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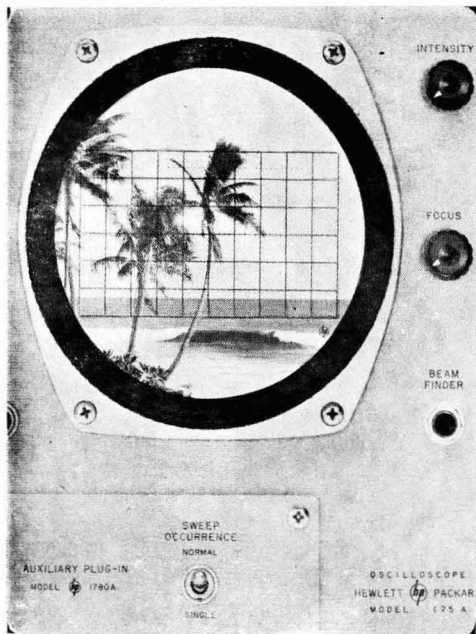
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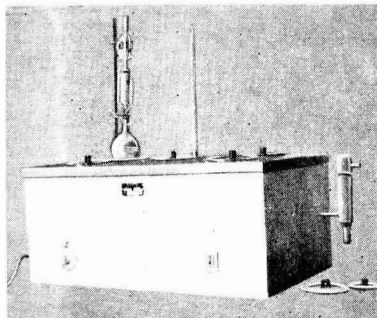
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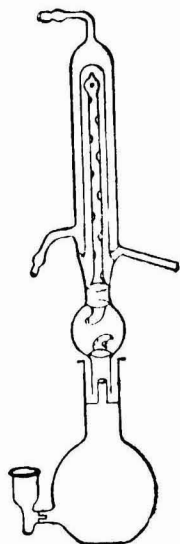
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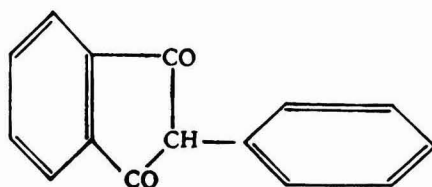
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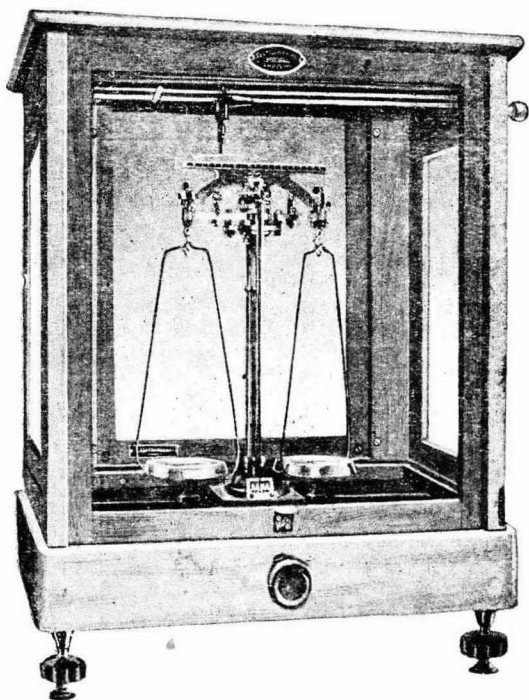
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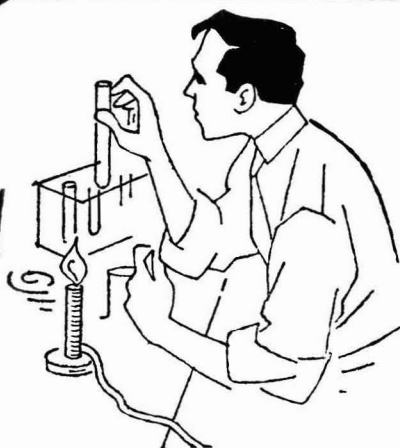
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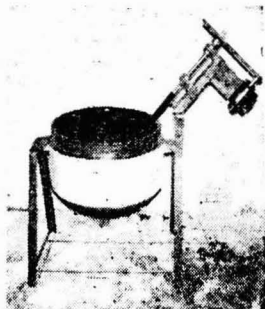
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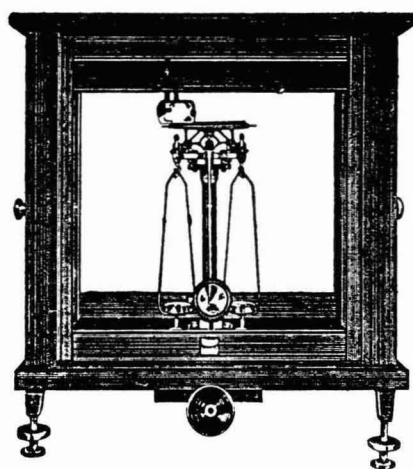
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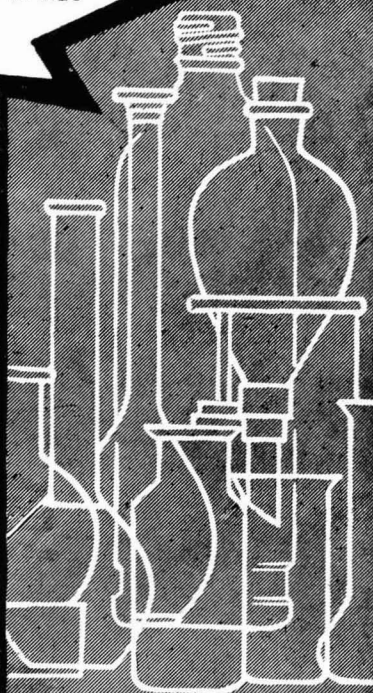
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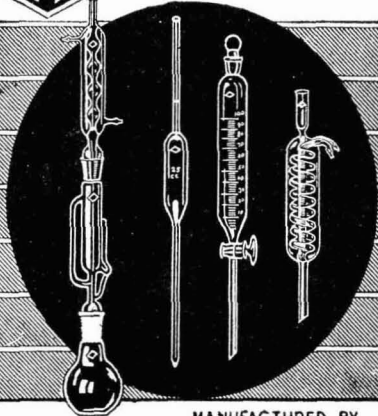
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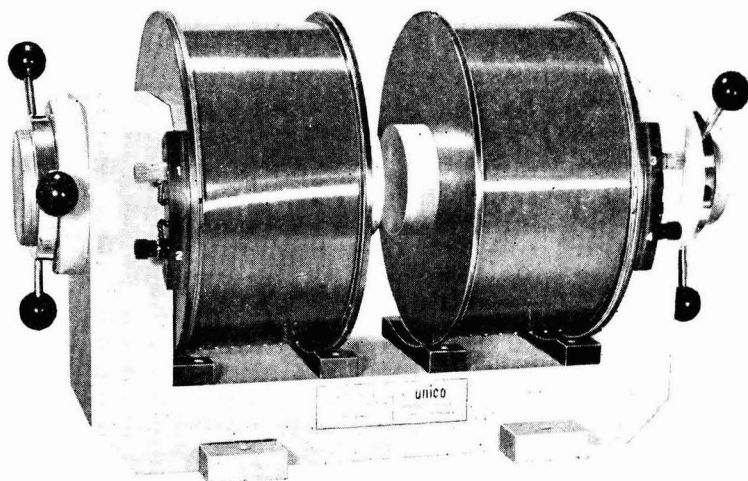
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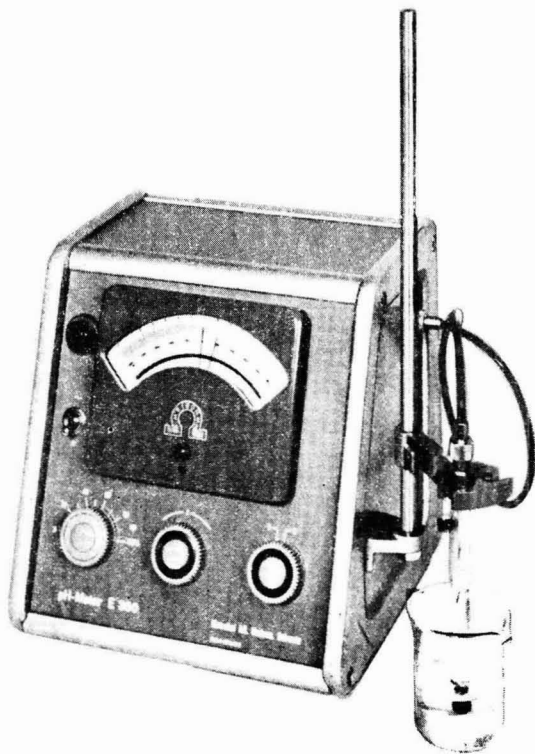
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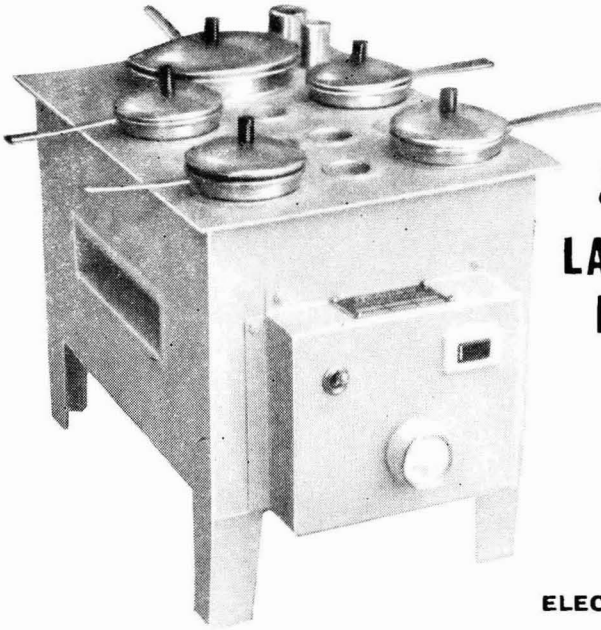
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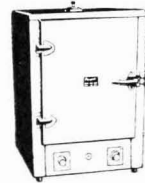
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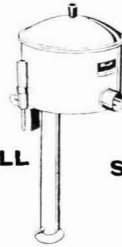
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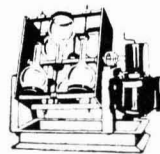


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Current Topics

The National Physical Laboratory: Foundation Day

FOR the first time since its inception fifteen years ago, the National Physical Laboratory (NPL), New Delhi, observed its Foundation Day on 21 January 1965. Coinciding with this, 'Open Days' were arranged on 21 and 22 January so that the general public could visit the laboratory and get a first hand knowledge of the achievements of the laboratory and the work in progress. An exhibition organized during these days helped to give a graphic picture of the many-sided achievements and activities of the laboratory. This occasion was also taken advantage of to arrange for the first Dr K. S. Krishnan Memorial Lecture which was delivered by Dr K. R. Ramanathan, Director, Physical Research Laboratory, Ahmedabad, on 21 January.

One of the earliest laboratories to be set up by the Council of Scientific & Industrial Research (CSIR), NPL got off to a fine start under the able stewardship of Dr K. S. Krishnan, its first director, who set the tune and tradition for its research activities. The main objectives of NPL are: (a) to undertake applied research on all physical aspects with a view to helping industries; (b) to undertake basic research in fields which have a bearing on problems of a physical nature associated with applied research as stated above; (c) to undertake developmental testing to help industry; and (d) to maintain basic standards of mass, length, time and temperature, as well as derived standards for electricity, electronics, acoustics and optics. In order to assess the contribution of NPL towards fulfilling the above objectives, a brief review of the work carried out is necessary. A brochure entitled "Fifteen Years at the National Physical Laboratory", brought out to mark the foundation day, presents an impressive record of the work carried out by the 19 divisions of NPL covering many branches of basic and applied physics, maintenance of standards and testing and certification of industrial products. The laboratory has well-established schools of research in the fields of ultrasonics, radio propagation, solid state physics, and rain and cloud physics. Over 700 scientific papers have emerged from the laboratory during the past 15 years and 49 patents have been taken out. The laboratory has developed a number of industrial products not previously manufactured in the country utilizing indigenous raw materials, thus opening the way for the establishment of new industries. Special mention may be made of the production of industrial carbons and electronic components on pilot plant scale. The laboratory has played an important role in the introduction of metric system

in the country. Another important achievement is the setting up of time and frequency standards.

Applied research is the basic objective of the work of the various divisions of NPL. Significant contributions of practical importance have emerged in the field of ultrasonics. For example, in view of the growing noise nuisance in major cities of India, a systematic survey of the prevailing noise due to vehicular traffic has been made with a view to formulating upper limits of acceptability for different vehicles. Design and fabrication of testing machines has been an important activity in the field of applied mechanics. Several instruments and devices have been designed and constructed for work connected with electrical standards. A valuable survey and study of the dielectric insulation materials available in the country has also been completed. Development of microwave electronic circuitry, with special reference to switching techniques and their application to instruments and devices has been the main activity in the field of electronics. Some of the instruments and techniques developed include a 10 cm. multicavity magnetron, a wide tuning-range magnetron, a 6 cm. klystron, electro-forming of microwave components like straight-wave guides, etc. Several optical instruments and accessories, such as microscope objective testing interferometers, megohmmeters, colorimeters, a wide range of logarithmic photometers, colour temperature meters, etc., have been developed which could be produced on a commercial scale.

A radio propagation service for radio traffic organizations in India and abroad, operation of an automatic ionosonde as a part of a world network, a solar flare radio patrol system feeding national and international networks, detection of atmospheric nuclear explosions, and conservation of radio frequency spectrum are some of the applied activities carried out in the field of radio propagation.

Basic research programmes of the laboratory by and large have a bearing on the applied research projects under investigation and are incidental to them. A fundamental contribution in the field of ultrasonics relates to the establishment of a quantitative relationship between sound energy absorbed and heat developed in a medium; this relationship has been utilized in devising a new thermosonic technique of measurement of absorption.

Programmes in the field of radio research are concerned with the physics of the upper atmosphere, radio-astronomy and space radio research involving both satellites and rockets. An exhaustive study of the characteristics of the equatorial ionosphere and physics of the D region is also being made. Space radio research programme includes studies on atmospheric densities from satellite drag data, satellite transmissions and rocket soundings of the

ionosphere. Utilizing satellite drag data, atmospheric models have been developed for sunspot maximum and minimum conditions giving the densities of different atmospheric constituents and temperatures.

In the field of electronics, an important contribution concerns a new effect of magnetic field on the propagation of microwaves in wave-guides and on the breakdown characteristics of diodes. A new type of calorimeter has been designed and built for the determination of atomic heats of pure metals at liquid helium temperatures. A technique, giving results with an accuracy of ± 0.5 per cent, has been developed for the determination of the elastic properties of metals and alloys.

Experimental studies into the efficacy of the present techniques of inducing, artificially, development of rain in non-raining clouds have yielded much useful basic data. Investigations on the concentration of hygroscopic nuclei in surface air layers around Delhi under various synoptic conditions have shown that the ice-phase plays a significant role in precipitation, more akin to temperate than tropical latitudes. Also, studies on the chemical nature of these nuclei have revealed that sulphates are predominantly aerosol during winter and chlorides during summer and monsoon seasons.

Thermionic emission phenomena and lattice defects in ionic crystals have been the major areas of study in the field of solid state physics. A method has been developed by which electrons can be introduced into the conduction band of alkali halides. A Greek band associated with divalent impurities has been demonstrated experimentally using Ni and Co as impurities. Systematic work on Z-centre has revealed the mechanism by which divalent impurities increase the sensitivity to colouration. An important programme of work of great practical and theoretical interest undertaken is on the physical properties and structure of thin films.

Work on standards and testing of instruments and appliances is a major function assigned to NPL from its very inception. Primary standards maintained by the respective divisions include those of mass and length, time and frequency, standard microphones for measurement of sound and absolute ohm and volt. In addition, a full range of sub-standard thermometers, and a set of tungsten strip lamps, platinum resistance thermometers and thermocouples are maintained. The laboratory has also a project for maintaining low temperature thermometer standards and secondary standards of light. The laboratory has been supplying standards of mass, capacity measures and length measures to manufacturers of scientific instruments, scientific institutions and central and state governments. The laboratory takes an active part in the work of the Indian Standards Institution by laying down standards for a variety of industrial products. Testing of a wide range of instruments and equipments for the benefit of industry has been an important facet of the activity of NPL. An idea of this can be had from the fact that the laboratory issued nearly 12,000 test certificates during the past 8 years and collected over Rs 4 lakhs testing fees.

Impressive as the record of the achievements of NPL is, much more could be achieved by judicious reorganization and reorientation of the work of the laboratory. The programmes of the laboratory have been recently reviewed by Prof. P. M. S. Blackett and by the Third Reviewing Committee of CSIR headed by Dr A. Ramaswami Mudaliar. It has been suggested that the work of the laboratory should be project-oriented. Dr K. R. Ramathan in his Krishnan Memorial Lecture has also drawn pointed attention to the need for reorienting the work of the laboratory on the lines of the National Bureau of Standards (NBS), USA. It is pertinent to quote *in extenso* his observations: "The functions of NBS as I understand are: (i) development and maintenance of international standards of measurement and provision of the means and methods of making measurements consistent with international standards; (ii) determination of the physical constants and properties of materials; (iii) development of methods and instruments for testing materials, devices and structures; (iv) advisory services to government agencies on scientific and technical problems; (v) invention and development of devices to secure special needs of the government; and (vi) development of standard practices, codes and specifications. You will notice in the above there is no division according to disciplines. They put down the outlook and the objectives which are required to meet the needs of the country. These include the development not only of materials, means and methods but also devices for special purposes. I think we have to some extent incorporated parts of this in the actual working of the NPL division dealing with the indigenous manufacture of radio components and materials, but we cannot say that we have kept in mind all aspects of the work of NBS.

"I feel that there are far too many divisions in the laboratory, and it would be a good thing if different related divisions could work together on common projects, planning and working together. Problems that come up for solution in a laboratory cannot often be fully dealt with in one particular division. I think that probably more can be done by coordinating the activities of related groups for solving the problems that come up before the laboratory. In some of our bigger laboratories, we have a collection of facilities and personnel which we do not have, and which we cannot hope to have, in many university laboratories, and it is important that this combination of facilities should be made use of in the fullest possible manner.

"Today there is a considerable amount of thinking going on for the development of electronics and radio industry in India. Probably many hundreds of crores of rupees will be spent in developing an indigenous electronics industry. The growth of a really worthwhile electronics industry to meet the needs of all our services including defence, communication and broadcasting services is imminent. It would require a very large amount of work by large groups of people, and it would require study of materials, techniques, instrumentation, and production of standard equipment for quantitative measurements. We have yet to produce in

our country all necessary materials and combinations to meet the requirements. I feel in a field like this, where it is possible for many disciplines to combine or many divisions in a laboratory like NPL to combine, there is much valuable work to be done. It should be possible to enlist the cooperation of big user services like the Defence, Posts and Telegraphs, by exchange of information, discussion of need,

etc., so that fullest use can be made of the facilities available. This is a large national objective and there should be some integrating element to get people to work together in an effective way."

Dr Ramanathan has admirably pin-pointed the directions in which the future programmes of NPL should be oriented. The laboratory would do well to pay heed to his constructive suggestions.

Science & the State*

I AM deeply grateful to the members of the Indian Science Congress Association for the honour they have done me in electing me President for the year. When I think of the many eminent scientists who have adorned this seat, my embarrassment becomes the greater, for I do not possess even a first degree in science. The only reason for your choice may be that during the last few years, I have to the best of my ability tried to serve the cause of science in India. I have, therefore, accepted your invitation in a spirit of humility and am beholden to you for this gracious gesture.

The Indian Science Congress has in the past had many distinguished Presidents and among them, Jawaharlal Nehru will occupy a position of special eminence. A student of science all his life, he may not have made a personal contribution to any field of scientific research, but perhaps no one in India has done more for science and scientists than our late Prime Minister. He devoted himself to the task of inculcating in the Indian people the scientific spirit and removing from their minds the attitude of superstition and fatalism which has so often sapped Indian vitality. He sought to infuse into our economy, politics and society the critical, objective and analytical approach of science. Science is essentially rational and according to him, the extension of the rational principle to every sphere of human activity is necessary for the prosperity and indeed for the survival of man.

It is in this spirit that throughout his life, Nehru worked for the development of science in India. Our magnificent national laboratories devoted to research in sciences and their application to industry, agriculture and generally to human life stand as a permanent monument to his vision and his faith. We of the Indian Science Congress owe him a special debt of gratitude. From the inception of independence, he attended every single session of the congress excepting two. We miss him today and shall always miss him, for he spoke to scientists as a fellow worker in the cause of science. In Jawaharlal Nehru's death, Indian science has lost one of its greatest supporters and friends.

Another great figure whose name comes to my mind on this occasion is that of Ashutosh Mookerjee.

*Address of Prof. Humayun Kabir, General President, Combined 51st and 52nd Session of the Indian Science Congress, Calcutta, 31 December 1964.

He was himself a mathematician of eminence, but his major service to science lay in the encouragement and support he gave to research by others. An educationist of international standing, he was primarily responsible for developing post-graduate studies and research in Indian universities. Some of the most notable names in Indian science were attracted to a life of study and research under his direct inspiration. The creation of the University College of Science and Technology at Calcutta is one of the shining monuments to his love of science and industry. The Indian Science Congress has a special link with him, for he was the first President of this Association and it is to mark the centenary of his birth that the congress is holding its present session in 1964 in the city of Calcutta. I must thank the Vice-Chancellors of the Punjab and the Calcutta Universities whose cooperation and understanding made this happy event possible.

I have said earlier that I am not a student of science and cannot, therefore, comment on recent scientific work in any field. There have been startling developments in almost every area of science, but their proper discussion and assessment must be left to specialists. I may perhaps speak to you about some general problems concerning science and measures necessary for accelerating scientific progress in India. I think there will be general agreement that facilities for study and research in science have been greatly expanded. The state is offering support and help on a scale that could not have been imagined two decades ago and yet there is a feeling that not enough is being done. The limiting factors, in India as elsewhere, are shortage of personnel and inadequacy of funds relative to demand. The number of scientific workers has enormously increased and yet the output appears inadequate both qualitatively and quantitatively. Similarly, funds are always short as modern science requires more and more elaborate and sophisticated machines which are costly and difficult to make. Even rich countries like the UK or West Germany are finding it difficult to meet all the demands for equipment, for a single piece of apparatus may in some cases cost as much as a hundred million rupees or more.

Before I take up some specifically Indian questions, I may refer generally to a few problems which affect all countries. While the importance of science and scientific research to modern society is accepted

by all, the full implications of the new scientific revolution have not always been recognized. Formerly, the advancement of science was the task of devoted students whose main interest was theoretical research in fundamental problems. Associations like the Royal Society of London have fostered the growth of science for over three hundred years, but till the beginning of the present century, no country, with the possible exception of Germany, made any effort at the state level to organize scientific research for industrial purposes. In the UK, it was only the impact of World War I which led to the establishment of the Department of Scientific & Industrial Research, though private industry both in the USA and the UK had gradually become conscious of the importance of research in order to face the competition of research-based German industries. The experience of the first and the second world wars convinced all nations that scientific research is necessary for survival itself.

With the growing recognition of the importance of science for military, industrial, commercial and other purposes, the state inevitably came into the picture as a conscious agent for promoting scientific research. This meant a growing realization of the practical utility of science and yet one of the characteristics of science is that some of the most spectacular advances have taken place without any reference to practical applicability. Scientific discoveries are as dependent on free imagination as artistic creation. That is why attempts to make scientific research too narrowly utilitarian are foredoomed to failure. Men engaged in scientific research in any field must, therefore, be given the widest possible freedom. Disinterested pursuit of truth has again and again proved more profitable than close adherence to prescribed objectives.

State participation often leads to state control and control is not conducive to scientific progress. In spite of this risk, increasing state participation in scientific work is inescapable in the modern world. Research today has become so expensive that it is almost impossible for an individual scientist or even a group of scientists in a university to find necessary funds. This refers to equipment which is becoming more and more complicated and costly, and even more to the need for documentation services and easy access to the vast volume of research carried out in many languages in many parts of the world. In fact, the scale of expenditure has increased so greatly that the state itself has to exercise economy in the allocation of resources to competing projects.

Practical application necessarily becomes an important consideration in such a context. Even the richest of states finds it difficult to justify and support pure research over long periods unless there are tangible results. This explains why the demand for applied research and development has been continually increasing and there is at times a risk that immediate demands may defeat long-term needs. The only redeeming feature in the situation is that pure research has generally led to results of great practical utility. As such, there has been no real clash between the pursuit of truth for its own sake and the pursuit of truth for its practical results.

I may refer here to another feature which is characteristic of modern research. In earlier times, it was possible for individuals working by themselves to make significant contributions to science or technology. In fact, this was often the only way in which science could advance. Today, with the enormous increase in the body of knowledge and the necessity for cooperative manipulation of data, it is almost impossible for an individual, however gifted, to achieve spectacular success entirely on his own. This is not to minimize the importance of the individual genius, for he will always have a role of the highest importance, but even the genius today must be supported by colleagues who provide him with the material for his intellectual adventures.

The splendid achievements of the USA and the USSR in the scientific field in the last two or three decades are due primarily to this fact of cooperative research. In both countries, great emphasis has been placed on building up teams and it has been found that the individual as a member of a team can make more significant contributions than when working on his own. This perhaps helps to explain why young Indian scientists who have shown great promise when working abroad do not always justify our hopes after they return. Some become disappointed with conditions here and leave the country and this is naturally a cause for concern. I am convinced that among gifted scientists, those who go abroad for money and position are in a minority. The majority are attracted to foreign countries by the more satisfactory conditions of work and the promise of earlier and greater achievement.

The problem of migration of scientists is not peculiar to India and fortunately for us, it has not yet assumed serious proportions here. Nevertheless, it deserves careful consideration and I may be excused if I digress and dwell on this for a moment. I have discussed this question with leaders of science in the UK, Germany, Switzerland and France. I found general agreement that there should be no objection to some circulation of scientists. Under modern conditions, every country should be prepared to allow a few of its promising scientists to work in other countries. Such movement must, however, be mutual. Objections arise, and validly, because it is at present a one-way traffic with most scientists moving to the USA, some of them permanently. Very few from America come to work in other countries.

I will repeat what Prof. Heisenberg told me in this connection. He said that apart from the question of easy access to equipment and other material, one major reason for migration of young scientists to the USA is the existence there of scientific teams which make it easier for a young scientist to make a name for himself. Under modern conditions, it is almost impossible for isolated workers to effect any significant breakthrough. In America, large groups of scientists are working with the most up-to-date instrumentation and the result is that any worker of first rate ability can hope to make valuable contributions in collaboration with his colleagues.

Prof. Heisenberg felt that the only way of checking this tendency of young scientists to migrate to the USA is to build up effective scientific teams

within the country, expand facilities of research in universities and laboratories and improve conditions of service of scientists. This requires planning and coordination by the state and academic bodies and also a great deal of cooperation between older and younger scientists. In addition, it is necessary to give young scientists liberal facilities of travel. Prof. Heisenberg said that some of his junior colleagues visit the United States every year and almost everyone has been given the option of going abroad at least once in two years. In this way, younger scientists are able to keep abreast with the work which is being done elsewhere and one of the major reasons for migration has disappeared.

The conditions which obtain within a university department or research laboratory also have a direct bearing on the movement of scientists. Where there is an atmosphere of freedom, where all members participate and are encouraged to participate in discussion and research and the head takes active interest in the work of his colleagues, a team can be built up quickly. Members in such institutions feel that they are engaged in a cooperative endeavour and generally everybody is active and therefore happy. The individual can make his best contribution in such conditions and the general quality of work in the laboratory immediately goes up. When, on the other hand, there is dictation, or in the alternative, indifference or aloofness from above, there is invariably friction at lower levels. In such institutions, scientists, specially the younger ones, feel frustrated and become incapable of really creative work. I am sorry that I should have to mention this, for it is obvious that discussion, free enquiry and questioning are the basis of any worthwhile scientific work. There must, therefore, be freedom and equality among scientists working in a team. Some will even then be leaders but the position will be attained by individual excellence and achievement and not by virtue of seniority or office. Status as such is generally a hindrance to scientific work. This applies particularly to India, where the consciousness about status is far stronger than in most western countries.

The question of leadership will even then remain and this is perhaps the crucial issue. There are hardly any complaints and certainly no stagnation in laboratories or university departments where a leader is both competent and cooperative, and encourages his junior colleagues. It is only where there is no atmosphere of creative activity that frictions abound. The creation of such an atmosphere is primarily the work of the senior scientists themselves. The state can help by removing impediments or creating conditions where scientific work can be easily carried out, but the state cannot create in scientists the spirit of cooperation or the incentive to research.

One measure may, however, help in this direction. This is the creation of a number of centres of research in each field, subject of course to the limitation of resources in manpower and funds. It is necessary to have several centres of comparable quality, both in order to stimulate internal competition and also to ensure that no important field is ignored. Existence of only one centre in a country generally

means that there is hardly any means of judging whether its work is fully satisfactory or not. There may, in addition, be a tendency to gloss over deficiencies and what is more serious, to limit the scope of research because of the personal taste and attainment of the leaders of the centre.

Some duplication may result from the existence of several independent centres, but of the two alternatives of (a) some duplication and (b) neglect of some important field, we should prefer the former. I may add that, strictly speaking, there can be no duplication in any field of research. Two scientists may attack the same problem, but their background, approach and treatment are bound to be different. Very often, such parallel attempts have led to extremely important discoveries that are complementary. If somebody had interfered with the work of Newton and Leibnitz on the ground that their research work appeared to be duplicatory, the world would have been the poorer for lack of differential or integral calculus. In order, however, to ensure that the duplication does not become wasteful, scientific councils with representatives of universities, important government and other organizations and independent scientists may be set up, but this is a point to which I shall return.

I may now turn to the distinction which is being increasingly drawn between fundamental and applied research. Fundamental research is recognized to be primarily the function of universities and similar scientific bodies. Applied research is generally left to industry or an operative department or ministry of government. This involves the risk that concern with immediate problems may impair the quality of applied research done under their auspices. It was mainly in order to guard against this danger that independent research councils were set up in western countries. Because they have as a primary aim research that yields practical results, governments have found it easier to finance them on the needed scale. Because they have no immediate administrative or executive responsibility, they can view the whole field of research and not be carried away by the need to deal only with day-to-day problems.

The question of the relation of such research councils and their laboratories to the universities is exercising the minds of scientists everywhere. They all agree that the two main functions of the university are the training of the younger generations and the advancement of knowledge for its own sake. As such, universities cannot always serve the immediate needs of society, and the research councils with their laboratories become unavoidable. If universities were asked to do the kind of work which the national laboratories do, they would be diverted from their true purpose and this would be a loss both to the universities and the nation. National research councils and national laboratories have thus come to stay, especially in the light of the spectacular advances of German industry in the latter half of the nineteenth and the equally striking advances of American and Soviet industry during the last three decades of the present century.

At the same time there is general agreement that if the research councils and their laboratories are

isolated from the universities, the long-term effects are harmful to both. It has been common experience that these councils and laboratories start with a great flourish and show striking results almost immediately, but after a few years, they seem to lose their initial energy. Prof. Heisenberg in Germany and Prof. Blackett in London offered a very interesting explanation of this phenomenon. They independently stated that it is the continual influx of young students and the pressures they exert on the accepted ideas of the teaching faculty which keep universities efficient and alive. In industry generally and to a lesser degree in the national laboratories, this revitalizing factor does not work to the same extent. Even though there are new recruits, they tend to fall in line and accept the pattern already in vogue in the industry or the laboratory. The result is a kind of 'scientific inbreeding'. Generally within ten years, and almost invariably within twenty years, these laboratories tend to become sterile unless they are renewed by exchange of personnel with universities or the inflow of new men with different ideas and programmes. Steps must, therefore, be taken to ensure that the research councils in India work in the closest co-operation with the universities.

The limitation of resources is a hard fact everywhere and even more so in India. In view of our shortage of trained manpower and paucity of material resources, we certainly cannot afford duplication of efforts and yet it seems some unnecessary duplication is taking place. The major reason for this is the comparative isolation from one another of universities, the Council of Scientific & Industrial Research, the Defence Science Organization, the Agricultural and the Medical Research Councils and the Atomic Energy Commission. Since each works independently and sometimes without knowledge of what the others are doing, it is perhaps inevitable that each should go its own way and at times tread on one another's toes. In the UK, there is a fairly clear demarcation in the functions of the defence laboratories, the national laboratories and the universities. In terms of resources and personnel, universities devote 90 per cent or so to pure research, some 10 per cent to applied research and almost nothing to development. For national laboratories, the major emphasis is on applied research with some attention to pure research while development is a marginal activity. Defence laboratories, on the other hand, are interested almost exclusively in applied research and development, and even more in development than in applied research. Hardly 1 per cent of the resources of defence laboratories are engaged in pure research and only about 20 per cent in applied research. Whenever any theoretical or basic problem arises, the defence laboratories use the resources of the national laboratories or the universities for the purpose. Development is such an expensive business that defence alone seems adequately placed to finance it, and hence any substantial diversion of defence funds for theoretical research is normally regarded as undesirable.

There is obviously need for some central agency in India to advise the state on allocation of functions, programmes and funds among different autonomous

bodies engaged in scientific research. The best solution may be to set up an advisory body with one representative each of the three research councils, the Defence Science Organization, the Atomic Energy Commission and the University Grants Commission, plus an equal or slightly larger number of independent scientists of eminence. Such an advisory body of 12-15 members could broadly review the programmes and consider the claims of the different authorities and then make recommendations for the allocation of funds among them. In addition, it could advise government in the relative priorities in research and where best they can be carried out. This is essential, as experience has proved that in matters of such vital importance, the collective wisdom of a group of experts is more dependable than the advice of a single individual, however brilliant and disinterested.

Ultimately, it would of course be for the government to take the decisions, as these are in the final analysis political. There are no scientific grounds for deciding whether more should be spent on biological or on space research. Nor is there any scientific criterion for deciding whether 2 or 3 or 10 per cent of the national income should be involved in scientific work. It would, however, be an advantage for government to have the advice of an expert body, for it could then consider its recommendations and take its decisions in view of available resources.

Once the allocation to an authority is made, it should be free to distribute it among universities, laboratories and other agencies at its discretion. This would ensure the best possible use of available national resources while maintaining the autonomy of the universities, the research councils and other authorities. The existence of such a body would also ensure that there is no undue duplication of laboratories or programmes nor undue encroachment by one authority on the functions or province of another. Without such an advisory body, there is a real risk that funds may be allocated, not according to the importance or urgency of projects, but because of the influence or personality of a powerful claimant.

The Indian Science Congress is the most representative body of scientists in the country and I would, therefore, place for its consideration the following broad conclusions:

(1) The state must play an increasing role in the support of scientific research without, however, trying to influence directly the aims or programmes of scientific organizations or individual scientists. At a conference of scientists held in August 1963, it was suggested that at least 1 per cent of the national income may be earmarked for support of scientific research. This seems to be the bare minimum, if India is to keep abreast with modern developments.

(2) Universities have in the past been the main centres of scientific research, but they cannot meet all the requirements of modern society. Special organizations have, therefore, been set up and the national research councils seem to be the most suitable instruments for the purpose, provided they work in the closest liaison with the universities and

share in the task of training future generations of scientists.

(3) National research councils can be most effective when they are given complete autonomy within their own fields and are not limited to programmes of immediate interest to government or industry.

(4) It is necessary to create in the country a number of advanced research centres, preferably three or four but at least two, in each major field of science with necessary staff, equipment and facilities like some free foreign exchange and the freedom of travel abroad for its members.

(5) Individual scientists must be given the freedom and indeed encouragement to pursue independent lines of research with special attention to the need of developing the initiative of younger scientists.

(6) There should be national councils in every field of science with representatives from government organizations, universities and other independent societies in more or less equal proportions and, finally,

(7) For effective guidance of scientific research, an advisory council consisting of representatives of the various national research councils, the Atomic Energy Commission, the Defence Science Organization, the University Grants Commission and independent scientists should be set up to advise government on the apportionment of funds to universities, non-official agencies and the national councils, the determination of priorities and programmes, and broad allocation of projects among the different bodies engaged in research.

The Indian Science Congress can and ought to take a lead in bringing about a new era in Indian science. Throughout her long history, India has

produced many men of the highest genius. The concept of zero and the evolution of the decimal system are among the greatest achievements of the human mind. In physics and chemistry also, Indian thinkers have reached great heights. In the fifty years before independence, we had again many brilliant scientists who achieved distinction in spite of severe handicaps. Any country can be proud of names like Ramanujam and Satyen Bose, Birbal Sahni, Meghnad Saha and C. V. Raman. I have named them only by way of example, for there are many others who have made significant contributions in many fields.

In spite of the fact that intermittently there have appeared great names in physics and mathematics, medicine and astronomy, chemistry, metallurgy and botany, we have to admit that there has been no climate of science in India till recently. After independence, there has been a great expansion of facilities and resources. Many new universities and laboratories have been established. Many more students are studying science and the number of research workers has increased substantially. We have some great names living among us and many young men have shown great promise. Nevertheless, India does not yet occupy in the world of science the position to which her traditions, her numbers and the intellectual quality of her people entitle her. With greater freedom and equality in discussion, with more large-hearted cooperation between older and younger scientists, I am confident that India can produce scientists of whom any country and any age could be proud. Towards that consummation, let the Indian Science Congress make a significant contribution.

Seminar on Recent Advances in Optics & Their Applications in Defence

THE new laboratory of the Instruments Research & Development Establishment (IRDE), Dehra Dun, of the Ministry of Defence, Government of India, was inaugurated by Shri Y. B. Chavan, Minister for Defence, on the forenoon of 30 October 1964. In continuation of this function, the Director, IRDE, organized a seminar on 'Recent advances in optics and their applications in defence' on 30 and 31 October 1964. The seminar was inaugurated by the Minister for Defence Production, Shri A. M. Thomas. Dr S. Bhagavantam, Scientific Adviser to the Defence Minister, presided over the deliberations. The seminar was attended, in addition to the delegates from IRDE, by 66 delegates from other organizations representing 43 different institutions which included organizations of the Ministry of Defence, defence research and development establishments and defence research laboratories, national institutes of technology, national laboratories, universities, industrial units in the public and private sectors, the Atomic Energy

Establishment and other scientific institutions and departments of the central government.

The aim of the seminar was to bring together senior representatives of the defence services, scientists engaged in defence research and those from the various other research institutions in the country with a view to developing mutual appreciation of each other's work, requirements and problems. Collaboration between the defence research and development organization and various universities and national laboratories is generally conceded to be an essential requirement for rapid development of technology in the country. The IRDE, being the only establishment of its kind in the country devoted to the development of instruments for the defence services primarily and for other requirements also in general, realized this need for co-ordinated effort and organized this seminar with a view to laying emphasis on the more sophisticated aspects of optics which represents yet another field of specialization of the establishment. The main

topics covered in the seminar were: (1) laser optics, (2) fibre optics, (3) infrared optics, (4) optical image evaluation, and (5) interferometry. In all, fifteen papers were presented at the seminar and discussions held on these topics. On the evening of 30 October 1964 there was also a popular lecture by Dr S. Bhagavantam on 'Symmetry: Its principles and practice', which was widely attended. Dr Bhagavantam lucidly explained the basic concepts of symmetry, taking examples from nature and interior decorations and indicated the spread of these concepts in the study of molecular and crystal structures.

Six papers were presented on lasers. Two of these by Prof. H. N. Bose (Indian Institute of Technology, Kharagpur) and Prof. A. K. Kamal (Roorkee University, Roorkee) discussed the physical principles involved in laser action and gave an account of the various possible applications of the lasers in range finding, in communication systems, etc., in addition to industrial and medical applications based on their thermal effects. Dr B. R. Marathe [Central Electronics Engineering Research Institute (CEERI), Pilani] gave a short account of the efforts made at the CEERI, to design a gas laser. Dr P. Venkateswarlu (Indian Institute of Technology, Kanpur) gave an account of the energy levels and the splitting of the energy levels of ions having d -electrons in doped single crystals and discussed the possibility of the development of maser action in trigonal and tetragonal crystals doped with ions having d^8 -electrons. Dr K. V. Narasimham (Defence Science Laboratory, Delhi) gave an account of the spectroscopic investigation of laser materials with particular reference to the rare earth ions (Nd^{3+}) carried out by him at the Johns Hopkins University, USA. Shri M. B. Khambaty (Atomic Energy Establishment, Trombay) gave an account of the GaAs laser currently under fabrication in their laboratories and the various applications proposed in communication systems. The papers read, lectures delivered and the discussions that followed gave an encouraging picture of the number of laboratories interested in this field of work and the efforts made so far at various centres for developing the technical know-how for fabricating laser components indigenously.

Dr V. Ramakrishna Rao (IRDE, Dehra Dun) described how the fundamental properties of infrared radiation are of strategic importance to military requirements. Two typical examples of active and passive devices were discussed. The scientific and technological aspects relating to the infrared studies such as sources and targets, materials, optics, atmospheric absorption, detectors and electronics were also discussed and the lines of work in which defence science can seek the collaboration of scientists in universities were indicated by him. Shri S. P. Singhal (Solid State Physics Laboratory, Delhi) gave an account of PbS detectors currently under development in the laboratory.

Dr N. S. Kapany, Director of the Optics Technology Inc., Belmont, California, USA, could not be

present but contributed a paper dealing with the optical properties of fibres and a number of instruments like fibre optics gastroscope, oximeter, hypodermic probe, etc. Shri S. K. Srivastava (IRDE, Dehra Dun) gave a detailed account of the technology of aligning, grinding and polishing. He pointed out the importance of factors like the impurities in glass, the surface cleanliness, etc., responsible for the absorption of light in fibres and indicated how improved transmission can be obtained by coating or cladding of fibres.

Prof. K. J. Habell (National Physical Laboratory, Teddington, UK), at present Professor of Instrumentation and Technical Optics, Indian Institute of Science, Bangalore, described the latest developments in interferometry such as the wave-shearing interferometers and their applications to a quantitative examination of large size optical elements, and the Moire fringe interferometry and its application in measurement of lengths and angles. Dr P. Hariharan (Hindustan Photo Films Ltd, Ootacamund) contributed, *in absentia*, a paper dealing with the testing of optical components (lenses and mirrors) using Twyman interferometer, with suitable modifications and improvements. Dr M. V. R. K. Murty (Madras Institute of Technology, Madras) described the construction and applications of simple interferometers using pairs of zone plates or scatter plates. Dr P. K. Katti (Indian Institute of Technology, Delhi) discussed the applications of multiple beam interferometry.

Dr M. De (University College of Science and Technology, Calcutta) dealt with the optical image evaluation and frequency response and described a method to study defects like coma, significance of phase shifts and the variation of contrast due to curvature and astigmatism. A method for differential correction of aberration in terms of frequency response was also indicated by him. Considerations governing the extension of these ideas to receptors like the human eye or the photographic emulsions were also discussed. Shri K. Swaminathan (IRDE, Dehra Dun) discussed the problems involved in the evaluation of an optical system and advocated the use of an electronic computer for this kind of work.

The proceedings were finally summed up by Dr S. Bhagavantam who observed that the background technology required for the development of laser optics and fibre optics is the main bottleneck in the rapid growth of applications of interest to the defence sciences. He expressed the hope that something useful could be expected in the immediate future in infrared applications and observed that the developments made so far in optical design and interferometry were of considerable interest and would help design test equipments for defence requirements.

The seminar ended in the evening of 31 October 1964 after Dr C. S. Rao, Director, IRDE, summarized the existing and proposed research and development activities of the IRDE in these subjects and thanked all the participants for making the seminar a success.

Annealing of Radiation Damage in Solids

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THE interaction of radiation with solids results in a number of effects depending upon the nature of the solid, and the nature and energy of the incident radiation¹. The direct effects are electronic excitation and ionization, displacement of atoms from normal lattice sites, and nuclear transformation. Fast charged particles generate chiefly electron excitation; a small fraction of their energy, only of the order of 0.1 per cent, is lost to atomic collisions². As the particles slow down, i.e. towards the end of their tracks, energy losses are predominantly through elastic collisions. The transition from inelastic to elastic behaviour is not abrupt; it can, however, be fairly well defined by certain considerations³⁻⁴. Fission neutrons produce only atomic displacements by elastic collisions with atomic nuclei, ionization processes being of negligible importance⁵ if the atomic number of the target material is greater than 10. Gamma rays generate primarily ionization, atomic displacements sometimes resulting as a secondary process from the elastic collisions of the Compton electrons⁶. Nuclear transformations occur to an appreciable extent only when materials of high cross-section are irradiated. Other special nuclear effects are observable under bombardment at extremely high energies (> 100 MeV.). Also of general occurrence is excitation of nuclear and electronic motion without permanent displacement.

Production and Nature of Radiation Damage

The four basic solid types, viz. molecular, ionic, metallic and valence crystals, behave in different ways under irradiation. In organic or molecular crystals, the individual molecules are relatively isolated from one another so that the atoms within the molecules relax rapidly when the electronic state is changed. Thus, free radicals are introduced and bonds rearranged principally as a consequence of electronic excitation. The excitation energy is also capable of dissipation, e.g. as light in aromatic compounds such as naphthalene and anthracene, without chemical action. Electronic excitation and (further) ionization produce predominantly chemical bond rupture in ionic solids with polyatomic ions⁷⁻⁹, such as NO_3^- , ClO_4^- , etc., whereas in simple ionic solids, e.g. the alkali halides, atomic displacements are generated with fairly high efficiency¹⁰⁻¹³. In valence crystals, such as diamond, germanium and silicon, the conversion of electronic energy into displacement energy is unlikely because the energy of recombination of electrons and holes is not large enough compared with the heat of formation. Actually, significant damage has been observed in these solids only when radiations which can knock atoms out of position are employed. In most good metals, the conduction electrons are so loosely coupled to the lattice that there is very little transmission of excitation energy from the electrons to the lattice. Electrons of the *d* and *f* type form a possible exception. In any case, there

seem to be no known cases in which damage related to lattice displacement has been observed to occur in metals purely as a result of electron excitation.

The energetics of the radiation damage process has been examined in considerable detail by a number of investigators^{2,14-20}. If the energy transmitted to a lattice atom in a collision is in excess of a certain minimum displacement energy E_d , the atom will be displaced from its normal lattice position. According to Seitz², the value of the displacement energy is approximately four times the binding energy of the atom in the solid, and hence is in the neighbourhood of 25 eV. for most materials. This prediction is in good agreement with experimental values obtained from electron bombardment studies²¹⁻²⁵. Atomic collisions range from the Rutherford type to the hard sphere type depending upon the distance of closest approach of the two nuclei, and hence on the energy of the bombarding particle. Whereas in Rutherford collisions small energy transfers are more probable than large ones, all energy transfers from zero to the maximum possible are equally probable in hard sphere collisions. The maximum possible energy transfer in the case of atomic projectiles is given by

$$Q_{\max.} = [4M_1M_2/(M_1+M_2)^2]E \quad \dots(1)$$

where M_1 and M_2 are the masses respectively of the incident particle and the target atom, and E the energy of the incident particle. The average energy transferred in those Rutherford collisions which displace atoms is given by

$$\bar{Q}_R = \left(\frac{E_d Q_{\max.}}{Q_{\max.} - E_d} \right) \ln \left(\frac{Q_{\max.}}{E_d} \right) \quad \dots(2)$$

The average energy transferred in a hard sphere collision, as also by a neutron, is

$$\bar{Q}_H = \frac{1}{2} Q_{\max.} \quad \dots(3)$$

The maximum energy which can be transferred in a collision by a relativistic electron of mass m is

$$Q_{\max.} = \frac{2(E+2mc^2)}{M_2c^2} E \quad \dots(4)$$

where c is the velocity of light.

In all these collisions, energies far in excess of the threshold energy for displacement may be imparted to the struck atom such that the primary displaced atom may itself displace other atoms by hard sphere collisions. Thus, for example, primary knock-on carbon atoms receive a mean energy of 280 keV. in irradiation with 2 MeV. neutrons. For materials in which there is no energy loss by ionization, the mean number of displaced atoms (i.e. vacancy-interstitial pairs) per primary knock-on is¹⁹

$$\bar{v} = \bar{Q}/2E_d \quad \dots(5)$$

Refined calculations yield the following values for \bar{v} for typical reactor irradiations (mean neutron

energy, 1 MeV.) in various substances⁴: carbon (graphite), 900; copper, 380; germanium, 290. The mean energy of a primary knock-on in light charged particle bombardment is much smaller⁵, a typical value being about 300 eV. A primary displaced atom of this energy produces about five additional displaced atoms, so that the total number produced by the incident particle as a result of a displacement collision is about six⁵.

A schematic presentation of damage in atomic particle irradiation is shown in Fig. 1. An incident particle collides with a lattice atom and produces a displacement. The primary displaced atom makes a collision and produces a secondary displaced atom whereafter both the primary and the secondary displaced atoms cause further displacements. Some of the collisions are of the replacement type which displace a lattice atom but leave the initially moving atom trapped at the vacancy thus created^{3,26}. It will be noticed that the damage becomes more densely populated at the end of each branch of the track than at the point of the primary impact. Moreover, the ratio of interstitials to vacancies is fractional near the point of primary impact and greater than unity at the periphery of the damage zone.

In addition to individual atomic displacements irradiation also produces collective effects in the target crystal. These are thermal and displacement spikes^{2,18}. The thermal spike consists of discrete or overlapping hot spots along the path of an incident particle or of a light displaced atom of energy $> 10^8$ eV. dissipating energy to similar light atoms, and has its origin in those close encounters in which energy less than the displacement threshold is transmitted. An energy transfer of about 10 eV., for example, would raise a region containing less than 100 atoms to a temperature near the melting point for a period of the order of 10^{-12} sec. A light displaced atom of energy $< 10^8$ eV. dissipating energy to similar light atoms undergoes hard sphere diffusive motion. Heavy displaced atoms in a heavy material also exhibit this type of motion unless they have extremely high energy. Most of the energy transmitted to the primary displaced atom reappears in the form of lattice vibration which, at least initially, is confined to a spherical region in that part of the path of the primary where it undergoes hard sphere diffusive motion. Brinkman¹⁸ has termed these spheroidal heated regions as displacement spikes. The average size of a displacement spike produced by 2 MeV. neutrons in copper has been estimated to be 75 Å. in diameter, and contains 2×10^4 atoms. Temperatures which are of the order of the melting point of the solid endure for 10^{-11} sec.

As distinguished from damage produced by atomic projectiles (Fig. 1), energetic electrons and γ -rays produce random distribution of interstitial-vacancy pairs in which the distance between the interstitial and the vacancy rarely exceeds 4 or 5 interatomic distances. This simplest form of damage arises from the fact that the primary knock-ons have generally insufficient energy to cause further displacements.

The lattice defects introduced by bombardment produce changes in the physical properties of solids²⁷⁻²⁹. Several of the properties affected by irradiation are shown in Table 1. Structural and

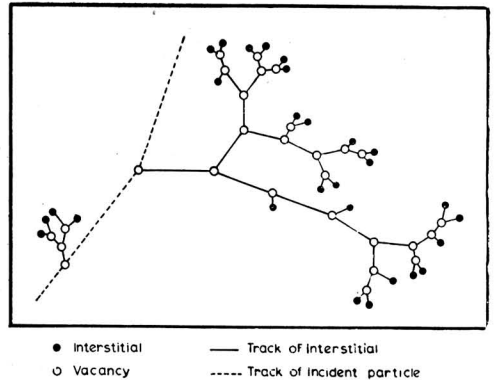


Fig. 1 — Schematic representation of interstitial-vacancy damage in solids

TABLE 1 — PROPERTIES AFFECTED BY LATTICE DEFECTS

Structural and mechanical	Electronic	Rate processes
Crystal structure	Paramagnetism	Diffusion
Density	Optical absorption	Ionic conductivity
Elastic constants	Photoconductivity	Phase change
Hardness	Dielectric loss	Chemical reactions
Thermal conductivity	Electrical conductivity	

mechanical effects are associated with localized strain and the change of vibrational frequencies in the damage zone, and electronic effects primarily with trapping of electrons or holes by the defects. It should be mentioned that such a separation of the causes of property changes is an over simplification. In fact, most changes are due to a combination of these and other causes. Fig. 2 shows changes in the electrical properties of graphite as a function of reactor exposure after Hennig and Hove³⁰. In general, the change in a given property is initially linear with respect to the time-integrated flux, but the rate subsequently diminishes due to the occurrence of radiation-induced recovery, i.e. the process of radiation annealing³¹. At low concentration of defects, the change in property is proportional to the concentration of defects. The number of defects can, therefore, be estimated in the proportional region from the magnitude of change of the property and the proportionality constant. The agreement between the experimental and theoretical values is within a factor of 2-5, the theoretical value being the greater.

To summarize, primordial radiation damage in solids consists largely of vacancies and interstitials with a variety of separations. The defects occur in groups in massive particle bombardment. The simplest form of damage consists of a random distribution of interstitial-vacancy pairs, and is produced in irradiation with electrons and γ -rays of energies near the threshold for displacement.

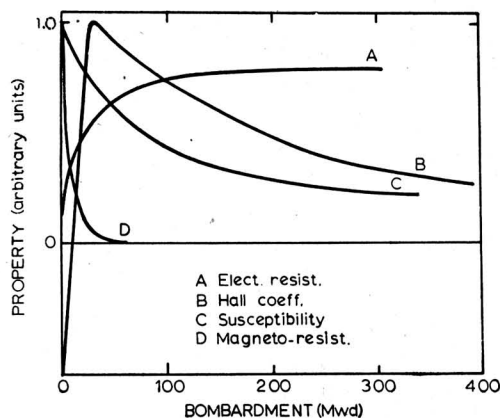


Fig. 2—Variation in the electrical properties of graphite induced by bombardment (after Hennig and Hove³⁰)

Annealing of Radiation Damage

It is a general phenomenon that when the temperature of a solid in which physical changes have been induced by irradiation is raised, the properties tend to revert to their original value. It is also known that partial recovery occurs even during irradiation³¹. The recovery, or annealing, is brought about by the interstitial atoms returning to their original positions in the lattice, i.e. by the mutual annihilation of the interstitials and the vacancies through recombination. Thermal annealing usually occurs in several stages, with different activation energies in different ranges of temperature; for example, recovery in copper manifests itself in five stages³²⁻³⁴ as follows: Stage I, 14-65°K.; II, 65-233°K.; III, 233-373°K.; IV, 373-473°K.; and V, > 473°K. A voluminous literature has accumulated in this field, and has recently been reviewed by Seitz and Koehler⁵ and by Dienes and Vineyard⁴. The present work is confined to the consideration of chiefly the kinetics of isothermal recovery with special emphasis on the mechanism involved.

In general, the kinetics of a given annealing process can be represented roughly by

$$-(dN/dt) = AN^\gamma \exp(-\epsilon/kT) \quad \dots(6)$$

where N is the number of defects taking part, ϵ the activation energy, A a constant, and γ the order of the reaction not necessarily integral. Thus, the processes are analogous to chemical reactions, although the rate is frequently limited by diffusion in which case the apparent order of the reaction is high and is not related to the number of constituents involved.

Theories of the Kinetics of Annealing

Annealing as a process with unique kinetics—Overhauser³⁵ studied the isothermal annealing of electrical resistivity induced in copper by bombardment with 12 MeV. deuterons at liquid nitrogen temperatures. He found that the annealing process which occurs with an activation energy of 0.68 eV. is accurately represented by Eq. (6) with $\gamma = 2.5$. The fact that the observed behaviour is close to a

bimolecular reaction has led to the assumption that the process involves the formation of bound pairs, which contribute less to the resistivity, from single diffusing imperfections which are responsible for the induced resistivity. Overhauser has shown, in fact, that the deviation of γ from the value 2 for an ideal bimolecular reaction can be explained in terms of the variation in lattice strain associated with the effects of irradiation. Simple second order kinetics have been found to obtain in annealing of neutron irradiation damage in lithium fluoride³⁶ and of γ -irradiation damage in sodium chloride³⁷. Waite^{38,39} has developed a theory of bimolecular reaction rates in condensed phases. It follows from the theory that bimolecular reactions in such phases follow second order kinetics when the rate is limited only by a barrier to reaction upon encounter. If the rate is also limited by the random diffusive motions leading to encounter between the entities, the rate is still of the second order in the reactants, but with a time dependent rate 'constant' which becomes truly constant, leading to simple second order kinetics, only after a definite transition period.

The thermal recovery of lattice expansion of fast neutron irradiated molybdenum⁴⁰ occurs in three stages, characteristic of different mechanisms of defect removal, at 100-200°, 400° and at 500-800°C. Although strict obedience to first or second order kinetics is not observed over the entire range of data, the first process, which anneals 20-30 per cent of the total radiation-induced lattice expansion, is grossly characterized by first order kinetics; however, a unique value of activation energy does not obtain. The process is believed to represent trapping of migrating interstitials at small impurity atoms.

Mixed kinetics model—Fletcher and Brown⁴¹ have developed a model for the kinetics of thermal annealing of the simplest form of radiation damage which consists of a random distribution of interstitial-vacancy pairs. It is considered that the interstitials remain stationary, and that the vacancies move. It is believed that the conclusions arrived at on the above assumption would also be valid for the reverse circumstance, viz. of stationary vacancies and mobile interstitials, which is generally found to be the case, in pure metals at least.

The migration of a vacancy occurs when an adjacent atom jumps into the vacancy whereby the vacancy moves to the former position of the atom. In a normal lattice, the average time τ required for an atom to jump into a vacancy is

$$\tau = \nu_0^{-1} \exp(\epsilon_m/kT) \quad \dots(7)$$

where ν_0 is the average lattice frequency, ϵ_m the potential barrier, k the Boltzmann constant, and T the absolute temperature. Vacancies and interstitials, however, cause the surrounding lattice to become distorted. Consequently, for a vacancy within the distorted lattice around the interstitial, the energy barrier and the jump time are lowered such that the vacancy has a preference for jumping towards the interstitial. Furthermore, since the atoms closest to the interstitial are most affected, the average jump time diminishes progressively as the vacancy approaches the interstitial. Thus, within the deformed region, the time required for a vacancy to become

annihilated will approximate to the jump time for the initial movement. Vacancies located outside the distorted region are capable of jumping in any direction with equal probability.³⁸ These vacancies, therefore, wander according to a random-walk process, some wandering back into the deformed region where they are subsequently annihilated, and the rest wandering off through the crystal. The vacancies which wander off are 'liberated' from their original interstitials, and will eventually be captured on dislocations, etc., or may recombine with other interstitials.

The interstitial-vacancy recombination process thus takes place in three stages:

(i) The first stage comprises the vacancies initially located within the deformed lattice; the time of recombination is less than the average jump time in the undistorted lattice.

(ii) The second stage involves those vacancies which are initially located outside the deformed lattice, but which wander back after a small number of jumps of time τ and are captured at their original interstitials.

(iii) In the third and final stage, vacancies which were liberated from their original interstitials will recombine or be captured after a large number of jump times τ .

Fletcher and Brown⁴¹ derive for an isotropic medium, the following relationships for the three stages of annealing:

$$(i) \quad N_M = \sum N_i \exp(-t/\tau_i) \quad \dots(8)$$

$$(ii) \quad N_L = \sum N_i \frac{r_o}{r_i} \operatorname{erf} \left[\frac{r_i - r_o}{2\langle b \rangle^2} \left(\frac{\tau}{t} \right)^{\frac{1}{2}} \right] \quad \dots(9)$$

$$(iii) \quad N_F = \frac{N_{FO}}{1 + 4\pi r_o^2 \langle b \rangle N_{FO}(t/\tau)} \quad \dots(10)$$

where N_i is the number of vacancies originally in the i th site, r_i and r_o radii of the initial vacancy position and of the deformed region measured from the interstitial, and $\langle b \rangle$ the magnitude of the change in radius r_i made at each jump in the appropriate stage averaged over all possible types of jumps. The total number of vacancies present after an annealing time t is given by the summation

$$N = N_M + N_L + N_F \quad \dots(11)$$

It is evident from Eqs. (8), (9) and (10) that the annealing depends upon the average jump time τ and the annealing time t only in the combination t/τ . Furthermore, the temperature dependence of annealing appears almost entirely through τ . Thus, it should be possible to superimpose the annealing curves for different temperatures by adjusting the time scales by proper factors. The barrier energy is obtained by considering the relative jump time as a function of $1/T$.

The model has been applied by Brown *et al.*⁴² to the isothermal annealing of bombardment damage in germanium. Fig. 3 shows the experimental composite annealing curve at 220°C. obtained by superposition of curves for various temperatures in the range 119-340°C. The continuous curve is the theoretical fit with two monomolecular recombination processes plus recombination during liberation.

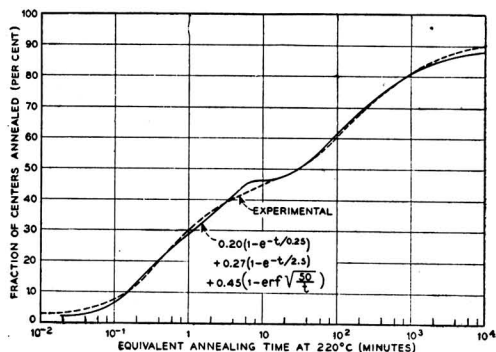


Fig. 3 — Theoretical fit of the composite experimental annealing curve for electron irradiated germanium with two monomolecular recombination processes plus recombination during liberation (after Brown *et al.*⁴²)

The curve is based on reasonable assumption regarding the distribution of the defects, and yields a lattice vibration frequency of the right magnitude ($\sim 10^{13}$ /sec.), and is, therefore, considered to represent the best description of the annealing process. The model requires that the barrier energy increase from a value characteristic of the stage of annealing governed by N_M and corresponding to early times (and low temperatures) to a constant value in the stages governed by N_L and N_F . Experimentally it is found that the energy is 1.78 eV. at higher annealing temperatures, and diminishes to 1.58 eV. at lower temperatures.

Kinchin and Pease³ have considered the two-dimensional diffusion in layer structures by replacing the spherical sink of the three-dimensional model by a circular one. There is no 'liberation' in this case. The solution is a good approximation to Eq. (6) with $\gamma = 6$.

Recent work has shown that annealing in semiconductors is more complicated than the simple interstitial-vacancy recombination envisaged in the Fletcher-Brown model. The annealing depends upon the charge state of the radiation defects^{43,44}. Moreover, interaction of the defects with impurities present in the crystal is of importance⁴⁵. Direct evidence for such interaction has been adduced by Bemski⁴⁶ and by Watkins *et al.*⁴⁷ from studies of paramagnetic resonance in irradiated silicon. The energy levels of the defects do not simply exist or vanish but change position during the migration of the defects through the lattice. The complications are inherent in semiconductors, and arise from variation in the position of the Fermi level with the experimental parameters.

Various workers have extended the Fletcher-Brown model to the annealing of chemical recoil and radiation damage in different systems. de Maine⁴⁸ observed that the model does not apply to the annealing of recoil damage in potassium chromate. Similar data of Zuber^{49,50} on cobaltic tris-ethylenediamine, as also those of Costea⁵¹ on hexamino-cobaltic nitrate, on the other hand, confirm to the model. Chemical radiation damage in nitrates is fairly simple and approximates to interstitial vacancy production

in irradiation. Annealing in these systems, therefore, as has been shown by Mohanty⁷, Maddock and Mohanty⁵² and by Mohanty and Upadhyay (unpublished work) is well represented by the model.

Diffusion-limited bimolecular recombination — Waite⁵³ has considered the annealing of radiation damage in solids as a diffusion-limited bimolecular reaction $A+B \rightarrow AB$ where A is an interstitial, B a vacancy, and AB a normal lattice site. This approach differs from that of Fletcher and Brown⁴¹ in that whereas these authors divide the annealing process into three stages corresponding to three distinct mechanisms of annealing, the Waite treatment combines the last two stages which appear to be the most significant. Moreover, the formulation of the random-walk process by Fletcher and Brown assumes independence in the distribution of the interstitials and the vacancies. There is, however, a certain correlation due to the recombination process; this correlation influences the rate of the reaction. Waite⁵⁴ has treated these problems by dealing directly with the joint probability distributions for each of the interstitial-vacancy pairs. The diffusion in the discrete lattice is approximated by diffusion in a continuum. The model envisages a spread in the separation of the interstitial from the corresponding vacancy, and a random distribution of the pairs with respect to one another.

The joint probability distribution for every pair $A_i B_j$ of the i th interstitial and the j th vacancy B_j is ρ_{ij} . Those $A_i B_j$ pairs for which $i = j$ are each produced in the same event, and have non-random initial distributions; all other $A_i B_j$ pairs ($i \neq j$) will have a uniform (random) distribution such that

$$\rho_{ij}(r, t = 0) = 1 \text{ for } i \neq j \quad \dots(12)$$

where $r (= r_A - r_B)$ is the interstitial-vacancy separation and will, therefore, be identical. The experimental data are not adequate to determine the form of $\rho_{ii}(r, t = 0)$. It is, therefore, assumed that

$$\rho_{ii}(r, t = 0) = Vn \exp \left[-\left(\frac{r}{\lambda r_0}\right)^2 \right], \quad r > r_0 \quad \dots(13)$$

which is equivalent to the condition that the probability that an interstitial-vacancy pair have an initial separation r is

$$\rho(r)dr = n \exp \left[-\left(\frac{r}{\lambda r_0}\right)^2 \right] 4\pi r^2 dr \quad \dots(14)$$

where V is the volume, λ the parameter which characterizes the radial distribution function, r_0 the capture radius, and n a normalization constant defined by the condition

$$\int_{r_0}^{\infty} \rho(r)dr = 1 \quad \dots(15)$$

Since both the interstitial and the vacancy are annihilated upon reaction, and the process is irreversible, the equilibrium concentration of vacancies and interstitials is negligible, so that

$$\rho_{ij} \rightarrow 0 \text{ as } t \rightarrow \infty \quad \dots(16)$$

Moreover, since it is assumed that interstitial-vacancy recombination is critically dependent upon r_0 , the Smoluchowski⁵⁵ boundary condition is valid:

$$\rho_{ij}(r \leq r_0, t) = 0 \quad \dots(17)$$

The boundary conditions provided by Eqs. (12), (13), (16) and (17) enable evaluation of ρ_{ij} and of ρ_{ij} for $i \neq j$. Differentiation with respect to r and substitution of the results into the appropriate rate relationship, viz.

$$\frac{dC_A}{dt} = \frac{dC_B}{dt} = \frac{4\pi r_0^2 D}{V^2} \sum_j^{N_A^0} \sum_i^{N_B^0} \left[\frac{\partial \rho_{ij}}{\partial r} \right]_r \quad \dots(18)$$

yield the expression for the kinetics of interstitial-vacancy recombination:

$$\begin{aligned} \frac{dC_A}{dt} = \frac{dC_B}{dt} = & -4\pi r_0^2 D C_A^2 \left[1 + \frac{r_0}{(\pi D t)^{1/2}} \right] - 4\pi r_0^2 D N C_A^0 \\ & \times \exp \left[\int_0^t f_{ii} dt \right] \left\{ \frac{\exp(-ar_0^2)}{(\pi D t)^{1/2}} \left(1 - \frac{4aDt}{4aDt+1} \right)^2 \right. \\ & \left. + \frac{\exp \left[-ar_0^2 \left(1 - \frac{4aDt}{4aDt+1} \right) \right]}{(4aDt+1)^{1/2}} \left[\frac{2}{r_0} \left(1 - \frac{4aDt}{4aDt+1} \right) \right. \right. \\ & \left. \left. - 4ar_0 \left(1 - \frac{4aDt}{4aDt+1} \right)^2 \right] \operatorname{erf} \left[a^{1/2} r_0 \left(\frac{4aDt}{4aDt+1} \right)^{1/2} \right] \right\} \quad \dots(19) \end{aligned}$$

where C_A and C_B are the concentrations respectively of the interstitials and the vacancies at time t , N_A^0 and N_B^0 their initial numbers, C_A^0 the initial concentration of interstitials, D the sum of the diffusion coefficients of the interstitials and the vacancies

$$D = D_A + D_B \quad \dots(20)$$

$$\operatorname{erf}(x) = \int_x^{\infty} \frac{\exp(-\alpha^2)}{\sqrt{\pi}} d\alpha$$

$$a = 1/\lambda r_0^2$$

and

$$f_{ii} = -4\pi r_0^2 D (C_A + C_B) \left[\frac{1}{r_0} + \frac{1}{(\pi D t)^{1/2}} \right] \quad \dots(21)$$

The model has been applied by Waite⁵³ to the annealing of bombardment damage in germanium, and by Corbett *et al.*⁵⁶ to copper. For early times, the fraction annealed

$$\varphi = (C_A^0 - C_A)/C_A^0 \quad \dots(22)$$

at time t is given by

$$\varphi = K(Dt)^{1/2} \quad \dots(23)$$

where

$$K = 8\pi^{1/2} r_0^2 N \exp(-1/\lambda^2) \quad \dots(24)$$

The data of Brown *et al.*⁴² for the initial annealing in germanium, and also those of Augustyniak⁵⁷ for

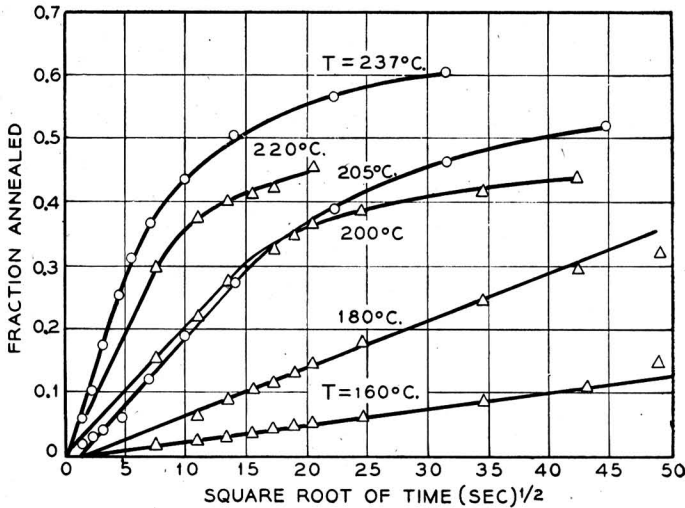


Fig. 4—Initial annealing of radiation damage in germanium [Δ , data of Brown *et al.*⁴²; \circ , data of Augustyniak⁵⁷ (after Waite⁵³)]

the same material are presented in Fig. 4 as a graph of ϕ against $t^{1/2}$. It is seen that as required by theory the curves are linear for early times. The initial value of $\phi/t^{1/2}$ for each temperature is a measure of the corresponding value of $KD^{1/2}$. Assuming that K is temperature independent, the variation of $\phi/t^{1/2}$ with temperature gives the temperature dependence of D . Moreover, if the diffusion coefficients of the interstitials and of the vacancies are very greatly different, D will have the form

$$D = D_0 \exp(-\epsilon_m/RT) \quad \dots(25)$$

It follows from Eqs. (23) and (25) that

$$\log [(\phi/t^{1/2})] = \text{const.} - \epsilon_m/2RT \quad \dots(26)$$

The value of ϵ_m has been calculated for germanium⁵³ from the linear plot of $\log(KD^{1/2})$ against $1/T$ as 1.37 eV.

An important feature of Eq. (19) is that the recovery is a function only of the parameter

$$z = \frac{2}{r_0} (Dt)^{1/2} \quad \dots(27)$$

This is indicative of the oft recognized circumstance that, provided the energy of activation is unique, a given recovery corresponds to the same microscopic configuration of defects irrespective of the time-temperature schedule employed. The same recovery is obtainable by annealing at different temperatures for times related by the Boltzmann factor. Physically, z is a measure of the number of jumps a defect makes during the time t . When the defects make the same number of jumps, regardless of the rate of jumping, the same amount of recovery takes place. It should be possible, therefore, to express isothermal recovery data taken at various temperatures as a unique function of $(Dt)^{1/2}$. The data of Augustyniak⁵⁷ and those of Brown *et al.*⁴² are shown in Fig. 5 (A and B) on graphs of ϕ versus $[D_0 \exp(-\epsilon_m/RT)t]^{1/2}$.

It is seen that data for $\phi < 0.45$ are adequately superimposed. The data for $\phi > 0.45$ scatter considerably, no doubt partly due to experimental error. Corbett *et al.*⁵⁶ find, on the other hand, that the recovery over 39.9-49.7°K. in substages I_D and I_E of stage I (14-65°K.) of electron irradiation damage in copper is superimposed in the entire range on to a single universal curve with $\epsilon_m = 0.12$ eV.

It is significant that Eq. (19) consists of two terms: the first term which is dependent on concentration gives the rate of interstitial-vacancy recombination with $i \neq j$, i.e. it corresponds to the recovery of a random distribution of interstitials and vacancies. The remaining term, on the other hand, is concentration independent, and relates to the correlated recovery of an interstitial with its own vacancy ($i = j$). The concentration independent term dominates at early times (low z) provided the initial distance between the interstitial and the vacancy of the pair $A_i B_j$ is small compared to the average distance between pairs. The concentration dependent term becomes dominant at high values of z where correlated recovery is no longer important, and has the simple form of a bimolecular rate process. At low concentration of damage, the composite recovery curve for copper calculated from Eq. (19) is clearly divided into two regions corresponding to the two types of recovery⁵⁶.

The Waite model represents the annealing behaviour of the simplest form of radiation damage (interstitial-vacancy pairs) with elegance and generality, and is accurately described by the attendant mathematics. Its original application by Waite⁵³ to semiconductor germanium is of doubtful validity in view of the subsequent discovery, already considered, that radiation damage in such systems does not consist of simple pair defects. Nevertheless, it is possible to prepare germanium crystals in which radiation damage anneals as indicated in Fig. 5A (Waite, T. R.,

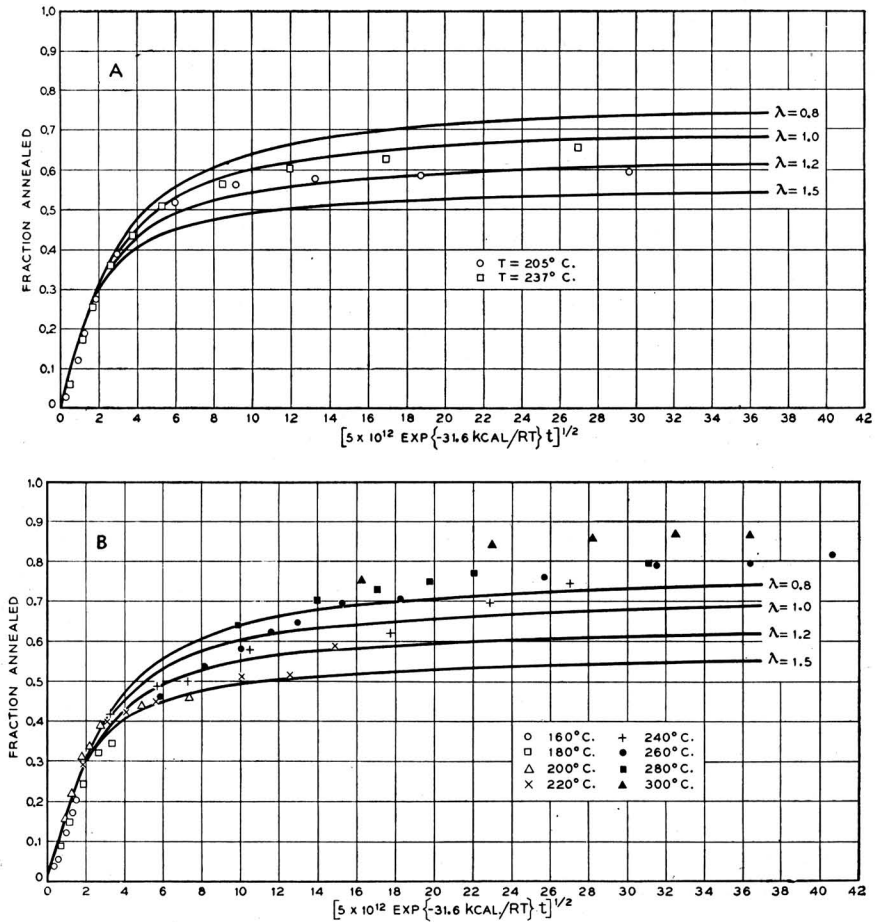


Fig. 5 — Annealing of radiation damage in germanium [The curves are calculated from Eq. (19) of text. A, data of Augustyniak⁵⁷; B, data of Brown *et al.*⁴⁸ (after Waite⁵⁹)]

private communication). The fact that the model accurately describes migration-induced annealing in pure copper⁵⁶ is indicative of the validity of the model for simple interstitial-vacancy recombination. The model considers a random distribution of correlated pairs and would, therefore, break down when a correlation exists between the interstitials and between the vacancies as at high defect densities, or is built up during the later stages of annealing at low defect densities⁵⁸.

Mohanty⁷ and Mohanty and Upadhyay (unpublished work) have applied the Waite treatment to the annealing in irradiated nitrates. As required by the theory, the plots of ϕ against $t^{1/2}$ are initially linear. Moreover, the annealing data at various temperatures can be represented as a unique function of $[D_0 \exp(-\epsilon_m/RT)]t^{1/2}$.

A process distributed in activation energy — The concept of a group of processes distributed in activation energy was originated by Vand⁵⁹ in his interpretation of the kinetics of the irreversible resistance

changes which take place when evaporated metal films are heated. Neubert⁶⁰ was probably the first to apply the concept to the annealing of radiation damage. Overhauser³⁵ found that annealing in copper bombarded at liquid nitrogen temperatures occurs below 200°K. with a spectrum of activation energies; between 200°K. and the room temperature, however, the process has a fairly sharply divided activation energy and an order 2.5. Honig⁶¹ considered the integral transformation of one of the equations arising in the kinetics of processes distributed in activation energy. The detailed mathematical analysis of the kinetics of recovery in the event of existence of a spectrum of activation energies has been provided by Primak^{62,63}.

As has already been pointed out, the general kinetics of isothermal recovery is representable by an equation of form (6). Since, however, N cannot be measured directly, it is necessary to consider a property p which is related linearly to the number of defects: $p = fN$. The rate Eq. (6) can then be

rewritten as

$$-(dp/dt) = Af [\exp(-\epsilon/kT)](p/f)^\gamma \quad \dots(28)$$

For a process with discrete activation energy, Eq. (28) may be integrated to give

$$p = p_0[1 - (1-\gamma)Bt \exp(-\epsilon/kT)]^{1/(1-\gamma)} \quad \dots(29)$$

where p_0 is the value of p at $t = 0$. The quantity B is given by

$$B = A(f/p_0)^{1-\gamma} \quad \dots(30)$$

and has the dimensions of frequency for all orders of reaction.

For processes distributed in activation energy, the measured value of the property P will be the integral of all the discrete processes occurring at the annealing temperature, and within a narrow band of activation energies $d\epsilon$:

$$P = \int_0^\infty p_0[1 - (1-\gamma)Bt \exp(-\epsilon/kT)]^{1/(1-\gamma)} d\epsilon \quad \dots(31)$$

$$P(t) = \int_0^\infty p_0(\epsilon)\theta_\gamma(\epsilon, t) d\epsilon \quad \dots(32)$$

The function θ_γ defined by Eqs. (31) and (32) is termed the characteristic isothermal annealing function.

The progress of recovery in isothermal annealing in the case of existence of a broad activation energy spectrum may be visualized as the horizontal movement of the sigmoid-shaped function θ_γ towards higher ϵ across the initial activation energy spectrum as shown in Fig. 6; the activation energy ϵ is given by

$$\epsilon = kT\{\ln[(1-\gamma)B] + \ln t - \ln[1 - \theta_\gamma^{(1-\gamma)}]\} \quad \dots(33)$$

The point of inflection ϵ_0 in the θ_γ function is

$$\epsilon_0 = kT \ln(Bt) \quad \dots(34)$$

and is referred to as the characteristic activation energy. The rate of movement of θ_γ diminishes with increase in t because of dependence on $\ln t$. At a given t , the portion of the initial activation energy spectrum to the left of θ_γ has already been annealed out, and that to the right is yet to be annealed. If the initial activation energy spectrum is very broad, i.e. many times γkT , the characteristic annealing function may be approximated to a step function. Eq. (32) then becomes

$$P(t) \simeq \int_{\epsilon_0}^\infty p_0(\epsilon) d\epsilon \quad \dots(35)$$

whence

$$p_0(\epsilon_0) \simeq -(1/kT)[dP/d(\ln t)] \quad \dots(36)$$

The relation given in Eq. (36) gives the initial distribution in terms of the isothermal annealing data.

Primak and Szymanski⁶⁴ have applied the Vand-Neubert-Primak model to the recovery of density changes introduced in vitreous silica by nuclear

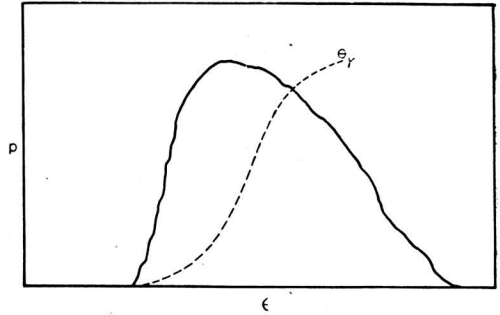


Fig. 6 — An activation energy spectrum in isothermal annealing

radiations. It is seen from Fig. 7 that the dependence, at various temperatures, of the per cent change in density on $\log t$ is almost linear. If $dP/d(\ln t)$ were constant for annealing at a given temperature, the portion of the initial distribution revealed at that temperature would be constant. Fig. 8 shows the plots of $p_0(\epsilon_0) = (1/kT)[dP/d(\ln t)]$ calculated on the assumption of linearity of $P(\ln t)$ against $\epsilon_0 = kT/\ln(Bt)$ by broken lines. The initial distributions at different temperatures form disconnected segments which reveal a peak. If, instead of fitting straight lines, the points in Fig. 7 are connected with the curves shown, and $p_0(\epsilon_0)$ calculated for every point from the slope $dP/d(\ln t)$ at that point, the initial distributions shown by continuous lines in Fig. 8 result. The value of the frequency factor has been arbitrarily chosen (10^9) to achieve a reasonably good coincidence of the overlapping sections of the distributions at different temperatures; the effect of B in isothermal annealing is to cause only a simple displacement along the activation energy axis. It would thus appear that the recovery data can be interpreted as revealing an initial distribution of per cent changes in density which is a peak over an activation energy spread of about 2 eV. Clarke⁶⁵ has applied the model to the annealing of neutron irradiation damage in magnesium oxide.

Overhauser³⁵ and Dienes⁶⁶ have considered the variation of the activation energy for recovery as arising from the change in the number of defects due to annealing. The lattice strain near a vacancy reduces the activation energy for migration of a nearby interstitial so that as the vacancies are progressively filled up during annealing, the activation energy increases to a constant value corresponding to the activation energy for migration in the undistorted lattice. The Dienes analysis assumes a linear dependence of ϵ on N of the form

$$\epsilon = \epsilon_0 - \alpha N \quad \dots(37)$$

where α is a constant. The general rate Eq. (6) becomes

$$-(dN/dt) = AN^\alpha[\exp(-\epsilon_0/kT)][\exp(\alpha N/kT)] \quad \dots(38)$$

At a fixed N , Eq. (38) may be written in the form

$$t = k'[\exp(\epsilon_0/kT)][\exp(-\alpha N/kT)] \quad \dots(39)$$

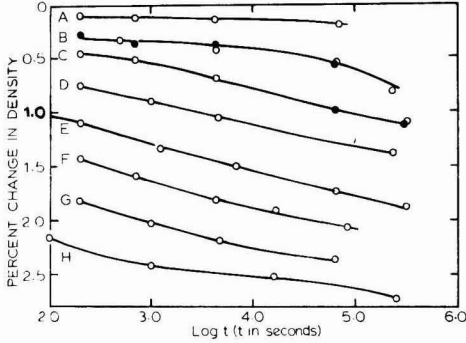


Fig. 7—Annealing of irradiation-induced changes in the density of vitreous silica [A, 300°; B, 450°; C, 550°; D, 650°; E, 725°; F, 800°; G, 900°; H, 1000° C. (after Primak and Szymanski⁶⁴)]

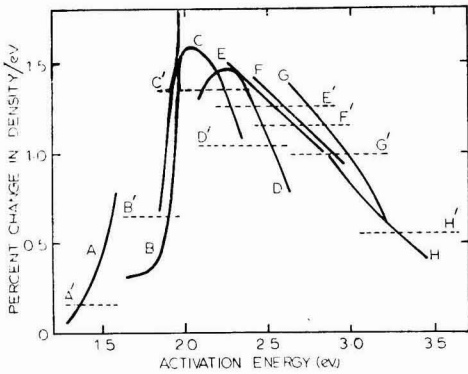


Fig. 8—Initial distribution of density changes over activation energy from the annealing data in Fig. 7 [A, A', 300°; B, B', 450°; C, C', 550°; D, D', 650°; E, E', 725°; F, F', 800°; G, G', 900°; H, H', 1000° C. (after Primak and Szymanski⁶⁴)]

where k' is a constant. Thus, although a plot of $\ln t$ against $1/T$ obtained at a fixed N is linear as in the simple case of discrete activation energy represented by Eq. (29), the variable activation energy manifests itself in a systematic change of the slopes of these lines as a function of the amount of recovery at which ϵ is being determined. Moreover, a small change in ϵ with N results in a large change in the time scale for a given isothermal recovery. It is also significant that a recovery process of a low order γ and variable ϵ is very similar in character to one of higher γ and of discrete ϵ .

The Vand-Primak treatment has been invoked in the annealing of chemical recoil and radiation damage by Harbottle and Sutin⁶⁰, Shankar and coworkers⁶⁷⁻⁶⁹, Costea⁵¹ and by Mohanty and Upadhyay (unpublished work). The plots of $\rho_0(\epsilon_0)$ against $1/kT[d\rho/d(\ln t)]$ are similar to those shown in Fig. 8.

Conclusion

The foregoing considerations show that annealing in even the simplest form of radiation damage, viz.

a random distribution of non-interacting interstitial-vacancy pairs, is very complex. The complexities arise from several factors. In the first place, there is a spread in the separation of the interstitial from the corresponding vacancy, depending on the energy transferred in the displacement collision and the crystallographic direction of the recoiling interstitial. In close pair recovery, the specific interstitial-vacancy configuration is of importance⁷⁰. The lattice deformity near a defect renders migration of other defects anisotropic in consequence of which the activation energy for migration varies inversely with the density of defects. Moreover, it is likely that some freely migrating interstitials escape to dislocations or grain boundaries, thus affecting the kinetics of recovery³¹. In such an event, subsequent to the annihilation of all the free interstitials by recombination, the excess vacancies diffuse to dislocations and grain boundaries with higher activation energy. The rate of diffusion-limited annihilation of excess vacancies has been calculated by Penning⁷¹. There is also the possibility of the formation of groups of interstitials, and of vacancies, which only break up with high activation energies⁷². Annealing in certain systems depends upon the charge state of the radiation defects, and the interaction of the defects with impurities present in the crystals^{40,45,73}. Clearly, further theoretical and experimental work is needed before the problem of damage recovery can be unravelled in its entirety.

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Spectroradiometric Methods for Daylight Studies

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IT is a matter of common experience that coloured objects in daylight under different conditions of weather appear different as the energy content of daylight at different wavelengths in the visible region varies with weather conditions. As these variations are so frequent and subtle, it is necessary to develop some artificial standard of light having some suitable colour distribution of daylight as its basis so that matching of coloured objects may be done properly. Also, because of the wide use of fluorescent dyes in coloured materials as well as white fabrics it is necessary to take into account the normal ultraviolet content also of daylight when choosing the artificial standard of daylight. A study of the spectral energy distribution of daylight, i.e. spectroradiometry of daylight, in the ultraviolet and visible regions will make available valuable material for developing a suitable standard for artificial daylight. In addition, such a study will throw light on the various processes operating in the atmosphere which are responsible for the variations. The general methods of spectroradiometry and the different assemblies developed by different workers for studies on daylight are briefly surveyed in this article.

General Methods of Spectroradiometry

To evaluate the spectral quality of a luminous source one requires a means for separating the light from the source into narrow spectral bands and for measuring the energy in these bands. For splitting the source into narrow spectral bands either filters or prisms or gratings are made use of. With monochromatic filters the readings can be obtained only at selected wavelengths depending upon the filters chosen. On the other hand, using a monochromator with either a prism or grating, one can separate quite narrow spectral regions and scan the whole spectrum continuously. If a single monochromator is used errors are introduced because of instrumental scattered light. A double monochromator is, therefore, preferred.

For measuring the energy in the spectral range studied a radiation detecting device is necessary. These devices can be either non-selective receivers like bolometers, thermopile, etc., or selective receivers like photocells, photomultiplier tubes or photographic plates. In spectroradiometry it is convenient to use a sensitive selective receiver like a photomultiplier tube or a fast photographic plate after calibrating the system point by point with a standard comparison source of known spectral quality. The output current from the photoelectric device can either be noted manually with the help of a sensitive galvanometer or recorded on a strip chart recorder. In the first case the energy can be measured at definite intervals of, say, 100 Å., whereas in the latter the energy can be measured continuously if the wavelength drive of the mono-

chromator is coupled to a suitable motor provided with a gear system. This gives the fine structure of the spectral distribution curve which sometimes is very valuable.

Spectroradiometry of Daylight

For the spectroradiometry of daylight either filters or prism or grating may be used. When using monochromatic interference filters for daylight—sunlight or skylight—one should see that the incident radiation on the filters is as nearly perpendicular to the filter surface as possible to avoid alterations in the filter spectral curves at oblique incidence. When the average shape of the spectral curve alone is of interest without any details, one can perhaps use the method of filters for the study of daylight. On the other hand, the use of a prism or grating monochromator is more convenient even when measuring the energy at selected intervals of wavelengths, as one has a greater control over the choice of wavelengths. The errors due to scattered instrumental radiation would be very serious in the ultraviolet region as the energy in the ultraviolet region in daylight is very low. Hence it is definitely advantageous to use a double monochromator in the ultraviolet region.

If the measurements required are on direct sunlight a heliostat or siderostat may be used to follow the path of sun and reflect the light on to the slit of the monochromator. It would, of course, be necessary to use neutral filters to reduce the intensity of sun's radiation. If the study is on sky radiation a mirror may be used to take the light from a chosen part of the sky. In both cases it is desirable to introduce a magnesium oxide block in front of the slit of the monochromator such that the light reflected by the mirror is again reflected by the magnesium oxide block into the slit. This keeps the monochromator optical system filled at all times, thus avoiding any error due to non-uniformity of the transmittance of the prism across the aperture. In the case of direct sunlight which is followed by a heliostat mirror, the plane of polarization would be continuously changing relative to the monochromator. This can be eliminated by the introduction of a magnesium carbonate block or may be corrected for in terms of the air mass as was done by Stair *et al.*¹ in their work on spectral distribution of energy from the sun.

Because of rapid changes in the spectral quality of daylight due to changes in the atmospheric contents like dust, clouds, ozone, carbon dioxide, etc., the energy measurements have to be made in an appreciably short time over the entire visible and ultraviolet regions if the ultraviolet region is also included in the study made. When the measurements are taken manually with a sensitive galvanometer, readings could only be taken at sufficiently long intervals of wavelengths to cover

the entire region in a reasonably short period of time. It is possible that even during the few minutes taken for this there may be variations in the intensity of the daylight. A correction may be applied for these variations in terms of the changes in the total illumination recorded by a light meter during the period of taking spectral readings, or in terms of a fixed wavelength, say 5600 Å. (as was done by Taylor and Kerr²). An alternative for these corrections is to take the average of a number of sets under apparently the same sky conditions. If one wants to study the spectral curve with all its finer details the automatic recording assembly is the only way. This consists essentially of a monochromator whose wavelength changing mechanism is driven by a variable speed synchronous motor and of a photocell whose output is recorded on a strip chart recorder. In addition to giving finer details of the spectral curve this device gives the result in much shorter time compared to the method where readings are taken manually. The quicker operation resulting from the automatic recording makes it necessary to keep the slit wide enough for obtaining a proper response of the recorder. But in the case of daylight with a continuous spectrum on which are superimposed thousands of Fraunhofer lines and absorption bands, large slit widths significantly alter the true character of the distribution. It is, therefore, necessary to use an amplifier before feeding the signal to the recorder.

Some Typical Designs Developed for Daylight Spectroradiometry

One of the earliest attempts at evaluating the spectral quality of solar radiation was made at the Smithsonian Institute. Coblenz and his colleagues at the US National Bureau of Standards, Washington, had done some work using mainly filters. The work done at the National Bureau of Standards was mainly centred round the ultraviolet region because of its biological importance. Later Stair³ and his colleagues continued the work at the National Bureau of Standards. In his earlier assembly for the evaluation of ultraviolet energy from the sun, he used an automatic recording method³. The assembly consisted of a double monochromator, RCA 935 phototube, 510 c/s. light modulator, amplifier, auxiliary meters and recording apparatus. Changes in the wavelength were accomplished through a synchronous motor drive coupled to the wavelength drum. Three speeds were available for scanning the spectrum both in forward and reverse directions. Wavelength marks were provided at suitable positions by means of an auxiliary pen on the record chart. A heliostat with a sufficiently large mirror was employed and a second stationary mirror reflected the light beam from the heliostat mirror into the spectroradiometer. No image of the sun was produced on the entrance slit with a lens or mirror as only the integrated solar energy spectrum was desired. The whole set-up was calibrated with a standard source whose distance from the slit and mirrors was so arranged that the illuminated area of the collimating lens was the same as when sunlight was falling

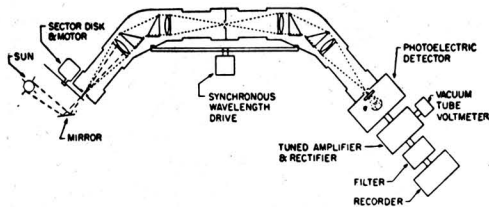


Fig. 1 — Block diagram of the spectroradiometer used by Stair *et al.*¹ (the heliostat is not shown)

on it. They introduced a correction for the change in polarization due to the rotation of heliostat mirror, in terms of the variation of the response of the instrument with the air mass. The block diagram showing the layout of the instrument is shown in Fig. 1. Tests made with this instrument showed that it was possible to employ it for studies on the spectral distribution of skylight also.

Stair and Johnston⁴ have described an improved version of the device described above. This consists mainly of a double monochromator as in the earlier design but mounted on a polar axis and driven by a synchronous motor to follow the path of the sun across the sky for hours without any significant readjustment. Any departures due to changes in solar declination or to atmospheric refraction effects are detected photoelectrically and are corrected manually. The need for polarization correction also is eliminated as the instrument is directly aimed at the sun.

In a recent paper MacAdam⁵ describes a continuously recording spectroradiometer designed and built at the research laboratories of Eastman Kodak Company. The instrument covers the range from 350 to 1000 $m\mu$ in about 3.5 min. which is roughly the same speed as for the one described earlier. The instrument is easily movable on caster wheels, both its overall length and height being 8 ft. It can be rotated both on horizontal and vertical axes.

The schematic diagram of the instrument designed by MacAdam⁵ is shown in Fig. 2. A constant deviation double monochromator consisting of two replica gratings is used for analysing the radiation. The first collimator is provided with a large number of baffles which permit rays to pass only in a direction parallel to the top and bottom sides of the collimator box and eliminate trouble from stray light. Light from the external source (ES) whose spectral distribution is to be studied and also that from a standard lamp pass alternately through the monochromator after approximate sinusoidal modulation by a rotating disc (D). After emerging from the third collimator (C_3) the light is focused by a Fresnel lens (N) on a photomultiplier tube (P). The output from the photomultiplier tube is a 60 c/s. signal whose phase depends upon the relative intensities of the two beams, viz. (i) from the external source and (ii) from the standard source at the particular wavelength. The 60 c/s. signal is amplified and made to drive a servomotor. The motor moves the mirror M' and controls the peak intensity of the beam passing through the monochromator

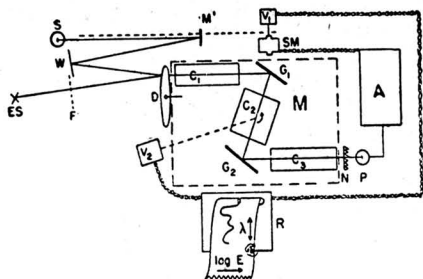


Fig. 2 — Schematic diagram of the set-up used by MacAdam [ES, external source; F, calibrated filter; D, rotating disc; C_1 , C_2 and C_3 , collimators; G_1 and G_2 , plane gratings; M, monochromator; N, Fresnel lens; P, photomultiplier tube; A, amplifier; SM, servomotor; V_1 and V_2 , potentiometers; R, recorder; S, standard lamp; M' , mirror; and W, white plate]

from the standard lamp. A potentiometer V_1 coupled to the mirror M' gives a small d.c. voltage proportional to the logarithm of the illuminance of the white plate W. This output d.c. voltage recorded on a chart which moves synchronously with the wavelength drive of the monochromator gives the relative spectral energy on a logarithmic scale ($\log E$). Another potentiometer V_2 geared to the wavelength drive of the monochromator may be adjusted to deliver a potential that is proportional to the logarithm of the spectral distribution of the internal standard lamp. This potential is added to that from V_1 and the curve on the chart gives the logarithm of the absolute spectral distribution of the external source.

In the case of sunlight and daylight, the spectral distribution curves of which might differ radically from that of the internal standard lamp, a calibrated filter can be placed in front of the entrance aperture of the instrument to make the energy from the external source roughly similar to that of the standard lamp.

Some of the specific advantages of this instrument are that no slits, lenses or mirrors are used in the monochromators and consequently there is no loss of energy by absorption and that the instrument can be directly aimed at the sun or the part of sky being studied. The spectral distribution curve is independent of the variations in the efficiency of the monochromators, the phototube power supply and gain in the amplifier. It was found that when the standard lamp was operated at 34 amp. the signal-to-noise ratio was about 10000:1 in the wavelength range 430-600 $m\mu$. The ratio decreased towards longer wavelengths, some typical values being 1000:1 at 850 $m\mu$, 100:1 at 900 $m\mu$ and 10:1 at 950 $m\mu$. In the visible region it has a very high signal-to-noise ratio and can be used with great advantage.

Another continuously recording unit which has been recently designed for studying sunlight is by Dunkelmann and Scolnik⁶. The block diagram of the instrument is shown in Fig. 3. It consists chiefly of a double monochromator adapted for

automatic scanning and recording. The instrument is thermostated in a light tight box at 85°F. Sunlight after reflection from a siderostat mirror (M_S) is incident on a magnesium carbonate block (C) in front of the slit of the monochromator. Light from a standard lamp L can be made to fall on the slit by interposing a mirror M_L . The photocurrent is amplified by a chopper amplifier after subtracting the dark current by means of a bucking box (B) and recorded on a strip chart recorder. With this instrument it takes about 5 min. to scan from 3000 to 7000 A.

Daylight Spectroradiometric Studies at the National Physical Laboratory

A programme of study of the spectral energy distribution of skylight was started some time back in the Division of Optics at the National Physical Laboratory, New Delhi. The equipment used was quite simple and employed a galvanometer and readings were taken manually. A start was made with a study of the western sky about 40° above the horizon, under different meteorological conditions during the monsoon months of 1960. The schematic diagram of the actual instrument used is shown in Fig. 4. It consists of a Hilger quartz monochromator, RCA photomultiplier tube and a sensitive galvanometer. The light from the sky was reflected by an aluminized mirror on to a block of magnesium oxide (1) which reflects it again into the slit (2) of the monochromator. The spectral region from 340 to 700 $m\mu$ was studied and readings were taken at 10 $m\mu$ intervals. After some preliminary experiments the time taken for the scan was reduced considerably by dividing the work between two persons, one exclusively attending to setting the wavelength drum and the other taking the galvanometer readings. In this way a scan of the region from 340 to 700 $m\mu$ took about 5 min. with readings taken at intervals of 10 $m\mu$. Though quite simple, this equipment yielded quite satisfactory results⁷.

These studies have shown that while continuous recording may be necessary for a study of finer details in the spectrum of sun or sky, a non-recording

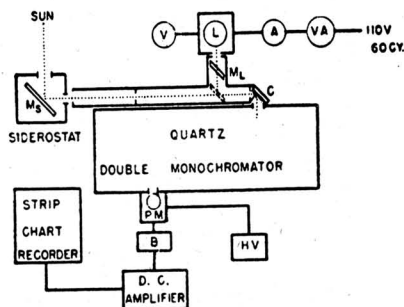


Fig. 3 — Block diagram of the instrument used by Dunkelmann and Scolnik⁶ for sunlight [M_S , siderostat mirror; M_L , mirror; C, magnesium carbonate block; L, standard lamp; V, voltmeter; A, ammeter; VA, variac; PM, photomultiplier tube; B, bucking box; and HV, high voltage power supply]

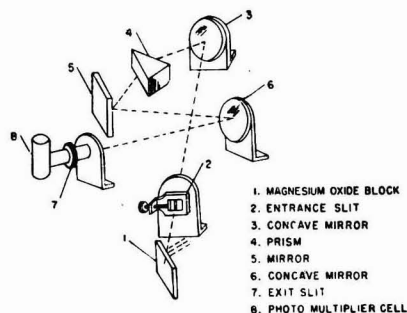


Fig. 4 — Schematic diagram of the assembly used at the National Physical Laboratory, New Delhi, for studying spectral energy distribution

unit with the energy measurements manually recorded at suitable intervals of wavelengths still gives valuable results on the spectral variation and colour of daylight. Taylor and Kerr² used such a unit for studies on skylight and evaluated the colour temperatures of daylight under different conditions. They took about 15-30 min. to cover the readings at intervals of 100 Å. in the region 4000-7000 Å. and introduced corrections for the variations in sky conditions during the time of observation in terms of the energy variations at wavelength of 5600 Å. and the total illumination measured separately.

In a recent study on the spectral energy distribution and colour of daylight, Henderson and Hodgkiss⁸ were able to get the intensity distribution in the range 3000-8000 Å. in about 10 min. from readings taken at 100 Å. intervals. Their results show that while it is a definite advantage to use a continuously recording unit, equally good results

on the evaluation of colour of daylight may be obtained even with a non-recording unit.

Summary

The need for developing an artificial standard of light having some suitable colour distribution based on that of daylight is pointed out and the necessity to take into account the ultraviolet content of daylight is stressed. The general methods adopted in studying the energy distribution at different wavelengths of daylight (spectroradiometry) and the different instruments used for this are described briefly. Special features of a newly designed instrument at the National Physical Laboratory, New Delhi, are described and discussed. It is concluded that while it is a definite advantage to use a continuously recording unit, equally good results on the evaluation of colour of daylight may be obtained even with a non-recording unit.

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Recent Advances in the Chemistry of the Cotton Plant*

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A SYSTEMATIC study of the various products obtained from the cotton plant (*Gossypium* spp.) has not been carried out until recently. No complete data are available on the presence of various compounds in the different species of the plant and their variation with the climatic and edaphic conditions, and the period of vegetation. Besides cellulose and oil, there are many other important compounds in the cotton plant, viz. organic acids, hydrocarbons, polyphenols (gossypol and its derivatives, flavonoids and tannins, anthocyanins, etc.), sterols, terpenes, vitamins, organic compounds of nitrogen and phosphorus and other substances which, evidently, play an important role in the life-history of the plant. However, the cotton plant as a source of these compounds has not been exploited. The physiological role of the compounds in the life-history of the plant is not known, due to lack of chemical, physiological and biochemical studies. For example, the root-bark of the plant, which is described in pharmacopoeias as having styptic properties, has hardly been studied. Since 1954, a comprehensive programme of study has been in progress in our laboratories with a view to separating and establishing the structure of the chemical substances present in the cotton plant, finding possible practical applications for them and studying the formation, distribution and the dynamics of accumulation of some of the substances which play a significant role in the life processes of the plant. In this review some of the results of work carried out in our laboratories on the substances separated from the various parts of the cotton plant are discussed.

Gossypol

The polyphenol, gossypol, which is a coloured and poisonous pigment of the cotton plant, was first separated from raw cotton oil by Marshlevosky in 1899. Gossypol is present in the seed-kernels and root-bark where, along with other pigments related to it, it is localized in the special morphological structures called the pigment glandules. The chemistry of gossypol has been studied by Zamishlyaevoya, Kozhevnikovaya, Markman, Rzhelin, Seshadri and coworkers, Clark, Adams and coworkers, and others. Smirnov, Yarosh, Bautner and others have studied the biochemistry of gossypol. However, investigations on the dynamics of accumulation and variation of gossypol concentration in different parts of the plant with particular reference to the variety and habitat of the plant are few. The derivatives of gossypol, which provide interesting data on the biogenesis of polyphenols in general and of gossypol in particular, have not been studied at all.

*Lecture delivered in Russian at the Advanced Centre for the Chemistry of Natural Products, Delhi University, and translated by (Mrs) Padma Vasudevan.

The study of the formation, distribution and dynamics of accumulation of gossypol in the various parts of the plant is of special importance for knowing the role of gossypol in the plant. The solution of this problem depends largely on the availability of an exact method for the estimation of gossypol in the various parts of the plant. The methods available in the literature are applicable only for the estimation of gossypol in the seeds and in the products obtained on processing it. A new method which can be used for quickly estimating gossypol in all parts of the plant has now been developed in our laboratory. The method is based on the facts that gossypol is most stable in borax solution; the properties of gossypol do not change on dissolving it in borax and borax does not dissolve other weakly acidic substances. The method consists in extracting the material with ether, dissolving gossypol in borax, extracting gossypol from the acidified solution of borax with chloroform and measuring the colour intensity of the product obtained by reacting gossypol with antimony trichloride.

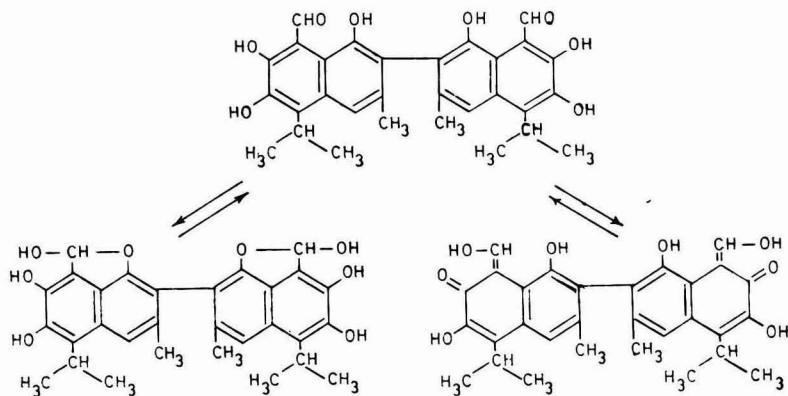
The dynamics of accumulation and variation of gossypol in the various parts of the industrial variety of the cotton plant have been investigated in our laboratories. The data obtained have enabled us to arrive at important conclusions. Contrary to the views found in the literature, it has been shown that gossypol is formed from the first day of the growth of the cotton plant and exists in all the vegetative and reproductive organs. The root-bark is richest in gossypol. Maximum accumulation of gossypol occurs at the end of the vegetative period.

In the seeds, there is intensive formation of gossypol between the 30th and 50th day of development of the bolls. The gossypol content in root-bark varies from 0.56 to 2.05 per cent and in the seed-kernels from 0.33 to 2.4 per cent.

From studies on the gossypol content of root-bark and seed-kernels it has been concluded that the presence of gossypol in the root-bark and seed-kernels varies widely depending on the species and variety of the cotton plant. Gossypol has not been detected in the seeds of other genera of *Malvaceae*. This shows the specificity of gossypol for the genus *Gossypium*. The root-bark which is rich in gossypol can be used as a raw material for the preparation of gossypol. A method for preparing gossypol from the root-bark has been worked out in our laboratory.

Adams and coworkers have proposed 2-2'[1,6,7-trihydroxy-3-methyl-5-isopropyl-8-aldehyde] binaphthyl (I) as the structure for gossypol. This structure has been confirmed by the synthesis of gossypol and from a study of its decomposition products, apogossypol and desapogossypol.

With a view to preparing physiologically active substances based on gossypol, a number of condensations involving its aldehyde groups have been



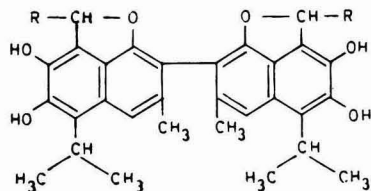
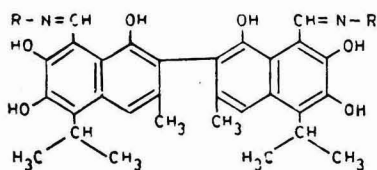
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Tautomeric forms of gossypol

carried out. The thiosemicarbazone (amizon) and isonicotinoylhydrazone (ftivazide) of gossypol have attained considerable importance as antitubercular drugs. In these substances, the aldehyde components are derivatives of amino- and hydroxybenzaldehyde. Starting from these considerations, and as gossypol is an aldehydophenol, it was suggested by us that the thiosemicarbazone and isonicotinoylhydrazone of gossypol can also have antitubercular activity. Nine derivatives of gossypol (II-X) having antitubercular activity have been synthesized.

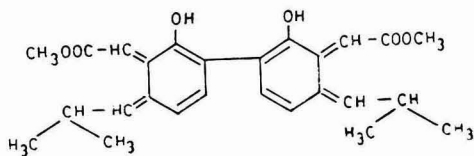
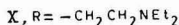
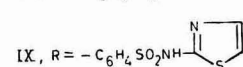
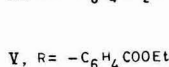
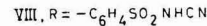
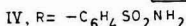
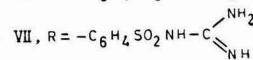
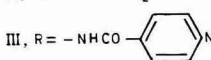
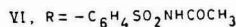
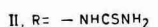
In analogy with the work of Seshadri and co-workers, who effected condensation of gossypol with malonic and acetoacetic esters, derivatives of gossypol with barbituric acid have been synthesized in our laboratory. A number of esters and derivatives of gossypol have been found to be water-soluble. The pharmacological activity of these compounds is under investigation.

Gossypol has also been found to react with Grignard's reagent to form compounds of the type (XI).

Oxidation of gossypol is an interesting reaction, but so far it has been found rather difficult to separate the products of oxidation and determine the course of oxidative decomposition of gossypol. A knowledge of the products of oxidative decomposition of gossypol, formed during refining of the oil, is important and is likely to form the basis of a process for their separation. The products of oxidation of gossypol in alkaline solutions with molecular oxygen have been studied in our laboratory. After methylating the product with diazomethane, it has been possible to separate a crystalline substance. This substance is unsaturated, contains two methoxy groups and does not contain any free carboxyl or phenolic groups. On the basis of this and chemical analysis, the structure (XII) has been proposed for the oxidation product.



XI R = C₆H₅ or C₆H₇CH₃



XII

Tannins

The tannins present in the different parts of the cotton plant, viz. seeds, leaves, bolls and flowers, have been investigated. The results of the studies on the dynamics of accumulation of tannins in seeds (Fig. 1, A), bolls (Fig. 1, B) and leaves (Fig. 1, C) of the variety 108-F have shown that the tannin content decreases with the growth of the plant with the exception of the bolls (Fig. 1, B) in which the tannin content increases towards the end of vegetative period. The flowers contain 5.6 per cent of tannins, the root-bark and stems 3.4 per cent and leaves 4.10 per cent. From the woody part of the root and stems no tannins could be isolated.

The separation of tannins has been effected by extracting the leaves with ethyl acetate. A mixture of tannins in the form of a light amorphous powder is obtained and it has been shown by qualitative reactions that the tannins from cotton belong to the pyrocatechin group. Employing paper partition chromatography, the presence of five catechins in the bolls and root-bark, viz. (+)-catechin, (\pm)-gallo-catechin, (-)-epigallocatechin, (+)-catechin, and (-)-epicatechin, has been established.

In the metabolism of the cotton plant, the tannins undergo considerable changes both quantitatively and qualitatively. Using partition chromatography on a column of silica gel, it has been possible to separate the mixture of tannins and obtain two of the catechins in the crystalline form. One of these has been identified as (+)-catechin and the other as (-)-gallo catechin. Thus, it has been shown that the tannins consist mainly of (+)-catechin and (-)-gallo catechin.

The changes in the quantitative and qualitative composition of tannins in the cotton plant affected by wilt have also been investigated.

Flavones

Flavones of the cotton plant had been studied earlier by Perkin and by Seshadri and coworkers,

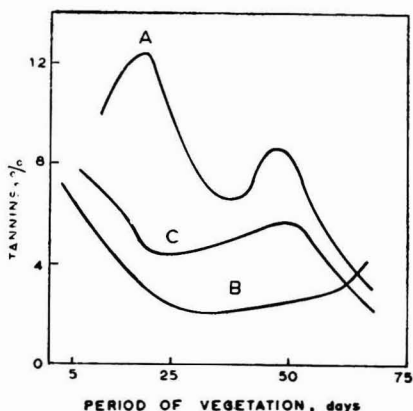


Fig. 1 — Change in the tannin content: A, in the seeds with the growth of the bolls; B, in the flap and folds with the growth of the bolls; and C, in the leaves with the growth of the plant

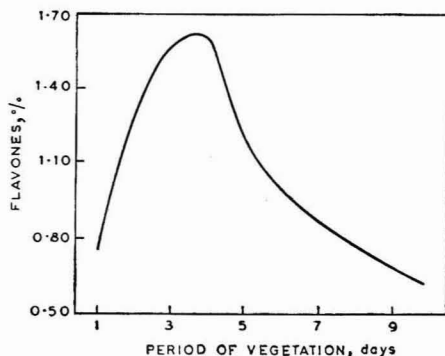


Fig. 2 — Change in the flavones content of the leaves with the period of vegetation

These workers separated five glycosides from the flowers of the cotton plant, viz. herbacitrin, quercimeritrin, isoquercitrin, gossypitrin, gossypin and one aglucone quercetin. The dynamics of accumulation of flavones in the leaves of the cotton plant during its growth have been investigated in our laboratory. The results, given in Fig. 2, show that flavones are formed in the leaves right from the first day of growth. They are present to the maximum extent in tender leaves and to the minimum extent in the mature leaves.

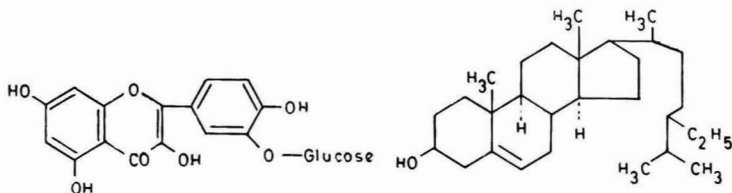
Employing paper chromatography, it has been shown that the flowers and leaves of the cotton plant contain six and three flavones respectively. From the flavones in the flowers it has also been possible to separate an aglucone, quercetin, in crystalline form. One of the glycosides has been identified as quercimeritrin; another identified as quercetin-3'-glucoside (XIII) has not been reported earlier.

Neutral Substances

Twenty neutral substances from the leaves, bolls and flowers of the cotton plant have been isolated and identified. These substances include: (a) hydrocarbons: tetracosane, hexacosane, octacosane, triacontane, dotriacontane and hexatriacontane; (b) alcohols: hexacosanol, octacosanol, triacontanol and dotriacontanol; and (c) phyosterols: β -sitosterol (XIV) and sitostanol. Sitostanol occurs in the plant as a fatty acid ester (XV). Of the triterpenes, β -amyrin, which has also been found to be present in the plant as β -amyrin montanate (XVI), has been separated and identified.

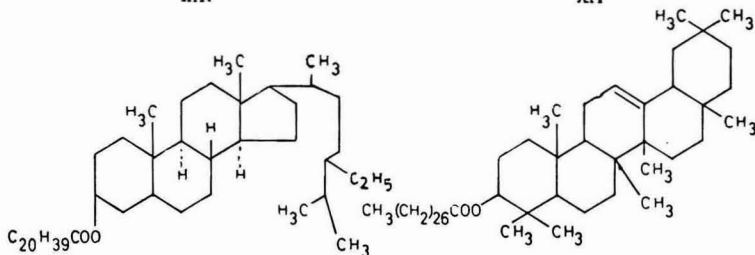
Vitamins

The leaves of the cotton plant are rich in vitamins such as ascorbic acid, nicotinic acid, riboflavin, inositol and vitamin P and especially the provitamin α -carotene. Further, the leaves are rich in protein, the amino acid composition of which is not inferior to those of proteins from the leaves of leguminous plants. The use of the cotton plant leaves to replace cut hay (source of carotene) in animal husbandry is worth a trial.



XIII

XIV



XV

XVI

Fatty Acids and Glycerides

The unsaturated fatty acids reported to occur in cottonseed oil are stearic, palmitic, oleic, arachidic, linoleic and myristic acids. Another unsaturated acid, palmitoleic acid, has recently been isolated in our laboratory from the oil obtained from the seeds of a special variety (108-F) of cotton. During a study of the triglycerides contained in the oil, the presence of 13 triglycerides (Table 1) has been reported by us for the first time.

Little information is available in the literature on the formation of oil in cotton seeds and when the oil begins to appear; some workers have noted the presence of oil in seeds which are 21 day-old and others in the seeds from 25 day-old bolls. But none of them has estimated the fatty acids in the oil. Keeping this in view the dynamics of accumulation of the oil and variability of the fatty acid composition of the seeds in the ontogenesis of the cotton plant have been investigated by us. The fatty acids have been separated by paper chromatography and estimated. The results suggest that the oil and fatty acids make their appearance during the first few days of formation of the cotton seeds and the amount of oil increases with the growth of the seeds. In the initial phase, the content of saturated acids is more than in the final phase, and depending on the degree of ripening, the content of unsaturated acids increases.

The fatty acids contained in the roots, stem, leaves, bolls and flowers of the cotton plant have been separated by adsorption chromatography on aluminium oxide, inverse-phase distribution and gas-liquid chromatography. The following 15 acids have been detected: lauric, myristic, palmitic, palmitoleic, palmitolinoleic, palmitolinolenic, stearic, oleic, linoleic, linolenic, arachidic (eicosanoic), eicosadienoic, eicosatrienoic, behenic and decosadienoic

acids. These fatty acids are present in the plant in the form of phospholipids, triglycerides, esters with sterols and in the free state. Not all parts of the cotton plant contain lipids of all classes. Thus, triglycerides are detected only in flowers and roots, and in very small quantities in the bolls. The triglycerides of the bolls resemble the glycerides from cottonseed oil in their composition and glyceride fractions of different polarity but differ somewhat from them by the higher content of palmitic acid and presence of small quantities of linolenic acid.

The glycerides from the root and flowers differ considerably from the glycerides of cottonseed oil. Of all the widely distributed fatty acids present in cotton fibres, palmitic acid occurs in largest amount followed by linoleic, linolenic and oleic acids. Palmitic acid occurs chiefly in the form of phospholipids and esters of sterols in all parts of the plant. Oleic acid is chiefly present as lipids of the

TABLE 1 — QUANTITATIVE COMPOSITION OF TRIGLYCERIDES FROM COTTONSEED OIL

Sl No.	Triglyceride	Composition %
1	Palmitodilinolein	26.58
2	Trilinolein	16.87
3	Palmitooleolinolein	15.93
4	Oleodilinolein	14.23
5	Dipalmitolinolein	9.59
6	Dipalmitolein	4.11
7	Dioloilinolein	3.12
8	Palmitodiololein	2.46
9	Stearodilinolein	1.68
10	Stearopalmitolinolein	1.52
11	Stearooleolinolein	1.08
12	Stearopalmitoolein	1.08
13	Triolein	0.37

axial organs and linolenic acid as lipids in leaves. The leaves differ from most of the vegetative and reproductive organs in the absence of triglycerides. The flowers show combined biochemical indications of both the axial organs and leaves by their high content of oleic and linolenic acids. Linolenic acid, which predominates over all other acids in the cottonseed oil, seldom exceeds 20 per cent in the vegetative and reproductive organs with the exception of bolls, where it forms triglycerides similar in composition to the ones in cottonseed oil. Myristic acid in the lipids of vegetative organs reaches up to 12 per cent. The other fatty acids are present in very small amounts.

From the various vegetative organs of the cotton plant, leaves and fibres, the following organic acids have so far been detected: citric, malic, oxalic, ascorbic, lactic, tartaric, succinic, fumaric, pyroracemic, formic, valeric, salicylic, acetic and glutaric acids. The content of organic acids in the cotton plant varies with the soil and climatic conditions, vegetative period and age of the vegetative parts and reproductive organs of the plant. The results of estimation of the total acid content of citric and malic acids in the leaves of the cotton plant from the 5th day to 60 to 70th day, from two levels and at two growth periods of the crop indicate that a sharp increase in the citric acid content occurs in the leaves of the first level from the 15th to the 20th day. The amount of citric acid accumulation is found to be maximum at the end of the vegetative period of the plant.

The accumulation of malic acid is at its maximum (up to 4 per cent) in 40 day-old leaves and then it decreases. The nature of the change in the content of total acids is quite different. However, in general the accumulation of organic acids with the growth of the leaves is the rule.

The total acid content of leaves is 10-14 per cent of which the titratable acid is only 0.78 per cent. The citric acid content towards the end of the vegetative period is 5-7 per cent and that of malic acid 4-5 per cent. Accumulation of citric and malic acids in considerable quantities in the leaves at the end of the vegetative period indicates that the leaves of the cotton plant can be used as a raw material for these acids. As a matter of fact, the leaves are being exploited on an industrial scale for these acids. With the aim of preparing physiologically active substances based on citric and malic acids, more than 20 new compounds have been synthesized and are under pharmacological testing.

Thus, at present, from the various vegetative parts of the cotton plant it has been possible to separate and study more than 40 individual compounds of different classes, some known and some isolated by us for the first time. The study of the chemical structures of the compounds separated, and solving the biochemical problems connected with the clarification of the role and changes of the various groups of compounds which accumulate in various vegetative and reproductive organs of the plant, will make it possible to reach definite generalizations of theoretical and practical value.

Synergic Extractions

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IN solvent extraction of metals by a mixture of two organic solvents the system may behave in one of the three ways: (1) neither solvent participates in the extracted metal complex (e.g. extraction of indium from hydrobromic acid with benzene + cyclohexane), (2) one of the solvents participates whereas the other is an inert diluent (e.g. extraction of chloroauric acid by tributylphosphate + xylene), or (3) both the solvents participate in the complex formation [e.g. extraction of uranium (VI) by thenoyltrifluoroacetone + tributylphosphate]. The last type represents the most interesting case. The distribution coefficients may be higher by a few orders of magnitude than those exhibited by either of the solvents alone. This phenomenon of greatly enhanced extraction was first termed 'Synergism' by Blake *et al.*¹ in 1958. It opened up a new area of solvent extraction which has attracted considerable attention in recent years.

The solvating solvent, tributylphosphate (TBP), has been employed in many extraction processes and it was observed as early as 1949 that the acid hydrolysis products of the reagent, mono- and dibutylphosphoric acids themselves were also effective uranium extractants. Blake *et al.*¹ reported that when a dialkylhydrogen phosphate, $(RO)_2PO.OH$, was used in conjunction with certain neutral organophosphorus reagents, e.g. $(RO)_3PO$, where R = *n*-butyl, the extracting power of the mixture exceeds the sum of the extracting powers of the components. According to Blake *et al.*, the synergic extraction seems limited to uranium and to dialkyl-phosphoric acid-neutral organophosphorus ester. This was too sweeping an inference since, later on, the phenomenon has been observed in a number of systems. Earlier Cunningham *et al.*² reported that a mixture of thenoyltrifluoroacetone (TTA) and tributylphosphate (TBP) extracts neodymium and praseodymium from nitrate solutions much better than either solvent alone and suggested an explanation based on mixed complex formation.

Extraction with Solvent Mixtures

Goble and Maddock³ investigated the extraction of protoactinium from hydrochloric acid by mixtures of diisopropyl carbinol with ketones, nitro compounds and nitriles. The extraction curves show pronounced maxima. A mixture of strong donor solvent and a solvent of high basicity is a better extractant than either of the pure solvents. Limited extraction occurs with the pure donor solvent alone because of the unfavourable electrostatic free energy of transfer, whereas the high dielectric constant solvent alone has limited donor power and hence limited extracting ability. If one solvent in a mixture contributes high basicity and the other a high dielectric constant, the distribution coefficient would be higher than in either of the solvents. Mottola and Sandell⁴ made similar

observations while extracting bismuth iodide with mixtures of isoamyl alcohol and acetate.

Maxima in the extraction curves are generally attributed to positive deviation from Raoult's law for the solvents⁵. In some cases mixed solvates may form which are more stable than the pure solvates leading to higher distribution coefficient. Vdovenko and coworkers^{6, 8} made such an observation in the extraction of nitric acid, uranyl nitrate and other nitrates with mixtures of diethyl ether and acetophenone, isoamyl alcohol and methyl-isobutyl ketone, or of dibutyl ether and 2,2'-dichlorodiethyl ether. When diluted with an inert solvent like benzene, each solvent was found to form a disolvate. In the mixture a mixed solvate is presumably formed resulting in increased extraction.

Synergic Systems

The most intensively studied synergic systems (HX-S) are those involving: (1) a chelating agent such as TTA (HX) and a solvating solvent such as TBP (S) and (2) a dialkyl-phosphoric acid (HX) and neutral phosphorus ester (S)⁹.

Systems involving a chelating agent and a solvating solvent — With TTA-TBP and TTA-TBPO (tributylphosphine oxide) mixture as extractant for uranium (VI), Irving and Edgington^{10, 12} found synergism of the order of 10^3 and 10^4 respectively. The extracted species were given as $UO_2X_2.TBP$ and $UO_2X_2.TBPO$ respectively from isopiestic as well as infrared measurements. The studies were later on extended to plutonium (VI), americium (III), europium (III) and thorium. The following species were identified: $PuX_3.2TBP$, $AmX_3.2TBP$, $AmX_3(NO_3)_3.2TBPO$, $AmX_3.TBPO$, $EuX_3.2TBP$, $EuX_3.TBPO$, $EuX_2(NO_3)_3.2TBPO$, $ThX_3(NO_3)_3.TBP$ and $ThX(NO_3)_3.TBPO$.

Irving and Edgington¹³ postulated that the conditions for synergic extraction are: (i) one of the active solvents (HX) should be capable of neutralizing the charge on the metal ion, preferably by forming a chelated complex, (ii) the second active solvent (S) should be capable of displacing any residual coordinated water from the neutral metal complex rendering it less hydrophilic, (iii) the second solvent (S) should not be itself hydrophilic and coordinated less strongly than HX, and (iv) the maximum coordination number of the metal and geometry of the ligands should be favourable. This explanation was satisfactory for uranium (VI) but invalid in the case of trivalent lanthanides and actinides which were apparently coordinatively saturated.

Healy¹⁴ studied synergism for uranium (VI), thorium, rare earths, actinides and alkaline earths employing TTA in conjunction with different organophosphorus esters such as TBP, TOPO (tri-*n*-octylphosphine oxide) and TPP (triphenylphosphate). The extracted species have been found to be $UO_2(TTA)_2S$, $UO_2(TTA)_2S_2$, $Th(TTA)_4S$, $Ca(TTA)_2S$, $Pm(TTA)_3S_2$,

Tm(TTA)₃S, Am(TTA)₃S₂ and Cm(TTA)₃S₂, where S represents the neutral organophosphorus ester. As the solvating solvent, TBP was replaced by esters varying in basicity from TOPO with its highly polar P→O bond to the very weakly basic TPP, the synergic effect was found to increase with increasing basicity, i.e. in the order TOPO>TBP>TPP.

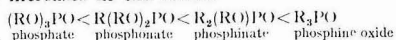
An interesting phenomenon in this respect is the influence of the so-called inert diluents on synergic extraction. In the synergic systems Mⁿ⁺/HTTA/S/diluent, the extracted species is the same, M(TTA)_nS_x, which is independent of the diluent but the distribution ratio varies over several powers of ten, depending on the diluent used. The synergism increases in the following order of diluents: chloroform<benzene<carbon tetrachloride<hexane<cyclohexane.

Subsequently, Irving and Edgington¹³ showed that the uranyl-TTA complex with TBPO is represented by UO₂X₂·3TBPO·H₂O, where uranium is octa-coordinated. They predict that synergism is possible with tri-, penta- and hexavalent ions of the octa-coordinated lanthanides and actinides, since here water displacement is feasible, but not with tetravalent ions where the bidentate chelating ligands will occupy all the coordination positions. In support of this, they have shown that plutonium (VI) extracts as Pu(TTA)₂·TBP and neptunium (V) as HNpO₂(TTA)₂TBP. If the chelating ligand is partly replaced by a simple anion such as nitrate, then only synergism is observed for thorium, neptunium (IV) and plutonium (IV). The thorium species is expressed as Th(TTA)₂(NO₃)₂TBP, Th(TTA)₂(NO₃)₂TBPO and Th(TTA)₂(NO₃)₂·2TBPO. These are different from those reported by Healy, viz. Th(TTA)₄TBP and Th(TTA)₄TOPO. This disagreement is probably due to the stronger complexing of thorium by nitrate (Irving) than by chloride (Healy).

Alternatives to phosphorus esters for producing synergism have been found among certain ketones, alcohols and amides such as *n*-decyl alcohol, ethylhexyl alcohol (EHA), methyl-isopropyl ketone, *N*-butylacetanilide (BAA), etc.¹⁵ The extracted species have been described as Th(TTA)₄EHA, Am(TTA)₃(EHA)₂, Pm(TTA)₃(EHA)₂, Am(TTA)₃·(MIK)₂, Pm(TTA)₃(MIK)₂, Th(TTA)₄BAA, Nd(TTA)₃·(BAA)₂ and UO₂(TTA)₂BAA. Two alternatives to TTA have been tried, viz. 8-hydroxyquinoline and cupferron, but both of these showed only limited synergism with TBP.

Systems involving a dialkyl-phosphoric acid and a neutral phosphorus ester—The important systems in this category are generally represented by acid phosphate (HX)-neutral phosphorus ester (S). Some examples of this category are: di-2-ethylhexyl-phosphoric acid (DEHPA)-TBP^{14,16,17}, mono-(2-ethylhexyl)-phosphoric acid (H₂MEHP)-TBP¹⁸, dibutyl phosphate (DBP)-TBP¹⁹ and dibutyl phosphate-TOPO²⁰. DEHPA-TBP was the first reported case of synergic extraction.

The position of maximum synergism depends on the nature of the neutral ester (S). The effectiveness of S increases in the series:



which is also the order of increasing basicity of the phosphoryl oxygen²¹. Synergism has been observed

with plutonium (IV) and (VI) and uranium (VI), but not with uranium (IV), vanadium (IV), aluminium, molybdenum, iron, titanium and thorium. The distribution coefficients in each case rise to maximum with increasing concentration of S and then decrease. The latter has been attributed to the increasing interaction between the acidic and neutral extractant through hydrogen bonding.

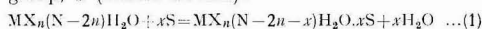
Mason and coworkers²² studied synergic effects in the extraction of lanthanides and actinides by mono-(2-ethylhexyl)-phosphoric acid (H₂MEHP) in combination with a synergist, viz. *n*-decanol (DOH), TBP or TOPO. The extraction curves reveal a region of enhanced extraction in the case of thulium, yttrium, europium and americium, the maxima becoming progressively more pronounced as the synergist was varied from *n*-decanol to TBP to TOPO. Marked differences were observed for lanthanides (III), thorium (IV) and uranium (VI).

Recently, Sato¹⁷ reported synergic effect of TBP in the extraction of uranium (VI) from sulphuric acid by DEHP. At low acidity (0.15*M*) and DEHP concentration <0.03*M*, the synergic effect is reversed.

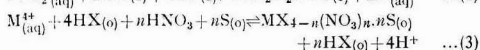
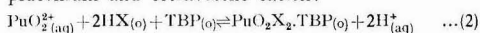
Mechanism of Synergistic Action

Although considerable amount of work has been done to explain the mechanism of synergism, it has yet to be clearly elucidated. The complexity of the problem is due to the fact that there are a large number of complicated factors involved such as the role of water, inert diluent, possible change in coordination and solvation. In certain cases there may be changes in the self-association in one of the solvents or there may be more favourable dielectric constants on the introduction of a second solvent. In other cases there may be specific solvation of the species extracted by the chelating solvent by the second solvent. It still remains to be ascertained how this solvation operates.

Irving and Edgington^{12,13} assumed that the synergic effect with uranium (VI) depends primarily on a mechanism whereby water attached to a formally neutral chelated complex MX_n(HX=TTA, a bidentate ligand) is replaced to some extent by a less hydrophilic group, S (second solvent):

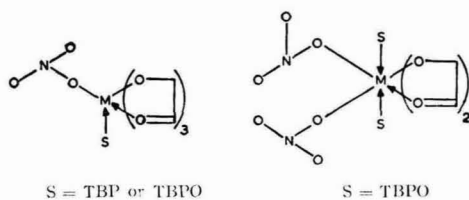


where N represents the maximum coordination number (C.N.) for the *n*-valent cation, M, and *x* is the bidentate ligand. So long as *n*<N/2, synergism is possible, the maximum number of neutral groups which could be attached being N-2*n*. If *n*=N/2 synergism will not be possible by the above mechanism. Of course, it might still occur by some other route, as pointed out earlier, viz. by partial displacement of the chelating groups by simple anions such as nitrate. These postulates have been substantiated by experiments with plutonium (VI), neptunium (V), thorium (IV), neptunium (IV), plutonium (IV), plutonium (III), americium (III) and europium (III). The following are typical reactions for hexavalent plutonium and tetravalent cation:



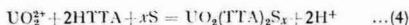
The value of n in Eq. (3) increases as the donor power of S increases and as the stability of the metal-TTA complex decreases.

In the case of M^{4+} , the octa-coordinated complexes $MX_3(NO_3)S$ and $MX_2(NO_3)_2 \cdot 2S$ are represented as:



It appears that one or more molecules of the chelating agent are displaced from an already coordinatively saturated complex by one or more molecules of the neutral donor component — an equivalent number of anions are at the same time coordinated to preserve electroneutrality.

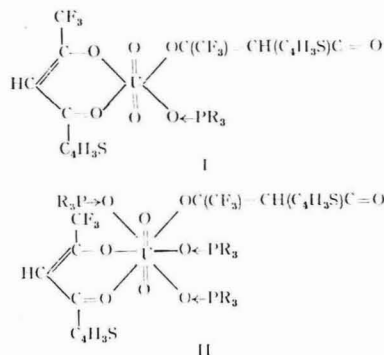
Healy¹⁴ suggested that the reaction between uranium (VI) and TTA plus TBP or TBPO occurs as follows:



on the basis of $\log K_D$ (distribution coefficient) versus $\log (HTTA)$ or $\log (S)$ keeping two of the three variables (H^+), (HTTA) and (S) constant at a time. Thus the extracted species are $UO_2(TTA)_2TBP$ and $UO_2(TTA)_2(TBPO)_3$. According to Healy, probably an aquo-metal-TTA complex such as $UO_2(TTA)_2(H_2O)_x$ is rendered less hydrophilic by the substitution of a neutral ester for the H_2O group such as $UO_2(TTA)_2TBP$. The neutral ester is probably attached through P=O bond to TTA. This is supported by the isolation of water-insoluble crystalline white thorium and yellow uranium solid complexes with the expected M/TTA/TBP ratios.

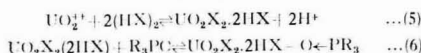
Later on, Healy and Ferraro²³ isolated stable solid synergic complexes — M/TTA/S — from the organic phase and confirmed the formulae by ultraviolet, visible and infrared spectral measurements. The complexes isolated and identified were: $UO_2(TTA)_2TBP$, $UO_2(TTA)_2TOPO$, $UO_2(TTA)_2 \cdot (TOPO)_3$, $UO_2(TTA)_2BAA$, $Th(TTA)_4TBP$, $Th(TTA)_4 \cdot TOPO$ and $Th(TTA)_4BAA$. From infrared studies, the reaction of neutral organophosphorus ester with metal-TTA complexes to form M/TTA/S complexes was found to lead to splitting of the single peak in the 1600 cm^{-1} region (coordinated carbonyl, C=O...M vibration) into two peaks. One peak was found at higher frequency and its position varied with the metal. This means that there is some uncoordinated (free) TTA-carbonyl. The second peak was observed at the same position as that found in M/TTA complexes, showing that in the M/TTA/S complexes part of TTA is still bonded as in the simple TTA compounds. Thus, the complexes contain TTA both as a monodentate and bidentate ligand. Typical

structures of $UO_2(TTA)_2TBP$ (C.N.= 6) (I) and $UO_2(TTA)_2 \cdot 3TBPO$ (C.N.= 8) (II) are suggested as:



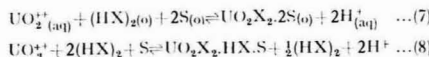
If only monodentate TTA were involved, C.N. for (II) would be 7 and coordinative saturation would be reached by coordination with 1 molecule of water. But this is ruled out since synergic complexes are invariably anhydrous.

Blake and group¹ were the first to suggest the following mechanism for the system $HX + TBP$, where HX is the dialkylphosphate:

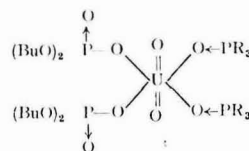


This implies increase in the coordination number of the uranyl ion.

Kennedy and Deane²¹ have shown that dialkylphosphoric acids, $HX [X = (RO)_2POO]$, are dimeric in inert diluents so that the probable extraction mechanisms for $HX-S$ system are:



These can explain the formation of the species, $UO_2(DBP)_2$, $HDBP \cdot TOPO$ as well as $UO_2(DBP)_2 \cdot 2TOPO$. A probable structure for $UO_2(DBP)_2 \cdot 2TOPO$ (C.N. for U = 6) is:

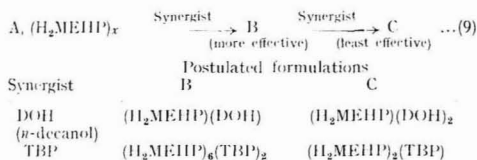


Further investigations have pointed to the possibility of replacing either one or two of the solvating HX molecules by S, the solvate composition depending on the strength and concentration of S^{19,20}. Thus, with $S = TBP$ and $HX =$ dibutylphosphate, $UO_2X_2 \cdot HXS$ is formed in carbon tetrachloride²⁴, but with $HX =$ diamylphosphate, UO_2X_2S and PuX_2S are found in xylene²⁵. Again with $S =$ phosphine oxide, $UO_2X_2S_2$ is found in carbon tetrachloride¹⁹.

According to Mason *et al.*²², the original extractant, A, mono-(2-ethylhexyl)-phosphoric acid (H_2MEHP) is converted by the synergist into an adduct, B, which

in turn is converted by further interaction with synergist into adduct, C.

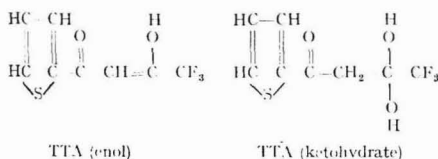
The association product, B, $(H_2MEHP)_6(TBP)_2$ has been identified by infrared and isopiestic measurements²⁶.



From infrared spectral studies of $UO_2^{++}/DEHPA/TBP$ system Sato¹⁷ has shown that the P→O band of DEHPA at 1230 cm^{-1} is shifted to lower frequencies, but the P→O band of TBP at 1270 cm^{-1} remains unchanged so that the uranium is bonded to the P→O of DEHPA. The combination of DEHPA and TBP presumably forms $(DEHPA)_2 \cdot TBP$ through hydrogen bonding.

Antisynergism

The reverse phenomenon of synergism, viz. anti-synergism, was noted by Blake *et al.* for high concentration of S in HX-S (alkylphosphoric acid-organophosphorus ester) system. This was probably the result of increasing interaction between the acid and neutral extractant through hydrogen bonding, whereby the concentration of the free chelating agent is reduced leading to smaller distribution coefficients. Peppard *et al.*²⁷ observed similar effects in the extraction of neptunium (IV) and thorium by H_2MEHP on the addition of TBP. In the TTA-TBP system anti-synergism was reported by Healy *et al.*¹⁵ on the addition of excess TBP. It is believed that excess of the donor solvent reduces TTA-enol activity and favours the formation of ketohydrate structure which in turn lowers the distribution coefficient, the resulting complex being more hydrophilic.



Conclusion

A wide range of analytical separations of metallic species is feasible because of the difference in the complexes formed in the synergic extractions of metals. For instance, among the rare earths, euro-

pium and promethium give complexes of the type $M(TTA)_3(TBP)_2$ which are different from other rare earths such as thulium which gives $M(TTA)_3TBP$. The vast scope for variations in extraction procedures opened up by synergic and anti-synergic phenomena holds many potentialities for separation techniques. So far, no general explanation has been given for the phenomena involved and synergism poses a challenging problem. Considerable exploratory work is necessary before a satisfactory explanation can emerge.

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Vitamin B₁₂ Coenzymes*

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SINCE the discovery of vitamin B₁₂ coenzymes in 1958 considerable amount of information has been collected on the structure and function of these compounds. Vitamin B₁₂ coenzymes are unique among the biologically active compounds in having a metal-carbon bond. Although metal chelates and metals are well known in biological systems, cobamide coenzymes are the first organometallic compounds found occurring naturally. The Grignard reagent and other organometallic compounds, commonly used as sources of carbanion for chemical synthesis, require ether or tetrahydrofuran as solvent. But cobamide coenzymes can achieve reactions in aqueous medium—an extraordinary feat indeed!

Structure and Synthesis of Corrin Coenzymes

Structure—The requirement of a derivative of pseudovitamin B₁₂ for the enzymatic conversion of glutamate to β-methylaspartate by cell-free extracts of *Clostridium tetanomorphum* was first reported by Barker¹. The structural relationship of this activating factor to vitamin B₁₂ was soon recognized when it was found that it was light-sensitive, adsorbed on charcoal and was converted to dicyanocobalamin on treatment with alkaline cyanide. Additional physical and chemical data suggested that cyanide is replaced by an adenine nucleoside in the corrin nucleus of vitamin B₁₂. Several groups have made important contributions towards the understanding of the structure of the coenzyme B₁₂. But probably the most significant single contribution has been made by Lenhert and Hodgkin² who determined the complete structure by X-ray analysis.

The main structural features (Fig. 1) are: (i) the presence of 5-deoxyadenosine (instead of cyanide in vitamin B₁₂); (ii) the nucleoside is attached to cobalt by a covalent bond by its 5-carbon; (iii) the adenine is 'approximately parallel to the planar corrin ring' while the sugar moiety is at right angles to it; and (iv) like vitamin B₁₂, coenzyme B₁₂ appears to be a cobaltic complex.

Properties—The properties of coenzyme B₁₂ and its analogues are similar to the corresponding vitamins except in some respects. All the cobamide coenzymes are characterized by a prominent peak at 260 mμ and the absence of the absorption maximum at 361 mμ. In general the absorbancy peaks of the coenzymes in the visible region are at a lower wavelength than those of the corresponding vitamins. The purine containing cobamide coenzymes can be differentiated from those containing benzimidazoles by the positions of the visible absorbancy maxima. At neutrality the purine containing coenzymes have maxima at approximately 460 mμ, while the benzimidazole containing analogues have maxima at

about 520 mμ. Differences in spectral characteristics are obtained in neutral and acid solutions which are interpreted as due to the differences in the strength of the coordinate bond between cobalt and nucleotide base, and that the main effect of 5-deoxyadenosine is to weaken this bond³.

Mild acid hydrolysis by 0.1N hydrochloric acid at 100°C. for 90 min. of coenzyme B₁₂ gives adenine, D-erythro-2,3-dihydroxypent-4-enal and aquocobalamin. The glycosidic bond in the benzimidazole nucleotide is stable and requires heating in 6N hydrochloric acid at 150°C. for 18 hr for hydrolysis.

Coenzyme B₁₂ changes colour from red to purple on treatment with 0.1M potassium cyanide forming pseudovitamin B₁₂ and adenine as products. Investigation on the sugar portion led to the identification of 5'-deoxyribose moiety.

Chemical synthesis—Soon after the recognition of the presence of cobalt-carbon bond in coenzyme B₁₂, its chemical synthesis was achieved using 5'-p-toluenesulphonyl (tosyl) ester of adenosine whose 2'- and 3'-hydroxyls were protected as an isopropylidene derivative. The isopropylidene tosyl adenosine was condensed with the fully reduced cobalamin (vitamin B_{12s}). The isopropylidene group was then removed

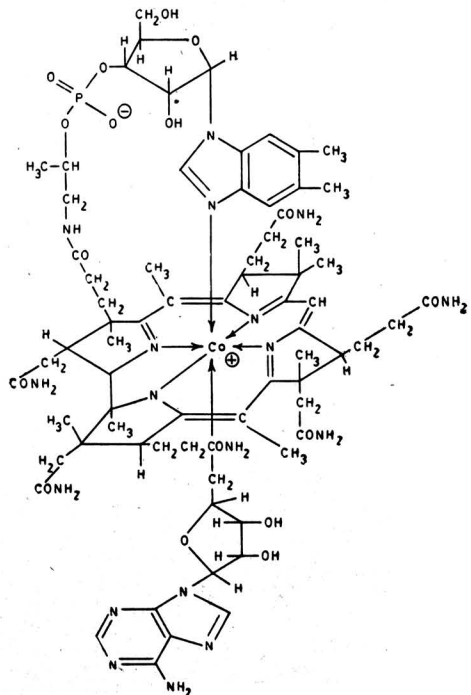


Fig. 1—Structure of coenzyme B₁₂

*Based on the proceedings of a conference entitled 'Vitamin B₁₂ Coenzymes', *Ann. N.Y. Acad. Sci.*, **112** (1964), 547-921.

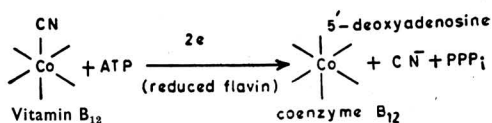
by mild acid hydrolysis (0.1N hydrochloric acid at 90°C. for 15 min.). This approach was conceived and worked out independently in three laboratories around 1961-62: (i) E. Lester Smith, Glaxo Laboratories, England; (ii) A. W. Johnson, University of Nottingham, England; and (iii) K. Bernhauer, Stuttgart, Germany. Syntheses of several analogues of coenzyme B₁₂ have been reported from these three laboratories. The approach was to react vitamin B_{12s} with alkyl and acyl halides. In addition, analogues containing Co-S link, such as sulphito-, tosyl- and mesylcobalamins, have been prepared by reacting the hydroxo-corrinoids with mercaptans. All the analogues, like coenzyme B₁₂, have trivalent cobalt and the same chromophore. They yield dicyanocobalamin on treatment with cyanide and on photolysis, hydroxocobalamin.

Biosynthesis — The biosynthetic pathway of porphyrins involves the formation of δ-aminolevulinic acid from succinyl-CoA and glycine (pyridoxal phosphate derivative) and the subsequent condensation of two moles of the latter to give the pyrrole, porphobilinogen. Then four moles of the pyrrole polymerize into porphyrin. This pathway is ubiquitous and further modifications of the side chains at the β-positions are characteristic of the different organisms⁴.

There are some differences between the corrin and porphyrin nuclei. Corrin is more reduced, one methylene bridge is less in corrin (between rings A and D) and there are 'extra' methyl groups. Similar pathway exists for the synthesis of vitamin B₁₂. Thus, δ-aminolevulinic-1,4-¹⁴C was found to be incorporated in vitamin B₁₂ in a streptomycete, and, as predicted, 15 carbon atoms possessed the radioactivity. The 'extra' methyls are derived from methionine-methyl group. This is one of the few examples of biological C-alkylation.

The conversion of vitamin B₁₂ into coenzyme B₁₂ was investigated by Brady and Barker in *Propionibacterium shermanii* and by Peterkofsky and Weissbach in *Clostridium tetanomorphum*. It was shown that ATP serves as the precursor of 5'-deoxyadenosine in coenzyme B₁₂. That both adenine and pentose moieties are derived from ATP was shown using ATP-8-¹⁴C and ATP-U-¹⁴C. Neither adenine nor ribose diluted the incorporation of ATP-¹⁴C; therefore, deoxyadenosyl group is transferred directly to cobalt displacing the cyanide group. The steps in the conversion of vitamin B₁₂ to coenzyme B₁₂ are: flavo-protein-dependent reduction to vitamin B_{12r}, release of cyanide, transfer of deoxyadenosyl group and the release of phosphates. However, these reactions appear to occur concertedly. Vitamin B_{12r} does not appear to be a free intermediate; nevertheless B_{12r} could replace B₁₂ as substrate, but the reducing agent was still required suggesting that further reduction was necessary. Consequent to the transfer of deoxyadenosine, the phosphates are released as inorganic triphosphosphate. The only other such example of the release of three phosphates from ATP is the activation of methionine which yields adenosyl-methionine, pyrophosphate and phosphate. Even in this case it was shown that methionine activating enzyme has an intrinsic hydrolytic activity breaking the triphosphosphate. The reaction involved in

the biosynthesis of coenzyme B₁₂ is represented below:



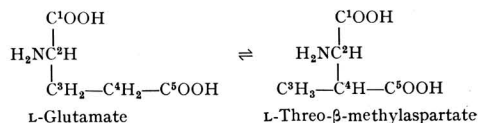
The enzyme responsible for this reaction, named corrin-coenzyme synthetase, has been partially purified and studied. It has been found that the reaction rate is inhibited by oxygen and increases on addition of hydrogen donors. The reaction requires no metal and is unaffected by RNase.

It is now considered that corrin-cyanides isolated from animal tissues are artifacts formed from the natural coenzyme forms. In view of the known clinical and nutritional activity of vitamin B₁₂, the animals must be converting it into the coenzyme. This conversion has also been reported in human and animal tissues.

Enzymic Roles of Cobamide Coenzymes

Since the discovery in 1958 of coenzymatic function of cobamides by Barker, several other reactions have been shown to require them. There are now at least seven different systems wherein coenzyme B₁₂ or its methyl analogue is shown to participate. Substantial progress has been made in our understanding of the mechanism of these reactions.

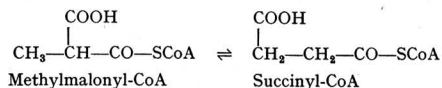
Glutamate mutase — This enzyme, formerly called glutamate isomerase, catalyses the direct rearrangement of the carbon skeleton of L-glutamate to yield L-threo-β-methylaspartate. This reaction is responsible for the fermentation of L-glutamate by *Clostridium tetanomorphum*. A 75-fold purified enzyme was prepared which was free of β-methylaspartase, glutamic dehydrogenase, glutamic racemase and transaminases. The reaction of glutamate mutase involves a transfer of 'glycine' moiety and hydrogen atom in opposite directions between α and β carbon atoms of a 'propionate' moiety (but the three pieces do not exist separately).



The reaction requires coenzyme B₁₂ specifically. The mutase can use other analogues of coenzyme B₁₂ with modifications of the nucleotide base but not of 5'-deoxyadenosyl group. The mechanism of the interesting carbon skeleton transfer reaction is still obscure. The interesting possibility of the coenzyme acting as a group carrier of the propionate moiety seems to be eliminated in view of the failure of carboxyethyl cobalamin to function as coenzyme (unless for the possibility that such an intermediate, although formed on the enzyme, is unacceptable to the enzyme when supplied exogenously). The transfer of hydrogen is not by way of a free proton since no isotope was incorporated into the product when

the reaction was carried out in D₂O (100 per cent). It has also been reported by others that the transfer of hydrogen from methyl group of methylaspartate to carbon 4 of glutamate occurs in a stereospecific manner.

Methylmalonyl isomerase — Both in the metabolism of pyruvate in animal tissues and its formation in propionibacteria, methylmalonyl isomerase plays an important role. Methylmalonyl-CoA is formed by the fixation of CO₂ on propionyl-CoA catalysed by propionyl carboxylase in animal tissues. It is broken down by transcarboxylase in propionibacteria. Both the enzymes are dependent on biotin and the carboxyl group is transferred through attachment of l'-ureido nitrogen of enzyme-bound biotin. In both systems methylmalonyl-CoA is converted to succinyl-CoA by the coenzyme B₁₂-dependent isomerase.



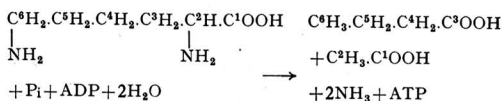
The enzyme preparations from the bacteria and animal tissues are different in two respects: firstly, in the animal enzyme, the cobamide coenzyme is more firmly attached than in the bacterial enzyme and yields a light-insensitive holoenzyme; secondly, the bacterial enzyme is less specific in the requirement of the coenzyme forms — the animal enzyme requires specifically dimethylbenzimidazolyl or benzimidazolyl forms. Similar to the glutamate mutase, any alteration in the 5-deoxyadenosyl group results in an inactive product.

Convincing evidence was obtained using ¹⁴C-label⁵ and ¹³C mass analysis^{6,7} that this is an intramolecular reaction involving a transfer of carbonyl thioester and the simultaneous transfer of the CoA esterified carboxyl group but not of CoA or carboxyl group. How exactly the coenzyme functions in this reaction also remains unknown. The accompanying hydrogen transfer does not involve free proton. But one proton is taken up in the overall conversion of methylmalonyl-CoA to succinyl-CoA, but this takes place in the methylmalonyl racemase reaction.

Dioldehydrase — Dioldehydrase, the enzyme that catalyses the conversion of propanediol to propionaldehyde was first discovered in *Aerobacter aerogenes* by Abeles and Lee⁸. The enzyme was purified 200-fold and a requirement for cobamide coenzyme and a monovalent cation was established. The reaction involves the displacement of (OH) on the carbon 2 by the hydrogen atom on the carbon 1 of a diol. The formation of the complex of enzyme and coenzyme was found to be a slow process but once formed the complex was light-stable. In the absence of the substrate, incubation of the complex leads to inactivation of both the components. Although the exact role of the coenzyme is not deciphered, spectral changes have been observed during the enzymatic action consistent with its participation in the reaction. A similar enzyme system found by Pawelkiewicz in another strain of *A. aerogenes* was used to test different corrinoids for their capacity to replace coenzyme B₁₂. Another enzyme, glycerol dehydrase, which converts glycerol to β-hydroxy-propionalde-

hyde, found in a *Lactobacillus* species⁹ also required cobamide coenzyme for activity.

Lysine fermentation — The fermentation of lysine by *Clostridium stricklandii* and *Clostridium* M-E. yielding butyrate, acetate and ammonia has been demonstrated by Stadtman¹⁰. The cofactors required for the degradation of lysine by bacterial extracts are: Mg²⁺, inorganic phosphate, ADP, pyruvate, Fe²⁺, acetyl-CoA, a disulphide catalyst, a flavin and B₁₂ coenzyme. Benzimidazole coenzyme was more effective than dimethylbenzimidazole form. Although full explanation of the requirement for the cofactors is not on hand the reaction seems to occur as shown below:



Although a transfer of glycynyl moiety as in glutamate mutase reaction is suggestive, no experimental proof is available.

Methyl transfer — The role of cobamide coenzymes in methionine synthesis has been investigated by a number of workers¹¹⁻¹³. Bacterial systems have two pathways for the synthesis of methionine from homocysteine: In one, the methyl group is transferred directly from N⁵-methyltetrahydrofolate (or the triglutamate). The other, a vitamin B₁₂-dependent enzyme develops when the cells are grown in the presence of the vitamin. Both require FADH₂ and S-adenosyl methionine. One interesting feature is that the B₁₂-dependent reaction operates only in the absence of oxygen, whereas the second one is oxygen-insensitive.

Since cobalamin acts catalytically it follows that methyl cobalamin may act as the intermediate in methyl transfer from N⁵-methyltetrahydrofolate to methionine. It has been shown by Woods and coworkers that methyl cobalamin in substrate quantities could be used for methylation of homocysteine or tetrahydrofolate. Adenosylcobalamin does not form the active enzyme, but its hydrolysis product, hydroxocobalamin, does. It is still not possible to demonstrate whether the B₁₂ enzyme accepts methyls from tetrahydrofolate. The fully formed B₁₂ enzyme still requires all the cofactors. The function of S-adenosylmethionine, which is not replaced by S-adenosylhomocysteine, in the reaction remains unexplained. The requirement of FADH₂ points out that a reduction step is involved. It has been considered that on transfer of methyl group, B₁₂ enzyme in oxidized form is liberated which has to be reduced by FADH₂ to prepare it to receive the methyl group from tetrahydrofolate. This is consistent with the fact that the highly reduced form, hydridocobalamin, is required to synthesize methyl or 5-deoxyadenosyl derivatives. In chicken-liver system, it has been shown by Weissbach and coworkers that the methyl transfer from methyltetrahydrofolate to homocysteine is markedly lowered in B₁₂-deficient animals and is restored on short-term dietary replenishment of the vitamin. The possible mechanism of the function of methyl cobalamin in methionine biosynthesis suggested by Woods and coworkers is shown in Fig. 2.

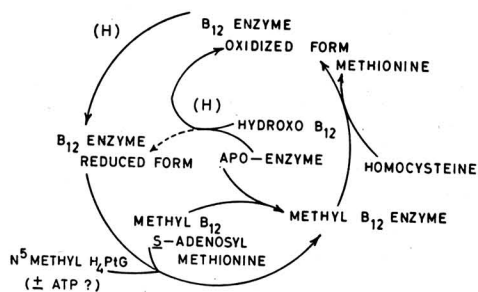


Fig. 2 — Possible mechanisms for a function of methyl cobalamin in methionine biosynthesis

Methane formation—Methane is produced by *Methanosarcina barkeri*, a strict anaerobe, utilizing methanol or acetate as sole carbon source. It has been found by Blaylock and Stadtman¹⁴ that in the presence of pyruvate substrate amounts of methyl cobalamin are utilized by cell-free extracts and that the methyl group serves as the source of methane. Also these extracts are found to have B₁₂ coenzyme activity in the test system of lysine degradation. These results, although inconclusive, suggest the role of cobamide coenzyme in methane formation.

General Aspects

Arnstein and White¹⁵ have discussed the possible relationship of known B₁₂-dependent reactions, viz. glutamate mutase, methylmalonyl isomerase, dioldehydrase and methionine biosynthesis, to the growth of a flagellate protozoan, *Ochromonas malhamensis*, whose growth requirements for vitamin B₁₂ closely resemble that of higher animals. Of the four systems tested, only methylmalonyl isomerase has been found to be completely blocked in vitamin B₁₂-deficient cells.

The action of vitamin B₁₂ coenzymes and their analogues can readily be studied in the chick and developing chick embryo since they can be maintained with very low reserves of vitamin and show well-defined deficiency effects. In the assay with chicks, aquocobalamin is equally potent, dimethylbenzimidazole coenzyme less effective, and methyl coenzyme about half as effective as vitamin B₁₂. All the three are more effective than vitamin B₁₂ in restoring the hatchability of chick embryos. Analogues of the coenzyme are not antagonistic to the vitamin in the chick.

From studies on the relative rates of absorption of the various forms of B₁₂ in the rat and man and their distribution in tissues, it appears that coenzyme B₁₂ is absorbed to a lesser extent than vitamin B₁₂ and it has no 'special virtue for the treatment of pernicious anaemia'. Data on vitamin B₁₂ activity in mammalian cells in tissue culture obtained by

Sanford and Dupree¹⁶ show that vitamin B₁₂ is not required for survival and growth of the cells of the nine strains tested and added vitamin does not increase proliferation of the cells.

It is generally considered that vitamin B₁₂ does not occur in plants although small quantities have been detected in tissues of some higher plants. There is no compelling evidence for the synthesis of cobamides in plants and its presence in some plants, in any case, may be of microbial origin. The nitrogen-fixing organisms present in nodules of leguminous plants have vitamin B₁₂ compounds. The leguminous plants grown in symbiotic association with these organisms, therefore, require cobalt. No evidence is presently available whether B₁₂ coenzymes have any specific role in the nitrogen fixation in these organisms.

Concluding Remarks

The types of enzymatic systems in which cobamide compounds participate seem to be transfer reactions involving one- or two-carbon groups. The evidence available establishes the involvement of vitamin B₁₂ compounds in these reactions. But the actual mechanism by which the compounds effect the group transfer is still obscure. It is not yet possible to demonstrate the intermediate cobamide compounds having the transferring group during the enzymatic reaction. Thus, the basic criterion to call the compounds coenzymes, instead of cofactors, is yet to be satisfied. In view of the large interest now generated in this field of study, it should be possible to have interesting new discoveries in the near future.

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REVIEWS

THE PROPAGATION OF ELECTROMAGNETIC WAVES IN PLASMAS by V. L. Ginzburg; translated from the Russian by J. B. Sykes & R. J. Tayler (Pergamon Press Ltd, Oxford), 1964. Pp. xix+535. Price £7

This is the English translation of a Russian book published in 1960 by Prof. Ginzburg of the Lebedev Institute of Physics in Moscow. Translations of three later papers by the author on electromagnetic wave propagation in dispersive media have been added. The present book may be considered to be a supplement to another Russian book on *Radio wave propagation and the ionosphere* by Prof. Ya. L. Al'pert whose translation also has recently appeared. While Al'pert's book deals descriptively and phenomenologically with the propagation of electromagnetic waves of all wavelengths from the millimetre to the kilometre range in the earth's atmosphere, Dr Ginzburg's book deals in a comprehensive way with the basic physics of electromagnetic wave propagation in ionized media. The treatment is mathematical in character, but the physical ideas are clearly explained. The following chapter headings will give an idea of the scope of the book.

The first chapter deals with the fundamental theory of electromagnetic wave propagation in plasmas followed by four chapters on homogeneous isotropic plasmas, homogeneous magneto-active plasmas, inhomogeneous isotropic plasmas and inhomogeneous magneto-active plasmas.

Then follow two chapters on reflection of radio waves from ionospheric layers, and radio wave propagation in cosmic condition. The eighth and final chapter deals with non-linear phenomena in a plasma with variable electromagnetic field, such as cross-modulation, combination frequencies, etc.

Like many other Russian advanced text-books, Ginzburg's book is comprehensive in its scope, and senior students and research workers who work in problems of radio wave propagation in ionized media and wish to dig deep into the fundamentals of the subject, whether in the earth's ionosphere, magnetosphere, interstellar space or the atmosphere of sun and stars, will find the book very helpful.

The book gives full references to Russian books and papers, and also to important publications in other languages. The book is provided with a subject index.

The price of the book is definitely high for Indian students and research workers. They will have to depend on libraries for the book — but it would be worth while for scientific libraries to have a few copies. It is a valuable addition to the existing literature of the subject in English — particularly its mathematical aspects.

K. R. RAMANATHAN

NUCLEAR ORIENTATION edited by M. E. Rose (Gordon & Beach Science Publishers Inc., New York), 1963. Pp. xiv+321. Price \$ 4.95

This book is a valuable contribution to the international science review series. The publication is

a collection of 48 important and interesting papers appearing in various journals of international repute. The papers include both theoretical and experimental works on an interesting aspect of nuclear science — nuclear orientation — attacked from various angles such as hyperfine structure studies, polarization of nuclei, saturation of paramagnetic resonance, electron-nuclear double resonance, etc. Various associated physical phenomena connected with oriented nuclei such as nuclear relaxation, nuclear cooling, anisotropy of the intensity of nuclear radiations, decay schemes, etc., have been discussed both from theoretical and experimental standpoint in some of the papers. The book offers a ready reference of the important works on nuclear orientations and alignment in many substances to the scientific workers engaged in this special line of nuclear research.

The main drawback of such books lies in the lack of coordination between the information available in the individual papers. It is a collection and not a critical review of the relevant papers, and this reduces the intrinsic value of the book considerably. At least a summing-up article by the editor was very much expected and would have increased the usefulness of the book.

A. BOSE

CHEMICAL KINETICS OF GAS REACTIONS by V. N. Kondrat'ev (Pergamon Press Ltd, Oxford) 1964. Pp. xiv+812. Price £5 5s.

This is an up-to-date and fairly comprehensive treatise on the rapidly developing field of kinetics of gas reactions. Prof. Kondrat'ev is the Permanent Chairman of the Scientific Council on Chemical Structure, Chemical Kinetics, Reactivity and Catalysis at the USSR Academy of Sciences. This designation of the author in a way reflects the breadth and depth of the subject matter covered by this book.

The first three chapters (general kinetic rules for chemical reactions, chemical mechanism of reactions and theory of elementary processes) serve as a good introduction to chemical kinetics and particularly to the subsequent more specialized treatments on bimolecular reactions, unimolecular and termolecular reactions, and energy conversion during molecular collisions (Chapters 4-6). Photochemical reactions, chemical reactions in electrical discharge and chain reactions are discussed in Chapters 7-9. The last chapter is a stimulating discussion of combustion processes, particularly the various theories forwarded to explain and the numerous problems associated with flame propagation.

The book gives a masterly survey of the many investigations on elementary chemical processes, the role of free radicals in the course of complex gas reactions, the concentrations of free hydrogen atoms and hydroxyl and other free radicals in combustion zones of various gases, the determination of velocity constants of reactions of radicals with different molecules, etc. The results obtained from various types

of investigations are summed up and then compared with theoretical postulates.

The entire book has a strong experimental bias. The treatment is very lucid and nowhere does it smack of 'translation English'. The mathematical treatment is confined to the essential minimum without sacrificing clarity and precision, a fact which gives this book some advantage over S. W. Benson's *The foundations of chemical kinetics*, at least as far as most chemists are concerned. Another distinctive point in favour of this book is its extensive coverage of the Soviet research in chemical kinetics, particularly the outstanding work of Semenov, Zel'dovich, Frank-Kamenetskii and the author himself, without in the least slighting or ignoring the work of western scientists. The bibliography at the end of the book gives 1334 references of which only the first 310 are to work by the Russian scientists.

All the ten chapters are developed rather independently so that one can fairly follow the discussions in any chapter without necessarily having gone through the earlier parts. The book is eminently suited as a base for an advanced course of about 50 lectures on chemical kinetics. It will also serve as a valuable ready-reference book to all those who are concerned in one way or other with the vast field of gas reactions and their kinetics.

P. G. MENON

ADVANCES IN ANALYTICAL CHEMISTRY AND INSTRUMENTATION edited by Charles N. Reilly (Interscience Publishers Inc., New York), 1964. Pp. vii + 523. Price \$ 15.00

This third volume, like the previous two of the series, discusses a few selected techniques in the widely expanding field of analytical chemistry. The usefulness of a new technique is not so much in its evolution as in its application to practical problems. Usually, there is a time lag between the two.

The last decade or so has seen the development of a variety of new techniques or approaches to meet the more exacting analytical demands as regards limits of detection, precision, accuracy and speed of analysis of a variety of materials. The development is far too rapid to be absorbed even by a dedicated analytical chemist within the short time at his disposal.

The aim of this continuing series is to deal with the significant new developments in ideas and techniques, their critical evaluation and the present status of important but more classical methods and approaches. The editor intends to present the topics from the point of a non-specialist but retaining a scholarly level of treatment. This object is understandable particularly from the point of view of an experienced analytical chemist, who desires to learn more but is neither a specialist in all the techniques nor a novice in any.

It would be apparent from the list of the topics given below that the editor has been quite choosy in his selection of what is important. The chapters have been written by scientists with intimate knowledge and experience in the subject. The subjects covered are: (a) Atomic absorption spectroscopy by R. Lockyer; (b) Photometric titrations by A. L. Underwood; (c) Analytical applications of enzyme-catalysed reactions by W. J. Blaedel & G. P. Hicks;

(d) Ion sources and detectors for mass spectrometric study of solids by L. F. Herzog, D. J. Marshall, B. R. F. Kendall & L. A. Cambey; (e) Galvanic analysis by P. Hersch; (f) Linear elution adsorption chromatography by Lloyd R. Snyder; (g) Concepts and column parameters in gas chromatography by J. Calvin Giddings; and (h) Thin-layer chromatography by René Maier & Helmut K. Mangold, with author index, subject index and cumulative index for Vols. 1-3.

Considering the aim the editor had kept in view, all the chapters have brought out the highlights of the techniques in instrumentation and application and discussed the possible future developments and limitations of the methods. The book certainly serves the purpose of keeping an analytical chemist fully informed about the latest developments and trends.

V. T. ATHAVALE

SOME PROBLEMS OF PLASTIC DEFORMATION OF METALS AT HIGH PRESSURES by B. I. Beresnev, L. E. Vereshagin, Yu. N. Ryabinin & L. D. Livshits; translated from the Russian by V. M. Newton (Pergamon Press Ltd, Oxford), 1963. Pp. xi + 79. Price 35s.

The book under review, which is an English translation of a Russian monograph incorporating the experiments conducted at the Institute for High Pressure Physics of the Academy of Sciences of the USSR on the plastic deformation of metals at high pressures, published in 1960, is a welcome addition to the significant, interest-growing and fast-developing subject of high pressure metal deformation.

The book has been conveniently divided into 4 chapters. In the first chapter, discussing the effect of increased plasticity under pressure, a number of interesting phenomena are highlighted such as the increase in area of the deformation stress and increase in plasticity, corresponding linearly to increase hydrostatic pressure. In the next chapter, the authors discuss the many conditions like methods of extrusion, the nature of the media and date of discharge. The third chapter is devoted mainly to the mechanical properties of metals extruded by high pressure, touching specifically the method of testing and mechanical property-deformation relationship. The authors, in the last chapter, discuss at some length the technological possibilities of extrusion of articles of complex shapes and the significance of hydraulic compressors.

This excellent 79-page monograph presenting concisely quite a number of experimental data of practical significance to industry for the extrusion of pipes and complex parts is a welcome addition to the important subject of high pressure metallurgy. Priced moderately and with the usual Pergamon standards, it is of equal value to both the research metallurgists and metals engineers interested in high pressure deformation problems.

A. A. KRISHNAN

FOUNDRY CORE AND MOULD MAKING by A. D. Sarkar (Pergamon Press Ltd, Oxford), 1964. Pp. viii + 182. Price 40s.

Considerable work has been done during the last decade on various aspects of the carbon dioxide

process and the author has successfully condensed the results of years of research and experience available in this field without loss of information or clarity. The author has also given lucid explanations of complex problems involved in the process, this being specially true with the chapters dealing with the mechanism of bonding. As many as 117 popular technical articles and research papers on the subject have been condensed and the matter enriched with the author's own personal experience to make this book highly informative and useful.

The work on high temperature properties of carbon dioxide sand has been dealt with exhaustively including various factors contributing to setting properties of the sand keeping in view both academic and practical interests. In addition there are chapters detailing practical aspects of the process including one on 'Choice of binder'. The author has spared no pains while analysing the various aspects of the process, the areas where further research work is required for a better understanding of the process.

This book can safely be recommended as a source of reference to both practical foundrymen and students alike.

R. M. KRISHNAN

VEHICLE EMISSIONS (Selected SAE Papers) (Society of Automotive Engineers Inc., New York), 1964. Pp. 321. Price £ 4 10s.

The word 'smog' appears to have been coined during the London Public Health Conference in 1905 and is a contraction of the words 'smoke and fog'. This type of air pollution is known as particulate and consists of particulated matter suspended in moist air and occurs mostly during the overcast winter months and continues day and night while it lasts.

As contrasted with this, there is the photochemical smog which is due to the reaction between sunlight and unsaturated hydrocarbons or olefines with nitrogen oxides in air. It occurs on sunny, warm periods during the daylight hours and may last over 5-7 hr.

Photochemical smog causes eye irritation, general discomfort, poor visibility and plant damage. This kind of smog is found to be common in southern California and in particular Los Angeles area where a combination of photochemical effects of high local concentration of ozone on excessive hydrocarbon emission from dense automotive traffic and frequently occurring intensive inversion layer due to the topographic and very low normal wind velocity, have caused acute smog problems. Both governmental and non-governmental agencies are working hard to find ways and means of combating this nuisance. Diesel fuel (0.12 million gallons) and gasoline (4.5 million gallons) are burned each day in Los Angeles county. From these figures it is obvious that gasoline-driven vehicles are more likely to cause air pollution. Consequently, most of the studies are directed to gasoline vehicle emissions. The book under review is a compilation of 22 selected papers dealing with the activities of many organizations which are engaged in combating the problem of photochemical smog for more than a decade. The presentation of the matter in this volume falls into four groups.

The first group of four papers brings out the following facts: Ozone is a substantial part of the oxidant characteristic of smog and automotive exhaust gas is capable of forming ozone in air either by irradiation or by photochemical process in presence of NO_2 . Shortly after sunrise the oxidants start rising and reach a peak at about midday and fall off towards the evening and are practically absent during nights. Smog occurs in the early afternoons on days when the traffic concentration is very intense. During this period, moderate eye irritation is felt.

A study of driving habits of motorists shows that 15 per cent of the driving time is spent on idling, 16 per cent on cruising at about 30 m.p.h., 37 per cent in accelerating to 22 m.p.h., and 32 per cent in decelerating. Most of the time, operation is at part throttle. These are responsible for excessive hydrocarbon emission. An attempt has been made at drawing up standards for vehicle operation such that undesirable exhaust emissions are minimized.

The second group of five papers deals with the evaluation of exhaust emissions. For this purpose the following up-to-date instruments are used: (i) Infrared gas analysers and recorders for continuous estimation of hydrocarbons, CO_2 and CO. (ii) Gas chromatography for estimation of non-oxidized hydrocarbons. (iii) Viscous flow air meters, electric-cum-electronic temperature and pressure indicators and multi-channel recorders used both in the laboratory and on the road for a detailed study of the exhaust products.

The findings of the third group of 8 papers pertaining to the influence of engine, fuel and lubricant on exhaust emission are as follows: Pollution of the fresh charge with residual gas is the major fact causing slow combustion under light load conditions. Also during deceleration too much of fuel would be admitted into the engine. These two are responsible for emissions of unburned hydrocarbons. Flame quenching and fuel condensation on combustion chamber walls occur under certain operating conditions which lead to excessive hydrocarbon emission. Lean mixtures and retarded timing lead to less hydrocarbon emission, but the former gives better and the latter worse fuel economy. The combustion chamber deposits also increase the hydrocarbon emission. Partial oxidation of these hydrocarbons may occur in the exhaust pipe if excess air or oxygen are made available or if the exhaust is made quite hot by retarding spark timing. Carburettor vent losses, sometimes amounting to 10 per cent of fuel used, add to the hydrocarbons escaping into the atmosphere. Vent losses are increased by slow speed driving in city areas.

The last group of five papers deals with the following methods for the control of vehicle emissions. Ventilating crankcase into the air inlet reduces emissions from the engines. Induction vacuum limiting devices reduce the rich mixture flow during deceleration, but it leads to difficulties while idling.

The exhaust gas treatment by catalytic oxidation or by after-burners will reduce the emission of hydrocarbons. However, life of such devices is limited and the cost of installation and maintenance is high.

Each one of the papers contains valuable information on modern instrumentation or refined experimental techniques and there is an exhaustive bibliography in the body as well as at the end of the volume.

This volume has succeeded in drawing the attention of the reader to the formidable nature of the problem of smog which is sure to affect many more communities in the future on account of very fast rise in automotive traffic. It has also brought out clearly the enormous amount of work that has already gone into understanding and solving this problem. Though there was no workable solution in the year 1962, as a result of continued effort, four successful exhaust emission control devices for new cars and one for used cars are now available (*SAE JI*, August 1964). There is also a fund of information useful to the engineers and scientists who are engaged in the basic studies of combustion in IC engines. This volume will be a valuable addition to the scientific and engineering libraries and laboratories.

M. R. K. RAO

FOOD DEHYDRATION: Vol. 2—PRODUCTS AND TECHNOLOGY edited by W. B. Van Arsdell & M. J. Copley (AVI Publishing Co. Inc., Westport, Connecticut), 1964. Pp. xi+721. Price \$ 24.50

Vol. 2 is the second of the pair of books dealing with food dehydration. Vol. 1 is devoted to discussion of the underlying scientific principles involved in dehydration.

Drying of foods in order to preserve them in seasons of surplus for use in times of scarcity is an ancient art. The modern era in food dehydration is considered to have begun about 1900. Preservation of foods by dehydration assumed great importance during World War II because of space and weight saving features of dehydrated foods. The chemistry of the deteriorative changes in stored dehydrated foods was not well understood at the time and several products came into severe criticism. Scientific and technical advances in the later years of World War II and the post-war years added much knowledge in the field of chemistry and technology of dehydration. Because of improvements in the flavour, texture and shelf-life of dehydrated foods processed by modern methods, they have regained popularity in civilian markets. Several new techniques such as freeze-drying, puff-drying and foam-mat drying have been developed in the last decade. With this background of the development of the industry, it became necessary to present the scientific, technical and engineering achievements in food dehydration in a consolidated manner and this object has been served by these two volumes on food dehydration.

Vol. 2 is organized into two major sections, one dealing broadly with principles and practice of food dehydration and the other with individual food commodities. It contains 12 chapters, contributed by 23 collaborators; the chapters are numbered serially with the 9 chapters of Vol. 1. The text contains 77 tables and 211 illustrations.

Introductory Chapter 10 is a summary statement of the scientific principles of dehydration, more or less a recapitulation of some of the subject matter of Vol. 1. Chapter 11 deals with drying methods and

equipment. Mechanical features of driers, instrumentation, various types of driers indicating their special features, and evaporators used to pre-concentrate liquid foods prior to drying are discussed. Chapter 12, titled 'Dehydration plant operation', contains information which should be of much use to the operating personnel as it covers various aspects of material handling, processing and inspection. Various types of equipment used for preparative purposes are well illustrated.

Chapter 13 describes briefly the dehydration of several vegetables; flow sheet for some of the vegetables and data on the characteristics of principal commercial varieties in USA are included. Chapter 14 deals with dehydration of potatoes in various forms; preparation, processing and quality evaluation are discussed. Chapter 15 gives a brief description of the processes for the manufacture of instant coffee and tea; product quality variables in production are referred to.

The fast developing industry of dry soup mixes forms the subject matter of Chapter 16; quite a few recipes of dry soup mixes and the pertinent military specifications have been included. Chapter 17 deals with sun-drying and dehydration of fruits with special reference to apples, prunes, raisins and cranberries; post-drying treatment of dried fruits and their shelf-life are also discussed. Chapter 19 describes the dehydration of meat, poultry and sea foods; emphasis is laid on freeze-drying as having distinct advantages over conventional air-drying. Chapter 20 summarizes the scientific and technological progress in the dehydration of milk and its products; product characteristics as influenced by the heat treatment are discussed. The last Chapter 21 deals with dehydration of liquid eggs into egg white, whole egg and yolk products; influence of drying on the physico-chemical, microbiological and functional properties of egg products have been discussed.

Three appendices at the end of the book are concerned respectively with peroxidase test, data on drying and shrinkage ratios of various vegetables, and glossary of terminology used in the text of the two volumes.

Considering that the editors have attempted to discuss the technology of dehydration, both in general terms and with reference to specific commodities, this volume is fairly comprehensive. It would be of great use to the various groups involved in research, quality control and production of dehydrated foods. The large number of illustrations increases the usefulness of this book for the production personnel.

D. S. BHATIA

METHODS OF ENZYMATIC ANALYSIS edited by H. U. Bergmeyer (Academic Press Inc., New York, and Verlag Chemie, GmbH, Weinheim/Bergstr.), 1963. Pp. xxiii+1064. Price \$ 30.00

This volume is intended to be a laboratory manual giving working directions of various methods in enzymatic analysis described by over one hundred authors professionally competent in their respective fields. It is divided into four sections. In Section A, the general principles of assay of enzymes are described, as also the experimental techniques such as handling biochemical reagents,

methods of measurement and instruments used, spectrophotometric, manometric and other methods as well as handling tissues for preparation of homogenates, extracts, etc. These should prove to be of immense help to a beginner because minute details of the principles, experimental techniques and interpretations are presented.

Section B deals with the estimation of substrates involved in carbohydrate metabolism, citric acid cycle, protein metabolism, lipid metabolism, nucleotide metabolism and others. Only methods adapted to enzymatic analysis are described.

Section C is devoted to methods of assay of enzymes. A noteworthy feature is the inclusion of discussion on the importance of measurement of enzyme activity in medicine, in food chemistry and in plant and agricultural chemistry. The wide use of enzymes and enzyme assays in these fields and their practical importance have been brought to focus. Methods have been described for all the classes of enzymes which have worked well in the hands of the expert authors. The details relate to the principle of the method, optimum conditions of measurement, reagents, preparation of solutions, procedure, calculations with one example, normal values, sources of error, stability of the enzyme samples and, where necessary, application to other sources of the enzyme.

In the last section (D), information on the commercially available enzymes, substrates and complete reagent kits are recorded. Some of the important properties have been summarized giving notes of guidance in handling the commercial preparations.

In the end a conversion table of transmission to extinction values is given. A special feature is that values up to first decimal of percentage transmission are given which are not found in other available books. References to original papers are given as footnotes, wherever necessary. The nomenclature recommended for enzymes by International Union of Biochemistry has not been used, except for their mention in parenthesis for the enzymes in Section D.

Classical chemical methods are still widely used for the measurement of metabolites. Several of these would involve invariably a separation step and then development of chromophoric group. These are relatively easier methods for most laboratories with limited facilities and are preferred where infrequent analysis is done. Since the introduction by Warburg of the spectrophotometric assay of reduced DPN and TPN at 340 m μ , this method has been exploited by the enzymologists in several ways. Several other enzymes are assayed coupled to one of the dehydrogenases so as to be able to measure the reaction by way of change in absorbancy at 340 m μ . Sometimes even two or three extra enzymes have been used to be able to couple to DPN reduction. This is made possible by the availability commercially in large quantities of a number of purified or crystalline enzymes which are relatively stable. The advantages of this type of assay are rapidity, specificity and sensitivity coupled to finding reaction rates accurately. One of the disadvantages is that the study of kinetics is made complicated by the presence of more than one enzyme. All the same the use of enzymes as analytical reagents has gained ground and can be expected to have wider application in the future, with the

commercial production of a larger number of enzymes at low cost.

This volume serves the purpose of a reliable laboratory guide giving working directions with minute details for the methods of enzymatic analysis. For a practising biochemist certain details like figures for pH , effect of substrate, etc., may appear superfluous. However, a comprehensive treatise of this nature should prove very valuable to all those interested in the use of enzymes in biochemical analysis.

P. S. SARMA & T. RAMASARMA

ADVANCES IN FLUORINE RESEARCH AND DENTAL CARIES PREVENTION edited for ORCA by J. L.

Hardwick, J. P. Dustin & Hans R. Held (Pergamon Press Ltd, Oxford), 1963. Pp. vi+354. Price 140s. The book is based on the papers presented at the 9th Congress of the European Organization for Research on Fluorine and Dental Caries Prevention and covers a wide variety of interdisciplinary fields, viz. biochemistry, crystallography, ultrastructure, histochemistry, tissue culture, microbiology, endocrinology, nutrition, etc., all impinging on the problems related to the tooth. Space does not permit the discussion of all these studies. Nevertheless, the following picture on the mechanism of cariostatic effect of fluoride seems to emerge from the reports.

Crystal seeding is an accepted indispensable first step in the process of biological calcification. The nature and the mechanism of crystal seeding seem to rest with the fluoride ion. Balance of ionic activities in body fluids was interpreted as not favouring crystal nucleation via hydroxyapatite, but via fluorapatite, suggesting a role for fluoride in crystal nucleation which triggers subsequent calcification (Perdok). From observations on the development of dental enamel in acute experimental fluorosis in pups, it was concluded that the fluoride influences the rate of mineral uptake in the enamel via a local factor which is closely associated with the organic matrix production (Allan).

Besides the earlier postulated theory that fluoride exerts its cariostatic action by transforming the apatite to more insoluble fluorapatite (by ion-exchange with the $-OH$ groups), it is now further suggested that such exchange of $-OH$ groups by fluoride ions, by increasing the number of hydrogen bonds between the mineral phase and the organic matrix, enhances the structural integrity and stability of the calcified tissue (teeth), thereby imparting to the tissues the property of greater resistance to chemical solution (Perdok). A further mechanism by which fluoride may exert its cariostatic action is made possible by the observation that the plaque material, from caries-free areas of teeth of individuals living in low fluoride regions, has a fluoride concentration higher than 6 p.p.m. (range 6-180 p.p.m.), a level which inhibits glycolysis of bacteria at pH 5.0, as reported earlier by Jenkins (Hardwick and Leach). In such a case the acid production from the substrate lodged in the plaque via glycolysis may be prevented by the inhibitory effect of fluoride on the plaque bacteria.

Owing to lower enzymatic activity of the saliva of caries-susceptible persons, sugars are broken down more slowly than in the case of people resistant to

caries. Therefore, more substrate for acid production is present in the plaque material of caries-susceptible persons (Bamstedt and Ahrens). In such a case the above postulated cariostatic effect of fluoride via inhibition of glycolytic production of acid by plaque bacteria assumes considerable significance.

A critical evaluation of the physiological results of implications of fluoride ingestion, and epidemiological survey of recent experiments in Europe, confirms the safety and advantages of fluoridation of public water supplies as a mass caries control measure (Dustin, Hornung, Adler and Polczer).

A careful electron microscopic study of amelogenesis in mammals which failed to detect 'fibrous' structural elements in exactly the form predicted by current concepts of enamel formation calls for a re-examination of the concept of 'fibrous' organic matrix (Fearnhead).

The complexity of structure of rat incisor enamel leading to possible errors in studying amelogenesis was also emphasized (Bouysson). Differences in the phosphate content and buffer capacity of human and rodent saliva was offered as a possible explanation for the conflicting reports on responses to dietary phosphate addition in humans and rodents (Ericsson). X-ray emission microanalysis and ion-beam erosion etching techniques were also applied to the study of dental tissues (Boyde, Switsur and Steward).

While the publication is undoubtedly a useful compilation of the observations of various investigators, its value would have been enhanced considerably more if the discussions following the presentations were also included.

P. VENKATESWARLU

SALIVARY GLANDS AND THEIR SECRETIONS edited by Leo M. Sreebny & J. Meyer (Pergamon Press Ltd, Oxford), 1964. Pp. xv+380. Price £7

Recent advancement of science is marked by rapid progress of detailed study of narrower facets. Biology is no exception to it. Enormous collection of facts, which are coming out every year from different laboratories are concerned with the studies in minute details of living systems. Each and every organ of human and animal bodies is explored by the application of the modern techniques to understand its morphology and physiology. The outcome of such an effort often appears bewildering; little time is left for an investigator to see what are the implications, what they actually mean. The symposium on which the book is based was organized to reduce this difficulty and it leaves no doubt that the present publication will present an overall picture of the development in this field of salivary gland research in a single volume.

For their diverse functions, salivary glands occupy a unique position in the animal body and any study to get the *modus operandi* of this organ will always be welcomed by the investigators and teachers. The present monograph is devoted to such studies as ultrastructure, hormonal control and neural control of the salivary gland. The contributors are able to present such a detailed account that it will be easier for many future investigators in cell biology and genetics to easily digest the new facts about the salivary glands and it will help, no doubt, to advance

further in finding answers to the perennial questions concerning cytodifferentiation and the genetic control of this important organ. The papers dealing with the chemistry of saliva also have thrown much light on the glands and have definitely opened new avenues to understanding. The chapter devoted to methodology will lessen the difficulties of future investigators in handling the organ in the course of an experiment.

To be precise, the present volume has fully justified the enterprise of the organizers and it may be said that 'the uncommon amount of effort and time' which the editors have invested has been fulfilled. The printing and the photographic reproductions are excellent.

B. GANGULY

PROGRESS IN OCEANOGRAPHY: Vol. 1, edited by Mary Sears (Pergamon Press Ltd, Oxford), 1963. Pp. vii +383. Price £5

Research in marine sciences is expanding at such a rapid pace that it necessitates the publication of periodical, authoritative reviews to keep the oceanographers and others interested in the sea conversant with the advances in the field. The volume under review is a new annual volume consisting of three types of papers: reviews of the present status of knowledge of certain fundamental problems, results of original research, and description of new methods and techniques.

Eugen Siebold describes the morphological methods (major features and structures like buttresses, bars, ripples, benthos), petrofabric techniques (grain fabric and bedding) and petrological methods (grain size distribution, single mineral studies and marker particles) for the study of the sand transport in the nearshore marine waters, and presents the results of his investigations on the North and Baltic Seas. The direction of transport of nearshore sands is stated to be directly related to the 'predominant wind directions and the resulting directions of oncoming waves and longshore currents' (p. 63). The paper is of considerable interest to the sedimentologist and coastal engineer.

The second paper by Blanchard on the 'Electrification of the atmosphere by particles from bubbles in the sea' is a summary of his Ph.D. thesis submitted to MIT. It is aimed at an evaluation of the quantity of electric charge that is separated at the surface of the sea. The paper is unusually long and does not seem to fit into a volume of this nature.

Parsons reviews the present status of knowledge regarding 'Suspended organic matter in sea water'. He describes the methods of measurement of particulate organic matter, and provides information regarding the composition of suspended matter (consisting largely of phytoplankton and detritus) and the quantity and distribution of particulate matter in the oceans. He evaluates the relative importance of various particulate components in the marine food chain.

'The salinity problem' is comprehensively surveyed by Cox. He reviews the historical background in respect of the parameters of salinity and chlorinity and describes the methods and apparatus for chlorinity determinations and conductivity measurements. He recommends the use of Volhard technique for the

former as it is capable of a precision of 0.0005 per cent in chlorinity. The modern salinometers yield results with reproducibility better than 0.01 o/oo in salinity. The relationship between conductivity and density is reasonably linear, but the relationship between chlorinity and density shows several times more scatter.

In 'Gulf Stream 1960', Fuglister summarizes the results of the studies undertaken by the Woods Hole Oceanographic Institution during the spring of 1960 on Gulf Stream. The investigations include the study of the path of the Gulf Stream, observations of deep currents with Swallow floats, temperature, salinity and oxygen profiles, velocity and transport studies, etc. (generally accepted value for transport, 70×10^6 m.³/sec.).

The volume is attractively produced and would be a valuable addition to any scientific library.

U. ASWATHANARAYANA

PUBLICATIONS RECEIVED

- RADIATION SOURCES edited by A. Charlesby (Pergamon Press Ltd, Oxford), 1964. Pp. vii+268. Price 80s.
- PRINCIPLES OF OPTICS — ELECTROMAGNETIC THEORY OF PROPAGATION, INTERFERENCE AND DIFFRACTION OF LIGHT by Max Born & Emil Wolf with contribution by A. B. Bhatia (Pergamon Press Ltd, Oxford), 1964. Pp. xxviii+808. Price £ 6
- DISLOCATIONS — International Series of Monographs on Solid State Physics by J. Friedel (Pergamon Press Ltd, Oxford), 1964. Pp. xxi+491. Price £ 6
- DIGITAL DIFFERENTIAL ANALYSERS by A. V. Shileiko; translated from the Russian by D. P. Barrett (Pergamon Press Ltd, Oxford), 1964. Pp. vi+111. Price 45s.
- FLUID DYNAMICS TRANSACTIONS: Vol. 1, edited by W. Fiszdon (Pergamon Press Ltd, Oxford), 1964. Pp. 397. Price £ 5
- INTEGRATION OF EQUATIONS OF PARABOLIC TYPE BY THE METHOD OF NETS by V. K. Saul'yev; translated from the Russian by G. J. Tee (Pergamon Press Ltd, Oxford), 1964. Pp. xvii+346. Price 80s.
- DIAMOND ABRASIVES AND TOOLS edited by John Burls (Pergamon Press Ltd, Oxford), 1964. Pp. x+127. Price 50s.
- SOLAR PLASMA GEOMAGNETISM AND AURORA by Sydney Chapman (Gordon & Breach Science Publishers, New York), 1964. Pp. x+141. Price \$ 1.95 (paper); \$ 4.95 (cloth)
- LECTURES ON MAGNETOIONIC THEORY by K. G. Budden (Gordon & Breach Science Publishers, New York), 1964. Pp. xiv+82. Price \$ 1.95 (paper); \$ 3.95 (cloth)
- L'EFFET MOSSBAUER ET SES APPLICATIONS À L'ÉTUDE DES CHAMPS INTERNES by A. Abragam (Gordon & Breach Science Publishers, New York), 1964. Pp. viii+70. Price \$ 1.95 (paper); \$ 3.95 (cloth)
- BASIC TECHNICAL MATHEMATICS WITH CALCULUS by Allyn N. Washington (Addison-Wesley Publishing Co.), 1964. Pp. xii+595. Price £ 8.75
- NEW TYPES OF METAL POWDER edited by Henry H. Hausner (Gordon & Breach Science Publishers, New York), 1964. Pp. ix+167. Price \$ 3.95
- INTRODUCTION TO INFRARED AND RAMAN SPECTROSCOPY by N. B. Colthup, L. H. Daly & Stephen W. Wiberley (Academic Press Inc., New York), 1964. Pp. xii+511. Price £ 12.00
- PHYSICAL ELECTRONICS by G. F. Alfrej (Van Nostrand Book Co., London), 1964. Pp. 208. Price 45s.
- IRON METABOLISM edited by F. Gross (Springer-Verlag, Berlin), 1964. Pp. xi+629. Price 45 DM (cloth)
- INFORMAL PROCEEDINGS OF THE BUHL INTERNATIONAL CONFERENCE ON MATERIALS — TRANSITION METAL COMPOUNDS, TRANSPORT AND MAGNETIC PROPERTIES edited by E. R. Schatz (Gordon & Breach Science Publishers, New York), 1964. Pp. vii+136. Price \$ 5.00 (paper); \$ 9.50 (cloth)
- MILLING METHODS IN THE AMERICAS edited by Nathaniel Arbiter (Gordon & Breach Science Publishers, New York), 1964. Pp. viii+486. Price \$ 7.50 (paper); \$ 11.50 (cloth)
- BIOLOGICAL CONTROL OF INSECTS, PESTS AND WEEDS edited by Paul De Bach (Reinhold Publishing Corp., New York), 1964. Pp. xxiv+844. Price \$ 22.50

Investigations conducted at the Technische Hochschule, Munich, have given evidence for the ferroelectric nature of ice for the first time. Substances which contain hydrogen bonds between two O-atoms (e.g. Rochelle salt) exhibit ferroelectric property and this is explained as due to the proton jumping from one possible position between the O-atoms to the other. It is known that ice contains hydrogen bonds of the above type and so it was expected to be ferroelectric in relevant temperature regions. But till now there has been no evidence for the ferroelectric nature of ice. In the observations made at Munich, the ferroelectric character has been observed at a very low temperature (100°K.) with a relaxation time of the order of hours. It is due to the large value of the relaxation time that the ferroelectric property of ice could not be observed earlier. It has been noted that the ferroelectric behaviour of ice could be obtained only if the water used for the crystal growth was not extremely pure. This shows that foreign atoms promote the appearance of ferroelectricity. It is not clear whether this influence is due to a shortening of the relaxation time of the ferroelectric polarization or whether the foreign atoms themselves contribute to the charge displacement [*Phys. Lett.*, **9** (1964), 291].

Element 104

The discovery of a new transuranium element, element 104, has been recently reported by the Russian research workers at the Joint Nuclear Research Institute, Dubna. Element 104 was produced by bombarding plutonium 232 with heavy particles of ionized neon-22. It has an atomic weight of 260 and a half-life of 0.3 sec. Its other physical and chemical properties are under study [*New Scientist*, **23** (1964), 650].

A new chemiluminescent reaction

A new kind of chemiluminescent reaction which involves removal of an electron from the radical-anion of a fluorescent species by

NOTES & NEWS

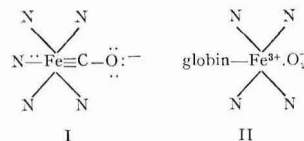
suitable oxidizing agents promises to be one of the most general types of chemiluminescent reactions known. The reaction apparently involves removal of an electron from the highest bonding orbital rather than from the antibonding orbital.

Potassium diphenylanthracene (K^+DPA^-), prepared by reacting slight excess of diphenylanthracene with potassium in boiling tetrahydrofuran, gives a bright blue chemiluminescence when reacted with 9,10-dichlorodiphenylanthracene ($DAPCl_2$). In another experiment it was found that sodium naphthalenide undergoes a similar reaction with $DAPCl_2$. To explain these reactions it is suggested that the $DAPCl$ radical formed as an intermediate can be reduced further to an excited state (DPA^*+Cl^-) by a good reducing agent such as DPA^- or $C_{10}H_7^-$. The rapid chemiluminescent reaction of K^+DPA^- with chlorine has also been explained on a similar reasoning. However, bright chemiluminescence which also accompanies in the reaction between K^+DPA^- with other oxidizing agents, viz. benzoyl peroxide, oxalyl chloride, mercuric chloride and aluminium chloride, cannot be explained as involving the intermediate $DAPCl$ radical. To account for this, it is suggested that the reaction of a good quenching oxidizing agent with DPA^- can produce singlet excited DPA^- ; no triplet state is involved. The nature of the oxidant also influences the luminescent reaction. For instance, the acridone ketyl which luminesces brightly on reacting with benzoyl peroxide gives no light when reacted with the analogous lauroyl peroxide. This might be due to a difference in the available orbitals in the two peroxides [*Chem. Engng News*, **42** (35) (1964), 32].

Nature of the iron-oxygen bond in oxyhaemoglobin

The structure of oxyhaemoglobin (and related haemoglobin compounds) has been proposed as (I)

by Prof. Linus Pauling of the California Institute of Technology, Big Sur, Calif., USA. The structure (II) proposed earlier by J. J. Weiss assumes that oxyhaemoglobin is haemoglobin peroxide, with the iron atom in the ferric state and the oxygen molecule present as an O_2^- ion, which is then taken up in the coordination shell of the ferric ion. The dot in the structure (II) represents not an electron but some sort of bond.



Oxyhaemoglobin is diamagnetic and the definition of oxidation number requires that the iron atom in any diamagnetic molecule has an even oxidation number. It is accordingly not possible to be described as ferric (oxidation number, 3+). In the structure (I) proposed by Prof. Pauling, the iron atom forms a triple bond with the carbon atom, and the outer oxygen atom or nitrogen atom has a negative electric charge. Oxyhaemoglobin and related haemoglobin compounds thus contain (i) ferrous iron rather than ferric iron, (ii) their electronic structure involves essentially the formation of a double bond between the iron atom and the nearby oxygen atom in oxyhaemoglobin (with the iron-oxygen-oxygen bond angle about 120°), and (iii) a triple bond to the carbon atom in carbonmonoxyhaemoglobin and the haemoglobin isocyanides (with iron-carbon-oxygen or nitrogen bond angle 180°). The iron-oxygen and iron-carbon interatomic distances in these compounds are predicted to have the values corresponding to these multiple bonds.

The negative charge assigned to the outer oxygen atom in structure (I) can be accounted for on the basis of the structure of myoglobin as determined by Kendrew. The structure (I) assigned places a

negatively charged oxygen atom in close approximation to the positively charged imidazolium group and in such a position as to permit hydrogen bonding with the negatively charged oxygen atom, thus further stabilizing the structure [*Nature, Lond.*, **203** (1964), 182].

A simple method of maintaining stock cultures

A simple method suggested by Mary T. Clement of the Division of Biosciences, National Research Council, Ottawa, for maintaining stock cultures overcomes most of the disadvantages encountered in the preservation of stock cultures in refrigerated rooms at very cold temperatures in the freeze-drying technique.

Cells from agar slants and centrifuged broth cultures are washed into about 3 ml. of glycerol-water and 0.2-0.3 ml. aliquots of the suspension distributed into standard freeze-drying ampoules (0.5 × 10 cm., constricted at one end for sealing), which may be corked and heat-sealed. The ampoules are then inserted into pockets formed by stapling 1½ in. strips of corrugated paper to 3 × 5 in. filing cards. The suspensions may be stored directly at -40°C. and pre-frozen by immersing the lower part of the tubes in an alcohol-dry ice bath. Although fast prefreezing is not generally considered beneficial, it reduces the time of exposure of the cells to the glycerol solution, which may not be universally innocuous, especially at room temperatures. The cards are filled in numerical order cabinets held at -40°C. Storage life of many strains exceeds their survival in agar slant cultures stored at 5°C. [*Canad. J. Microbiol.*, **10** (1964), 613].

Species specificity of purified interferons

Interferon, the antiviral particle, has a marked species specificity in a highly purified preparation as reported by Thomas C. Merigas of the Stanford Medical School, Palo Alto, and Samuel Baron *et al.* of National Institute of Allergy and Infectious Diseases, Bethesda, USA. The chick interferon produced by a WS strain of influenza

virus in embryonated eggs and by Chikunguna virus in tissue culture, and the mouse interferon produced by Chikunguna virus in tissue and *in vivo* by intravenous injection of Newcastle disease virus were obtained in highly purified form. The interferons obtained exhibited 6000-fold increase in unit activity per milligram of protein over the starting materials. The host cell specificity of the antiviral activity evaluated by concurrent assay on homologous and heterologous cells indicated that mouse interferons do not protect chick cells against virus attack and vice versa.

This species specificity is not explained by a demonstrable difference in adsorption rates. There is no difference in charge between the interferons as measured by combined zone electrophoresis or ion-exchange chromatography. However, differences in the two interferons could be distinguished by thermal inactivation studies and by precise chromatography. Purified chick interferon has been found to be more heat labile than purified mouse interferon. The chromatographic studies indicated that interferons produced by the same cell species *in vivo* or *in vitro*, or in response to different viruses are identical. These observations led to the conclusion that the same virus stimulates the production of physically distinguishable molecules in two different cell species, and that the interferon is a virus-induced product of the host genome. The complete species specificity exhibited by mouse and chicken interferons suggests that this striking property should be more generally applied for characterizing interferons [*Science*, **145** (1964), 811, 814].

Standardization of tissue culture media

The errors usually encountered in the cultivation of animal cells *in vitro* are mostly due to variation in the purity of reagents used and the lack of a precise recipe for preparing the culture media.

Recently Lionard Hayflic of the Eistai Institute of Anatomy and Biology, Philadelphia, and Pat Jacobs and Frank Perkins of the National Institute of Medical Research, London, have made investigations with a number of widely

used media and indicated that standardized media of constant composition could be prepared. Contrary to the conventional method of preparing media by dissolving the reagents in specific groups or blocks as suggested by Swim and Parker [*J. Lab. clin. Med.*, **52** (1958), 309], the simple procedure of pulverizing preweighed components and adding the mixture to water has been found to be successful. All media were prepared by combining the weighed ingredients and desiccating the aggregate over sodium hydroxide for 18 hr under vacuum. The mixture was then ball-milled until a free-flowing fine powder was obtained, re-desiccated to remove moisture acquired during the milling procedure and then packed for use.

Eagle's basal medium thus prepared contains all the original formulae with the exception of sodium bicarbonate, which could be added depending on the individual requirements like (1) the pH of water used, (2) variations of gas phase and liquid phase ratios in culture vessels of differing design, (3) variation in acid production and pH tolerance by different cell populations, and (4) the interrelationship of these parameters with cell inoculation density. Powdered medium was added slowly to deionized or distilled water at room temperature, agitating with a magnetic stirrer for 20 min. and the resulting solution was sterilized by 'millipore' filtration. Cell cultures of human diploid strain WI-26 and WI-38, which are considered to be fastidious in their media requirements and are more likely to be sensitive to the presence of toxic substances, have not shown any variation in their cell counts during serial passages for as many as forty generations.

The numerous advantages of dry powdered media are: (1) large amounts can be prepared from a single source of reagents and their composition standardized, (2) the hygroscopic powder which can be preserved at 5°C. in dark has been found to be stable for one year, and (3) contrary to the usual practice of storing prepared media at 0-10°C., the Eagle's basal medium is stable at least a month at room temperature [*Nature, Lond.*, **204** (1964), 246].

A microsomal inhibitor of amino acid incorporation in rat liver

Studies with cell-free systems have focused attention on the striking difference in the activity of amino acid incorporation systems in normal and regenerating rat liver. This has been explained as being due to the greater activity in regenerating liver cytoplasm of a fraction having certain properties similar to those of messenger RNA. Microsomal fractions, however, contribute more to this difference [Hoagland, M. B. & Askonas, B. A., *Proc. nat. Acad. Sci., Wash.*, **49** (1963), 130].

A microsomal inhibitor of amino acid incorporation whose action is antagonized specifically by guanosine triphosphate (GTP) has been reported [Hoagland, M. B., Scornik, O. A. & Pfeffersson, L. C., *Proc. nat. Acad. Sci., Wash.*, **51** (1964), 1184]. Microsomes from regenerating rat liver (M_R) incorporated amino acids at a higher rate and for longer periods than microsomes from adult normal liver (M_N). Mixtures of equal quantities of M_R and M_N always incorporated at a lower rate than that expected if their activities were additive. This suggested that M_N in some way inhibited the activity of M_R . GTP reduced the relative difference between the activity of M_R and M_N . M_R and M_N which had been incubated at 37°C. for more than 3 hr to destroy their protein synthetic capacity showed more inhibitory activity than the fresh M_R and M_N , indicating the presence of an inhibitor.

The inhibitor could be obtained in soluble form by sonication of microsomes. The inhibitory activity of sonic extract was reversed by GTP. Other nucleoside triphosphates — ATP, CTP, UTP — had no effect. In sucrose density gradient centrifugation it behaves as a polydisperse system, the activity being concentrated in the region 4-10s. It has been shown that the inhibitor does not function by (i) depleting GTP in the assay system or (ii) impairing the binding of messenger RNA to ribosomes or (iii) reduced release of nascent protein.

The presence of a microsomal inhibitor of amino acid incorporation suggests that it may have a

role in the control of protein synthesis. The low rate of protein synthesis in normal liver being due to an increased concentration of the inhibitor and the high rate in regenerating rat liver due to decreased concentration of the inhibitor, the reversal by GTP is more in the case of assay systems of normal liver than regenerating rat liver system.

Since the finding that GTP played a role in protein synthesis [Keller, E. B. & Zamenick, P. C., *J. biol. Chem.*, **221** (1956), 45], it has been assumed that it supplies energy for the process in some way. The presence of an inhibitor in microsomes and its reversal by GTP suggests that the role of GTP in protein synthesis may be to regulate the concentration of the inhibitor. This might be accomplished by altering the molecular configuration of a protein or a class of proteins in some way as to inactivate their inhibitory function. It has been observed by Frieden [*J. biol. Chem.*, **238** (1963), 3286] that GTP and/or GDP dissociate glutamic dehydrogenase.—M. R. SAIRAM

Biosynthesis and methylation of transfer RNA

The intracellular site of transfer RNA biosynthesis has not been clearly established. Support for a nuclear origin is implied in the finding of complementary sequences of bases in homologous DNA, able to form specific hybrids with transfer RNA [Goodman, H. M. & Rich, A., *Proc. nat. Acad. Sci., Wash.*, **48** (1962), 2101]. Additional support for a nuclear origin is the demonstration that isolated nuclei are able to incorporate labelled nucleotide precursors into low molecular weight RNA [Chipchase, M. I. H. & Birnsteil, M. L., *Proc. nat. Acad. Sci., Wash.*, **49** (1963) 692]. Other studies, however, have postulated that a template other than DNA may be utilized for the replication of this cellular RNA component [Spencer, M., Fuller, W., Wilkins, M. H. F. & Brown, G. L., *Nature, Lond.*, **194** (1962), 1014]. It has been clearly established that once the primary structure of transfer RNA is synthesized, some alteration of the molecule occurs. The methylation of bases in transfer RNA occurs at the polynucleotide

level with S-adenosyl-L-methionine acting as the methyl donor [Flaissner, D. & Borek, E., *Fed. Proc.*, **22** (1963), 229]. Recent evidence also suggests that conversion of uridine to pseudouridine may also take place at the polynucleotide level [Robbins, P. W. & Kinsey, B. M., *Fed. Proc.*, **22** (1963), 229]. Therefore, during the course of biosynthesis of transfer RNA, precursor RNA molecules which contain neither methylated bases nor pseudouridine may be anticipated to exist.

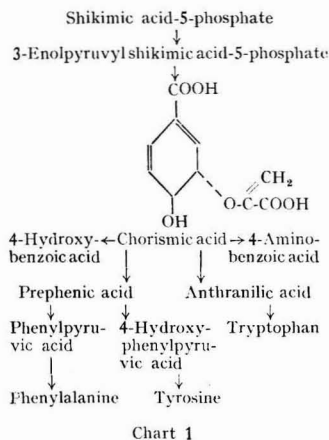
In a recent paper D. G. Comb and S. Katz [*J. mol. Biol.*, **8** (1964), 790] have presented evidence for such a precursor to transfer RNA. A rapidly labelled RNA fraction of the nucleolus has been isolated and partially characterized by them. This RNA component has been tentatively identified as a precursor to transfer RNA. It contains neither pseudouridine nor methylated bases. However, it resembles transfer RNA in base composition and molecular weight. It serves as a substrate for *in vitro* methylation to a greater extent than transfer RNA. The isotope studies reported suggest that a transfer RNA precursor arises in the nucleolus, moves to the cytoplasm where base methylation occurs and perhaps other alterations, and then moves back to the nucleolus.—B. SRINIVASA ACHAR

Chorismic acid, a new intermediate in aromatic biosynthesis

One of the major unsolved problems in the biosynthesis of aromatic compounds having the benzene ring is the process by which shikimic acid-5-phosphate is converted into anthranilic acid, a precursor of tryptophan, and prephenic acid, a precursor of phenylalanine and tyrosine. It was shown that 3-enolpyruvyl shikimic acid-5-phosphate is a likely precursor for the three aromatic amino acids [Levin, J. G. & Sprinson, D. B., *Biochem. biophys. Res. Commun.*, **3** (1960), 157]. Mutants accumulating 3-enolpyruvyl shikimic acid and requiring phenylalanine, tyrosine, tryptophane, 4-aminobenzoic acid and 4-hydroxybenzoic acid for growth have been described [Davis, B. D. & Mingioli, E. S., *J. Bact.*, **66** (1953), 129].

These observations suggest that there is at least one further common intermediate beyond 3-enolpyruvyl shikimic acid-5-phosphate.

A new intermediate in aromatic biosynthesis, named chorismic acid, has been isolated recently [Gibson, M. I. & Gibson, F., *Biochem. J.*, **90** (1964), 248]. This was made possible by the isolation of an auxotroph of *Aerobacter aerogenes* (strain 62-1) which accumulates chorismic acid. Chorismic acid was also formed from shikimic acid by cell-free extracts of strain 62-1. The auxotroph also accumulated anthranilic acid and presumably had a block in the conversion of chorismic acid to prephenic acid or prephenic acid to phenylpyruvic acid. Chorismic acid has been shown to be converted enzymatically into anthranilic acid in the presence of glutamine and cell-free extract of strain 62-1. Chorismic acid was also converted enzymatically to prephenic acid, phenylpyruvic acid and 4-hydroxyphenylpyruvic acid by wild strain of *A. aerogenes* in the absence of glutamine. It was also converted enzymatically to 4-hydroxybenzoic acid by the strain 62-1. Based on these results these authors have outlined a pathway of biosynthesis of aromatic compounds as shown in Chart 1.



F. Gibson [*Biochem. J.*, **90** (1964), 256] has established the structure of chorismic acid as the 3-enolpyruvic ether of trans-3,4-dihydroxycyclohexa-1,5-diene carboxylic acid. The barium salt, on warming, was readily converted into a mixture of prephenate and 4-hy-

droxybenzoate. Under acid conditions the prephenic acid was further converted into phenylpyruvic acid.

The isolation and characterization of chorismic acid, and its enzymatic conversion to several aromatic compounds, is bound to stimulate active research in the field of aromatic biosynthesis.—V. C. JOSHI

Intermediary steps of ribosome formation in *Esch. coli*

An aggregate of the ribosomal subunits gives rise to polyribosomes, which have been implicated as the actual sites of protein synthesis. However, very little is known regarding the steps leading to the formation of the ribosomal subunits (30s and 50s particles containing 16s and 23s RNA). An earlier concept [Britten, R. J., McCarthy, B. J. & Roberts, R. B., *Biophys. J.*, **2** (1962), 83] holds that the formation of 'eosome' or free 'unfinished' polynucleotides is the primary step in the origin of the ribosomal subunits.

Kono and Osawa [*Biochim. biophys. Acta*, **87** (1964), 326] have put forward certain other evidences to clarify the question of ribosome formation. *Esch. coli* cells in 'shift-up' culture, a condition under which there is little messenger RNA synthesis but where a preferential synthesis of ribosomal and soluble RNA can take place, have been allowed to incorporate (H^3)-adenosine or ($8-C^{14}$)-adenine for various intervals of time. The incorporation of the label into the various particles obtained by sedimentation analysis of the cell extract with sucrose density gradient centrifugation has been evaluated.

The results indicate that after 15 sec. of contact with the isotope, two components of about 17s and 22s become labelled. With increase in the period of contact with the isotope, newer peaks appear corresponding to 25s, 29s, 32s and 38s. After 10-15 min. of incubation, the bulk of the radioactivity can be detected in 30s and 50s subunits and some in 4s RNA. It has been shown that the earliest labelled particles (17s and 22s) are free 'ribosomal' RNA [Mitsui, H., Ishihara, A. & Osawa, S., *Biochim. biophys. Acta*, **76** (1963), 401]. In

the presence of an inhibitor like chloramphenicol the bulk of the label appears in the 25s and 19s particles and little, if any, in the 30s and 50s subunits. Similarly, the presence of flurouracil results in the accumulation of radioactivity around the 30s region which is actually composed of at least two distinct components of 32s and 28s and which contains the 17s and 22-23s RNA. The 'CM particles' and the 'FU particles' have a sequential relationship and when the inhibitors have been removed and the cells incubated further, the entire radioactivity from the intermediary particles migrates to the 30s and 50s subunits.

These results have been interpreted to indicate the following steps as the stages in the formation of ribosomal subunits: (1) the formation of free 'ribosomal' RNA of the size 17s and 22-23s which is probably the first phase of ribosome synthesis; (2) the formation of 'CM particles' (25s and 19s) and then the 'FU particles' (32s and 28s) which can also be detected under normal conditions at different periods of incubation after 15 sec. and before 10 min.; and (3) the formation of 30s and 50s subunits, through the intermediary particles 38s and 43s before the completion of the 50s subunit.

It is believed that the protein molecules become associated in a stepwise fashion to the ribosomal RNA molecules which have been detected in the fully completed stage at a very early stage of ribosome synthesis. Though a probable modification in the secondary structure of 'ribosomal' RNA has been envisaged at a later stage of ribosome synthesis, the formation of 'eosome' or 'unfinished polynucleotide' as the first step has been contradicted.—G. PADMANABHAN

Progress Reports

Mellon Institute

The Institute celebrated its Golden Jubilee during the year under review. Major events of the celebrations were a science symposium, Fiftieth Anniversary Lecture by Sir John Cockcroft, and a series of talks presenting the account of the researches carried out in the Institute. With a view

to finding the solution of the manifold problems inherent in a rapidly evolving technological society, the Carnegie Institute of Technology, the University of Pittsburgh and Mellon Institute have taken steps to pool their intellectual and physical resources. More than 150 research papers covering the fields such as theoretical chemistry, organic chemistry, continuum physics, metal physics and metallurgy, biochemistry, etc., were published during the year 1963.

In the following is given brief account of research studies carried out in the Institute.

Theoretical chemistry—It has been found that a judicious application of the principles of molecular orbital theory and its simplification, ligand field theory, can yield a striking clarification to the various colours exhibited by transition metal ions. The optical rotatory power of certain inorganic and organic compounds has been assigned to local field asymmetries about certain centres in these materials. This assignment has led to a fruitful and pictorial description of rotatory ability and also of dichroism. Procedures for obtaining accurate solutions to the molecular Schrodinger equation have been further improved with the incorporation of Monte Carlo integration techniques and with the development of an extrapolation method which permits one to estimate true energy eigenvalue with exceptional accuracy. Work on the H_3^+ system has been concluded and it is now possible to state that this molecule ion exists in the equilateral triangular configuration with a bond length of 1.68 Bohr radii and an energy, relative to infinitely separated particles, of -1.37 atomic units. The entire energy surfaces for the isosceles systems H_3^+ and H_3^{2+} have been determined accurately by calculation.

Continuum and molecular physics and spectroscopy—In the course of studies on the axiomatization of thermodynamics, mathematical methods were developed for finding the restrictions which the Second Law places on constitutive equations. A special frictionless creep instrument employing a levitated rotor and an eddy-current drive has been designed and built for use in exploring the elastic component of creep,

which is normally masked by viscous flow in linear amorphous polymers.

The electron spin resonance studies on the structure of free radicals produced by ionizing radiations have revealed that the vinyl and cyclohexyl radicals undergo conformational changes at frequencies of 10^9 and 10^5 c.p.s. respectively. The kinetic studies using ESR methods have been developed to the point where direct measurement of the radical lifetimes are possible.

A new vacuum ultraviolet spectrophotometer having low dispersion (8 Å./mm.; resolution ≈ 0.12 Å.) has been fabricated with a view to obtaining absorption spectra of systems which have electronic transitions of interest lying beyond the range of most commercial instruments. It will now be possible to show as to how the electrons of ammonia are perturbed by the formation of metal-liquid ammonia solution. The other instruments for use in spectroscopy work either completed or nearing completion are: (i) ultrarapid scanning infrared spectrometer, and (ii) electron spectrometer for studying the scattering of electrons by molecular gases.

Structure and properties of inorganic and organic materials—Studies on the formation of complex compounds have given interesting results. Infrared study of new metal-nitrosyl derivatives, $[C_5H_5Mn(CO)]_2$, $[C_5H_5Cr(NO)]_2$, has indicated the presence of bridging nitrosyl groups, the existence of which had previously been doubtful. The cycloheptatrienyl derivatives have also been prepared which contain a new type of metal-cycloheptatrienyl bond with only three-carbon atoms of the ring bonded to the metal atom rather than all seven as in the previously reported compounds, $C_5H_5VC_7H_7$ and $C_7H_7V(CO)_3$.

In the field of synthetic organic chemistry, successful synthesis of a few diterpenes and diterpene alkaloids, cyclononatrienes, strained systems and certain pseudo-aromatic compounds have been achieved.

Nuclear magnetic resonance spectra of a number of olefinic compounds have been recorded and analysed completely in terms of fundamental NMR parameters,

chemical shift and coupling constant. The same technique has been extended to studies of butadiene-like compounds. The effect of ring size on the nuclear magnetic resonance shifts of the saturated cyclic hydrocarbons from cyclopropane to cycloheptadecane has been studied. No correlation could be found between the carbon and hydrogen shifts. It was also observed that for cyclopropane the carbon and hydrogen shifts were quite high compared to other members of the series. This fact has been tentatively ascribed to an effective ring current in the three-membered ring.

Investigations on polymer systems—A novel initiator α -phenylethyl potassium has been developed for the synthesis of linear monodisperse polystyrene with the proton end group structure. These macromolecular polystyryl potassium compounds react readily and stoichiometrically with suitable tetrafunctional terminators to form the desired monodisperse tetrafunctional star molecules, without the complication of minor side reactions encountered in reactions of polymeric anions with multifunctional terminators. The study of these polymers is likely to yield valuable insights into the influence of structure on physical properties. For the first time, a soluble polycyclopentadiene with relatively high molecular weight has been obtained using a new homogeneous catalyst system, which is conveniently formed *in situ*. Elucidation of the structure of this polymer has shown that it is formed predominantly by 1,4-addition. This rigid polymer with active double bonds derived from a readily available inexpensive monomer could be a valuable intermediate for the further preparation of polymeric substances having useful thermal and electrical properties. Some of the other problems which are being pursued include: properties of dilute polymer solutions, crystallization of polymers, branched polystyrenes, acrylic resins, silicones, and ultrapure polymers.

Tropical Products Institute, UK

The annual report of the Institute for the year 1963 reveals that besides the major project on the

study of aflatoxin and its presence in groundnuts and other materials, two new projects were taken in hand, viz. (1) study of insect attractants and (2) study of methods used for local processing of tropical products with a view to improving the equipment or method or designing machinery. In naturally infested groundnuts, aflatoxin B₁ has been found to be the predominant metabolite of biological importance. When *Aspergillus flavus* is grown in artificial culture, the metabolites B₁ (with B₂) and G₁ (with G₂) are normally produced in equal proportions. Three methods utilizing thin-layer chromatographic separations of 'Kieselgel G', followed by an assessment of the fluorescence of the separated spots *in situ*, are under study for the qualitative analysis of aflatoxins. Structural investigations on aflatoxins B₁ and G₁ have led to the isolation and characterization of two minor aflatoxins, B₂ and G₂; their relationship to B₁ and G₁ has been established. The relationship of morphology to aflatoxin production by strains of *A. flavus* is under study.

Studies are in hand on the isolation of the sex attractant of the female moth of the red bollworm, *Diparopsis castanea* (Hamps), a common cotton pest. From studies on the effect of mode of drying fish on its nutritive value, it has been found that in the case of *Tilapia nilotica*, the fresh frozen fish contains maximum available lysine (10.7 g./16 g. N), sun-dried fish the least (6.1 g./16 g. N) and kiln-dried fish gives an intermediate value (6.9 g./16 g. N).

During studies on toxins of fungal origin, chick embryo test showed promise as a means of detecting acute toxicity. Hatching followed by post-mortem examination has been found to be a useful method of detecting chronic effects of toxic fungal metabolites, though the technique is too time-consuming for use as a routine test.

A new compound, named jasmolin II, has been isolated in 1 per cent yield from pyrethrum extract.

Its structure also has been worked out; it has a jasmone side chain which indicates that the compound may have biogenetic significance.

Shri M. M. Suri

Shri Man Mohan Suri has been appointed Director, Central Mechanical Engineering Research Institute, Durgapur.

Born on 13 January 1928, Shri Suri received his early education at Lahore and after graduating from the Government College, Lahore, joined the Superior Establishment of the Mechanical and Transportation Departments of the Indian Railways at Jamalpur. In 1954, he visited Italy, Germany, Switzerland, Austria, France, Belgium, Sweden and Britain on deputation as a Junior Inspecting Officer attached to the Director General of the Indian Stores Department, London. On his return to India, Shri Suri was posted as Deputy Director (Diesels) in the Diesel Department of the Research Designs and Standards Organization.

As early as 1956 Shri Suri hit the headlines with an invention which revolutionized diesel locomotion engineering, now known as Suri transmission. The Suri transmission marked a completely new trend in diesel locomotion and forms a valuable basis for design concepts of locomotives of this kind. It provides a simple but highly efficient means for transmitting diesel power in rail traction units, employing only two circuits, a Brockhouse type of convertor-coupling and a fluid-mechanical coupling, arranged in parallel.

In 1961 Shri Suri was promoted Joint Director (Diesels). The same year he was awarded the Padma Shri. In 1962, he was the recipient of the Shanti Swarup Bhatnagar Memorial Award for outstanding contribution to engineering sciences for the year 1962.

Announcements

■ *The Second International Congress of Food Science and Technology*

will be held in Warsaw during 22-27 August 1966. The plenary sessions of the congress will be devoted to lectures by outstanding scientists as well as discussion of plans for the formation of an international union of national scientific and technical societies or bodies dealing with food science and technology. Other sessions will be devoted to discussions on the following topics: New protein sources and their utilization; Chemical and biochemical changes in food; Modern technological aspects of food processing, manufacture and preservation; Advances in food engineering; Technical problems of producing wholesome food; Assessment of food quality; Modern trends in the academic training of food scientists and technologists; and Economic, nutritional and sociological aspects of food processing, manufacture and consumption. Special invited papers will be selected for presentation. Titles and abstracts of papers intended for contribution should be sent to the Congress Secretariat by 1 November 1965. Further details can be had from the Secretary, Executive Committee, Instytut Przemysłu Mięsnego, Warszawa 12, Ul. Rakowiecka 36, Poland.

■ *The Second European Symposium on Food — Recent Developments in Heat Treatment* will be organized from 31 March to 2 April 1965 in Frankfurt (Main) by the Working Party on Food of the European Federation of Chemical Engineering and the Gesellschaft Deutscher Chemiker. This symposium will be the fifty-eighth event of the European Federation of Chemical Engineering. The lectures of this symposium will be divided into two groups: A — Physical and technical points of view of heat transfer; and B — The influence of heat on food. Further details can be had from the secretariat of the working party, Gesellschaft Deutscher Chemiker, Dr rer. nat. Wolfgang Fritsche, 6000 Frankfurt (Main), Postfach 9075, Varrent-rappstr. 40-42.

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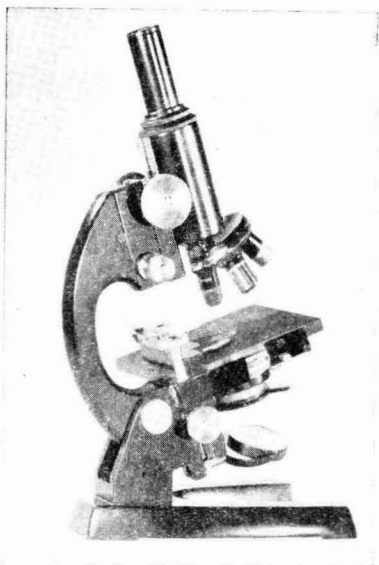
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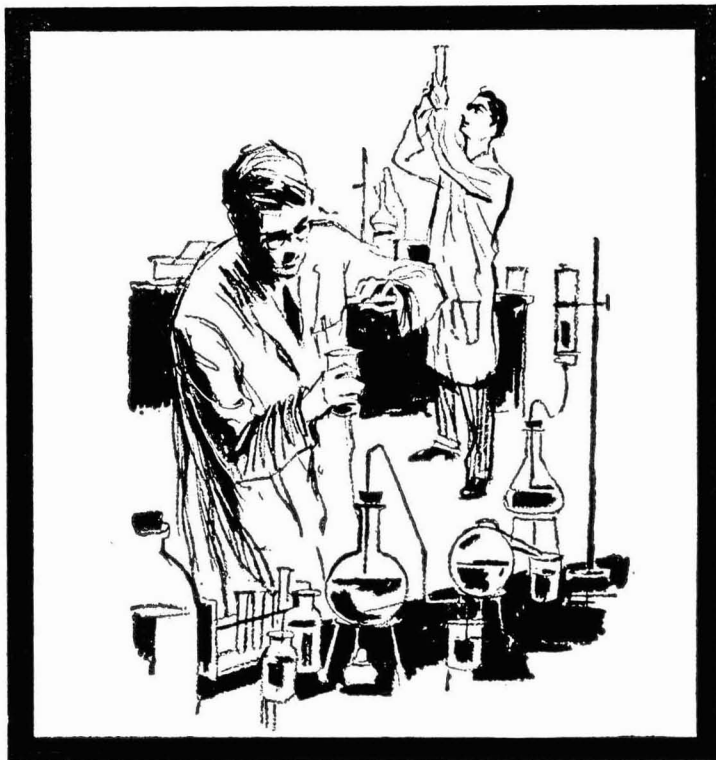
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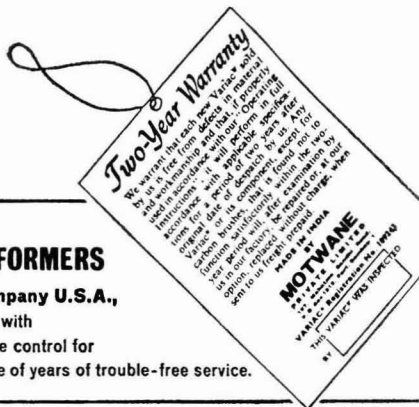
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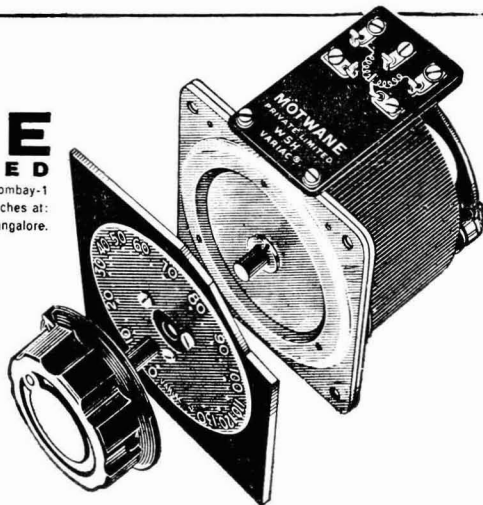
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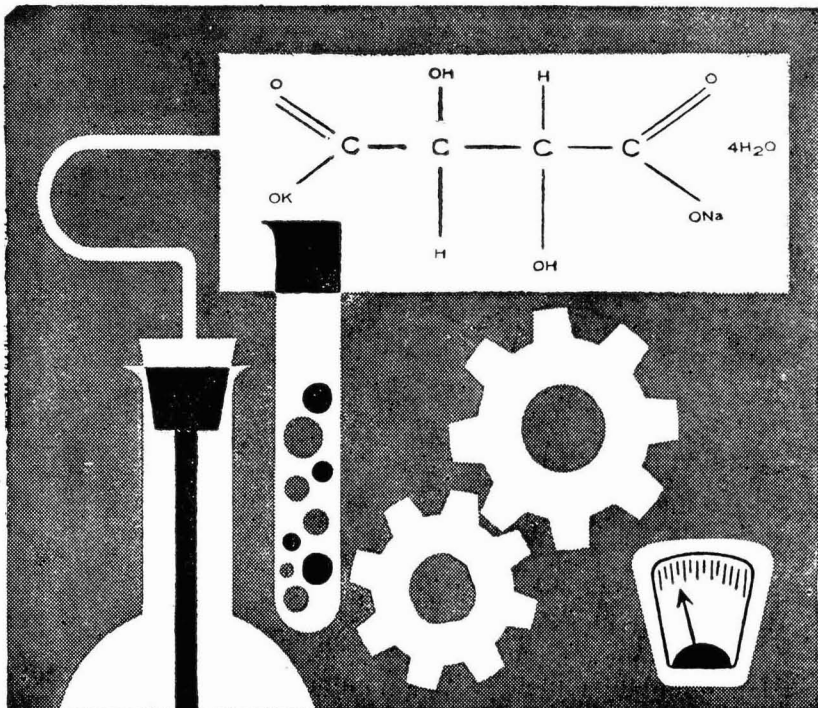
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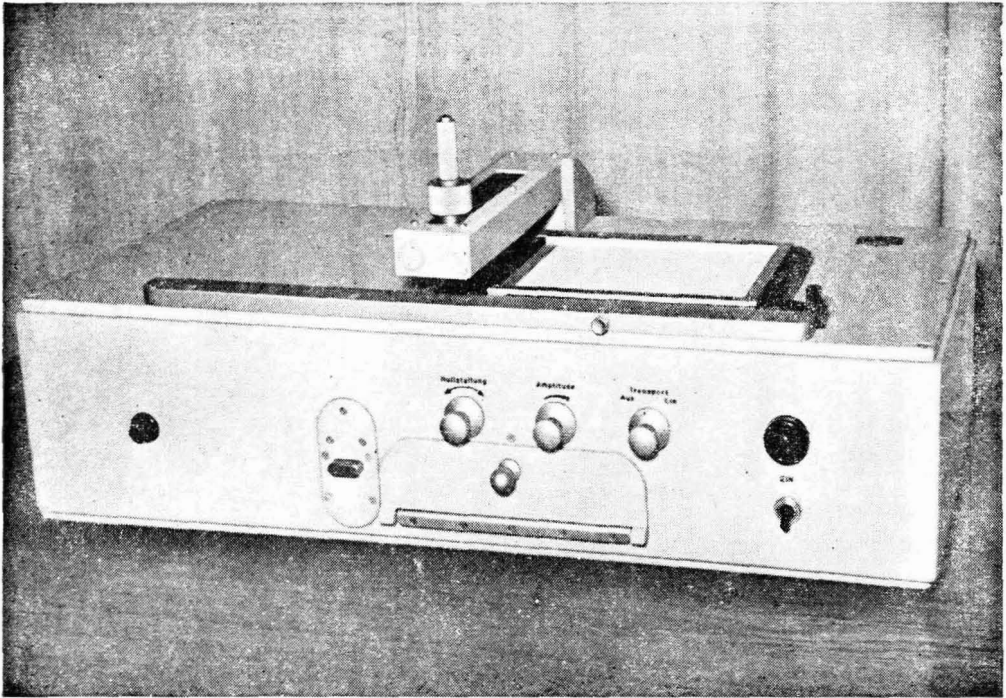
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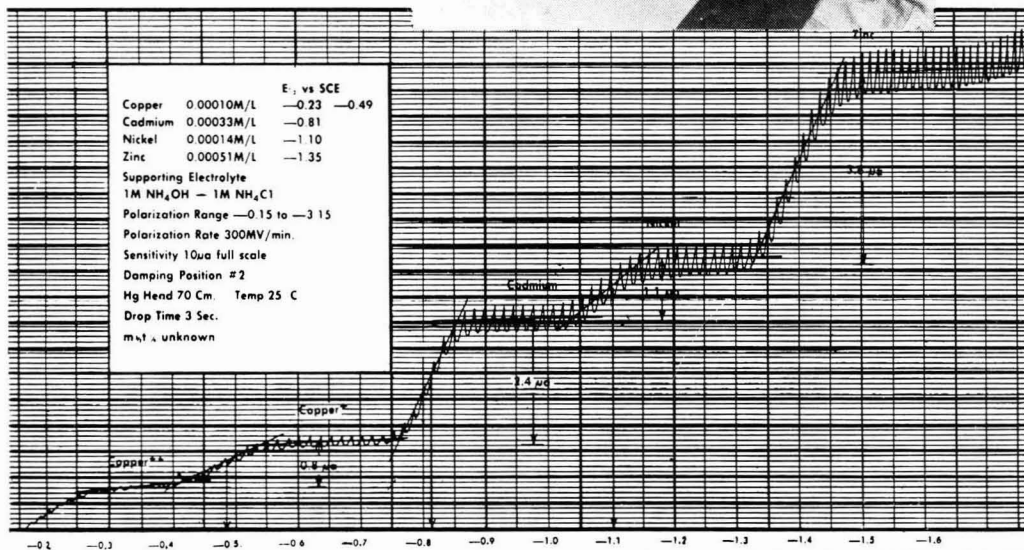
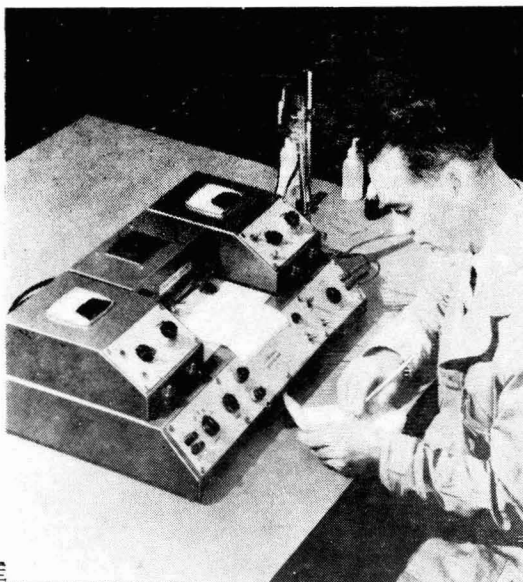
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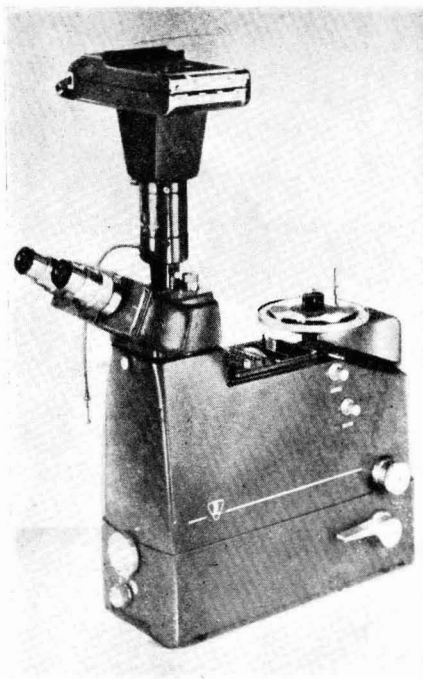
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