallmatrix} \longrightarrow CH_3-\underset{\underset{OH}{|}}{C}=CH_2 + CO_2$$

(II)

Westheimer and Jones[10], on the other hand, have proposed that in the decarboxylation of α,α-dimethyl acetoacetic acid the intermediate is a hydrogen bonded structure and not a zwitterion as believed by Pedersen[2].

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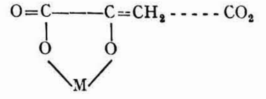
*Published literature up to June 1966 has been considered in this paper.

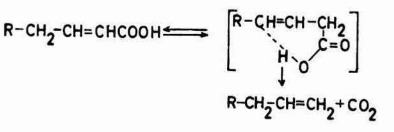
In support of their argument, these workers showed that the rate of decarboxylation of α,α-dimethyl acetoacetic acid is virtually independent of the dielectric constant of the medium.

The rate of decarboxylation of picolinic acid seemed to involve both a hydrogen bonded structure and a zwitterion. Cantwell and Brown[11,12] found it difficult to decide between these two forms of the decarboxylating species in the case of picolinic acid and its methyl derivative.

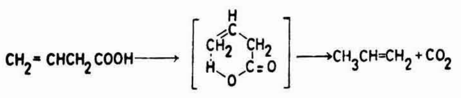
A similar difficulty is encountered by Dunn and Prysiazniuk[13] in the case of substituted anthranilic acid. It has been pointed out by Davies[14] that heavy metal ions exert a strong positive catalytic effect upon the decarboxylation of keto dicarboxylic acids, while the metals have no effect on the decarboxylation of β-keto monocarboxylic acids. Thus the decarboxylation of oxaloacetic acid[15-25], acetone dicarboxylic acid[26-29] and dihydroxy tartaric acid[30,31] has been reported to be catalysed by metal ions, while the rate of decarboxylation of acetosuccinic acid[31] seemed to be hardly affected at all. The rate of decarboxylation of oxaloacetic acid has been best expressed in terms of the concentration of the free acid, monoanion and the bivalent ion[17]. It appears that the metal ion tends to form a chelate[20,21] and decarboxylation proceeds by a transition state:



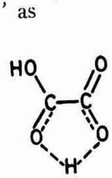
A number of unsaturated acids seemed to decarboxylate via the formation of a cyclic 'transition state'. The first step involved is an αβ to βγ isomerization[32-35], e.g.



Unimolecular vapour phase decarboxylation of 2-butenoic acid[36] also proceeded through a cyclic 'transition state' as



Similarly, Lapidus *et al.*[37] have shown that the vapour phase decarboxylation of oxalic acid is a unimolecular decomposition involving intramolecular hydrogen transfer through the formation of an 'activated complex' as



Bimolecular Thermal Decarboxylation

Decarboxylation of Malonic Acid and Its Derivatives

One of the most exhaustively studied decarboxylation reaction involves malonic acid and its derivatives. In aqueous solutions, Hall[38] found that the undissociated acid decomposed about ten times faster than its equivalent anion $HO_2CCH_2COO^-$, the bivalent ion $^-OOCCH_2COO^-$ not decomposing at all. However, for dibromomalonic acid the analogous anion $HOOCCBr_2COO^-$ decarboxylated readily and the free acid was stable. Substitution by bromine thus seemed to reduce the stability of the anion of dibromomalonic acid so much that its decarboxylation completely masked that of a zwitterion or a hydrogen bonded structure causing it to resemble the trihaloacetic acids in its completely anionic mode of decarboxylation. It might be interesting to consider the decarboxylation of phenyl malonic acid in aqueous solutions[39,40]. The rate data obtained at 45°C. over a range of concentrations and *p*H indicated that the singly charged anion decomposed about three times more readily than the undissociated acid, while the doubly charged anion appeared to be stable.

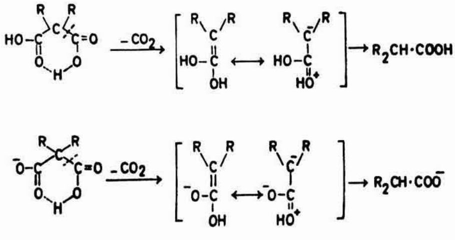
The rate of decarboxylation has been expressed as

$$\frac{d[CO_2]}{dt} = k[H_2A]+k'[HA^-]+k''[A^-]$$

In the *p*H range 4-6, however, the rate was given by

$$\frac{d[CO_2]}{dt} = k'[HA^-]$$

Both the unionized acid and the singly charged anion have been proposed to decarboxylate unimolecularly as shown below.



The decarboxylation of malonic acid in non-aqueous polar liquids has been found by Fraenkel *et al.*[41] to proceed by a bimolecular mechanism. In the rate determining step an electrophilic, polarized carbonyl carbon atom of a carboxyl group unites with an unshared pair of electrons on a nucleophilic atom of the solvent. Thus in quinoline and related media, the mechanism is as shown in Chart 1.

The rate of decarboxylation of malonic acid and substituted malonic acids will, therefore, depend upon the polarizability of the carbonyl carbon atom in the carboxyl group as well as on the nucleophilicity of the solvent. As is evident, these two factors will be controlled by the structure of the solvent and the electronic displacements (due to the inductive, electromeric and inductometric effects brought about by the substituents) in the substituted and

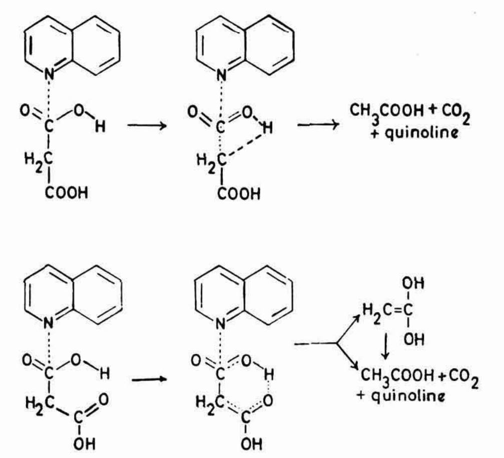
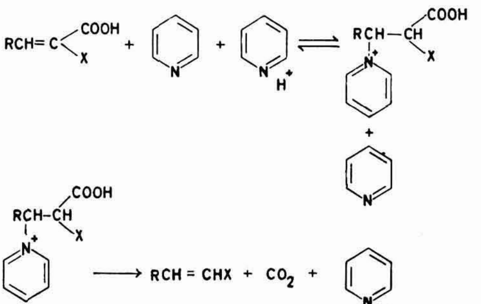


Chart 1 — Mechanism of decarboxylation of malonic acid in non-aqueous polar liquids

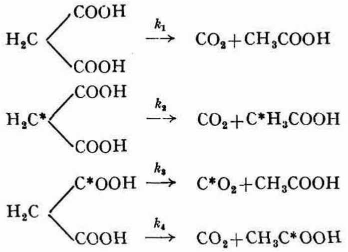
unsubstituted malonic acids as well as the solvents. These ideas have found extensive support in the work of Clark on the rates of decarboxylation of malonic acids in a large variety of solvents. Clark has reported rate data for malonic acid in over fifty solvents of different homologous series, viz. aromatic amines[42-44], aromatic[45] and aliphatic alcohols[46], monocarboxylic acids[47], aromatic nitro compounds[48], ethers[49], thiols[50,51], aldehydes[45], phosphates[52], sulphoxides[53], phenols[50,51] and polyhydroxy compounds[54]. Similar studies have been carried out by the same worker with substituted malonic acids like cinnamyl malonic acid[55], benzyl malonic acid[56], hexyl malonic acid[57-59] and butyl malonic acid[58,59]. The mechanism of decarboxylation in all these cases has been reported to be similar to that for malonic acid. Among a few other examples of the same mechanism are unsaturated malonic acid derivatives, viz. ethyl hydrogen isopropyline malonate[59] and benzylidene malonic acids[60]. In these the mechanism can be indicated as shown below.



β-Resoriylic acid[61], oxalic acid[62-65], oxamic acid[66-68], oxanilic acid[69,70], picolinic acids[71] as well as trichloroacetate ion[72-78] also decarboxylate with similar mechanism. An exception to this general pattern was maloanilic acid[79].

Clark also established the existence of an isokinetic temperature for the decarboxylation of these acids. The isokinetic temperature is the temperature at which the rates of decarboxylation of certain acid are the same in a number of solvents (mostly belonging to the same homologous series) and is arrived at by determining the slope of a line obtained by plotting $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for the decarboxylation in these solvents. A linear relationship between the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in a number of solvents is a proof of the mechanism of decarboxylation being the same in all these solvents[80-82]. It is interesting to note that the isokinetic temperature for the decarboxylation of malonic, oxalic, oxanilic and certain other acids was equal to or very nearly equal to the melting point of these acids.

Decarboxylation of malonic acid has been studied from yet another angle, viz. determining ^{13}C and ^{14}C isotope effects on the rates. Two types of isotope effects have been studied, viz. intermolecular and intramolecular. Considering the decarboxylation of isotopically labelled malonic acid, we can write the rate process as:



$$\mathrm{H_2C}\left\langle\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array}\right. \xrightarrow{k_1} \mathrm{CO_2+CH_3COOH}$$

$$\mathrm{H_2C^*}\left\langle\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array}\right. \xrightarrow{k_2} \mathrm{CO_2+C^*H_3COOH}$$

$$\mathrm{H_2C}\left\langle\begin{array}{l}\mathrm{C^*OOH} \xrightarrow{k_3} \mathrm{C^*O_2+CH_3COOH}\\ \mathrm{COOH} \xrightarrow{k_4} \mathrm{CO_2+CH_3C^*OOH}\end{array}\right.$$

The quantity $(k_1/2k_3)$ is a measure of intermolecular and (k_4/k_3) that of an intramolecular isotope effect. Some of the results of Yankwich *et al.*[83-93] and a few other workers[94-105] are found to be in close proximity to the theoretically predicted values[106-108]. Apart from malonic acid, decarboxylation of oxaloacetic acid[109,110], trinitrobenzoate ion[111], benzylpropionic[112], picolinic[113], quinaldic[114] and oxalic acids[115,116] have also been studied for isotope effects. Such studies extend an explanation for the rate determining step in the decarboxylation as well as a general support for the 'transition state' theory of rate processes. A detailed review on the isotope effect throwing light on the kinetics of reactions has been reported by Halevi[117].

Bimolecular S_E2 Mechanisms

Schenkel and Schenkel-Rudin[118] proposed that some organic acids decarboxylated by a bimolecular electrophilic substitution mechanism

$$H^+ + RCO_2H \rightarrow HR + CO_2 + H^+$$

in which the rate determining step is the attraction of a proton by the carboxylic acid. The kinetics are then governed by the equation

$$\text{Rate} = k[H^+][RCO_2H] \qquad ...(1)$$

Two possibilities arise: (i) the proton may attack the undissociated acid molecule yielding the rate equation given above; and (ii) the proton may attack the anion of the acid,

$$H^+ + RCC_2^- \rightarrow HR + CO_2$$

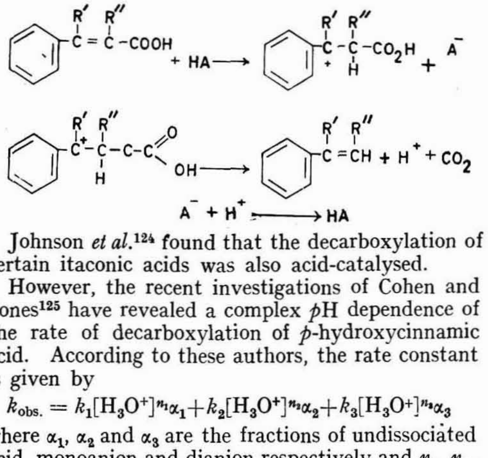
when the kinetic equation will be

$$\text{Rate} = k[\text{RCO}_2^-][\text{H}^+] \qquad \ldots(2)$$

For either mechanism, the rate will be dependent on the attraction between the α-carbon atom of the acid molecule and a proton. Since the formation of the anion will tend to increase the electron density on α-carbon atom, it may be expected that mechanism (Eq. 2) will require less activation energy than the first. It is possible that each of these mechanisms may operate separately or together.

There have been two lines of approach to the study of S_E2 mechanisms: (i) to determine the exact relationship between the rate of decarboxylation and concentration of hydrogen ions; and (ii) to study a number of acids of the same electronic type. As mentioned before, Schenkel and Schenkel-Rudin[118] gave the example of anthracene-9-carboxylic acid to exhibit an S_E2 mechanism. They reported that the decarboxylation of this acid took place more readily in acidic than in basic medium. The decarboxylation of mesitoic acid[119], substituted mesitoic acid[120], trimethoxy benzoic acid[121] and 2,4,6-trialkylbenzoic acids[122] has been reported to be acid-catalysed.

First application of the approach to study the decarboxylation of some acids of the same electronic type was made by Johnson and Heinz[123] who studied a number of substituted cinnamic acids. The order of rates of decarboxylation could be correlated to the electronic effect of the substituents R′ and R″ on the basis of the following S_E2 mechanism.

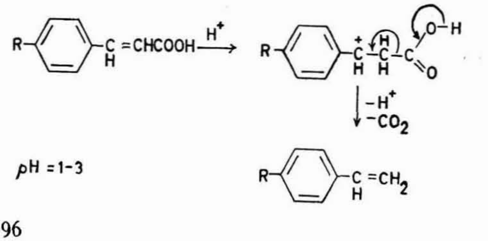


Johnson *et al.*[124] found that the decarboxylation of certain itaconic acids was also acid-catalysed.

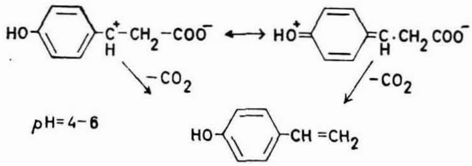
However, the recent investigations of Cohen and Jones[125] have revealed a complex *p*H dependence of the rate of decarboxylation of *p*-hydroxycinnamic acid. According to these authors, the rate constant is given by

$$k_{\text{obs.}} = k_1[\text{H}_3\text{O}^+]^{n_1}\alpha_1 + k_2[\text{H}_3\text{O}^+]^{n_2}\alpha_2 + k_3[\text{H}_3\text{O}^+]^{n_3}\alpha_3$$

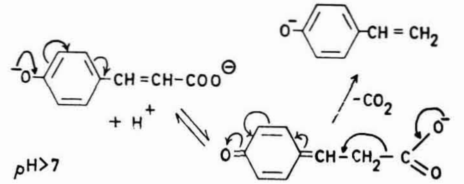
where α_1, α_2 and α_3 are the fractions of undissociated acid, monoanion and dianion respectively and n_1, n_2, n_3 the orders of reaction with respect to H_3O^+ ion for each of the species. The values of n_1, n_2 and n_3 have been reported to be 2/3, 1/2 and 2/3 respectively. The mechanism seems to be as under:



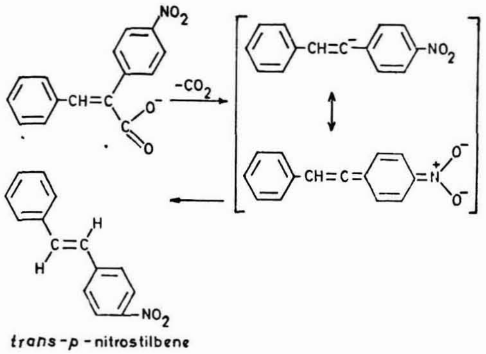
In *p*H range 1-3 a carbonium ion may be an intermediate. In *p*H range 4-6 probably a zwitterion is responsible for the decarboxylation.



In definitely alkaline media, the decarboxylation took place via quinonemethine which is formed by the protonation of the dianion.

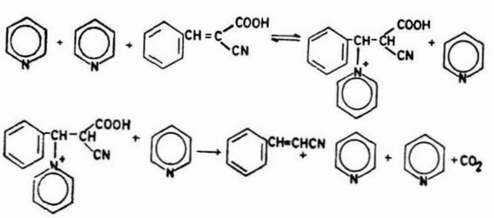


Jambotkar and Ketcham[126] have reported the decarboxylation of α,*p*-nitrophenyl-*trans*-cinnamic acid to take place as shown below.

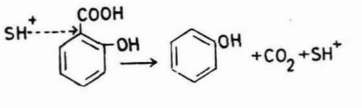


trans-p-nitrostilbene

Decarboxylation of α-cyano- and α-carboxy-cinnamic acids[127] also proceeds by a bimolecular mechanism but seems to be more like unsaturated acids in this respect. Thus in pyridine, the decarboxylation proceeds as shown below.



The rates of decarboxylation of a series of hydroxybenzoic acids were studied by Brown *et al.*[128] under comparable conditions in resorcinol and the results were best explained in terms of a bimolecular S_E2 mechanism. The rates increased and the activation energies decreased in the order benzoic, *o*-hydroxybenzoic, 2,4-dihydroxybenzoic and 2,4,6-trihydroxybenzoic acid which is the order in which the substituents facilitate the approach of a proton to the anionoid α-carbon atom.



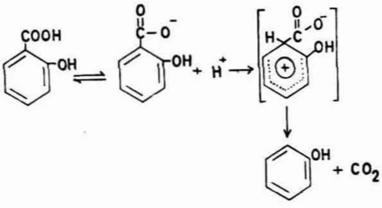
To explain the rate data, attack of a proton on both the unionized acid and the anion has been presumed. A similar example was reported by Pressman and Lucas[129] for the decarboxylation of β-hydroxyvaleric acid.

Brown *et al.*[130] carried out a rather detailed study on the decarboxylation of 2,4,6-trihydroxybenzoic acid. The rate data could be explained in terms of a bimolecular attack of protons on both the acid and the anion of the acid. Activation energy for these processes were 21·5 and 15·2 kcal./mole respectively. The activation energy for the decarboxylation in resorcinol was 13·6 kcal./mole indicating the mechanism in this case to be the attack of a proton on the anion of the acid. Schubert and Gardner[131] extended the study of decarboxylation of 2,4,6-trihydroxybenzoic acid to perchloric acid solutions of concentrations up to 50 per cent. The results were found to be consistent with those obtained in HCl solutions.

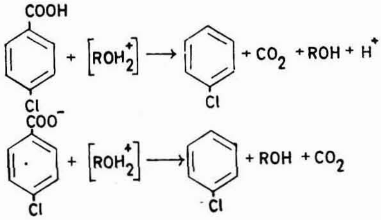
Decarboxylation of substituted as well as unsubstituted salicylic acid has been studied by a number of workers. The rate data for *p*-ammonium salicylic acid[132] and sodium-*p*-ammonium salicylate[133,134] is best explained by assuming simultaneous bimolecular reaction between a proton and *p*-ammonium salicylate ions as well as *p*-ammonium salicylate zwitterion. An interaction between a proton and an anion as well as the acid molecule seems to explain the rate of decarboxylation of 2,4-dihydroxybenzoic acid in water[135] and in D_2O solutions[136]. This is further supported by the studies of Lynn and Bourns[137] on the ^{13}C isotope effect for the same reaction in perchloric acid solutions.

A more detailed investigation on the decarboxylation of substituted salicylic acids has been carried out by Willi[138]. He studied the decarboxylation of 4-methyl, 4-methoxy-, 4-hydroxy- and 4-ammonium salicylic acids in aqueous solutions in the temperature range 50-85°C. The rates were found to be proportional to the product [anion] × [H$^+$]. Bimolecular pseudo first-order rate constants increased and the activation energies decreased with the electron donating power of the substituents.

Consistent with the results of Willi is the recently reported work of Kaeding[139] who studied the decarboxylation of salicylic acid and a number of its derivatives in benzoic acid solutions. The decarboxylation was found to be catalysed by metal salts of benzoic acid. The mechanism is indicated as shown below.



The decarboxylation of 2-hydroxy-1-naphthoic acid[140] and chlorobenzoic acids[141,142] seemed to proceed by a mechanism similar to that of salicylic acid. For *p*-chlorobenzoic acid in glycerol and resorcinol Muhammad[142] reported the mechanism shown below. [ROH$_2^+$] arising from the reaction HA+ROH ⇌ [ROH$_2^+$]+A$^-$.



Addition of aniline minimized the rate which was attributed to the fact that aniline removed the hydrogen ions and thus retarded their attack on the carboxylic acid.

Decarboxylation of Benzoic Acid

It is evident from literature that the decarboxylation of benzoic acid has not received much attention, one of the reasons being that it is an extremely slow reaction. Radiation induced decarboxylation, however, has been studied by Downes[143] as well as Sugimari and Tsuchihaski[144]. Muhammad and Siddiqui[145] studied the thermal decarboxylation of benzoic acid in resorcinol between 255° and 267°C. The kinetic data could be represented as

$$k = 1{\cdot}1 \times 10^{15} e^{-40{,}500/RT}$$

Another study of the same reaction has been made by Bolton[146]. The results indicated that the reaction in the temperature range 150-180°C. was very slow which was in contradiction with the published work of Muhammad and Siddiqui[145]. It was also noticed by Bolton that the pseudo first-order rate constants fell off with the time of reaction.

A study of decarboxylation of benzoic acid in aqueous medium has been carried out in detail (Pande, G. S. & McCallum, K. J., unpublished data) after the method of Conway and Libby[147]. The rate constants fell off as noticed by Bolton mainly due to an impurity, salicylic acid, in the benzoic acid. In one set of experiments the rates of decarboxylation were found by using benzoic acid in which the carboxyl carbon was labelled with ^{14}C and in the other set of experiments, the acid used was labelled with ^{14}C in the benzene ring. In either case at

160°C., the first-order rate constant in water was found to be $2{\cdot}3\times10^{-8}$ min.$^{-1}$ indicating a half-life of the reaction to be about 56 years at that temperature.

Summary

Recent work on the mechanism of decarboxylation of organic acids has been reviewed. Unimolecular thermal decarboxylation through an anion and a zwitterion, metal-catalysed first-order decarboxylation through chelation, bimolecular decarboxylation of malonic acid and its derivatives, S_E2 decarboxylation of hydroxybenzoic acids and their derivatives have been discussed.

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Eighth Seminar on Electrochemistry

The Eighth Seminar on Electrochemistry will be held at the Central Electrochemical Research Institute, Karaikudi, from 26 to 29 December 1967. Among the technical sections to be held at the seminar are: (i) Electrode kinetics, electrochemical equilibria and electroanalyses; (ii) Solid state electrochemistry; (iii) Corrosion; (iv) Electrodeposition and metal finishing; (v) Batteries; (vi) Electro-organic and electro-inorganic products; (vii) Electrothermics and electrometallurgy; and (viii) Techno-economic aspects of electrochemical processes. A special technical session on adsorption at solid electrodes will be held on 28 December 1967.

The last date for the submission of abstracts is 1 December and for full papers 15 December 1967. Further detail can be had from Dr P. B. Mathur, Convener, Eighth Seminar on Electrochemistry, Central Electrochemical Research Institute, Karaikudi 3.

REVIEWS

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

This volume reports the proceedings of a symposium held in Chicago during the annual meeting of the AIME in February 1965. The stated purpose of the symposium, namely to provide a review of the quantitative measurement and interpretation of X-ray diffuse scattering with an emphasis on the advances made during the last decade, seems to be fairly well fulfilled. There are, in all, eleven chapters grouped under two parts. The first part deals with the study of short-range order effects in disordered binary alloys and liquid alloys and the second with the effects of cold work distortion on the X-ray diffraction pattern.

The chapters are all by authors who are competent and active workers in the field. It contains an introduction by Prof. B. E. Warrem, and includes two additional chapters, not presented in the symposium. The volume will be useful to workers in different fields of material sciences, solid state physics, metallurgy, and particularly to those interested in the applied sciences related to the above fields.

R. SRINIVASAN

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

The volume under review comprises the lectures delivered at the First Pacific International Summer School in Physics held in Honolulu in August 1965. It starts with a course on the particle picture in field theory by Haag which touches the very foundations of the subject. The discussions are based on certain basic assumptions of a general nature. These are: (i) quantum physical assumptions regarding (a) an algebra of observables defined by algebraic structure relations like commutation rules and (b) superselection rules which stand in the way of the superposition principle and which are effective in the cases of integral and half integral spins and the electric charge; (ii) Lorentz invariance; (iii) locality and causality (in view of a theorem Zeeman has proved which states that causality implies Lorentz invariance, assumption (ii) appears redundant but this aspect has not been looked into in the literature); and (iv) the spectral condition which states that the vacuum is the lowest eigen state of the energy in Hilbert space and is invariant under all transformations and this together with all other physical states of the universe forms a complete set. A particle description is introduced into true quantum field theory (not the field theory in interaction representation which is really an S matrix theory) by the association that a particle is an asymptotic localization centre. With these assumptions, scattering theory is considered using the generalized LSZ formalism. The lecture ends with a discussion of spontaneous breakdown of symmetries and the Goldstone theorem using the apparatus of C^* algebra.

There are two further articles which are concerned with symmetry-breaking. In the first of these, Miyazawa discusses, with various examples, how spontaneous symmetry-breaking can arise in theories in which the vacuum does not share the symmetries of the Hamiltonian. The problem of the appearance of massless bosons in such cases is considered and the computation of mass-differences among members of a multiplet carried out for various examples.

In the second article, Frautschi considers symmetry-breaking from the point of view of Bootstrap theory. Using the N/D method, the result of a small mass-shift in the exchanged-particle mass is used to compute the corresponding mass-shift in the straight channel and hence the mass-differences of members of a multiplet. The topics dealt with are: (i) the neutron-proton mass-difference; (ii) octet dominance in $SU(3)$ symmetry-breaking; (iii) symmetry-breaking in baryon-baryon-pseudoscalar meson and baryon-decuplet-pseudoscalar meson couplings; and (iv) Bootstrap theory of electromagnetic and weak interactions.

The topic of Bootstrap itself which, in its extreme form, wishes to establish a 'nuclear democracy' among the strongly interacting particles (including nuclei) is dealt with by Zachariasen. The existence and fresh discovery of vast numbers of unstable particles would make such a hypothesis highly desirable. The Bootstrap idea is discussed using simple models and the connection of lack of elementarity in field theory with the $Z_3 = 0$ condition is discussed. The N/D technique arising in practical Bootstrapping problems is described at length. Bootstrapping of Reggeized particles and the origin of symmetries as revealed through the Bootstrap mechanism are the other topics discussed.

Neeman, one of the originators of the unitary symmetry scheme for elementary particles, discusses the symmetries generated by the algebra of the current components and the sum rules that can be derived from them. The failure of unitarility in Salam's $U(12)$ scheme is pointed out and a way out of this by considering certain infinite dimensional representations (which are unitary) of non-compact algebras, some of the generators of which do not commute with the Hamiltonian, is described by considering the analogy of the hydrogen atom and the strong-coupling theories.

In the last article of the book, Moravcsik describes features of particle reactions which are independent of specific assumptions about the forces acting between the particles. The necessary information arises by enforcing the conservation of momentum and energy, angular momentum and the discrete operations C, P, T individually and in combination and the most general form of the amplitudes for particle reactions under these constraints are worked out. Some of the results are stated as theorems which can be verified by experiments in the future.

All the articles in the volume have been written out in detail and hence the volume will be found exceedingly useful.

K. VENKATESAN

ELECTRONIC AUTOMATIC CONTROL DEVICES by A. A. Bulgakov; translated by R. Grabiec & F. Immirzi and edited by P. H. Walker (Pergamon Press Ltd, Oxford), 1966. Pp. xviii+320. Price 35*s*.

The original Russian text, translated by R. Grabiec and F. Immirzi and edited by P. H. Walker, provides a comprehensive review of applications of thermionic and ionic devices to the automatic control and regulation of industrial processes. Although the Russian version was published in 1958, the first English edition appeared in 1966.

Usually, in the case of a scientific text, the necessity for translation into other languages arises when the subject is of topical interest and is likely to benefit immediately the working engineer and scientist. As it happens, between 1958 and 1966 the whole of the electronics and control system technology has undergone a complete change. New devices and techniques have been developed and adopted; even the editor has pointed out the shortcomings of this text in the context of the existing state-of-art. The necessity of translating the text into English is, therefore, not very clear.

The use of thermionic and ionic valves has become almost obsolete and has been superseded by the use of semiconductor devices which have been given very little coverage in the original text. In addition, use of computer techniques for real-time control application from the point of view of automation and efficiency has not been spotlighted.

The general layout of the book also appears to be a little confused. It cannot be considered as a reference book, nor does it formally conform to a text-book, because of the fact that certain portions have been over-emphasized; to make the point, 40 per cent of the written matter has been devoted to applications of thyratrons in control systems. Very little has been devoted to silicon control rectifiers which today have almost completely replaced thyratrons for such applications.

One who is interested in conventional applications for thermionic and ionic valves to control system, the text would be of considerable interest. However, one would have very much appreciated a parallel treatment of the subject in terms of circuits employing semiconductors. The author has tried to make the subject sufficiently exhaustive by introducing topics concerning induction motors, rotary amplifiers and electronic voltage regulators, electronic control in servo and follow-up drives, matched speed regulation for multi-motor drives, etc.

Two chapters, devoted to ' Programmed machine-tool control ' and ' Principles of the design of multi-loop automatic control systems ' respectively, should have taken into account modern techniques of real-time process control which are essentially computer-based systems. An exhaustive bibliography is one of the attractions of the book; in particular, the reference to the Russian literature on the subject.

Everything said, the book is a good addition to the extensive literature in English already available on this interesting topic. In particular, it projects the image of the development in electronic automatic control systems in Russia up to 1956-57. It will be useful to the practising engineer and a student of the subject.

P. K. PATWARDHAN

HYPERSONIC FLOW THEORY : Vol. 1 — INVISCID FLOWS by W. D. Hayes & R. F. Probstein (Academic Press Inc., New York), 1966. Pp. xv+602. Price $ 16.50

This is the first volume of an extensively revised second edition of the volume *Hypersonic flow theory* by the authors. A unified and authoritative account of the basic problems in inviscid hypersonic flow theory is provided by the two authors who have a high reputation in this field. Although of comparatively recent origin, the volume of research on hypersonic flows has grown so rapidly that the material in the first edition had to be broken up into two separate volumes. This volume essentially deals with inviscid hypersonic flow, including non-equilibrium effect past slender, blunt and blunt-nosed slender bodies. The geometrical shapes of the bodies treated are quite general which includes three-dimensional and conical flows.

The book is divided into seven chapters. The first chapter deals with the salient features and assumptions underlying inviscid hypersonic theory, which the reader will find necessary to absorb in order to digest the following chapters. The authors discuss in great depth, in the second chapter, the small disturbance theory and the similitudes, including the non-equilibrium effects. The limitation of the self-similar solutions have been brought out very clearly. The confusion existing in the available literature regarding the entropy wake (the authors own coinage), and the entropy layer due to bluntness effects has been removed. Work as recent as 1964, on the effect of the entropy layer on the asymptotic shock layer properties, has been discussed. It is really gratifying to note that the continental views on this current problem have been given due recognition. Chapters III and IV deal with the Newtonian theory, based on thin shock layer concept and constant density solutions as applied to two-dimensional and asymmetric bodies. In Chapter V, the theory of thin shock layers has been improved to treat general three-dimensional flows; conical flows in particular. Much of the material in this chapter forms the recent work done by Prof. Hayes. Section 5.4 of the first edition, entitled ' Variable stream-tube area approximation ', has been treated in a more rational way for the case of two-dimensional and axisymmetric blunt-faced bodies. The method is essentially a two-layer approach based on asymptotic expansion technique taking into consideration the Bernoulli effect in the inner layer. Chapter VI deals with the numerical computation of blunt-body flows. The method of integral relation developed by Belotserkovskii and Chuskin has been discussed in sufficient detail. Extension to non-equilibrium flows has also been indicated. In Chapter VII, the authors discuss in detail the adaptation of the method of characteristics to hypersonic flows. The improvements in the shock expansion theory within the hypersonic framework have been critically examined. The singularities in the solutions for the conical flow have been treated in detail, and the method of characteristics has been generalized to cover non-equilibrium flows.

The authors have to be congratulated for bringing out such an original and illuminating book. It is a pleasure to recommend this book to the specialist in hypersonics as well as to the advanced students of theoretical aerodynamics, who will find in it a lot of new problems in basic hypersonic flow theory. A comprehensive list of references is appended at the end of the book. Vol. 2 of this book dealing with viscous effects scheduled for 1969 will be eagerly awaited by specialists in this field.

N. R. SUBRAMANIAN

THE THEORY OF EQUILIBRIUM OF ELASTIC SYSTEMS AND ITS APPLICATIONS by C. A. P. Castigliano (Dover Publications Inc., New York), 1966. Pp. lxiv+360+15 plates. Price $ 3.00

This classic book, originally written in French in 1879, was translated into English by E. S. Andrews in 1919. The book was then highly acclaimed by structural engineers as it gave detailed and rigorous proofs of its theorems and a large number of very carefully worked out practical applications.

This long overdue reprint of the 1919 English edition published by Dover in 1966 has its value considerably enhanced by the addition of a biographical portrait section prepared painstakingly by G. A. Oravas. It is very interesting to read through the life history of Castigliano and his various contemporaries as also the historical review of ' Extremum principles in elastomechanics '. It has been very truly remarked by Oravas that " despite the elapsed time, Castigliano's last major work is still one of the most penetrating expositions of structural mechanics based on the principle of work ". The book comprises two parts; Part I consisting of eleven chapters dealing with theory and Part II running from Chapters XII to XXIV and consisting of practical applications. In Part I the various principles and theorems of the theory of elasticity have been described fully and rigorously and illustrated with the help of standard examples. In Part II calculations for tensions, maximum stresses, lines of pressure and effects on stresses due to temperature variation, have been presented in detail. The topics considered in order are framed structures, elastic structures, general equations of the elastic equilibrium of a solid, approximate applications, theory of lattice girders, formulae for the internal work of different solid bodies, theory of straight beams, theory of columns, theory of ribs and arches, theory of composite structures and imperfectly elastic structures, such as masonry arches, studies of beams strengthened by two or three tie-rods and one or two cast iron struts, a roof with iron-trusses without tie-rods, an arched roof-truss with a single tie-rod, a roof-truss of the Poloncean type, an arched roof-truss with several tie-rods or tie-bars (Crescent truss), an iron arch bridge with flat springings or rounded ends, a brick masonry arch bridge and a stone bridge.

Although many standard books, incorporating recent advances in the subject have been published, Castigliano's book still has its own charm and importance. The book is highly recommended to practising structural engineers and others interested in principles of work in elastomechanics and their applications.

AVTAR SINGH

WORLD ENERGY SUPPLIES, 1961-64 (United Nations, New York), 1966. Pp. 99. Price $ 2.00; Rs 12.00

This useful publication — ninth in the series entitled ' World Energy Supplies Statistical Papers Series — J ' by the Department of Economic and Social Affairs, Statistical Office of the United Nations — provides data on the production, trade and consumption of energy in each of the four years 1961-64 for approximately 170 countries. Conveniently grouped into thirteen tabulated statements employing a computerized programme for collection and collation of data, they refer comprehensively to coal (including lignite, where peat is important it is also included), coke, petroleum and its products, natural and manufactured gas and electricity. Data for each type of fuel and summary tables of all fuels together are shown for individual countries and territories and are aggregated into regional and world totals. Metric units have been used throughout.

Comparison of all fuels with one another is made in metric tons of coal equivalent and on the basis of the heat energy which can be obtained from them under ideal conditions; heat energy was taken as the yardstick, since most of the energy sources are put to use after their conversion into heat energy. A point to be borne in mind when expressing the fuel value as coal equivalent is that even among coals the heat content varies widely, depending on their maturity, so that the energy production and consumption equated in terms of coal equivalent introduces a certain fallacy.

In recording the data on production, care is taken to see that double counting is avoided. This is achieved by referring only to the primary sources of energy, such as production of coal and lignite at the mine-head, crude petroleum and natural gas at the oil and gas wells, and hydro, nuclear and geothermal electricity. Processed (secondary) energy sources, such as coke, refinery products, manufactured gas and electricity have not been included in the computation of energy production figures, though data on their production individually are also tabulated for reference. The data tables on consumption refer to ' apparent inland consumption ' which is obtained by subtracting from the total of the production and imports, the sum of exports, addition to stock and bunker fuel supplied to foreign-bound ships and aircrafts. Data related to bunkers are also given separately where possible.

The table on world movement of solid fuels is interesting, indicating the trade bias in fuel procurement by various countries.

Presenting an overall view of the pattern of energy production and consumption statistics, the compilation is a valuable reference volume to students of economics and energy planning in various countries. Compilation of this sort requires appreciable amount of effort. To be authentic, the sources of information have to be reliable and the data obtained have to be checked and rechecked to ensure accuracy. These call for considerable effort and organization. By systematic and regular compilation and publication of such useful data, the United Nations Statistical Office is rendering yeoman's service indeed.

S. RANGA RAJA RAO

INSTITUTE OF AGRICULTURE, ANAND, INDIA, SILVER JUBILEE SOUVENIR, 1940-65 (Director, Institute of Agriculture, Anand), 1966. Vol. I — Education, Pp. 64; Vol. II — Research, Pp. ix+xxii +250; Vol. III — Extension, Pp. 33

The Institute of Agriculture, Anand, was founded in 1939 under the initiative of the late Sardar Patel and Dr K. M. Munshi. The institute began with a School of Agriculture; with the addition of more schools and training centres later and with the establishment of a College of Agriculture and provision for postgraduate studies, the institute has grown into a large complex.

Vol. I deals with the several constituent units, their organization and activities. Scientific work of the institute is presented in Vol. II, which includes brief accounts of the investigations conducted during the past 25 years. The investigations covering a wide field fall under three major heads: (1) the various aspects of crop science such as agronomy, physiology, breeding, plant pathology and entomology (all relating mainly to the principal crops of Gujarat like bajra, paddy, wheat, tobacco and cotton); (2) animal husbandry, including dairying and dairy technology; and (3) other ancillary subjects, like agricultural economics, engineering, statistics, meteorology and extension. Vol. III is devoted to an account of the extension activities of the institute. The research findings of the institute, which are ready for extension, numbering some 134, have been listed.

Of particular interest in the context of the sluggishness visible in the contemporary agricultural scene in our country is the novel way the institute has adopted in taking the results of research to the farmer's door. Farmers' camps in the form of night classes, usually of a week's duration, are held in their own villages. Each day a subject matter specialist talks to the gathering and this talk is followed by discussion with farmers asking questions and the specialists giving possible solutions. On the last day the specialists are present at a general discussion with the farmers on all topics. This is a very imaginative development and is perhaps the best way by which our agricultural schools, colleges and research institutions can make their impact on the rural scene.

A 14-page list of popular articles in Gujarati published so far in the institute's monthly, *Krishigovidya*, given at the end of this volume, shows the wide coverage of aspects covered.

The get-up of the volumes is satisfactory.

R. S. CHAKRAVARTHY

MIXING—THEORY AND PRACTICE: Vol. I, edited by V. W. Uhl & J. B. Gray (Academic Press Inc., New York), 1966. Pp. x+340. Price $ 15.50

Mixing is the operation which is carried out to reduce gradients in composition and properties (e.g. temperature) of materials in bulk. Hence it is an important chemical engineering operation inasmuch as it promotes heat and mass transfer and chemical reactions. Though there is extensive published work on the theory and practice of mixing, an attempt has been made in this book, for the first time, to review and organize this information in a systematic manner so as to make it available to research workers and practising engineers in a comprehensive form. The book has five chapters and each chapter has been written by one or more acknowledged specialists who are authorities in their respective fields.

The first chapter by the editors is introductory in nature and discusses the definition, applications and theoretical relationships of mixing. There is also a discussion on prediction of performance of equipment.

In the second chapter entitled 'Fluid motion and mixing' by R. S. Brodkey, there is a description of diffusion and mixing processes; criteria for mixing, laminar mixing and turbulent mixing have also been discussed.

'Impeller characteristics and power' is the title of the third chapter written jointly by R. L. Bates, P. L. Fondy and J. G. Fenic and covers power requirement, flow pattern, agitator drives, future needs, etc., of impellers.

Chapter 4 deals with flow patterns, fluid velocities and mixing in agitated vessels and is written by J. B. Gray. The last chapter by V. W. Uhl covers mechanically aided heat transfer and discusses industrially important problems, like scale up and design of agitated heat transfer equipment for heating and cooling.

This book is a valuable addition to the chemical engineering literature and will be welcomed by teachers, research workers and practising design engineers. We look forward to the publication of the second volume.

N. R. KULOOR

MODERN ASPECTS OF ELECTROCHEMISTRY: No. 4, edited by J. O. M. Bockris (Plenum Press, New York), 1966. Pp. viii+316. Price $ 12.50

This is the fourth volume in the series on *Modern aspects of electrochemistry*. Studies in electrochemistry have become highly specialized as a result of modern approaches to the subject. Considerable amount of work has been carried out in recent years and unless there are attempts like this to bring out summarized critical accounts of the same, developments of vital interest are likely to be missed by those who are actively engaged in research work. From this point of view, the value of this work to those engaged in advanced work is considerable.

Prof. Van Rysselberghe has been contributing greatly to the thermodynamic aspects of electrochemistry for a number of years. In Chapter 1 of this volume, he deals with some aspects of the thermodynamic structure of electrochemistry. Chapter 2 contains an excellent review on the mechanism of oxidation of organic fuels by Gileadi. Oxidation of organic compounds at an anode has been a much neglected field and much of the work done earlier has been of a sketchy nature. In recent years, as a result of continued interest in using organic compounds in fuel cells, renewed efforts to understand the mode of such reactions in the light of modern concepts have yielded results of significance. The chapter is a well-written account of the recent work on this subject. Anodic and electronic currents at high fields of oxide films by Prof. L. Young form the subject matter of Chapter 3. Formation of films on metals by oxidation is an aspect which is not only of theoretical interest, but also has some very good practical applications in corrosion behaviour of metals, preparation of capacitors, metal oxide resistors, etc. This chapter summarizing the present knowledge on this subject is a welcome one and is quite useful. Chapter 4 deals with an economic study of electrochemical industry in USA by Wenglowski. This chapter highlights the importance of the electrochemical industry in the economy of chemical industry as a whole. This is perhaps the first time that such an effort has been made. Normally, it was regarded as having only a small contribution to make; at least a perspective account was not available to indicate the importance of electrochemistry.

Vol. 4 is thus a very valuable addition to the series of three volumes on modern aspects of electrochemistry published earlier.

H. V. K. UDUPA

REFRACTOMETRY AND CHEMICAL STRUCTURE by S. S. Batsanov; translated from the Russian by Paul Porter Sutton (D. Van Nostrand Co. Inc., Princeton, New Jersey), 1966. Pp. 250. Price $ 4.95

This book gives a general review of the present status of refractometry as a physical tool in the determination of structures. Although X-ray analysis, supplemented by electron diffraction studies, is used quite extensively for the determination of structures, it is necessary that attention should be focused on alternative physical methods for this purpose, particularly those which may be less time consuming and less exacting as regards the degree of purity of the material to be examined. This book on refractometry, indicating the potentialities of this technique in solving structural problems, is thus most welcome.

The history and development of refractometry are given in the first chapter, followed by a chapter on methods for calculating atomic, molar, bond and ionic refractions and the last chapter describes the application of refractometry to the study of the hydrogen bond, structures of silicates and organic compounds and in the calculation of interatomic distances. The book contains a large number of tables giving refractometric data and has a very extensive bibliography.

NITYA NAND

PUBLICATIONS RECEIVED

SMALL SCALE POWER GENERATION (United Nations, New York), 1967. Pp. xvi+215. Price $ 3.50 or Rs 21.00

COMPLETENESS IN SCIENCE by Richard Schlegel (Appleton-Century-Crofts, New York), 1967. Pp. xi+280

HIGH ENERGY BATTERIES by Raymond Jasinski (Plenum Press, New York), 1967. Pp. xv+313. Price $ 17.50

THE DESIGN AND ANALYSIS OF SCIENTIFIC EXPERIMENTS by K. C. Peng (Addison-Wesley Publishing Co. Inc., London W1), 1967. Pp. xi+252. Price $ 12.50

PESTS AND PESTICIDES by N. P. Rao (Scientific Information Bureau, Defence Science Laboratory, Delhi), 1967. Pp. 93

ELEMENTARY GENETICS by W. R. Singleton (D. Van Nostrand Book Co., New York), Second Edition, 1967. Pp. xii+576. Price $ 9.50

LIQUID PHASE OXIDATION OF HYDROCARBONS by N. M. Emanuel, E. T. Denisov & Z. K. Maizus (Plenum Press, New York), 1967. Pp. xiv+350. Price $ 22.50

THE BIOCHEMISTRY OF ANIMAL DEVELOPMENT: Vol. 2, edited by R. Weber (Academic Press Inc., New York), 1967. Pp. xiv+481. Price $ 21.00

ELECTROCHEMISTRY OF MOLTEN AND SOLID ELECTROLYTES edited by A. N. Baraboshkin & S. F. Pal'guev and translated from the Russian by Habina Wrollowa (Consultants Bureau Enterprises Inc., New York), 1967. Pp. viii+65.

INTERPRETED INFRARED SPECTRA: Vol. 3, by H. A. Szymanski (Plenum Press, Data Division, New York), 1967. Pp. ix+275. Price $ 12.50

NOTES & NEWS

Proton-produced X-rays

The surface density of thin films may be determined by X-ray production by proton bombardment. A method evolved by J. M. Khan *et al.* (University of California) has certain advantages inasmuch as it yields absolute densities.

The physical basis of the method lies in the observation that positive ions of sufficient energy are capable of ejecting electrons from bound inner levels of atoms. On the filling of resulting vacancies, X-rays, characteristic of the target atom, are emitted. If the cross-section for X-ray production and the rate of energy degradation for the projectile are known, the absolute value of the number of atoms/cm.^{2} for thin films can be determined.

The target chamber of the apparatus used has double collimating discs that define the beam and an electron shield which is a part of the current collection system. Care is taken to collect the photoelectrons produced on the electron shield in such a manner that they do not disturb the current measurement. Ultra high vacuum conditions ($<10^{-7}$ mm. of Hg) should exist in the target chamber to avoid build-up of contamination and to retain the initial surface conditions. The apparatus also comprises: (i) r.f. electrodeless ion source, (ii) 100 kV. accelerating column, (iii) 2-6 in. oil diffusion pumps, (iv) 5 kg. analysing magnet and (v) X-ray detector (proportional counter) and associated amplifying, discriminating and scaling circuitry.

Even though no specific measurements are presented, the X-ray yield for an infinitely thick target of aluminium is employed to calculate the performance of a typical system. The calculation of X-ray yield (X-ray proton) is based on the formula

$$I = n\int_0^R e^{-(\mu/\rho)(R-r)} \quad \sigma_x[E(r)]dr$$

where μ/ρ = mass absorption coefficient for self-absorption of the X-rays produced, in units of cm.^{2}/μg.; σ_x = cross-section of X-ray production, in units of cm.^{2}/atoms; n = atoms/μg.; r = surface density, in units of μg./cm.^{2}; and R = range of incident particle, in units of μg./cm.^{2}.

The cross-section, in general, is a function of energy. A knowledge of stopping power is also required to relate energy to penetration depth. In the case of low energy ions, as the penetration depth is small compared to X-ray absorption length, the self-absorption of the X-rays can be neglected.

The aluminium X-ray yields (X-rays/proton) as functions of proton densities are calculated for the range 0-115 μg./cm.^{2} at an incident proton energy of 100 keV. When a 10 μa. proton current is incident on a thick target, a typical detection system will record 10,000 counts/sec. with a counter signal-to-noise ratio of 10^4. At a signal-to-noise ratio as low as unity, the calculated surface density is 0·005 μg./cm.^{2} or 10^{14} atoms/cm.^{2} approximately. The method is at present applicable to 11 elements.

The accuracy of the method is dependent chiefly on (i) the experimental measurement of X-ray yield and (ii) reliability of cross-sections and stopping powers. The errors in first can be decreased to a small value ($\pm$15 per cent) but serious limitations are associated with the uncertainty in the cross-section and stopping power. The latter is used to obtain the cross-section as well as to calculate the curve of yield as a function of surface density and may have an uncertainty as high as $\pm$25 per cent. However, the technique of observing X-ray yield offers a good sensitivity and surface densities spanning almost four orders of magnitude can be measured. The use of standard samples could easily limit the errors to $\pm$10 per cent and serve as a cross check [*J. appl. Phys.*, **37** (1966), 564].

Carbon-13 NMR spectroscopy

A number of new approaches to the study of molecular spectroscopy have been made possible with the use of carbon-13 NMR spectroscopy. Recently developed techniques have considerably broadened the scope of this branch of spectroscopy. Some of the important applications envisaged include (i) determination of electronic structures of molecules, (ii) study of molecules with no hydrogen, (iii) study of compounds whose proton spectra are not sufficiently informative, and (iv) use of ^{13}C as a tracer.

Carbon-13 NMR spectroscopy studies have shown appreciable differences in ^{13}C nuclear shieldings for carbon nuclei bearing axial and equatorial functional groups in substituted cyclohexane systems. Another useful field of application of this technique is the study of carbonium ions and carbonions. In the former the technique allows for differentiation (by labelling the potential carbonium ion carbon atom with ^{13}C) between the real carbonium ions (with sp^2 hybridization) and the highly polarized donor-acceptor complexes (with sp^3 hybridization). For example, ^{13}C NMR spectroscopy shows that *tert*-butyl chloride in antimony pentafluoride-sulphur dioxide solution ionizes to the trimethylcarbonium ion. The ^{13}C resonance spectrum indicates a large deshielding effect. This, in turn, indicates sp^2 hybridization in the molecule and substantial positive change on the carbon atom.

Carbon-13 NMR spectroscopy has been used to study the structures of paramagnetic transition metal cyanides by noting the large paramagnetic ^{13}C NMR shifts for these complexes containing ^{13}C in natural abundance. The isotropic shifts for the aqueous solutions of these complexes and for polycrystalline substances yield an estimate of unpaired electron spin density in s orbitals at the carbon nucleus. Variation in the ^{13}NMR shift for a single $K_3Fe(CN)_6$ crystal with the change in orientation of the crystal has also been studied. These anisotropic shifts give a measure of unpaired spin density in p orbitals at the carbon nucleus. They can also yield information about the orientation of the complex in the crystal [*Chem. Engng News*, **45** (No. 13) (1967), 46-47].

Long distance power transmission by superconducting lines

For supply of power to population centres, the generating stations may either be built near these centres or near the sources of energy, i.e. near coal or oil fields (leaving aside hydel and nuclear power). In the first case, coal or oil will have to be transported to the generating stations, often from a considerable distance. In the second case, electricity may have to be carried by transmission lines over a long distance. The recent growth in utility industry in USA (and the projected growth in the future) has forced the authorities to put the economics of the first and long practised procedure of coal/oil transportation to a re-examination. Moreover, the utilities have recently become aware of the advantages of power pooling. By tying together formerly independent power systems they can save in reserve capacity (particularly if the systems are in different regions of the country), because peak loads occur at different times of the day, or in different seasons. In addition, the location of fossil fuel or, for that matter, nuclear power plants near densely populated locality entails the problem of health hazards.

After consideration of the points mentioned, the balance naturally tips towards the long distance transmission of electricity. The economics is, of course, a big hurdle to cross. Garwin and Matisoo have considered the problem of economical transmission of large blocks of power of the order of 10^5 MW over a distance of 1000 km. [*Proc. IEEE*, **55** (1967), 538-48].

Their solution is a transmission system using superconductors to carry current. The superconductors would, of course, be refrigerated so that their resistivity is zero. The major power loss then would be the power required to maintain the line at 4°K. The power line would be made of Nb_3Sn and the power must be transmitted as direct current, rather than alternating current, because the very large alternating current losses would require excessive refrigeration capacity.

The authors have given a design and have discussed at length a line at 200 kV. carrying $0{\cdot}5 \times 10^6$ amps. of current, the power capacity and length of line being 10^5 MW and 1000 km. respectively. The investment in the line will be approximately $ 806 million or $ 8.06/kW. Of this, some $ 6.06/kW. is line cost, the remainder being converter cost. By dividing the power transmitted less the power drawn off to run refrigeration equipment by the transmitted power, the efficiency of the system comes to more than 99 per cent.

Cleavage of oximes with bisulphite

So far, the cleavage of oximes to the parent oxo compounds was based either on direct acid hydrolysis or acid-catalysed exchange with formaldehyde, pyruvic, or levulinic acids. A simple, inexpensive and mild procedure involving reaction with bisulphite has been reported [*J. org. Chem.*, **31** (1966), 3446]. The reaction is carried out under neutral non-reversible conditions and brief exposure to acid (in the cold) is required only for the isolation of the product. The method gives near-quantitative and chromatographically pure yields of 'crude' product.

The oxime, dissolved in 10-12 vol. of 50 per cent aqueous ethanol, is refluxed with 3·5 molar equivalent of sodium bisulphite until TLC indicates complete reaction. After distilling out ethanol, the residue is admixed with chloroform and an excess of dilute hydrochloric acid, and the ketone or aldehyde is extracted into the organic layer. In the case of aldehydes, hydrolysis of the bisulphite adduct requires stirring with acid for about 30 min. to obtain two clear layers.

Simultaneous titrimetric determination of bicarbonate and titrable acid of urine

A new simple acid titration method for the simultaneous determination of bicarbonate and titrable acid in urine is reported [*Aust. J. exp. Biol. med. Sci.*, **45** (1967), 141]. The method consists in adding an excess of $1M$ HCl to the urine sample after its *p*H has been determined. The amount of acid needed depends on the *p*H of the urine sample, but up to *p*H 7·6, 2·0 ml. of HCl is sufficient for 25·0 ml. of urine. The acid is allowed to react with the bicarbonate present in the urine sample and then the carbonic acid formed is driven off. This is followed by back titration of the remaining acid with standard alkali ($0{\cdot}1M$ NaOH). If the back titration is carried out to a *p*H of 7·4, then only titrable acid minus bicarbonate is determined. If, however, back titration is first carried out to the original *p*H of the urine and then to *p*H 7·4, the first volume gives the amount of bicarbonate present and the difference between the two volumes gives the titrable acid present.

The new method has the advantage over the Van Slyke method in that it is simple and combines into one single operation the determination of urinary bicarbonate and titrable acid or titrable base where the *p*H of the urine is above 7·4. Also titrable acid in urine can be measured without titrating H_2CO_3, which is always present.

Simple isotopic assays for thymidylate synthetase and dihydrofolate reductase

The estimation of thymidylate synthetase and dihydrofolate reductase by the release of tritiated water from their labelled substrates has been simplified [*Biochemistry*, **5** (1966), 3546, 3548].

The simplification involves removal of the residual substrate by adsorption on to charcoal instead of the product from the remaining substrate involving collection of the tritiated water in a cold trap and assaying the supernatant fluid by liquid scintillation counting. Besides being simple, the method is rapid and extremely sensitive and can be applied to crude homogenates of mouse ascites tumour cells.

A suitable aliquot (about 5 µl. for thymidylate synthetase, 20 µl. for dihydrofolate reductase) of the supernatant fluid of tissue homogenate is incubated for

40 min. at 37°C. with a suitable amount (about 5 µl. for reductase and 15 µl. for synthetase) of the reagent containing labelled substrate. After the reaction is terminated by the addition of trichloroacetic acid (also oxidation of the tetrahydrofolate by KNO_2 in the case of reductase), the residual substrate is adsorbed on to charcoal. The suspension is centrifuged at 200 *g* for 10 min. A 100 µl. aliquot of the supernatant fluid is removed and added to 10 ml. of 2,5-bis-2-2-(5-*tert*-butylbenzoxazolyl)-thiophene scintillation solution for counting by liquid scintillation.

High solubility fibrinogen of human plasma

For the first time, the preparation of high solubility fibrinogen, almost completely free from the low solubility fibrinogen, has been rendered possible by the development of a new method based on glycine precipitation and ethanol fractionation [*Biochemistry*, **5** (1966), 2829]. Unlike the conventional methods, employing cold ethanol fractionation for initial isolation, the new method involving glycine precipitation entails little loss of clottable material and affords almost complete isolation of the fibrinogen of high solubility and clottability (about 95 per cent) from those of lower solubility.

The method involves initial precipitation of plasma by 2·1*M* glycine at 5°C. followed by dissolution of the initial precipitate in 0·15*M* NaCl, 0·01*M* sodium phosphate buffer (*p*H 6·4), reduction of the original volume (O.S.) to one-third and reprecipitation with glycine. The second glycine precipitate is dissolved, brought to one-tenth of the O.S. with 0·10*M* sodium phosphate and made free of the cold-insoluble fraction according to Laki [*Archs Biochem. Biophys.*, **32** (1951), 317]. Fractionation of this supernatant with 8-16 per cent ethanol concentration yields fibrinogen of higher solubility than that precipitable at 8 per cent ethanol concentration employed in the conventional methods. Further subfractionation with ethanol has led to a more complete recovery of the high solubility fibrinogen from that of lower solubility.

Indian Statistical Institute

The annual report of the institute for the year 1965-66 presents in detail the achievements of the institute during the year along with reports of the various meetings held, activities of its research and training school, honours and awards and staff news pertaining to appointments, promotions, etc.

The Planning Division of the institute at Delhi continued its research work on economic planning and regional survey and, in collaboration with the London School of Economics and the Planning Commission, submitted a memorandum entitled " Manpower and Educational Development in India (1961-1986) " to the Education Commission. The main fields of research covered by the Calcutta unit of the Planning Division were national income and allied topics, consumer behaviour, macro-economic programming and econometrics. In addition, 12 seminars and lectures were arranged by this division.

National sample survey was one of the major projects in which work was continued. Activities pertaining to this project were: (a) the statistical planning of surveys, including sample design concepts and definitions, methods of collecting primary information, preparation of schedules of enquiries, and training of field workers and the technical workers relating to field enquiries; (b) the programme of statistical process and the laying down of detailed specifications; (c) the conduct of the field work in West Bengal and Bombay City, together with experimental researches for the improvement of sample design and techniques; and (d) the processing of NSS data.

Research, incorporating statistical and psychometric theory, was oriented towards the development of improved methods of educational evaluation and personnel selection. Empirical studies were conducted on psycholinguistic meaning systems in the Bengali language, effect of medium of instruction and examination on performance of science students and ' new mathematics ' at the elementary education level. Theoretical studies were carried out on sampling estimates for psychometric errors of measurement and on component scores for selection and classification. Pilot studies for a project on psychological gerontology have been undertaken.

The statistical quality control unit of the institute functioned in nine centres at Bangalore, Baroda, Bombay, Calcutta, Coimbatore, Delhi, Ernakulam, Madras and Trivandrum. These units rendered quality control services to 75 factories during the year. Training in quality control resulting in a one-year postgraduate diploma was imparted to 26 engineers, technologists and scientists.

Important activities of the Documentation Research and Training Centre (DRTC), Bangalore, included the continuation of the work on the design of depth schedule, formulation and testing of a methodology for increasing the productivity in the design work and working out of over 50 depth schedules largely for subjects in commodity production engineering. The problem of homonym in class index heading derived by chain procedure was examined and solution for resolving the homonyms was also worked out. The use of the methodology for the design of depth classification, developed at DRTC, is now being extended so as to cover subjects in social sciences also.

Besides the computation services rendered, the Electronics Division continued its researches on computer technology and allied topics with emphasis on computer logic and reliability studies for digital systems as a preliminary investigation for the design of second computer. Fundamental research on network analysis led to a mathematical deduction of the Kirchhoff's laws in their true natural forms.

Plastics in building — A seminar

A seminar on " Plastics in Building ", organized under the joint auspices of National Buildings Organization and the Plastics Institute, was held in New Delhi during 9-10 March 1967.

This first ever get-together of the plastic industry was attended by engineers, architects and those concerned with the building industry. The aim of the seminar was to create an awareness, in the prospective users of plastic building materials in India, of the potentialities, advantages and limitations of these materials. In this connection, a plastics development house was fabricated and kept open to the visitors.

Shri K. Raghu Ramaiah, Union Minister of Supply, Technical Development and Materials Planning, inaugurated the seminar. He emphasized the need for constant research in the use of plastics in general and in buildings in particular. He also appealed to the industry to keep the quality high and the price down as it is only with these ideas that any industry can come to the fore and contribute towards the industrial development of the country.

Sixteen papers, covering various aspects of the application of plastics in the building industry, were presented at the seminar. The papers also generally reviewed the developments in this field in other countries.

In the concluding session of the seminar, nine recommendations were passed. The most important among these dealt with the study of long time behaviour of plastics in building materials, ensuring of safety from toxic effects of plastics and the development of polyester and epoxy-based compounds for heavy duty floor materials.

Solar Physics

Solar Physics is the latest addition to the existing family of astronomical journals and is devoted solely to the happenings in the interior, atmosphere and immediate environment of the nearest star, the sun. The sun is the only star which presents to us a sizeable disc that makes details of its surface accessible to planned observation. Hence, close scrutiny with corresponding logical inferences of this very typical star has been a significant factor in the progress of astrophysics.

The new journal will cover a wide range of astrophysical topics pertaining to the sun. It will also treat solar terrestrial physics, though coverage of this area of interest will be confined to only those aspects that further knowledge of solar phenomena. Apart from original research papers and research notes, it will also feature invited review papers on topics of general interest to solar physicists. It will also contain reports from the different astrophysical institutes on recent progress made by them in research as well as instrumentation.

The first number of this journal contains papers on granulation effects, chromospheric and coronal phenomena, solar activity, and some magnetic aspects of interplanetary space. The electromagnetic spectrum is well covered from the soft X-rays through the visible range on to the radio regions. Reports of research at three solar observatories located on three different continents together with the different countries of the contributing authors depict well the international character of the journal.

Inhomogeneities characterize the small-scale structure of the solar atmosphere. The facility to study these fine-structure details is perhaps the prize-asset of solar physics and is best studied by high quality photographs of either the disc in monochromatic or white light or of spectra of individual features. In these days of high printing costs, it is refreshing to read in the information provided to prospective authors on the cover page that " the amount of information contained in a good picture should not be underestimated. Photographs and diagrams supplied with good captions are stepping-stones to a better and rapid understanding of a paper ". The high standard of printing, of illustrations as well as text, indicates that the publishers are as appreciative of this requirement as the editors. The astronomical community at large, and solar physicists in particular, owe a debt of gratitude to the editors for their painstaking efforts in presenting a new medium for the publication of scientific results in the field of solar physics.

VAINU BAPPU

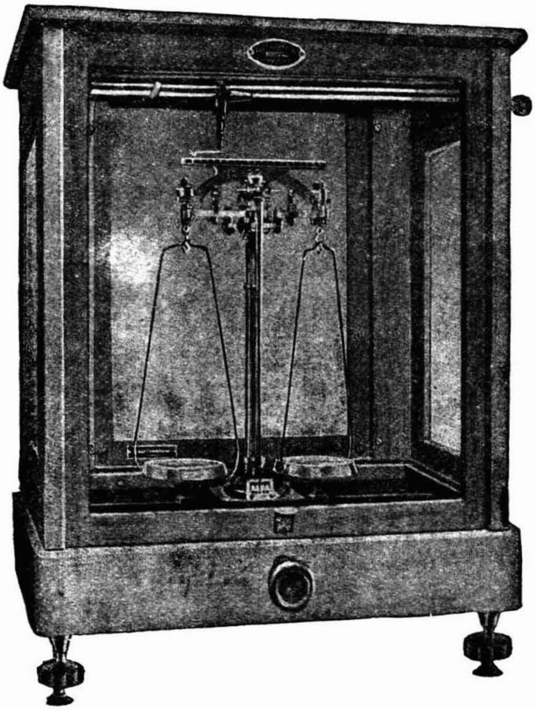
Announcements

▪ *Theoretical and Applied Mechanics Congress* — The Twelfth Congress on Theoretical and Applied Mechanics will be held at the Indian Institute of Technology, Hauz Khas, New Delhi 29, during 18-21 December 1967. The congress will be presided over by Dr V. M. Ghatage, Deputy General Manager, Hindustan Aeronautics Ltd, Bangalore.

Research papers for the congress should be on (i) mechanics of solids, (ii) mechanics of fluids, (iii) statistical mechanics, (iv) mathematical methods, (v) computation methods, and (vi) experimental techniques. There will be invited addresses on special topics.

Forms for registration are available from the Secretary, Indian Society of Theoretical and Applied Mechanics, Indian Institute of Technology, Hauz Khas, New Delhi 29, to whom the papers should be submitted along with (i) three copies of abstract (one in proforma attached with registration form), (ii) registration form duly filled, and (iii) registration fee of Rs 10.00.

▪ *Oil Technologists' Symposium and Convention* — A symposium and convention of the Oil Technologists' Association of India will be held at Hyderabad during 9-11 February 1968. The symposium is being sponsored by the Oil Technologists' Association of India, the Council of Scientific & Industrial Research, the Soyabean Council of America and various organizations connected with vegetable oils and oilseeds. The symposium, besides covering the areas of sources and utilization of oils and fats, will cover the currently important areas in the field, such as sources of oil, detergents, hydrogenation, detection of adulteration of fats, and current researches in various areas. Further information can be had from the Convener, Oil Technologists' Symposium and Convention, Regional Research Laboratory, Hyderabad 9.



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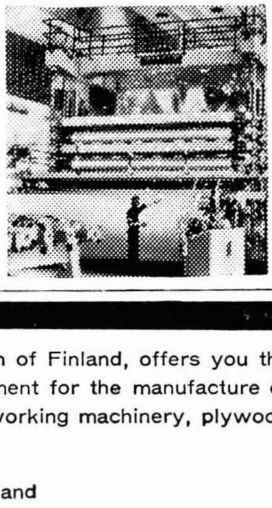

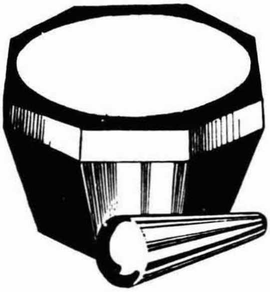

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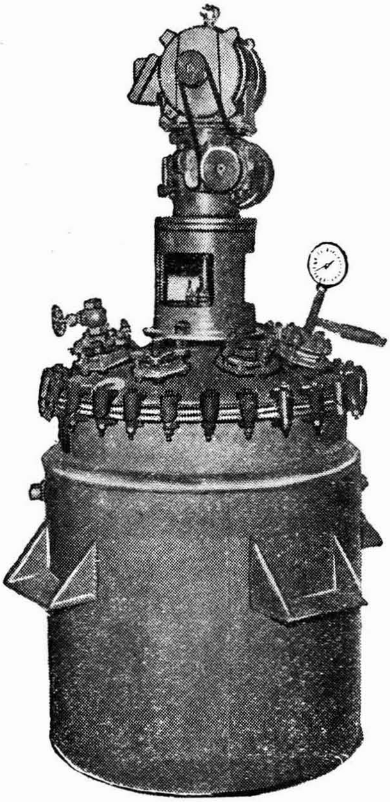

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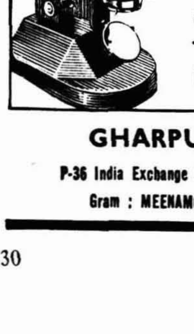

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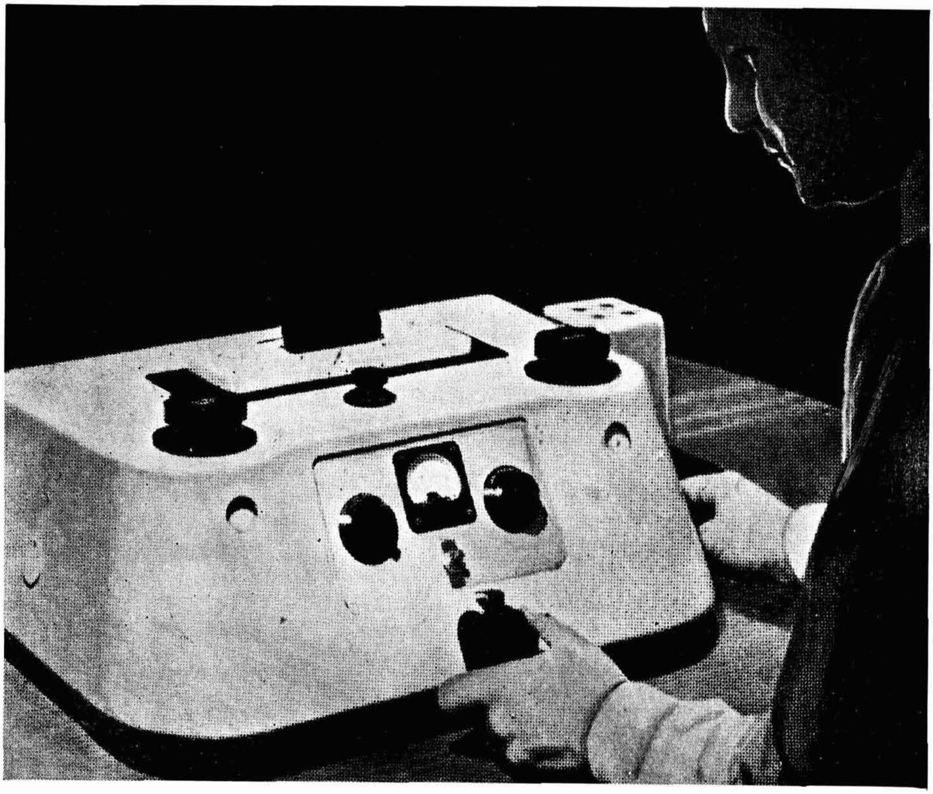

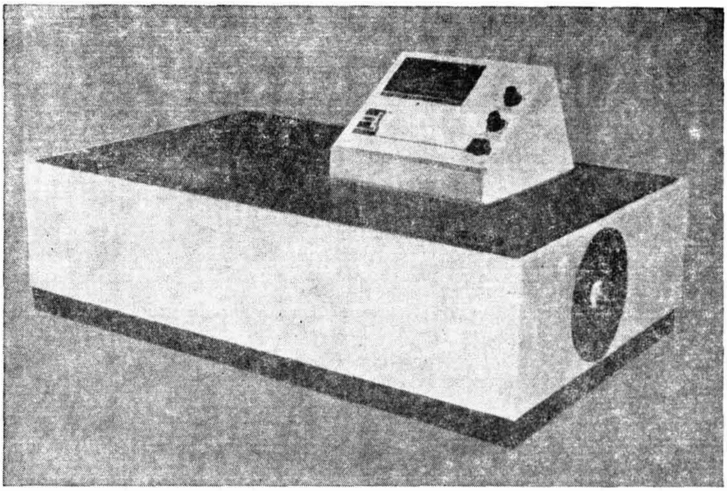

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