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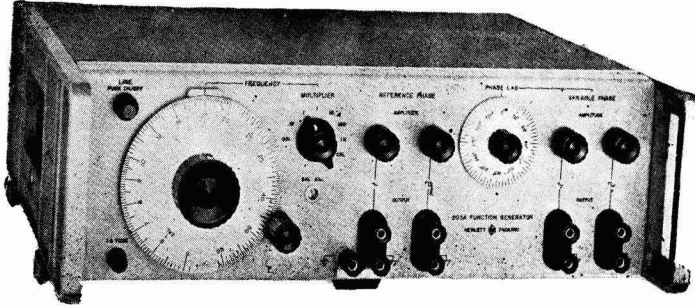
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VOLUME 24

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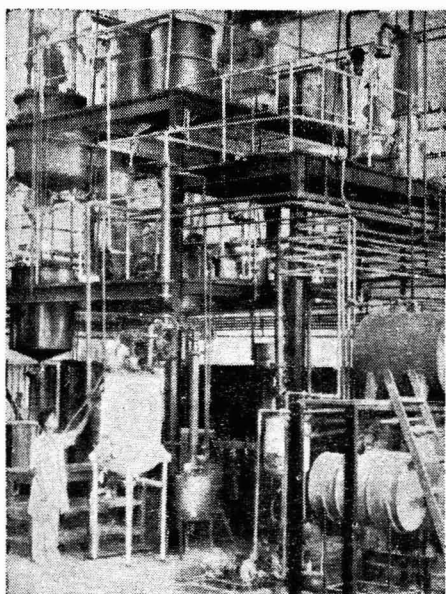
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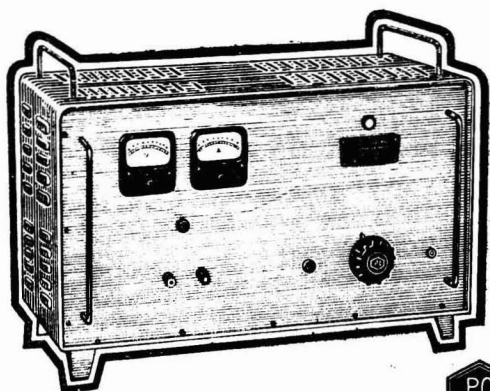


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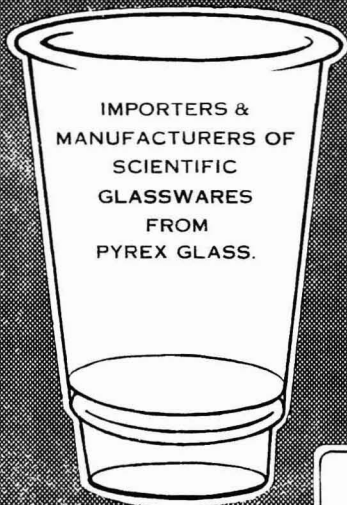
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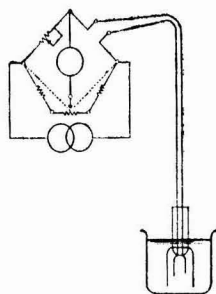
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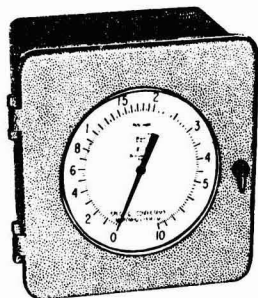
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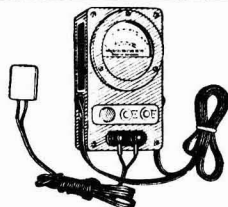
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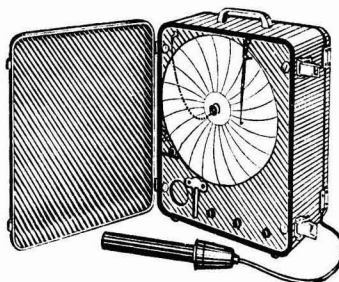
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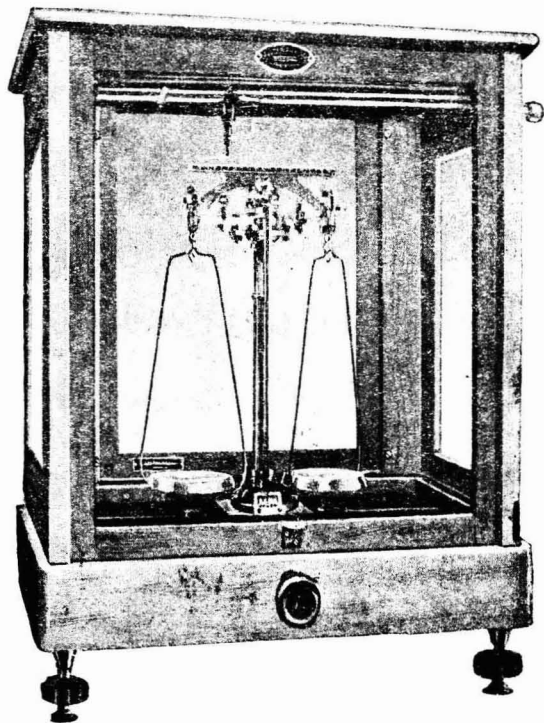
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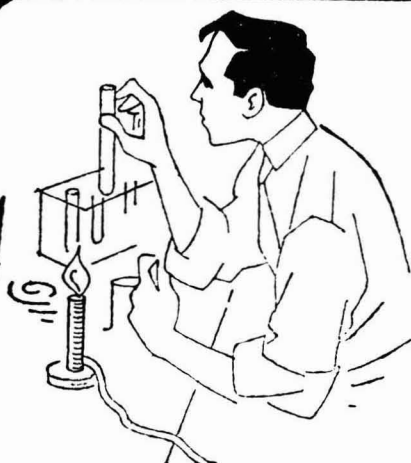
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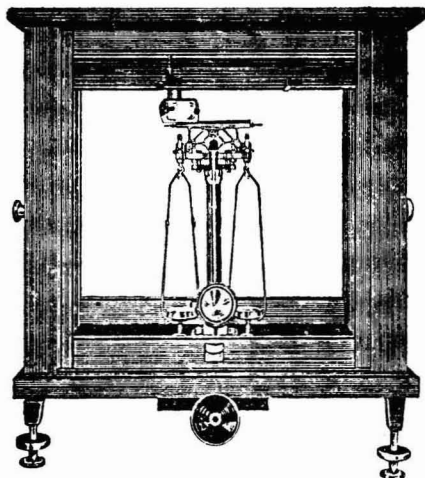
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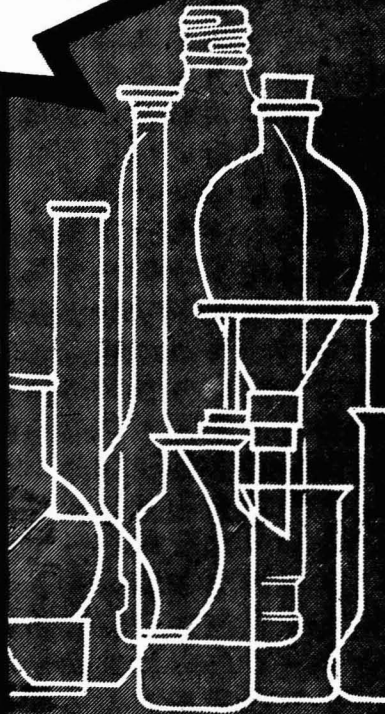
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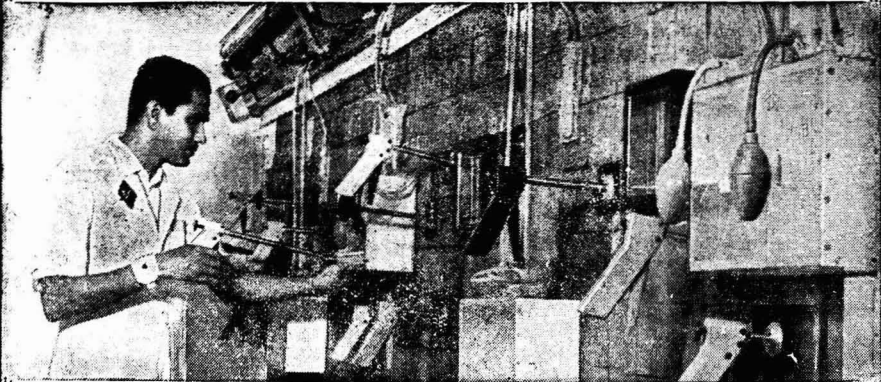
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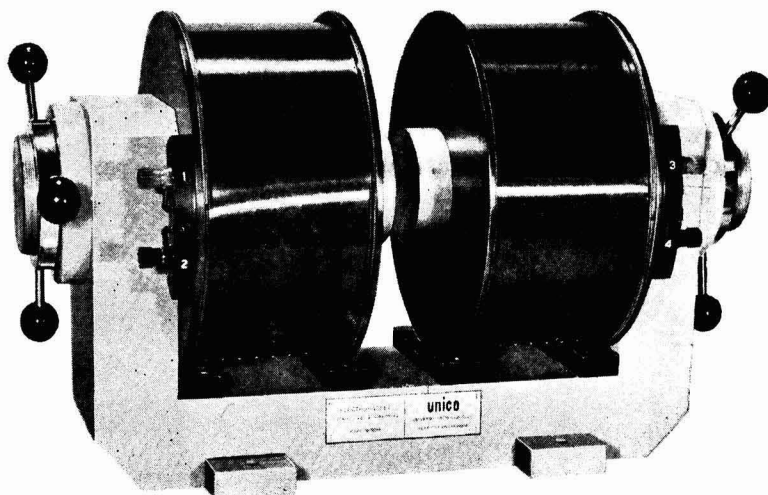
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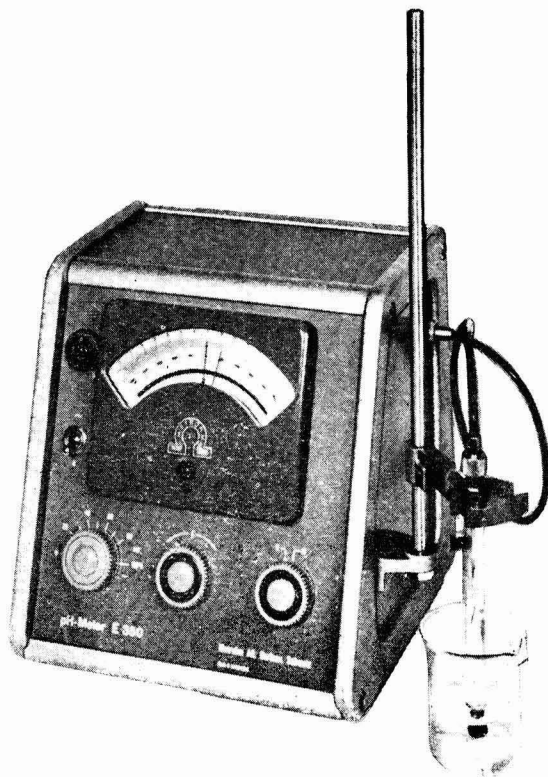
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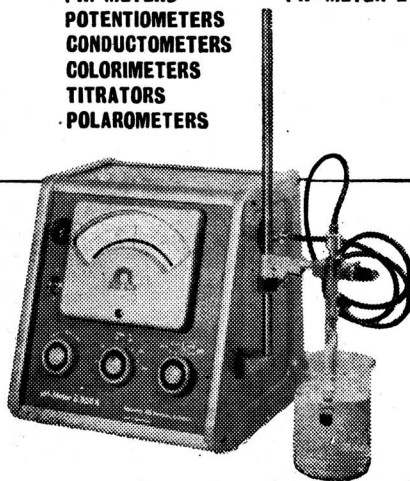
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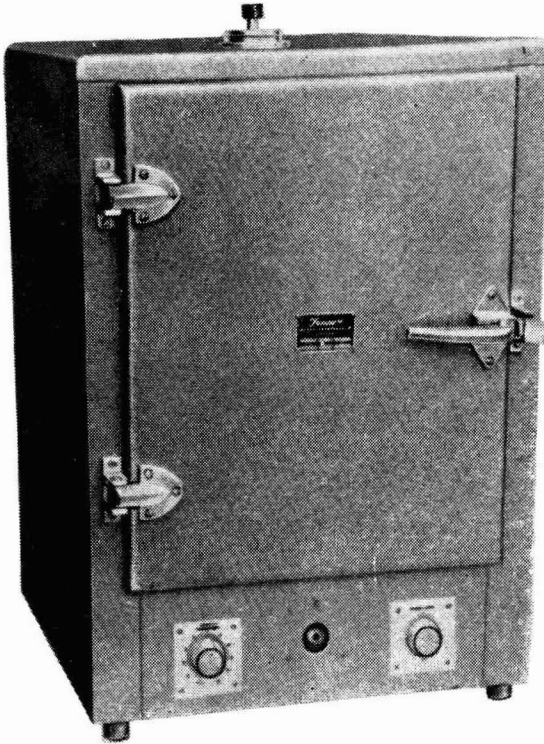


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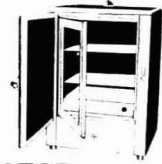
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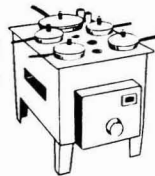


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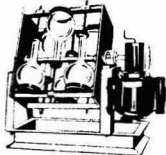


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Current Topics

Atomic Energy Research & Development in India: A Decade of Sustained Progress

THE Department of Atomic Energy completed in 1964 a remarkably active and fruitful decade of research and development. A well-illustrated and documented brochure, issued recently to mark the occasion, sets out the many and varied contributions of the Department. Although the Atomic Energy Act was passed in 1948, it was only in 1954 that the Government of India embarked upon a full-fledged programme of work in atomic energy. The Atomic Energy Commission, set up under the 1948 Act with Dr H. J. Bhabha as Chairman, was assigned the following responsibilities: to do research on scientific and technical problems connected with the release of atomic energy for peaceful purposes; to train and develop the necessary scientific and technical personnel for this work; and to foster fundamental research in nuclear sciences in its own laboratories, and in the universities and research institutions in India. In 1954, the Atomic Energy Establishment was set up at Trombay, and later in the same year, the Government of India created a separate Ministry, the Department of Atomic Energy, for the development of peaceful uses of atomic energy.

It has been rightly pointed out that any review of atomic energy research and development in the country would be incomplete without referring to the basic foundations laid by the Tata Institute of Fundamental Research — which incidentally completes 20 years this year — in this field. Putting forward the proposals for the establishment of the Institute to the trustees of the Sir Dorab Tata Trust in 1944, Dr Bhabha had observed that the Institute would be “an embryo from which I hope to build, in the course of time, a school of physics comparable to the best anywhere” and “when nuclear energy has been successfully applied for the production of power, in say a couple of decades from now, India will not have to look abroad for its experts but will find them ready at hand”. This prophecy has been more than fulfilled, and with an academic staff of 200, the Institute is today India's national centre for advanced study and fundamental research in nuclear sciences, mathematics, cosmic rays, space research, radioastronomy, etc. Ever since its establishment in 1945, the Institute devoted its attention to building up a team of scientists in different branches of science and technology related to atomic energy. The small electronics group, then set up to design and fabricate electronic instruments and equipment needed for atomic energy work, formed the nucleus of the present Electronics Division at the Atomic Energy Establishment, Trombay.

Much of the early work of the Atomic Energy Commission during the years 1948-54 in the fields of chemistry and metallurgy was carried out in a small way in the Commission's laboratories at Bombay, and work in the fields of biology and medicine at the Indian Cancer Research Centre. A Rare Minerals Survey Unit was set up for prospecting and developing atomic minerals; this unit is now the Atomic Minerals Division of the Department of Atomic Energy. Among the many achievements of this Division, mention may be made of the discovery of large deposits of uranium and the location of extensive thorium-rich minerals in Ranchi plateau of Bihar, and the location of valuable beryl and lithium ores.

During the past 10 years, the Department of Atomic Energy initiated studies on various types of reactors and on the availability of raw materials and finished products necessary for the setting up of the reactors. Three research reactors were set up during the period 1954-61. The swimming pool reactor, Apsara, became critical on 4 August 1956. The control system for the reactor was designed and built by the scientists of the Department and the General Engineering Group was responsible for its erection. This provided valuable experience for the scientists and engineers of the Department. So much so, in building the Canada-India reactor later in collaboration with Canada, Indian scientists and engineers made significant contributions. An important development in connection with the Canada-India reactor, which became critical on 10 July 1960, was the use of fuel elements completely fabricated in India from Indian uranium. India's third reactor, the Zerlina, which became critical on 14 January 1961, was designed and built entirely by Indian personnel. The fuel elements and the complicated control system for the reactor were fabricated at Trombay. The experience gained in the building of these reactors has become extremely useful and handy now that India has planned to set up reactors for power generation.

A major objective of the Department of Atomic Energy is to make India self-sufficient in respect of atomic fuels and other materials required for nuclear energy work. Reactor grade uranium is being produced at Trombay since 1959 in the Fuel Element Fabrication Facility, and the Uranium Metal Plant is now in a position to produce enough uranium to feed the three nuclear power stations. Also, the plant is being used for research and development work on new fuels and materials. Thorium oxide and sintered thorium metal have been produced; a small pilot plant is in operation for obtaining thorium metal in kilogram quantities by reduction of thorium oxide with calcium. Trombay scientists and engineers have also successfully built and commissioned a fuel element reprocessing plant for reprocessing uranium rods

to extract plutonium and other fissionable materials. This is a significant achievement as plutonium reactors can be used to breed uranium-233 from thorium and plutonium itself can be directly employed in small and medium sized reactors. India has now offered, through the International Atomic Energy Agency, to reprocess used fuel elements for other countries.

Heavy water is being produced since August 1962 at Nangal by the Fertilizer Corporation of India. The plant set up with the active assistance of Atomic Energy Establishment has an installed capacity of 14.5 tonnes of heavy water per year; a bigger water plant is being designed to produce 200 tonnes of heavy water per year.

A variety of radioisotopes and radiation sources are being produced by the Department of Atomic Energy in quantities not only sufficient to meet the needs of the country but also for export. Over 250 types of radioisotopes and radiation sources are being produced at Trombay and supplied for research purposes and medical uses. Labelled fertilizers are being produced and supplied; the Department is one of the few suppliers of ^{32}P labelled fertilizer in the world. Expert services are also provided to industry in the use of radioisotopes. Studies on movement of silt on river and sea beds, and of flow of water in rivers have been carried out using radioisotopes. Investigations on silt movement in a number of harbours have resulted in working out suitable measures which have helped to effect considerable savings by way of dredging operations. The experience and knowledge gained in this field have been placed at the disposal of the International Atomic Energy Agency for the benefit of other countries.

From the very beginning, considerable emphasis has been placed by the Department of Atomic Energy on the indigenous development of instruments and equipment needed for atomic energy work. From a small beginning in 1952, today the Atomic Energy Establishment at Trombay produces most of the electronic instruments required for its own work, and for the use of institutions employing radioisotopes and radiation sources. The design and development capabilities of the electronic engineers are now comparable to those in the developed countries. So much so, the Electronics Production Division at Trombay will soon form the nucleus of a company producing electronic instruments on a commercial scale.

In agriculture and related fields, the Atomic Energy Establishment has done much useful work. Biological effects of ionizing radiations, induction of mutations in economic plants such as rice and groundnut, preservation of food products such as fruit, fish, etc., are some of the problems investigated. New strains of rice and groundnut with improved characters have been developed. Significant advances have also been made in the control of insect pests in stored grain by irradiation. Extensive studies are being carried out on the use of radioisotopes in the diagnosis and treatment of diseases at the Radiation Medicine Centre

set up in 1963. Investigations on oral cancer in animals have shown that specific nutritional deficiencies play an important role and that early lesions could be controlled by adequate and sustained administration of B-vitamins. Good progress has been made in investigations relating to thyroid disorders in the Tata Memorial Hospital, and the Indian Cancer Research Centre, Bombay, both of which are now under the administrative control of the Department of Atomic Energy.

One of the important goals the Department of Atomic Energy has before it is the generation of power from atomic energy to augment the power resources of the country. In August 1959, the Planning Commission approved the setting up of an atomic power station in the industrial area of Maharashtra-Gujarat states during the Third Plan period. Plans for two more atomic power stations in Rajasthan and Madras are now ready, and are being included in the Fourth Five Year Plan programme. While the Maharashtra-Gujarat station is being set up with Canadian collaboration, the Rajasthan station will be built by Indian personnel working with Canadian designs. The Madras station will be designed and built entirely by Indian scientists and engineers. Each of these stations will be producing about 400 MW. of power which will be cheaper than thermal power.

The Department of Atomic Energy is one of the few organizations in the country with a well-planned programme of recruitment and training of scientific and technical personnel to meet its requirements. Graduates in science and engineering are selected on an all-India basis and are given specialized training in disciplines related to nuclear science and technology. This system of recruitment and training has been quite successful and effective, and the Department of Atomic Energy is provided with the required complement of well-trained and well-qualified scientific and technical personnel. The Department is also proposing to set up inter-university centres for nuclear research. These centres, which will be provided with such facilities as a reactor, an accelerator or a sub-critical assembly for advanced studies in various branches of nuclear science, will form additional training centres for scientific and technical personnel.

The achievements of the Department of Atomic Energy during the short span of 10 years have been indeed impressive and have helped to earn India a high place among the advanced countries engaged in nuclear research and development of atomic energy. The significant progress made by the Department is mainly due to its clear-cut programmes and objectives. India, unlike other countries engaged in nuclear research, is committed to the development of nuclear energy for peaceful purposes only. With this commitment and with Dr Bhabha to guide the work of the Department with his characteristic foresight, India could be expected to make further significant contributions to the peaceful uses of atomic energy.

Some Investigations on Terpenes & Macrocyclic Musk Compounds*

IN the National Chemical Laboratory, Poona, my colleagues and myself have been engaged for the last several years on the chemical examination of commercially important Indian essential oils with a view to finding better uses for them and to have a better knowledge of the constituents present therein. We have also been interested in the synthesis of some commercially important chemicals which are widely used in the perfumery industry.

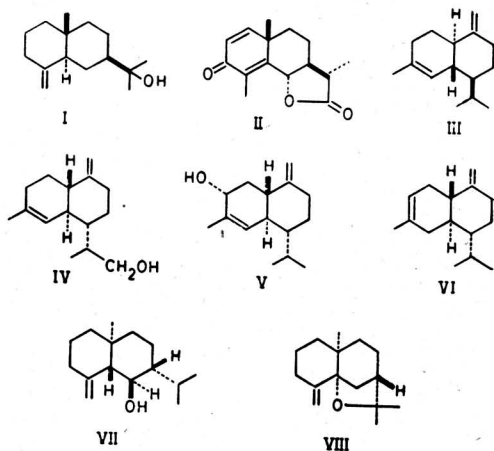
Isolation and Structure of Terpenes

In connection with our work we have examined a large number of essential oils and separated their constituents by using modern practices. Of these, special mention may be made of costus root oil, agarwood oil, jatamansi oil, valerian root oil, vetiver oil, ginger oil and wild ginger oil. We have isolated a large number of new and hitherto unreported constituents with unusual structural features. Some of these contain 15 carbon atoms and belong to the group of sesquiterpenoids. A few odd members contain 14 carbon atoms as well. We have been fortunate to isolate about 30 such new products and determine their structures and, in many cases, their absolute configurations.

Organic molecules of the type handled by us, containing mainly carbon, hydrogen and oxygen, have often a three-dimensional structure. Workers interested in the biogenesis of organic compounds occurring in plants have found that nature takes a very methodical attitude in making these compounds and is able to do so under extremely mild conditions, which is the envy of any organic chemist. In making these compounds, which also include terpenoids, it adopts a well-defined three-dimensional pattern.

A few years ago, an organic chemist would have been satisfied if he could determine the relative disposition of various functional groups in a particular molecule within the framework of a two-dimensional picture. But in recent years, due to the development and elaboration of the concept of absolute stereochemistry, a three-dimensional picture is considered essential. This can, of course, be neatly determined by X-ray crystallographic method, but can also be done equally well within certain limits by adoption of chemical and physico-chemical methods.

Considering the relative disposition of the various atoms, there are several thousand stereo possibilities for a molecule like cholesterol, but only one cholesterol occurs in nature. This is also generally true for sesquiterpenoids which, in the overwhelming majority of cases, also follow certain set stereochemical patterns. In this context I am reproducing the stereo formulae of three typical terpenoids: eudesmol (I), santonin (II), and cadinene (III).



In the course of our work on sesquiterpenes of Indian essential oils, we have come across several compounds which belong to the rather unusual antipodal or the mirror image group. Some of these are: khusul (IV), khusinol (V), γ_2 -cadinene (VI), (-)-junenol (VII), and agarofuran (VIII). Occurrence of a series of such products in Indian essential oils, obviously, raises interesting problems of biogenesis and stereochemistry. A few of the other important terpenoids, structures and stereochemistry of which have been determined by us, are costunolide, dihydrocostunolide, saussurea lactone, tetrahydro-saussurea lactone, methoxycostunolide, agarofurans and agarospirol, khusitone, khusalil, zingiberol, β -bergamotene, valeranon, hydroxy valeranon, etc.

Extraction of Essential Oils

Besides scientific interest, our work on Indian essential oils is also of considerable commercial significance. The low temperature solvent extraction procedure developed by us and as applied in the case of costus root, jatamansi and agarwood oils has led for the first time to the isolation of the oils and the respective constituents in the form in which they exist in the roots without any polymerization or denaturing. Many of the labile constituents which can be isolated by applying this procedure are expected to have medicinal properties.

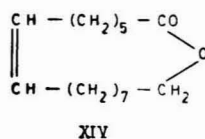
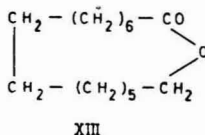
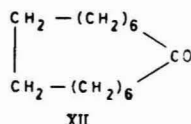
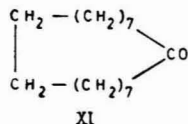
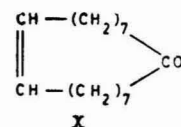
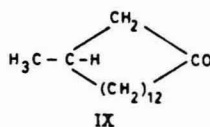
Macrocyclic Musk Compounds

We have also taken deep interest in another type of products. These are the macrocyclic musk compounds. A product belonging to this group is muscone, the active principle of 'kasturi', obtainable from the Indian musk deer. Kasturi (musk) has been known to the oriental people for centuries and has found use in the indigenous system of medicine. A musk pod, for the collection of which a musk deer has to be killed, weighs approximately an ounce (28 g.), of which only about 0.3 g. is the active principle muscone. The musk odour is a

*A dissertation by Dr S. C. Bhattacharyya, Scientist, National Chemical Laboratory, Poona, on the occasion of the presentation of the Shanti Swarup Bhatnagar Memorial Award in Chemistry for the year 1962 at the National Physical Laboratory, New Delhi, 14 January 1965.

typical impression which cannot be explained, but is to be felt and appreciated.

Musk-like odour has also been observed in natural civet, certain excretion of American musk rat, and also in some plant products, namely angelica root oil and ambrett seed oil. Many distinguished scientists have worked on these perfumery principles, one of the most glorious names being that of L. Ruzicka of Switzerland. From their researches, it is known that the musk odorous principles belong to the group of macrocyclic (large ring) ketones or lactones. At the time when the structures of these products were elucidated, it created almost a sensation, as the existence of such products, on theoretical grounds, was not considered feasible. However, once the structures were determined, ways and means were found to synthesize them. This interest still continues and has also found favour with us. By using easily available indigenous raw materials and following simpler chemical reactions, we have been able to develop practical syntheses of all the naturally occurring musk odorous compounds and the related products. These include, amongst others, muscone (IX), civetone (X), dihydrocivetone (XI), exaltone (XII), exaltolide (XIII), and ambrettolide (XIV). These products find use in the industry and sell at very high rates. But the results of our researches, which were partly motivated by an industrial bias, should bring down the price of this inaccessible



group of aristocratic chemicals to a more approachable democratic level. With adequate efforts it should be possible to develop a foreign market for these products. Besides these, we have also established several other commercially important processes, such as (i) synthesis of dihydrojasnone from octanone, (ii) a composite method for the synthesis of peach aldehyde and isojasnone from undecylenic acid, (iii) 1-menthol from citronellal, and (iv) vitamin A-grade β -ionone from lemongrass oil. Some of these processes have been released to the industry.

Conference on Research & Industry

At the suggestion of Shri M. C. Chagla, Union Minister for Education and Vice-President, Council of Scientific & Industrial Research (CSIR), it is proposed to organize a 3- to 4-day conference of scientists and representatives from industry in New Delhi under the auspices of CSIR during the second week of November 1965. The basic objective of the conference is to bring about better awareness of the problems and difficulties of the industry by the scientists and appreciation by the industry of the role of scientific research in industrial development. The specific problems to be discussed at the conference include: (i) Development of substitutes for imported raw materials; (ii) Indigenous manufacture of essential components hitherto imported; (iii) Development of indigenous know-how at a sufficiently advanced level as to be commercially utilizable in respect of those articles on which repeated foreign collaboration has been sought; and (iv) Measures through which the programmes of industrial research could be oriented to the needs and requirements of industry. The conference may also consider how technical personnel from industry could be more closely associated with the research programmes and projects of the research establishments. The possibility of exchange of ideas with other sectors engaged in research such as Defence, Railways and the Atomic Energy Establishment, and institutes in public and private sector who have their own research organizations will also be considered.

The conference will begin with a general session and split into specialized sections devoted to different fields such as chemicals, metallurgy, fuels, coal, petroleum, glass and ceramics, drugs and medicine, etc. The sections would consist of research scientists engaged in the particular field, officers of Directorate General of Technical Development, Planning Commission and industrialists and technical personnel from industry in the same field. The participants in the various sections will set before themselves the task of putting across a picture of the industry in their specific field and identify the major problems necessitating research and investigation. These investigations could relate to essential raw materials, components, level of technology, future developments and improvements and such other matters. At the end of discussions, the conveners of the sections would set out a paper summarizing their deliberations on the problems of the industry and their recommendations. These and the general problems would then be considered at a plenary session.

A small committee has been set up at CSIR Headquarters to make arrangements for the organization of the conference with Shri Baldev Singh, Research Coordination, Industrial Liaison and Extension Officer, as the Convener. Nominations for participation in the conference and suggestions on the problems to be discussed may be addressed to the Director-General, Council of Scientific & Industrial Research, Rafi Marg, New Delhi 1.

Twenty-second International Geological Congress

U. ASWATHANARAYANA*

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THE twenty-second session of the International Geological Congress held in New Delhi during 14-22 December 1964 marks a significant event in the annals of Indian geology. India had the proud privilege of being the first Asian country to play host to the congress since the establishment of the latter in 1878. The congress was attended by over 2100 geologists, geophysicists, geochemists and mining engineers from about 100 countries, the contingents from USA and USSR being by far the largest. About 390 papers were presented in 16 sections devoted to different subjects. Several commissions of the congress, international associations and scientific societies and the International Union of Geological Sciences held their meetings at the time of the congress. For the benefit of the visiting geologists, numerous pre-congress and post-congress geological excursions were organized to different parts of the country. The Posts and Telegraphs Department of the Government of India brought out a special stamp (with hammer through the globe as the motif) to commemorate the congress.

The Organizing Committee of the congress issued the following brochures to acquaint the delegates with the present status of knowledge of various aspects of Indian geology and mineral resources: *Geology and mineral resources of India* by P. V. Rao, *Gondwanas of India* by D. R. S. Mehta, *Structure of the Himalayas* by D. N. Wadia and W. D. West, *Stratigraphy of the Sivalik group* by M. R. Sahni and L. P. Mathur, *Age determination of rocks and geochronology of India* by U. Aswathanarayana, *Iron ores of India* by M. S. Krishnan, *Mica fields of India* by M. V. N. Murthy, *Oil in India* by L. P. Mathur and P. Evans, and *History, function, organization and plans of the Geological Survey of India* by B. C. Roy.

The congress was inaugurated by Dr S. Radhakrishnan, President of India. Dr D. N. Wadia, F.R.S., Geological Adviser to the Government of India and doyen of Indian geologists, was elected President of the congress. In his Presidential Address, Dr Wadia referred to some of the outstanding problems of Indian geology. The congress then broke up into smaller groups to discuss the papers presented before the various sections.

The papers presented at the congress were so many and so good that it is impossible to do justice even to a fraction of them. The reviewer is, therefore, restricting himself to an analysis of the outstanding results presented in each section, though such an approach may tend to be subjective.

Geology of Petroleum

The Russian geologists submitted detailed information regarding geological structure and oil and gas

*Permanent Secretary, Twenty-second International Geological Congress.

content of the Volga-Ural region, Caspian depression, Mesozoic strata of the middle Asian Epi-Hercynian Platform, West Siberian Lowland and Siberian Platform. Vassilyev *et al.* (USSR) classified the oil- and gas-bearing basins of USSR on the basis of tectonic-structural criteria. The occurrence of high molecular organic compounds — bitumens — in the igneous and metamorphic rocks of the Kola Peninsula, USSR, reported by Petersilie (USSR) is of great scientific interest. Sometimes the bitumens are close to oil type and contain large amounts of paraffin hydrocarbons and smaller amounts of naphthene, along with some aromatic hydrocarbons. Mueller (UK) presented evidence to indicate the existence of petroleum of different origins: maturing of sapropelic sediments, mild distillation from kerogen-type organic sediments, intensive distillation and hydrogenation of coal-type sediments and distillation and condensation of juvenile abiogenic substances.

Geological Results of Applied Geophysics

Geophysicists from the Oil and Natural Gas Commission (India) presented results of gravity/magnetic/seismic surveys for oil in the plains of Punjab, Cambay Basin, Western Uttar Pradesh, Brahmautra Valley, etc. The progress of geophysical prospecting for chromite in Cuttack District, Orissa, for copper ore in Dariba and Khoh areas in Alwar District, Rajasthan, and for diamondiferous volcanic pipes in the Panna area, Madhya Pradesh, was outlined by the geophysicists of the Geological Survey of India.

Bondarenko *et al.* (USSR) gave an account of the advances in the techniques of underground geophysical prospecting. The intensity and phase structure of the radio fields can be employed as an aid in prospecting for massive impregnated sulphide ores, uranium ores and highly watery zones. Gravity surveys and gradiometer observations are useful in the location and estimation of size of ore bodies. An examination of the intensity and energy spectrum of cosmic rays in the mines can lead to an idea of average density of overlying rocks. The geological results of off-shore geophysical exploration (mainly seismic) for oil in the Caspian, Azov, Black and Kara Seas of USSR were presented by Vartanov *et al.* (USSR). Subbotin *et al.* (USSR) delineated the deep structure of the Ukraine area from geological and geophysical data, and attempted to relate the deep structure to the formation of mineral deposits in that region.

Cretaceous-Tertiary Boundary Including Volcanic Activity

On the basis of K-Ar dating of plutonic and volcanic rocks from the Basin and Range Province, Arizona, Damon *et al.* (USA) showed that the most intense Laramide activity occurred at the Mesozoic-Tertiary boundary. Shafiqullah *et al.* (Canada)

placed the Cretaceous-Tertiary time boundary at 63 ± 1 m.y. (K-Ar ages of bentonites in diachronous coal beds of the Cretaceous-Tertiary boundary). The lithofacies and biofacies relationships at the Cretaceous-Tertiary contact in the Sirte Basin, Libya, were described by Lehmann (Libya). M. V. A. Sastry and B. R. J. Rao (India) presented foraminiferal and other evidences to show that the Maestrichtian marks the close of the Cretaceous period in South India.

Rock Deformation and Tectonics

The validity of the generally held view that magmatic massifs ride at the head of big overthrust nappes was questioned by Ciric (Yugoslavia). According to him, the magmatic and crystalline massifs of the Dinaric Alps are really autochthonous in relation to their surrounding rocks. They played the role of solid nuclei during tectonic movements and inhibited the tectonization of the surrounding and overlying rocks. Das Gupta (India) expressed the view that the Khetri Copper Belt was affected by a single period of orogeny during which several episodes of superposed deformation, related igneous intrusions and metamorphism took place. He did not find any systematic relationship between the structure and grade of metamorphism except in the eastern part of the belt where the metamorphic grade increases with progressive tightening of the folds and with enhanced temperature induced by the emplacement of granite.

Structural, petrological, stratigraphic, palaeontological, palaeoclimatic and palaeomagnetic data regarding East Antarctica were shown by Hamilton (USA) to be consistent with the concept of the Palaeozoic and Early Mesozoic supercontinent of Gondwanaland. Ichikawa and Kojima (Japan) compiled, on the basis of geological and geophysical data, a crustal profile of south-west Japan in which region the pre-Neogene basement is better preserved. Karunakaran *et al.* (India) delineated three tectonic cycles (Upper Cretaceous-Palaeocene, Eocene-Oligocene, Miocene) in the Andaman and Nicobar islands, which brought about changes in palaeogeography and sedimentation patterns.

Khain (USSR) traced five main stages of evolution of the earth's crust. The Catharchean stage (3500 m.y.) was characterized by the formation of geosynclines amidst oceanic platforms (thalassocratons). During the Archaean stage (2900 m.y.), the nuclei of future continents took shape. Early to Mid-Proterozoic (Gothian) stage (1700-1200 m.y.) was characterized by the existence of large but unstable platforms repeatedly subjected to breaking up. During the Proterozoic (Sinian, Riphean) stage (1200 m.y.), the structural pattern of the earth's crust took place and then steadily developed till the recent time. The fifth stage was marked by the gradual decline of geosynclinal activity and extension of continental platforms (epeirocratons). Qureshy (India) related the gravity anomalies to the regional tectonics of the Peninsular India.

Genetic Problems of Ores

According to Adler and Ninninger (USA), unoxidized uranium deposits in sandstones are formed

due to the deposition of uranium from ground water when it encounters zones of organic debris in immature arkosic and conglomerate sands that were eroded from an orogenic high land and accumulated in tropical, savannah-like low lands. P. K. Chatterjee and P. K. Banerjee (India) described the early kinematic chromite deposits of Orissa which, incidentally, do not fit into either Bushveld class or California class of chromite deposits. They proposed a new classification of chromite deposits, based upon their origin and tectonic environment. In the gold fields of South India, the gold-quartz mineralization is associated with amphibolites, greenstones and chloritic schists. The gold mineralization is found by Narayanaswami (India) to be localized in zones of dextral and sinistral drag folds associated with cross-fold structures within the Dharwar schists, or in shear zones and faults in zones of regional cross-fold structures in the bordering charnockitic terrain.

Radkevich (USSR) related metallogeny to the fracturing and activation of ancient platforms and post-Cambrian areas with completed folding. Several examples were cited to show that different types of activated structures usually bear mineralization of different ages. Supriya Roy (India) brought out the role of metamorphism in the formation and transformation of manganese oxide phases in the Gondite-type manganese deposits of Maharashtra and Gujarat.

Minerals and Genesis of Pegmatites

Gerassimovsky (USSR) described the mineralogy of apgaitic nepheline syenite pegmatites of Lovozero alkaline massif. Pegmatites are richer in rare elements and poorer in nepheline relative to rocks. They are also characterized by an abundance of sodium minerals and virtual absence of calcium minerals. The intermittent immigration of alkali-alumina-siliceous fluids into slip planes has led, according to Mahadevan and Murthy (India), to the development of different types of pegmatites (homogeneous, zoned or composite) in the Bihar Mica Belt. Nedumov (USSR) considered the pegmatite melt solution as a homogeneous multicomponent system with mutual solubility of components limited by certain intervals in temperature and pressure. He described the process of differentiation of pegmatitic melt and pointed out the role of tectonics in the formation of rare metal pegmatites. Solodov (USSR) related the rare metal content of a pegmatite to its mineralogy. For instance, Be characteristically occurs in microcline pegmatites, while Ta, Cs, Pb, Li, Nb and Tl minerals are common in microcline-albite pegmatites.

Plateau Basalts

Deccan Traps are generally believed to constitute a tholeiitic basalt province. S. C. Chatterjee (India) described alkali-olivine basalts from the Pavagadh Hill near Baroda, Gujarat State. Sinha and his associates (India), who investigated the geochemistry of the Deccan basalts in general and Pavagadh basalts in particular, observed that in traps generally there is a progressive decrease in water and alkalis and an increase in lime and

magnesia from the lowest to the uppermost trap horizon. The Pavagadh rocks appear to provide a good example of coexistence of both olivine basalt and tholeiitic basalt magma types. The structure, mineralogy and geochemistry of the carbonatites of Amba Dongar, Gujarat, associated with Deccan Traps, were described by Sukheshwala and Udas (India). The metasomatic aureole is rich in fluorite and several other economic minerals.

Palaeontology and Stratigraphy

Bandy and Chierici (USA and Italy) reported that deeper bathyl foraminiferal zonation off southern California is not duplicated in the Mediterranean. The discovery by Dombrowski (West Germany) of 'living' bacteria in the palaeozoic salt deposits raises a series of questions of far-reaching scientific importance. Gromov *et al.* (USSR) postulated that as a consequence of favourable combination in space and time of biological, geological and cosmic factors, optimum conditions are created for the rapid development, wide distribution and adaptation of fauna. Applying this concept, they distinguished two main stages in the Late Neogene characterized by Hipparion fauna and equid and elephant fauna. Field studies by Kummel and Tiechert (USA) demonstrated the existence of a lithofacies change, besides the well-known faunal break, at the boundary of the marine Permian and marine Triassic of the Salt Range in Pakistan. S. S. Sarkar (India) has computed the rate of evolution of some Tertiary mammals (Proboscidea, horse and Bos) on the basis of dimensions, at different geological times, of a particular molar or bone of a vertebrate belonging to a particular lineage.

Gondwanas

Evidence was presented by Bowen (Australia) to show that north-west Tasmania and the north-eastern New South Wales were the two principal loci from which glaciers radiated out during the Late Palaeozoic times. He maintained that assumption of connection with other continental masses is not required to explain the various characteristics of the eastern Australian glaciation. Kar *et al.* (India) reported that heavy mineral assemblage can be employed to distinguish the Raniganj Series from the Barakars and Barren Measures in the West Bokaro Coalfield. The technique was found useful in the correlation of coal seams. The Parana Gondwana Basin in South America was shown by De Loczy (Brazil) as a cratonic intershield embayment, sedimentation in which was never affected by tangential folding. According to Niyogi (India) the glaciofluvial and glaciolacustrine sediments of the Talchirs were deposited in natural depressions bounded generally by strike ridges. The depressions acquired the characters of intercratonic basins during the Late Talchir times.

Archaeon and Pre-Cambrian Geology

On the basis of field and radiometric age data, Allen (UK) divided the younger Granite Group of British Guiana into five petrographic units: alkali-quartz syenite and potassic granite, quartz diorites, granodiorite-tonalite association, granite-adamellite

association and post-Iwokrama granite. Basu (India) described the petrology and structure of the alkali rocks (theralite, nepheline syenite and camptonite) of Kishangarh, Rajasthan. The emplacement of the alkali rocks in the Pre-Cambrian metasediments is broadly syntectonic. Keller (USSR) outlined the lithology, structure, fossil content (stromatolites, oncolites, etc.) and classification of the Riphean group (1550-650 m.y.) which forms a part of the Upper Pre-Cambrian of USSR. Kirwan (Canada) questioned the existence of through-going fault along the Grenville Front. He accepted that the Grenville Front is faulted in places but maintained that there are areas of complete metamorphic gradation from the Huronian, Temiskaming and Keewatin to the Grenville. He suggested that the term Grenville be given metamorphic rather than chronostratigraphic connotation. According to Mahadevan (India), the charnockites of Western Ghats were deformed, and rendered gneissose due to recrystallization. The granites were emplaced as syn- to late-kinematic bodies and appear to be at least partly responsible for the recrystallization of charnockites. Ravich (USSR) gave an account of the geology and petrology of the Antarctic basement. Most rocks of the crystalline basement of Antarctica are characterized by charnockite association of minerals.

The manner and history of the emplacement of the Singhbhum granite batholith (mainly granodiorite-adamellite, trondjhemite and leucogranite, with patches of granitized basic metamorphic rocks) was ably dealt with by Saha (India). The preliminary results of K-Ar dating of some Pre-Cambrian minerals and rocks of Peninsular India were presented by Sarkar, Polkanov, Gerling and Chukrov (India and USSR). Simonen (Finland) discussed the lithology, structure and metamorphic chronology of the Svecofenides of Finland which represent an ancient geosynclinal belt. He described the synorogenic, intraorogenic and late orogenic phases of the orogenic evolution of Svecofenides.

Himalayan and Alpine Geology

Bodenhausen *et al.* (Netherlands) reported the occurrence of graptolites of Lower Silurian (Llandoveryan) age at a relatively high level in the succession of the so-called Tibetan Zone of the northern part of the central West Nepal. Hence parts of the succession may be considerably older than was formerly realized. The thick basal gneisses together with overlying sediments were thrust in southerly direction over the low grade metamorphic rocks of the Lesser Himalayan Zone. The relationship between the post-Palaeozoic volcanism of the Caucasus and the development of certain geosynclinal troughs (eugeosynclines or volcanogenic geosynclines) was ably deciphered by Dzotsenidze (USSR).

Karunakaran *et al.* (India) delineated three episodes in the history of the Andaman geosyncline: Formation during Upper Cretaceous times, sediment-filling (with turbidites and other terrigenous sediments) between Eocene and Miocene periods and orogenic movements during Upper Oligocene and Middle to Upper Miocene times. The orogeny

resulted in the elevation of the geosyncline and its modification into an island arc. Geological and geophysical studies outlined by Supriya Sen Gupta (India) indicate a northerly slope of the basement below the Gangetic alluvium and the thickening of the sediments in the same direction. The depth of the Mohorovicic discontinuity progressively increases towards the Himalayas where it attains a depth of about 70-75 km. below the mountains. Valdiya (India) described the lithology and structure of the following zones in the Himalayas: Autochthonous Siwalik zone, Para-autochthonous Lesser Himalayan zone, Krol Nappe System, Kashmir Nappe System and the Tethys Himalayas.

Hydrogeology

Babushkin *et al.* (USSR) explained the new techniques for artificial replenishment and recharge of ground waters, specially in the piedmont regions, and for the most economical way of exploitation of lens waters in the desert regions without triggering the ingress of underlying saline water. Three hydrogeochemical ground water zones were delineated by Honda and Maitra (India) in West Bengal. Ogilvie and Vostokova (USSR) presented an excellent paper on the geological, geographic and geophysical methods for the exploration of fresh ground water in the desert regions. They described new, continuous aero-electrical methods of search for small bodies of fresh, free ground water and electrical methods for locating the boundary where the ground water salinity changes slowly. Rogovskaya (USSR) discussed the horizontal and vertical differentiation of ground water in irrigated areas in arid zones.

Charnockites

According to Hepworth (UK), charnockites of south-west Nile, Uganda, form part of the layered Granulite Group which is partly metasedimentary. The retrogression of the granulites is ascribed to the superposition of a 'Grey Gneiss', metamorphism of Mozambiquian age. Klimov *et al.* (USSR) described the numerous geological and mineralogical characters common between the charnockites of East Antarctica and India and other Gondwana areas. They believed that charnockites were formed under conditions of high temperature, low partial pressure of water and oxygen and high content of alkalis (particularly potassium). The charnockites of Anabar Massif in Siberia are products of metamorphism of sedimentary and volcanic rocks under conditions of granulite facies metamorphism (estimated temperature and pressure: 600-900°C. and 3000-10,000 bars respectively). Mahadevan (India) agreed with the view that the 'basic' charnockites (pyroxene-hornblende-plagioclase granulites) are genetically unrelated to the 'acid' charnockites. He believed that acid members were produced by the replacement of country rocks by the alkaline fluids of varying composition under conditions of high mobility. Partial replacement of basic granulites led to the formation of 'intermediate' charnockites.

According to Searle (Cyprus), the charnockites of Ceylon originated as basic volcanic rocks intrusive

into the sedimentary Highland Series. Both the volcanic rocks, and the sediments were later subjected to Vijayan metamorphism which converted the volcanic rocks into charnockites. Wilson (Australia) described the tectonic and metamorphic setting of four groups of charnockites of different ages (more than 2500, 1500, 1200 and 1000 m.y.) in Australia.

Laterite

In warm, wet climates, the liberation and chemical removal of silica readily takes place and leads to the formation of laterites and bauxites. The observation of Bushinsky (USSR) that the solubility of silica in water rapidly increases with temperature — from 100 mg./litre at 0°C. to 300 mg./litre at 50°C.—explains the phenomenon. According to P. K. Chatterjee *et al.* (India), the laterites of Orissa are apparently formed *in situ* by residual weathering. They occur at different altitudes, overlie rocks of different composition and range in age from Archaean to Tertiary. Mature topography is a prerequisite for the development of laterite in Orissa. John Hays (Australia) described the relationship between laterite and land surfaces in the northern territory of Australia. He delineated two periods of lateritization — during the Late Cretaceous and the Early Tertiary times. Roy Chowdhury *et al.* (India) gave the profile of laterite overlying the Traps in some parts of Madhya Pradesh: Pisolithic laterite at the top, followed downward by aluminous laterite and bauxite, highly porous or cavernous laterite and, at the base, lithomargic clay.

Sedimentology and Sedimentation

Indranil Banerjee (India) employed stratigraphic and petrographic data to outline the broad features of tectonic control of the Vindhyan sedimentation. Microscopic, thermal, chemical and X-ray studies by Bardossy *et al.* (Poland) of rock samples of Silurian age from Poland, Germany, Bohemia, Hungary and Bulgaria clearly show that the depositional environment during the Silurian was uniform throughout the region. Glennie and Ziegler (Netherlands) pointed out the complications involved in the subdivision of the Siwaliks of Nepal which are fluvial sediments derived from the rising Himalayas and deposited in giant alluvial fans. They proposed a simple twofold lithologic subdivision — conglomerate facies and 'sandstone' facies — which does not carry a time implication. The directions of palaeocurrents in different types of basins were deciphered by Grossgeim (USSR) on the basis of grain directions, orientation of elongated biogenic remains, etc. Siddiqui (India) gave an account of the origin of the Tertiary bentonitic clay deposits of Barmer embayment, Rajasthan. He showed that the volcanic rocks gave rise to Namontmorillonite clay under hot, humid conditions (on land) and when the clay was subsequently deposited in the embayment, it got converted into Mg-montmorillonite by cation exchange.

Other Studies

Cherdyntsev (USSR) employed the variations in the $^{234}\text{U}/^{238}\text{U}$ ratio as a tool for studying the

geological conditions of uranium migration, particularly, in natural waters. The association of certain magmatic formations with specific structures in the earth's crust was brought out by Kuznetsov (USSR). Spilitic keratophyre group of extrusives and gabbroid intrusions are associated with geosynclinal stage of development of mobile zones, andesitic lava flows with the formation of geanticlines and the general closing of geosynclines, basalts with stable regions (old and recent platforms and oceanic blocks), and migmatites and charnockites with the Archaean bases of old platform. Rozhkov and Kovalsky (USSR) gave an account of the mode of formation and occurrence of the kimberlite. Intrusive kimberlite bodies are devoid of diamonds. Explosive kimberlite bodies are diamondiferous, but the quality and richness of diamonds vary for different pipes. The formation of diamond-bearing placers largely depends upon the degree to which the kimberlite pipe was eroded. Volborth (USA) described equipment (US \$ 50,000) involving the use of X-ray fluorescence and neutron activation, for rapid, non-destructive analysis of rock samples. All major elements (including oxygen) and practically all trace elements can be determined. The limits of detectability vary from 1 to 100 p.p.m., depending upon the element. Timothy Whitten (USA) reported some conceptual models for the analysis of three-dimensional variability of rock units.

Other Meetings

Concurrently with the sessions of the International Geological Congress, the following commissions of the congress held their meetings: Commission on Stratigraphy (with ten subcommissions devoted to different geologic periods); Geological Map of the World (with two subcommissions dealing with Metallogenic and Tectonic Maps); Geological Map of Europe; Meteorites; Study of clays; Coordination of geological and geophysical research; Problems of

the role of geochemistry in international scientific meetings; and Group discussion on International Indian Ocean Expedition. The Spendirov Prize was awarded to D. K. Ray (India).

The following international associations and scientific societies also met at the time of the congress: International Palaeontological Union; International Association of Hydrogeologists; International Mineralogical Association; Association of African Geological Surveys; Society of Economic Geologists; and the Geochemical Society. The International Union of Geological Sciences organized a fruitful symposium on the Upper Mantle Project and a commission of the Union discussed the study of economic elements in the earth's crust.

Concluding Remarks

The congress was memorable in many ways. It was a thrilling experience to the young geologists of India to come into contact with eminent earth scientists from different parts of the world. The sessions went on with clock-work precision. With numerous good papers scheduled for presentation at different places, one had to keep on moving from session to session and very regretfully skip some fine papers. The delegates who went to Kashmir for pre-congress geological excursion got marooned there due to heavy snow-fall. As attempts to arrange for their transportation to Delhi were not successful, the resourceful delegates organized scientific meetings in Srinagar itself. While it is proper that the Geological Survey of India, as the largest geological agency in the country, should play the principal role in the organization of the congress, the geology departments in the universities could have been brought into the picture to a greater extent. Notwithstanding some minor shortcomings in respect of arrangements which are probably inevitable in the organization of a conference of this size, the congress was a great success.

Sixth Seminar on Electrochemistry

The Sixth Seminar on Electrochemistry will be held at the Central Electrochemical Research Institute, Karaikudi, during 27-29 December 1965. The technical sessions of the seminar will cover the following fields: (1) Electrode kinetics, electrochemical equilibria and electro-analysis; (2) Electro-organic and inorganic products; (3) Electrothermics and electrometallurgy; (4) Batteries; (5) Electro-

deposition and metal finishing; (6) Corrosion; and (7) Miscellaneous.

Abstracts of papers intended to be presented at the seminar should be sent to the Convener, Dr K. S. Rajagopalan, Scientist, Central Electrochemical Research Institute, Karaikudi, by 15 September 1965. Full papers should be sent, in duplicate, by 15 October 1965.

Detection, Modulation & Generation of Optical & Sub-millimetre Wave Radiation Using Semiconducting Materials*

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GENERATION of coherent radiation for bridging the gap between the micro and the optical waves has made significant progress in recent years. In the wake of this progress have come certain very novel suggestions not only for generation but also for detection and modulation of these waves. The present paper is intended to outline and discuss the basic principles involved in some of those suggestions which require the use of semiconducting materials. As it is not convenient, within a modest review, to cover the entire family of semiconducting materials, the scope would be restricted to Ge, Si and the semiconducting group III-V compounds. The emphasis will be on descriptions, as far as possible, of the performance in terms of the basic physical parameters of the semiconducting material used in the device. Critical comparison of the performances of the different types of devices will be included and a few possible avenues of new developments in the field suggested.

DETECTION

Basic Considerations

Discussions are most conveniently initiated with detection of waves. Methods of detection are readily provided by some of the well-known techniques in spectroscopy. As a result, this topic lends itself to more thorough examination than any other and one can find in the literature quite a number of interesting publications giving useful background of the art at its present stage of development¹⁻⁵. Some of the most promising results obtained till now are those concerned with the use of semiconducting materials. Both bulk semiconductors and junction devices have been used in these studies — the former depending for operation on thermal as well as optical effects, and the latter on optical effects alone. Irrespective of these, the basic physical process required for detection is the absorption of the desired radiation. Considering a rectangular slab of material placed in vacuum and a monochromatic radiation flux I_0 per unit area incident normally on one face, the radiant power absorbed is easily shown to be⁶

$$I'_0 = \frac{\alpha I_0 (1 - R') [1 - \exp(-kd)]}{1 - R' \exp(-kd)} \quad \dots(1)$$

α being the surface area; k , the so-called absorption coefficient of the material of the slab for the radiation; and R' , the reflection coefficient for the

vacuum-material boundary given by

$$R' = \frac{(\sqrt{\epsilon} - 1)^2 + k'^2}{(\sqrt{\epsilon} + 1)^2 + k'^2} \quad \dots(2)$$

$$k' = \frac{k\lambda}{4\pi} \quad \dots(3)$$

ϵ being the dielectric constant and λ the wavelength.

For small values of k such that $kd \ll 1$

$$I'_0 = \alpha I_0 kd \quad \dots(3a)$$

and for $kd \gg 1$

$$I'_0 = \alpha I_0 (1 - R') \quad \dots(3b)$$

The radiation absorbed produces a secondary effect which may cause a change in the resistance (R), or the voltage across the two terminals (V) or the current flowing through the body (i) of the specimen, thus affording a means for detection. The secondary effect may be either thermal or optical.

A simple experimental arrangement suitable for observation with either type of detector is shown in Fig. 1. It is at once seen that even this simple arrangement introduces certain complications through the presence of the electrical leads, bias current (i) and the bias supply arrangement. In the following we shall consider first of all the behaviour of the intrinsic detector ignoring these disturbing factors. The possible effects of these on the performance of the detector will be discussed for a few typical cases — by performance

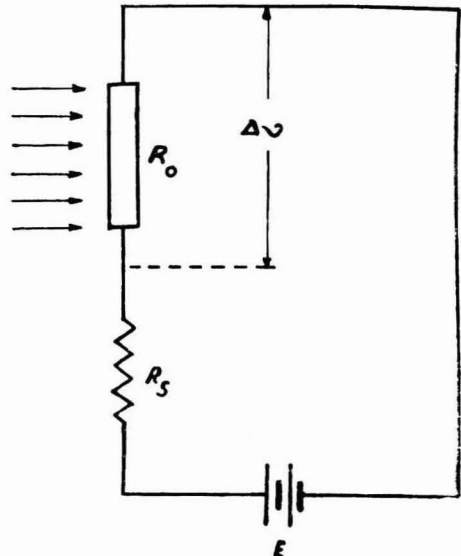


Fig. 1 — Simple arrangement for detection of radiation

*Based on a talk given at the Symposium on Solid State Physics held at the National Physical Laboratory, New Delhi, in April 1964.

being meant (i) the response per unit incident power or the responsivity, (ii) the speed of response or the time constant (τ), and (iii) the minimum detectable power — the noise equivalent power (NEP) or the sensitivity (I_m) and the noise factor (NF) of the detector*.

Thermal Detectors

The Intrinsic Detector

The bolometer type of thermal detectors has long been in use as detector of electromagnetic radiations and has been amply discussed in literature^{1,3,7-9}. The particular variety used in the microwave and infrared range consisted of beads of amorphous semiconducting materials. For these the performance had not been found to correlate strictly with the basic physical parameters of the materials themselves. With the advent of detectors using single crystals¹⁰ one should, however, expect a better correlation in this respect. For such materials the event leading to detection is primarily the rise in temperature due to lattice agitation caused by the incident radiation. New hole-electron pairs are thus created and the consequent change in resistance of the element provides the means for detection. For the intrinsic detector of Fig. 1 the heat balance equation for small rise in temperature can be written as

$$\frac{d\Delta T}{dt} = \frac{1}{C} (I_0 - G\Delta T) \quad \dots(4)$$

C being the heat capacity of the detector and G its effective thermal conductance with respect to the surroundings. Under steady state

$$\Delta T = \frac{I_0}{G} \quad \dots(5)$$

Responsivity — For an intrinsic semiconductor, the change in carrier density consequent to ΔT is

$$\Delta n_i = n_i \frac{E_g \Delta T}{2KT_0^2} \quad \dots(6)$$

T_0 being the ambient temperature; E_g , the band gap energy; and K , the Boltzmann's constant, giving a change in resistance

$$\Delta R = \frac{R_0 E_g k d (I_0 \alpha)}{2KT_0^2 G} \quad \dots(7)$$

wherein the possible dependence of mobility (μ) on temperature has been ignored. This may not be valid at low temperature. Further, use has been made of Eq. (3) signifying weak absorption. With a doped sample E_g should be replaced by the impurity ionization energy E_i . If i is the current flowing through the element, then the responsivity may be obtained as

$$r_0 = \frac{d(i\Delta R)}{d(I_0 \alpha)} = \frac{R_0 E_g k d i}{2KT_0^2 G} \quad \dots(8)$$

The physical constant of primary importance is the absorption constant k . The values compiled by Lax and Burstein¹¹ for Ge and Si (Fig. 2)

*The term detectivity defined by $\sqrt{\alpha}/\text{NEP}$ is currently being used as a figure of merit of the detector. This may be easily inferred from the parameters considered here.

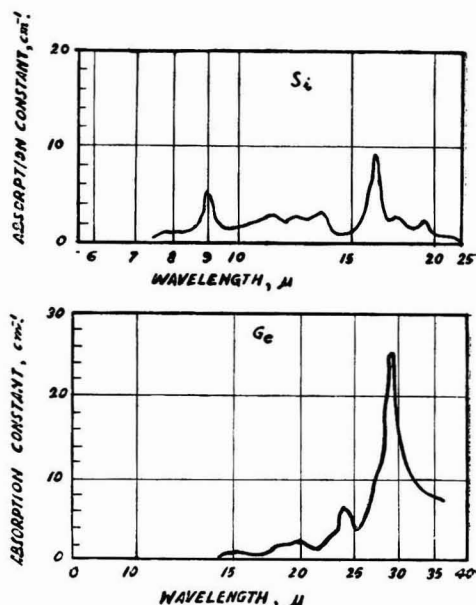


Fig. 2 — Lattice absorption spectra of Si and Ge (after Lax and Burstein¹¹)

indicate that these materials together should give very good performance over the range 8-35 μ . Operation, with somewhat poorer performance, should also be possible outside this band. Since $R_0 \propto \exp(E_g/KT)$, Si should give a better value of r_0 , GaAs should have been better still but for its extremely peaky nature of variation¹² of k with λ . At low temperature G varies roughly as T^3 both for ordinary radiation and conduction processes^{1,3,14}. The possibility of having a large value of r_0 through low temperature operation is thus immediately apparent. With such technique r_0 value as high as 10^5 V/W. appears attainable.

Time constant and frequency response — For communication applications a quick response of the detector becomes of utmost importance in order that the device has a wide frequency response. With the incident power modulated as $\exp j\omega t$, analysis as above leads to a responsivity.

$$\left. \begin{aligned} r_\omega &= \frac{r_0}{1+j\omega\tau} \\ \tau &= \frac{C}{G} \end{aligned} \right\} \quad \dots(9)$$

The bandwidth as defined by the 3 db. point is thus given by G/C . This last ratio should, therefore, be as high as possible.

Recalling Debye's T^3 law of variation of specific heat, one should expect that a low temperature of operation would lower τ , provided measures have been adopted to ensure a high value of G through special techniques. Highly conducting heat sinks in close proximity with the element have been used for the latter purpose — one of the best results being obtained with flakes cemented on Z-cut

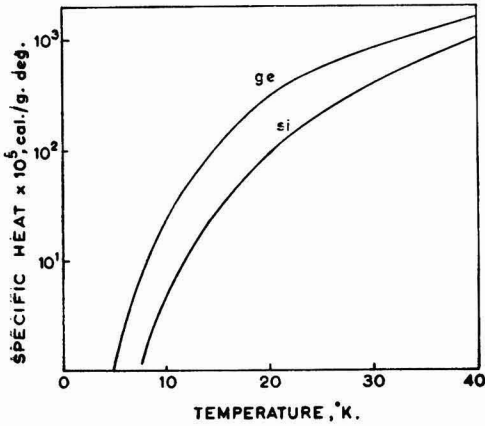


Fig. 3a — Specific heat of Ge and Si versus temperature

quartz¹⁵. Low¹⁰ obtained excellent results using the electrical leads as the heat sinks. For Ge at 3°K., the density $\rho' = 5.3$ g./cc., specific heat¹⁶ $s = 10^{-5}$ cal./g., thermal conductivity 1.25 W./cm.°C. and for a sample of thickness $d = 1$ mm.,

$$\tau \approx 100 \text{ } \mu\text{sec.}$$

a value roughly that achieved by Low around the same temperature. For Si at the same temperature ρ' and ρ' s are smaller¹⁷ (Fig. 3a) and thermal conductivity a little higher¹⁴ and hence τ may be lower by an order. It is to be noted that thermal conductivities of Ge and Si pass through maxima¹⁴ around 20°K. (Fig. 3b). Below this limit both s and G in normal cases should have T^3 laws of variation, indicating difficulties in securing adequate return in fastness of response through further cooling below this range. The thermal conductivity of Cu also passes through a maximum near 20°K. at which point its value is at least 10 times higher than the best expected¹⁸ of Si or Ge. Some improvement may, therefore, be effected by the use of Cu leads as heat sink to stimulate losses¹⁰. But in any conceivable arrangement involving either the leads as the sink or any other, promoting conduction, a temperature gradient would inevitably appear in the body of the element, making some of the above relations only approximate. Moreover, as discussed below, G cannot be indefinitely increased, without affecting seriously the sensitivity of the device. To date the figure 100 μ sec. seems to be the best realized of a purely thermal type of detector, thus limiting the maximum usable modulation frequency to a few kc/s.

Semiconductors are unique in the sense that they have an intrinsic cooling process arising out of a decreased i^2R loss consequent to the lowering of R by the incident radiation. At low temperature certain materials may have an α large enough to make this appreciable compared with either the radiation or the conduction loss thus increasing the G -value. It appears that, in principle, a $\tau = 10^{-6}$ sec. can be realized provided such a condition of cooling

has been established all over the detector element. Too high a value of G may reduce responsivity to an unworkable value, the maximum attainable value can be shown to be kd/i .

Sensitivity and noise factor — In the absence of poor electrical contacts — thus eliminating the so-called excess $1/f$ noise — three main sources limiting the minimum detectable power of a normal detector may be visualized. These are the photon noise, the phonon noise and the Johnson noise. Of these the photon noise may be minimized by using a small aperture¹⁰; at 300°K. an aperture 180° would suffice. Under this condition the minimum detectable power W_m per cycle or the NEP is given by

$$W_m = \sqrt{\left(4KT_0^2G + \frac{4KT_0R}{r_0^2}\right)} \quad \dots(10)$$

The first term within the bracket represents the phonon and the second the Johnson noise. For a good detector having $r_0 \gg 1$ phonon noise becomes the main contributing factor and sensitivity is improved through a reduction of both T_0 and G or of T_0^2G taken singly. Recalling the nature of variation of G for both conduction and radiation at low temperature as stated above, it would appear that more improved sensitivity can be realized with a lower temperature of operation within that range. With an ideal noiseless detector

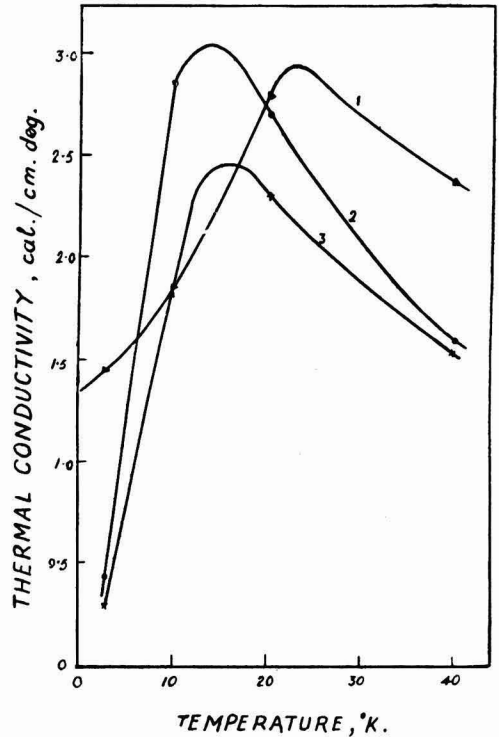


Fig. 3b — Thermal conductivities of Ge and Si versus temperature (after White and Woods¹⁴) [1, Si: n-type; 2, Ge: p-type; 3, Ge: n-type]

the only limiting factor is the background photon noise and for this and a detector element of suitable dimensions at 2°K., an ultimate sensitivity of 10⁻¹⁶ W./cycle has been estimated to be theoretically possible, the experimental value realized (ref. 10) so far with Ge at such temperature being 5 × 10⁻¹³ W./cycle. A low *G*-value, of course, increases τ and affects the speed of response.

In conformity with the usual practice we can define the noise factor as

$$N = 1 + \frac{W_m \text{ for the real detector}}{W_m \text{ for ideal detector}} \dots(11)$$

For the case referred to above $N \simeq 5000$. Thus, in spite of its exceptionally good sensitivity the limit of excellence is far from being reached and thermal detectors with better performance still remain worth searching for. With Si, for example, responsivity being higher and thermal conductivity at 2°K. nearly the same as that of Ge, one should expect to have a lower noise factor. With elements in which purely intrinsic cooling, as referred to above, is prominent noise factor should be higher.

Effect of Bias Current

The bias current, which must inevitably be used, incidentally provides for a means for varying r_0 . All but too small values of *i*, however, cause some heating, raising the temperature of the element to some value T'_0 even in the absence of a signal. Denoting by ΔT the rise in temperature above this value due to the incident radiation alone, the equation for heat balance is written as

$$\frac{d\Delta T}{dt} = \frac{1}{C} \left[I_0' - G\Delta T - \frac{R_0 E_g}{2K} \left(\frac{i}{T} \right)^2 \Delta T \right] \dots(12)$$

For small values of ΔT such that $T \simeq T'_0$, r_0 and τ are thus obtained from Eqs. (8) and (9) provided *G* is replaced by

$$G + \frac{R_0 E_g}{2K} \left(\frac{i}{T_0} \right)^2$$

This newly added term in i^2 is the intrinsic cooling conductance and in semiconductor under certain conditions might be quite comparable to *G*. The bias current, therefore, lowers both the responsivity and the time constant. It also follows from Eq. (10) that the decreased r_0 and the effective increase in *G* should deteriorate the sensitivity and the noise factor of the detector.

Effect of End Cooling

The presence of electrical contacts at the ends gives rise to end cooling, making the temperature non-uniform and causing additional losses due to conduction. These decrease r_0 but improve the τ -value. Sensitivity and noise factor are adversely affected. The problem of end cooling assumes particular importance because of its recent ingenious use for realizing a fast thermal detector. In general the temperature distribution along the length (2*l*) of the element may be shown to follow the relation¹

$$\left. \begin{aligned} \Delta T_x &= \frac{Q}{P} \left[1 - \frac{\cosh \sqrt{Pl} x}{\cosh \sqrt{Pl} l} \right] \\ P &= \frac{G + \frac{R_0 E_g}{2K} (i/T'_0)^2}{K_s \beta} \\ Q &= \frac{\Delta W}{G + \frac{R_0 E_g}{2K} (i/T'_0)^2} \end{aligned} \right\} \dots(13)$$

K_s being the thermal conductivity of the material and β the area of cross-section of the element. In Eq. (13) *x* is to be measured from the centre. It is clear that a higher *P*-value will help to minimize the effects of end losses.

Effect of Bias Supply Arrangement

The bias supply arrangement does not matter if $R_s \gg R_0$. For $R_s \gg R_0$ the responsivity would be reduced by a factor $R_s/(R_s + R_0)$.

Other Modes of Thermal Detection

Thermal effect in semiconductors may be made the basis of detection in quite a number of other ways. Thus, the current I_{co} in a reverse-biased *p-n* junction, which also varies¹⁹ as $\exp(-E_g/KT)$, provides a means for detection. The high resistance of the reverse-biased junction permits one to put a sufficiently large resistance in the external circuit to achieve the responsivity of the more conventional detector (Fig. 4). This external resistance will now contribute Johnson noise. Nevertheless, its sensitivity, noise factor and time constant may not be much different from those stated for ordinary detectors.

Thermoelectric and thermomagnetic phenomena²⁰ in semiconductors may also be conceivably used for detection. Responsivity of such devices cannot, however, be as high as those discussed earlier.

In summing up we note that thermal semiconductor detectors have the merit of covering a large range of wavelengths with excellent sensitivity and reasonably good responsivity. Their great drawback is, however, the sluggishness of response. Moreover, a large wavelength range necessarily also means a large inherent noise bandwidth. Practical use of intrinsic cooling may help to achieve a faster response.

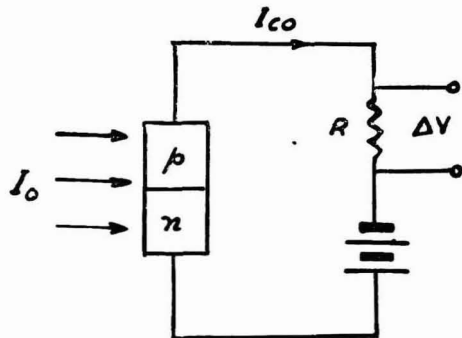


Fig. 4 — Detector using reverse-biased *p-n* junction

Photodetectors

Photons of suitable energy can create free carriers through direct interaction with bound electrons without invoking the aid of lattice agitation. The carrier created might be either a hole-electron pair or an electron or a hole depending upon the frequency of radiation and the nature of the semi-conducting crystal. In any event, however, the electrical property of the crystal changes, thus providing a means for detection. In a different type of detector interaction with photons and free carriers causes a change in mobility but not the density of the carriers leading to a change in conductivity of the material. Thus, we can have three broad classes of optical detectors, viz. those involving creation of hole-electron pairs or the intrinsic photo effect, those involving the creation of a single type of carriers or the extrinsic photo effect, and those involving absorption of radiation by free carriers⁵. A detector of the last type may be made tunable over a narrow frequency band. Either bulk semiconductor or *p-n* junction photodiode may be used to realize an intrinsic photodetector. Both straight and heterodyne types of operation of such detectors have been discussed in literature²¹⁻²⁵.

Detectors Using Intrinsic Photo Effect

In intrinsic photoconduction the incident photon causes a valence band electron to make a transition to the conduction band (Fig. 5), thus creating a hole-electron pair. The process is an extremely rapid one having a time constant less than 10^{-14} sec. The creation of additional carriers disturbs the thermal equilibrium and a countering mechanism by way of recombination of electron and hole appears. This latter process involves a time constant, the so-called lifetime τ , of 10^{-4} to 10^{-8} sec. for a typical semiconductor. Solution of equation

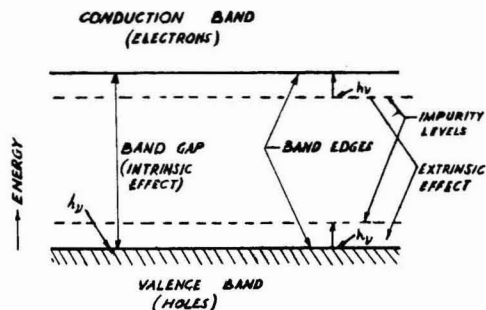


Fig. 5 — Energy band structure of a semiconductor showing photo effect of different types

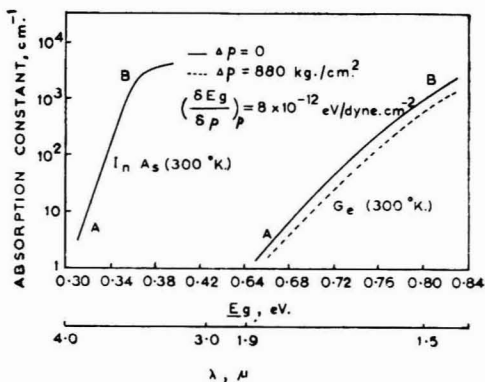


Fig. 6 - Absorption edges of Ge and InAs and dependence on pressure (Ge)

governing these rate processes has been discussed in detail by Rittner²⁶ and others both for bulk semiconductor and junction photodiodes²⁷. Such studies provide bases for a number of distinct classes of detectors using intrinsic photo effect, viz. bulk photoconducting detectors, photoelectromagnetic detectors, photoconductive *p-n* junction detectors, photovoltaic *p-n* junction detectors and heterodyne detectors.

A common drawback of all intrinsic photo effect detectors is that there is a maximum or threshold wavelength (λ_0) of response defined by the requirement that photon energy should be at least equal to the band gap energy as given in Table 1 for several materials at 300°K.

For reasons associated with peculiarities in energy band structure the approach to the limiting wavelength is gradual (Fig. 6). The band gap is also an apparently decreasing entity with increasing temperature. Thus, InSb has its limiting wavelength reduced from 7.2 to 5.6 μ if the temperature is changed from 250° to 77°K.

Bulk photoconductive detector — Let the sensing element be a thin rectangular slab of thickness d , length l and breadth b receiving radiant power I_0 per unit area normally on one of the wider faces of area bl . In the absence of trapping, drift and surface recombination the density of excess carrier generated would be governed by the equation²⁶

$$\frac{d\Delta n}{dt} = \alpha' I_0 - \frac{\Delta n}{\tau} \quad \dots(14)$$

where α' is the quantum efficiency giving the number of carriers generated per quantum absorbed.

TABLE 1 — BAND GAP ENERGY AND THRESHOLD WAVELENGTH FOR VARIOUS CRYSTALS

Crystal	E_g eV.	λ_0 μ	Crystal	E_g eV.	λ_0 μ	Crystal	E_g eV.	λ_0 μ
Ge	0.68	1.9	InAs	0.35	3.4	GaSb	0.71	1.8
Si	1.08	1.2	InP	1.25	0.91	GaP	2.4	0.55
InSb	0.18	7.2	GaAs	1.35	0.88	BN	10	0.12

Intrinsic absorption is characterized by k -values 10^2 - 10^6 cm.⁻¹ and for such strong absorption f is related to I_0 as [vide Eq. (3b)]

$$f = (1-R') \frac{\lambda I_0}{hcd} \quad \dots(15)$$

provided also the diffusion length is large compared to d .

Responsivity: For small signals τ is independent of Δn and the steady state density of excess carriers obtained from Eq. (14) is

$$\Delta n = f\tau\alpha' \quad \dots(16)$$

The consequent change in resistance measured across the length is thus

$$\Delta R = \frac{R_0 \Delta n}{n_0} = \frac{R_0 \alpha' f \tau}{n_0} \quad \dots(17)$$

R_0 and n_0 being the initial values of R and n . With a constant current i flowing along l a change in voltage drop $i\Delta R$ will result and the responsivity will be given by

$$r_0 = \frac{i\Delta R}{I_0 b l} = \frac{i R_0 \alpha' \tau (1-R') \lambda}{n_0 h c v} \quad \dots(18)$$

v being the volume of the sample. With $\alpha' \simeq 1$, the highest responsivity should be obtained near the limiting wavelength. As (R_0/n_0) increases rapidly with decreasing temperature the advantage of low temperature operation is also obvious. This, however, decreases the limiting wavelength as stated already. With $\tau \simeq 100$ μ sec., $i = 10$ μ a., a Ge sample at ordinary temperature may have $r_0 \simeq 10^4$ V./W. Improvement by at least one order may be possible by low temperature operation. In a practical element, surface recombination and the presence of the electrical leads would make r_0 appreciably lower than that predicted by Eq. (18). Increasing r_0 by using a larger bias current is limited by the onset of appreciable Joule heating. The difficulty may be overcome partially if a conducting heat sink is used.

Frequency response: If I_0 is modulated as $\exp j\omega t$, then Eq. (14) may be used to show that the responsivity

$$r_\omega = \frac{r_0}{1 + \omega^2 \tau^2} \quad \dots(19)$$

The device will, therefore, have a cut-off frequency $1/2\pi\tau$. For Ge and Si, τ may be a few μ sec. With group III-V compounds like GaAs or InSb values less than 10^{-8} sec. may be realized, permitting a bandwidth of about 100 Mc/s. Too low a value of τ , of course, reduces the responsivity [Eq. (18)]. Some compromise is, therefore, essential. In case deep lying traps are present τ cannot be uniquely specified, but its effective value becomes higher, improving r_0 but reducing the cut-off frequency. Unfortunately, traps are present in many of the practical photoconducting materials and τ depends on temperature, increasing with decreasing T under ordinary conditions²⁸.

Sensitivity and noise factor: The main sources of noise at low levels of illumination are the Johnson noise associated with R_0 and that due to photons associated with the background radiation. Judicious

selection of aperture reduces photon noise. Under this condition the NEP (W_m per cycle)

$$W_m = \sqrt{(v_j^2/r_0^2)} \quad \dots(20)$$

as

$$v_j^2 = 4R_0KT_0$$

$$W_m \propto n_0 \sqrt{T_0/R_0} \quad \dots(21)$$

indicating a lower NEP at a lower temperature. With $r_0 \simeq 10^5$ V./W. and low temperature W_m may be 10^{-13} W./cycle or even lower. Thus, in respect of sensitivity the photoconducting detector performance at the present time is as good as the best Ge thermal detector developed so far.

InSb promises the longest threshold wavelength and should give one of the most wide band detectors^{29,30}. Roberts⁵ reports the following values regarding the performance of a practical intrinsic InSb detector:

Dimension = 6×0.01 mm. glued to Cu block heat sink

$\tau = 5 \times 10^{-8}$ to 10^{-6} sec.

$W_m = 10^{-11}$ W./cycle for 77°K. operation.

For an ideal detector of this area limited by background radiation alone the W_m value is roughly 3×10^{-12} W. at the temperature. Thus, the NF realized is within 10 — a remarkably good achievement. For high illumination level the NF might deteriorate due firstly to the presence of the so-called generation recombination noise and secondly due to a reduction in r_0 arising out of a sublinear photoresponse at such levels.

Photoelectromagnetic detector — Observation of photoelectromagnetic (PEM) effect³¹ provides an alternative type intrinsic photodetector. In this a Hall type of voltage is generated through interaction between the current due to the diffusion of optically generated carriers towards the interior of the semiconductor sample, and a steady magnetic field B acting at right angles (Fig. 7). This voltage enables

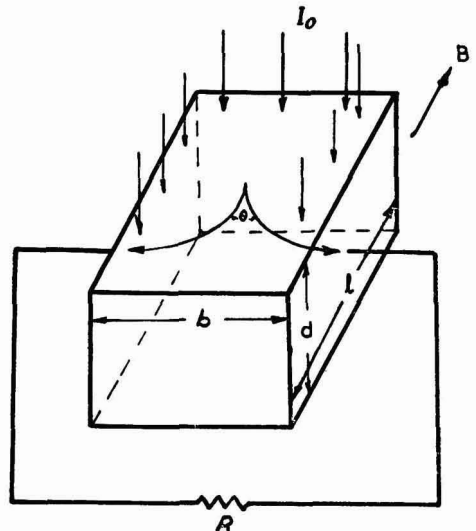


Fig. 7 — A photoelectromagnetic detector

a current to be drawn through an external path without the use of a battery. The theory of the effect is a little involved and we will neither reproduce it nor discuss the general results. We shall only recall the expression for the short-circuit PEM current for the simple case when B and the Hall angles are small and the sample thickness d several times the diffusion length L , viz.

$$J_{sc} = \frac{q_0 \alpha I_0 \alpha' (1-R') \lambda L}{\left(1 + \frac{S\tau}{L}\right) hc} \quad \dots(22)$$

θ_H being the sum of the Hall angles for electrons and holes and S the surface recombination velocity at the surface of incidence. The responsivity is

$$r_0 = \frac{q_0 \theta_H \alpha' (1-R') \lambda L}{\left(1 + \frac{S\tau}{L}\right) hc} \quad \dots(23)$$

Detection is also possible through measurement of the PEM open circuit voltage V_{oc} with the help of probes, thus eliminating complications due to the presence of conducting leads. For this

$$V_{oc} = J_{sc} / \sigma_0 d \quad \dots(24)$$

Very little can be gained through a detailed discussion of Eqs. (22)-(24) because of the simplifying assumptions on which these are based. For $d \gg L$ the frequency response will be limited by the effective lifetime. On the other hand, with a small d -value, this limitation will arise through the carrier transit time from one face to the other, the far side being chosen to have a high enough recombination velocity to enable all excess carriers to recombine upon it. Usually PEM detectors permit the use of thicker semiconductor samples than a photoconductive detector. A detector of this type can be made to have a good response up to a few kMc/s. However, Eq. (23) will no longer give its responsivity, which may not be as high as that of an ordinary photoconductive detector, its output voltage being established by a diffusion rather than drift field. Details of the design procedure for a practical PEM detector have been discussed by Sommers and Teutseh²⁵.

Photon and Johnson noise will determine the NEP in this case too and as such its noise performance should be as good as that of the photoconductive detector. For a temperature of about 77°K. PEM detector sensitivity is usually better than that of the other type. Practical InSb and InAs detectors having sensitivity 10^{-10} W. have been described¹². For these, response time is less than 10^{-6} sec. An InSb PEM detector capable of responding to 1 kMc/s. modulation frequency at room temperature has been described by Zitter³².

Photoconductive and photovoltaic detector using p-n and p-i-n junctions — An excellent detector of light is the reverse-biased junction diode. The depleted junction region under such a bias is an ideal intrinsic region with a strong electric field (Fig. 4). The hole and electron generated by the light, therefore, drift rapidly in opposite directions causing a current i to flow through an external path. Either the short-circuit current or the voltage across an

external load R_L may be measured for detection. Such a junction detector using InSb at 77°K. has been found to approach a photoconductive cell in performance.

Responsivity: It may be shown that in case the light is incident normal to the junction flooding the same wholly the photocurrent,

$$i = \frac{q \alpha I_0 \alpha' (1-R') \lambda \tau}{hc T_r} (1+b) \quad \dots(25)$$

where b is the hole to electron mobility ratio; α , the junction area normal to the direction of incidence; and T_r , the transit time of a carrier across the junction (i.e. d/v_d , d , the junction width and v_d the drift velocity). With increasing field v_d increases tending ultimately to a limiting value 10^7 cm./sec.²⁵. Hence, we might easily realize a condition $\tau \gg T_r$, signifying considerable gain in the basic photo effect³³. Observing the voltage across R_L , the responsivity is obtained as

$$r_0 = \frac{q R_L \alpha' (1-R') \lambda \tau}{hc T_r} (1+b) \quad \dots(26)$$

With $R_L = 10^4$ ohms, 1.2 μ radiation (the limiting value for Si) and $\tau/T_r = 10$, r_0 approaches a value 10^5 V./W.

For radiation incident parallel to the junction, of course, a slightly different set of equations must be used.

Frequency response: Detailed analysis due to DiDomenico Jr and Svetlo²⁴ shows that with $T_r \ll \tau$ the frequency response, as is to be anticipated, should be determined by T_r . The limiting frequency of operation is now $1/2\pi T_r$. A small junction width is, therefore, preferable. Too small a value, however, increases the junction capacitance and makes stringent a subsidiary condition:

$$R_L C \leq 1/2\pi f_0$$

f_0 being the modulation frequency. Because of the saturation in v_d mentioned above, increasing the field indefinitely does not bring proportionate return. In any case, with $T_r \ll \tau$, a junction device may have a much higher bandwidth than a bulk type detector for the same responsivity.

Sensitivity and noise factor: At high frequencies the chief sources of noise are the shot noise associated with diode dark current i_d and signal current i and the Johnson noise in R_L . At low temperature the first source may be disregarded. Hence, the NEP

$$W_m = \sqrt{[2qiR_L^2 + 4R_L kT_0] / r_0} \quad \dots(27)$$

With $i \simeq 10^{-5}$ amp., $r_0 \simeq 10^5$ V./W., $R_L \simeq 10^4$, $T_0 \simeq 100^\circ\text{K.}$, W_m approaches a value 10^{-13} W. which, it may be shown, is equivalent to a noise factor of the order 10.

In a p-n junction without bias the normal built-in field existing in the depleted region separates the optically generated hole-electron pairs to cause a photovoltage to appear across the diode. This voltage may be made to drive a current through an external low impedance path. Either the open circuit photovoltage³⁴ or the short-circuit current may be utilized for detection. Absence of a strong field across the junction, of course, does not enable us to have a means for external control of

performance through the factor τ/T_r . Junction resistance KT/qi_{co} contributes Johnson noise in the open circuit mode while shot noise affects the performance in the short-circuit mode of operation.

Pruett and Petritz³⁵ and Pagel and Pruett³⁶ have discussed the relative performances of the photo-voltaic and photoconductive modes of detection with reference to an InSb photodiode and concluded that the former mode should have a greater sensitivity but a more stringent cooling requirement. A grown junction, InAs photovoltaic cell may, however, be operated even at room temperature. It appears that the photovoltaic detector has not yet been as much adequately studied as its photoconductive counterpart. An ordinary solar cell, which has been shown³⁷ to be suitable for measurement of coherent luminous power up to 10^{-8} W., may also be used as a photovoltaic detector of radiation in the visible and near infrared region.

Heterodyne detectors using bulk semiconductor p - n junction — Optical detectors described above are all linear on a power basis. In other words, the response must be proportional to the square of the electric field vector associated with the radiation. This fact may be utilized to achieve mixing action with two coherent waves incident simultaneously, with a view to realizing a heterodyne detector. Such a detector reproduces the envelope of the incident wave in a faithful manner. Heterodyne detectors using both bulk materials and p - n junctions have been discussed recently.^{21,23,24,38-40} In case the two radiations have frequencies ω_1 and ω_2 and are polarized in the similar fashion, the associated field strengths being $E_1 \cos \omega_1 t$ and $E_2 \cos \omega_2 t$, the number of excess hole-electron pairs created and as such the response will be proportional to

$$[E_1 \cos \omega_1 t + E_2 \cos \omega_2 t]^2 = \left[\frac{E_1^2}{2} + \frac{E_2^2}{2} + E_1 E_2 \cos(\omega_1 - \omega_2)t + E_1 E_2 \cos(\omega_1 + \omega_2)t + \frac{E_1}{2} \cos 2\omega_1 t + \frac{E_2}{2} \cos 2\omega_2 t \right] \dots(28)$$

If ω_1 and ω_2 are both optical frequencies, electrical detection is possible only of the difference frequency $(\omega_1 - \omega_2)$. The photocurrent at this beat frequency will, therefore, be of the form

$$i = \frac{4\pi q \alpha \alpha' (1-R')}{h} \sqrt{\frac{I_1 I_2}{\omega_1 \omega_2}} \frac{\tau}{T_r} \frac{(1+b)}{(1+\omega_3^2 \tau^2)^{1/2}} \dots(29)$$

I_1 and I_2 being the incident power per unit area associated with the radiations and $\omega_3 = \omega_1 - \omega_2$. The response due to the signal frequency ω_2 may, therefore, be increased by using a strong local source of frequency ω_1 . It must be remembered, however, that at too high radiation intensities the response-power relation becomes non-linear and Eqs. (14) and (16) cease to be valid. i versus E_1 relation being linear the device works well as an envelope detector. (With an ordinary photodiode detector when the output is measured across a matched load the increasing mismatch at higher power level may be utilized to obtain a linear E - i relation under certain circumstances.)

Eq. (29), which applies to a bulk semiconductor, indicates that the frequency response should be limited by τ . With reverse-biased junctions the transit time T_r tends to take over this role. Better performance is, therefore, expected of a junction diode. If I_2 is modulated at a frequency ω_4 then $\omega_3 \gg \omega_4$. Since T_r may be 10^{-12} sec., a difference frequency 100 Mc/s. with a modulation in the microwave frequency range may be detected provided a suitable second detector is available.

The main types of noise are Johnson noise in the load resistance R_L , photon noise and shot noise associated with the d.c. photocurrent contributed by the terms $E_1^2/2$ and $E_2^2/2$ in Eq. (28). Neglecting photon noise the NEP

$$W_m = \sqrt{\left[4R_L K T_0 + \frac{4R_L^2 \pi q^2 \alpha \alpha' (1-R')}{h} \left(\frac{I_1}{\omega_1} + \frac{I_2}{\omega_2} \right) \frac{\tau}{T_r} (1+b) \right]} / r_0 \dots(30)$$

where $r_0 = d(iR_L)/d(\alpha I_1)$ is the power responsivity, a less meaningful concept in envelope detection.

Experimental results on detection using Ge, Si, GaAs and InAs diodes have been presented by Lucovsky *et al.*²³. A successful practical heterodyne detector for detection of microwave modulated light has been described by Targ⁴¹.

Detectors Using Extrinsic Photo Effect

With the currently available semiconducting materials of the category under discussion, the longest wavelength for operation of an intrinsic type of photodetector is limited to the threshold wavelength for InSb which for optimum performance is, as already noted, no more than 5.6 μ . Operation at longer wavelengths is, however, possible through the use of photo effect in doped samples which require for carrier generation only enough energy for transfer of a bound carrier from a level located inside the forbidden gap to either the valence or the conduction band edge (Fig. 5). Fig. 8 shows

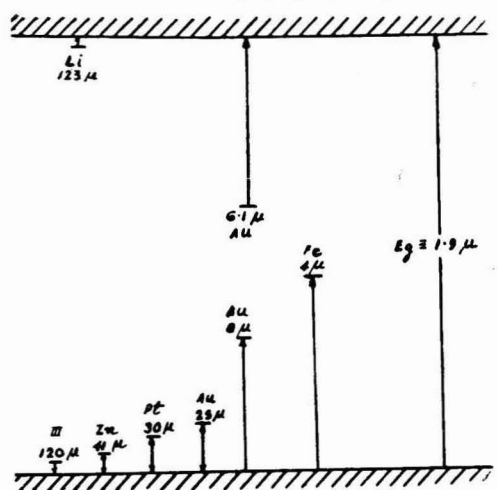


Fig. 8 — Threshold wavelength for extrinsic photo effect in Ge with different doping elements

TABLE 2—THRESHOLD WAVELENGTH AND ELECTRON ORBIT RADIUS OF DOPED SEMICONDUCTING GROUP III-V COMPOUNDS

Compound	p-type			n-type		
	Doping material	λ_0 μ	a_0 A.	Doping material	λ_0 μ	a_0 A.
InSb	Cu, Mg, Zn, Cd, Si, Ge	40	14	Li, Sn, S, Se, Te	1600	640
InAs	Mg, Zn, Cd	25	12	Cu, Si, Ge, Sn	617	310
GaSb	Cu, Mg, Zn, Si, Ge	40	15	Li, Se, Te	411	150
GaAs	Na, Cu, Mg, Hg	25	12	Li, Sn, S, Se, Te	153	85

threshold wavelengths for free carrier generation in Ge with a number of doping elements. In Table 2 are given the doping materials and the theoretically estimated threshold wavelengths for a few group III-V compounds. It will be seen from Table 2 that with proper choice of doped material, operation can be extended up to 1.6 mm. waves (*n*-InSb). In extrinsic photo effect absorption of a photon creates a single type of carrier—either a hole or an electron. Further, absorption of photon is a rather weak process (*k* small) for which Eq. (15) must be replaced by²⁶

$$f = \frac{\lambda I_0 k}{hc} \dots(31)$$

under small signal conditions. Eq. (14), however, holds, and hence the responsivity is obtained by multiplying the right side of Eq. (18) by $kd/(1-R')$. *k* for extrinsic absorption is typically 10^{-1} cm., hence with $d < 1$, $kd/(1-R') \approx 1$. Since λ is much larger, $I_0 \lambda/hc$ is much larger for a given power. As against this, a doped sample tends to have a lower resistance than an intrinsic one at a given temperature. The responsivity cannot, therefore, be much different from that for an intrinsic detector.

The highest frequency of response is, of course, limited by τ which, for doped Ge and Si at extremely low temperature, may be as low as 10^{-10} sec.⁴² For ordinary conditions, the performance is similar to that of the intrinsic type. The same applies to NEP and noise factor.

A few peculiar aspects of extrinsic type detector deserve special mention. Energy required for free carrier generation being small, the sample must invariably be cooled to a very low temperature to avoid thermal ionization of impurities and to obtain a large R_0 value. Again, even with cooling the performance may not improve if the energy level pertaining to the doping material is broad enough to approach the valence or the conduction band edge. For a given density of doping element the breadth of this level increases with increasing radius of the associated Bohr type orbit in the semi-conducting material, this again being larger for material having a lower effective carrier mass. Values of this radius are given in columns 4 and 7 of Table 2. It will also be noticed that this value tends to be larger for material with longer λ_0 or smaller separation between the impurity level and the band edge. In *n*-InSb a density of doping

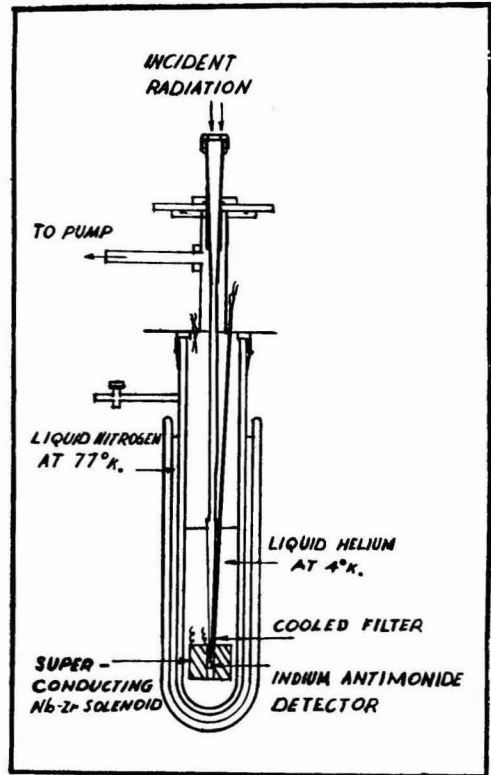


Fig. 9 - InSb extrinsic photodetector

10^{13} /cc. is enough for the impurity level to broaden out and merge with the conduction band edge. Under this condition, λ_0 tends to infinity and no amount of cooling will be able to decrease thermal ionization, i.e. to increase the R_0 value. Electron orbits may, however, be squeezed to a small circle artificially through the application of an external magnetic field of adequate strength⁴³.

Intrinsic detectors with excellent properties have been described^{44,45}. The one used by Harding and Roberts is illustrated in Fig. 9. The operating temperature 1.7°K. was attained by using a liquid He bath. A magnetic field of 6000 oersteds was realized through the use of a superconducting Nb-Zr solenoid. This helped to prevent broadening of impurity level. The *n*-InSb detecting element was of size $5 \times 3 \times 2$ mm. The detector was found to possess a bandwidth of 10^7 c/s., sensitivity of 10^{-13} W. and a threshold wavelength of 8 mm. The extension of the threshold beyond the theoretical limit 1.6 mm. (Table 2) was believed to be due to an entirely different mechanism of absorption arising out of the presence of free carriers. The detector had been designed to study radiation from plasma sources.

Detectors Using Free Carrier Absorption

As in the case of metallic conductors free carriers in semiconductors also absorb radiation under certain

conditions, the coefficient of absorption at high frequencies being determined by

$$k \propto \frac{\lambda^2 n}{m^{*2} \mu} \quad \dots(32)$$

For long waves in the mm. and sub-mm. range, a temperature low enough to make impurity scattering the dominant process and hence μ low in consequence of the relation $\mu \propto T^{3/2}$ and a material like n -InSb with an effective carrier mass as low as $0.015 \times$ the electronic mass, this absorption process may be strong enough ($k \approx 10\text{--}10^{-2} \text{ cm.}^{-1}$) to provide a basis for a satisfactory detector. Here, absorption increases the energy or the effective temperature of the carriers and a change in resistance follows in consequence of the resulting change in mobility. Such a detector has been proposed by Rollin⁴⁶. Responsivity of the device may be expressed as

$$r_0 \approx \frac{R_0 i \tau_E k d}{n_0 K T_0 v} \quad \dots(33)$$

τ_E being a relaxation time governing the energy exchange between an excited carrier and a phonon. For a particular n -InSb detector at 2°K., an r_0 value of $2.4 \times 10^3 \text{ V./W.}$ has been shown to be possible.

At high frequencies r_0 is frequency dependent through k as

$$k_{\omega} \approx \frac{k_0}{1 + \omega^2 \tau^2}$$

τ being the momentum relaxation time for the carriers and is typically of the order 10^{-13} sec. τ_E for the detector mentioned above was estimated to be 10^{-7} sec., thus establishing the possibility of detection of mm. and sub-mm. waves modulated at a few Mc/s.

Assuming Johnson and photon noise to be the main sources of noise, the NEP has been shown to be in the region 10^{-14} to $10^{-13} \text{ W./cycle.}$

Kinch and Rollin⁴⁷ have described a practical mm. and sub-mm. wave detector using free carrier absorption in n -InSb. The NEP at 1.8°K. for this was $3 \times 10^{-13} \text{ W./cycle}$ with a response time 10^{-7} sec.

Tunable Detector

All the aforesaid detectors are capable of operation over a large wavelength range which makes them open to noise from other than signal channel unless preceded by an optical filter cooled at the operating temperature. Such an arrangement is not flexible, however. A more flexible detector may be realized by making the device tunable through the use of cyclotron resonance and diamagnetic Landau effect as explained below.

Ordinarily, the energy states for free carriers in the conduction and the valence bands are continuously distributed in the form of bands. As predicted originally by Landau these bands may be stratified into a number of discrete levels by a magnetic field. For this we must have

$$\omega \tau \geq 1 \quad \dots(34)$$

Neglecting the effect of spin, the separation between successive Landau levels may be shown to be $\hbar \omega_c$, ω_c being the cyclotron frequency Bq/m^* (Fig. 10), m^* effective mass of a hole for the valence and

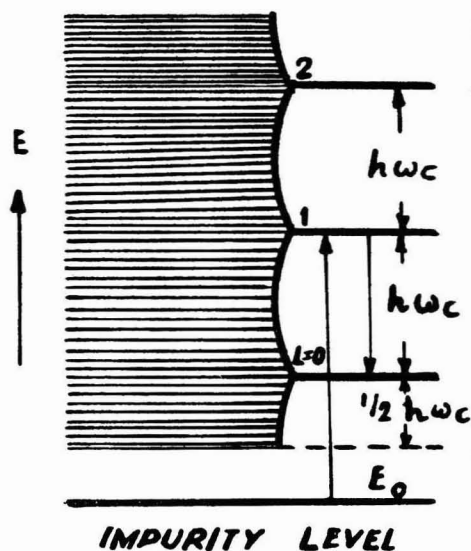


Fig. 10 — Landau splitting of energy bands under a strong magnetic field and the two possible methods of realizing tunable detectors

of an electron for the conduction band. If, further

$$\hbar \omega_c > K T_0 \quad \dots(35)$$

free carrier, if any, would settle to the lowest level in case the impurities are wholly or partially ionized. Conditions (34) and (35) are generally realized at very low values of temperature. With photon energies lower than that of the band gap two types of selective absorption are possible (Fig. 10): (i) With ionized impurity states the carrier in the lowest Landau level might absorb selectively photons of frequency $\omega_c/2\pi$ making transition to the higher level. This actually means cyclotron resonance. (ii) With non-ionized impurity states, bound electrons from these might absorb photons of right energy making a transition to the second Landau level and then be scattered back to the first. In the first case the absorption coefficient reaches a maximum for resonance giving a tunable detector under the family of detectors using free carrier absorption and in the second case the number of free carriers increases attaining a maximum at resonance giving a tunable detector under the family of detectors using extrinsic photo effect. The latter type of operation will naturally be possible at shorter wavelengths.

Goodwin and Jones⁴⁸ achieved cyclotron resonance detection at 34 kMc/s. using Ge at 4.2°K. and a magnetic field 1.8 kilo-oersteds — the sample being placed inside a cavity. Response time achievable was claimed to be as low as 10^{-9} sec. Rollin had also suggested the possibility of such a detector.

Brown and Kimmitt⁴⁹ have described a detector of the second type using n -InSb at 4.2°K. and an arrangement similar to that shown in Fig. 9. The response obtained by them at 100 and 250 μ

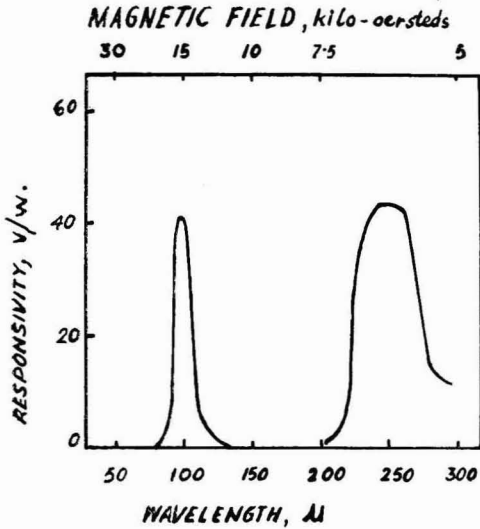


Fig. 11 — Response curve of a tunable detector (after Brown and Kimmitt⁴⁹)

is shown in Fig. 11. The bandwidth is roughly 12 per cent at 100 μ. Its NEP and response time were estimated to be 5×10^{-11} W. and 10^{-6} sec. respectively. A narrower bandwidth and a four-fold responsivity were obtained by operating the sample at 1.5°K. Bandwidth varied roughly as $2/\pi$.

In a tunable detector the magnetic field has to be adjusted for resonance (upper scale in Fig. 11). A semiconductor with a lower effective carrier mass requires a lower value of field to realize a given resonance frequency; *n*-InSb for which $m^* = 0.015 m_e$ is the best possible material from this point of view. Nevertheless, even with this the required magnetic field is 75 kilo-oersteds for operation at 26 μ. Recent developments like the Nb₃Sn, Nb-Zr alloys^{50,51} have opened up ways for superconducting magnets giving 100 kilo-oersteds and even above. It may be noted that a subsidiary effect of such high fields is the rise in the detector resistance because of magnetoresistance effect and this affects NEP.

Other Types of Optical Detectors

Optical detectors in which the photoconductance is sensed by a probing microwave signal, rather than a d.c. bias, are also possible. A waveguide method has been proposed by Brand *et al.*⁵². GaSb tunnel diodes have been used for detection and mixing of mm. waves⁵³. Such detectors are claimed to be much better than ordinary diodes in respect of sensitivity and NF at 55 kMc/s. Saito *et al.*⁵⁴ have described a method in which silver-bonded point contact Si and Ge diodes were used for detection and simultaneous amplification through parametric action.

Detection of Frequency Modulated Waves

The methods described above relate to the detection of amplitude modulated waves. Semiconductor

detector devices are useful for other types of detection also. Thus, confining operation near the band edge (AB in Fig. 6) where *k* varies with $(\omega - \omega_0)$ one can, for small frequency deviation, obtain a linear detector for frequency modulated waves.

Thus we note that optical detectors cover a wide frequency range bridging infrared and microwave regions. Their response can be quite fast and sensitivity approaches that of the best thermal detector. These also permit realization of heterodyne and tunable detectors.

MODULATION

In any practical communication system, modulation constitutes a vital operation. Amplitude, frequency and phase are the parameters of a wave which can be modulated. For the wave bands under consideration interest has so far been restricted mainly to the possibilities of amplitude modulation^{55,56}.

Schemes for amplitude modulation using semi-conducting materials invariably involve a wave transmitted through a slab or a junction of that material (Fig. 12). In the most general case, a polarized wave of intensity I_0 passes through the semiconductor slab having an absorption constant *k* for the wave and with an externally imposed electric or magnetic field. The wave next passes through an analyser, the instantaneous strength of the wave finally transmitted being

$$I_1 = I_0 F(k, R', \pi) = \frac{I_0(1-R')^2 e^{-kd}}{1-R'^2 e^{-2kd}} \pi \dots (36)$$

where π takes into account the change in the state of polarization of the wave while traversing the slab of thickness *d*. The external field may be made to vary any of *k*, *R'* and π with time in the desired fashion to enable transmission of an amplitude modulated wave. We have, therefore, three main families of modulators to be discussed, viz. the *k*-, the *R'*- and the π -modulators.

Performance will be assessed in terms of the following parameters:

(i) Modulation efficiency η defined by the ratio of the maximum change in light intensity at the fundamental component of the modulation signal to that when the same incident power I_i is modulated 100 per cent at the fundamental frequency.

(ii) Depth of modulation *m* measured by the change in intensity with the modulating signal to the total intensity in the absence of the signal.

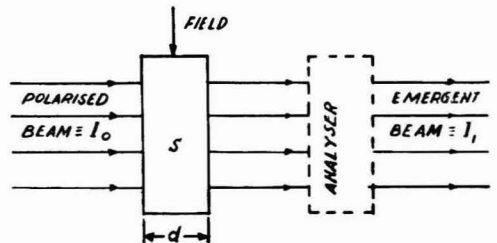


Fig. 12 — A general scheme of modulation

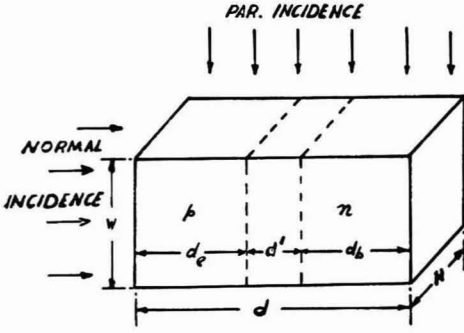


Fig. 13 — A p - n junction showing the geometry and two modes of irradiation

(iii) Frequency response measured by the reciprocal of the longest characteristic time constant of the modulator.

Also of interest is the power required to obtain a given modulation depth.

k -Modulators

As seen already, photo effect might involve either free carrier or extrinsic or intrinsic absorption. Each one of these is a potential basis for a k -modulator. Of these, the most extensively discussed are those involving free carrier absorption.

Free Carrier Absorption

The simple theory of absorption due to free carriers gives

$$k = \frac{q^2 n \tau}{k' m^* (1 + \omega^2 \tau^2)} \quad \dots(37)$$

k' being constant for a given material. For infrared and deep sub-mm. region $\omega \tau \gg 1$ and relation (32) holds while for longer waves

$$k \propto n \mu \quad \dots(38)$$

Modulators using expressions (32) and (38) appear to have received attention of a number of workers⁵⁵⁻⁶⁰. Suggestions involve modulation of both n and μ .

n -Variation — In a semiconductor carrier concentration may be readily varied through carrier injection across a p - n junction. With the forward-biased junction, there exists in the n -type base region an excess of holes above the thermal equilibrium value distributed according to the relation

$$p_x = p_n \left(\exp \frac{qV}{kT} - 1 \right) \exp \left(-\frac{x}{L} \right) \quad \dots(39)$$

p_n being the thermal equilibrium value; V , the bias voltage; and x , the distance measured from the base end of the junction. A beam of light transmitted through the base region will, therefore, suffer more absorption in the presence of a forward bias. The exact intensity of the transmitted beam will depend upon whether the beam travels in a direction parallel^{57,59} or perpendicular^{58,60} to the plane of the junction (Fig. 13).

It may be noted that k is normally involved in the transmitted intensity through an exponential function. Under this condition faithful modulation is assured only for small signals or, in other words, for small modulation depths. Further, it is more convenient to treat such a diode as a current-controlled device. Subject to this reservation simple analysis can be made using Eq. (39), neglecting surface reflection and assuming absorption due to sources other than free carriers to have a coefficient k_0 , to show that for light traversing normal to the junction

$$\eta' = \left| \frac{4jqx_p p_n' X \Delta V}{KT} \exp[-z_n(n_p d_c + n_n X)] - k_0(d_c + X) \right| f(\omega \tau_p, X/L) \quad \dots(40a)$$

$$m' = \frac{qXx_p p_n' \Delta V}{KT[1 + z_p p_n' X f(0, X/L)]} f(\omega \tau_p, X/L) \quad \dots(41a)$$

where z_n , z_p are the absorption cross-sections due to electrons and holes; and d_c , X , the widths of the emitter and the base region; ΔV , the modulating signal, while for the parallel case with the dimensions in the direction of incidence equal to W

$$\eta'' = \left| \frac{4jqx_p p_n' W \Delta V}{KT} \exp[-(k_0 + z_n n_n)W] f(\omega \tau_p, X/L) \right| \quad \dots(40b)$$

$$m'' = \frac{qx_p p_n' W \Delta V f(\omega \tau_p, X/L)}{KT[1 + z_p p_n' W f(0, X/L)]} \quad \dots(41b)$$

$$p_n' = p_n \exp \left(\frac{qV_0}{kT} \right) \quad \dots(42)$$

$f(y, Z) = \left\{ \exp(-\sqrt{1+jyZ}) - 1 \right\} / \sqrt{1+jyZ}$ where V_0 is the bias voltage. With normal incidence the background absorption tends to be higher.

The frequency response of the modulator is limited by the recombination lifetime τ_p of the injected holes. With Ge and Si, values of τ_p are such that operation may be possible up to 1 Mc/s. As pointed out already, injected carrier density varies exponentially with voltage and this tends to make distortion high unless m is small. As a way out of this difficulty a current rather than a voltage drive may be used.

Fig. 14 taken from a recent study of the problem by McQuistan and Schultz⁵⁹ with a Ge p - n junction shows the typical performance one

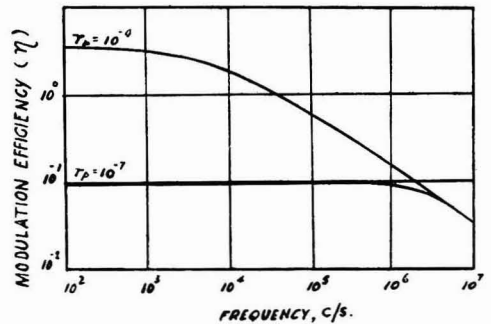


Fig. 14 — Typical η versus frequency curve with τ_p as a parameter for a p - n junction modulator with forward bias and parallel illumination (after McQuistan and Schultz⁵⁹)

should expect, of such a modulator, using parallel irradiation.

τ_p must be made the smallest possible in order to obtain the widest possible frequency response. It is to be noted that with a reduced τ_p , L is reduced, which, for a given injection, gives a steeper concentration gradient of holes. The diffusion current through the injection, therefore, increases, heating the diode and demanding a higher power of the modulating source. An alternative arrangement involving the use of a reverse-biased junction is, however, free from this trouble⁶¹. In this the signal voltage is made to vary the width of the depletion junction layer intervening the p and n regions and hence the total number of carriers encountered by the light beam in traversing the diode, for the total number per unit cross-section normal to the junction should be roughly $d_e p_p + (d_0 - d_e - d)n_n$, d_e , d and d_0 being the respective widths of the emitter, the depletion layer and the entire diode and $d \propto \sqrt{\text{junction voltage}}$. In this, absorption is predominantly due to the majority carriers p_p and n_n . The response time is, therefore, not limited by τ_p but by the product $C\tau_b$ of the junction capacitance and base resistance of the diode. The modulator should, therefore, have a wider frequency response with a much lesser modulating power requirement. Distortion is also smaller than in the previous mode and may be reduced to a negligible value by squaring the voltage and using parallel incidence⁶².

μ -Variation — It would be seen from relations (37) and (38) that k can also be varied by changing the mobility μ of the free carriers. This, as is now well known, may be done with the help of an externally applied electric field of sufficient strength to generate the so-called 'hot carriers'. Thus, for Ge, it has been shown⁶³⁻⁶⁵ that the drift velocity v_d of carriers follows a non-linear law of variation with external field tending to a limiting value of 10^7 cm./sec. when the field $E \approx 10^4$ V./cm. That means μ , as given by (dv_d/dE) , decreases with field strength tending to a value zero, the variation being as

$$\mu = \mu_0(1 - aE^2)$$

at low and

$$\mu = bE^{-1/2}$$

at high fields, a and b being constants. Experimental results show that satisfactory modulation should be obtainable with Ge for fields between 5×10^3 and 10^4 V./cm. Using the high field expression for μ stated above we have, for the small signal case $\Delta E \ll E_0$, E_0 being the bias value,

$$\eta' \approx \left[\frac{4jb'd\Delta E}{2E_0^{3/2}} \exp[-(k_0 + b'E_0^{-1/2})d] \right] \dots(43)$$

and

$$m' \approx \frac{b'd\Delta E}{2E_0^{3/2}} \dots(44)$$

when $\omega\tau \ll 1$, k_0 taking into account the background absorption due to sources other than free carriers; and

$$\eta'' \approx \left[\frac{4jb''d}{2E_0^{1/2}} \exp[-(k_0 + b''E_0^{1/2})d]\Delta E \right] \dots(45)$$

$$m'' \approx \frac{b''d\Delta E}{2E_0^{1/2}} \dots(46)$$

for $\omega\tau \gg 1$. If d is optimized Eqs. (43)-(46) reduce to

$$\eta' = \left[\frac{4jb'\Delta E}{2E_0^{3/2}(k_0 + b'E_0^{-1/2})e} \right] \dots(47)$$

$$m' = \frac{b'\Delta E}{2E_0^{3/2}(k_0 + b'E_0^{-1/2})} \dots(48)$$

$$\eta'' = \left[\frac{4jb''\Delta E}{2E_0^{1/2}(k_0 + b''E_0^{1/2})e} \right] \dots(49)$$

$$m'' = \frac{b''\Delta E}{2E_0^{1/2}(k_0 + b''E_0^{1/2})} \dots(50)$$

b' , b'' being the absorption coefficients for unit field. Eqs. (47)-(50) show that the lowest possible biasing field, consistent with the validity of the relation $\mu \propto E^{-1/2}$ and the requirement $\Delta E \ll E_0$, should be used. This rather adverse dependence on field is evidently the same and modulation indices roughly $\frac{1}{2}(\Delta E/E_0)$ for both the high and the low frequency approximations, provided background absorption due to sources other than the free carrier is small.

The response time of the mobility variation type of modulator should be limited by the relaxation time for the 'hot electrons', i.e. the time required to dissipate the excess energy gained from the field when it is switched off. This can be as low as 10^{-11} sec. for Ge. It is, therefore, possible by this method to achieve modulation even at microwave frequencies.

For high modulation frequencies the carrier frequency also tends to be high. Inspection of relation (37) reveals that for very high frequencies of radiation, e.g. infrared radiation, k tends to be small unless the doping is enough to make n large. This, along with the high value of field requirement mentioned above, makes severe power demand on the modulating source even up to the sub-mm. wave region. It is mainly on this account that the μ -variation type carrier absorption modulator is unlikely to be of much use except for low frequency waves modulated at frequencies much below its intrinsic permissible limit.

Impurity ionization variation — In an extrinsic semiconductor, at sufficiently low temperature, the free carrier concentration n can, in principle, be varied by varying E_I the ionization energy of the doping elements. A possible method for doing this may be visualized by recalling the facts outlined for an n -InSb carrier absorption detector. There, it had been seen, that a magnetic field may be used to control the separation between the impurity band and the conduction band edge. Putley's⁴³ experimental results suggest that for a sample with donor density 3×10^{14} /cm.³, E_I roughly varies from 5×10^{-4} eV. at 4000 oersteds to 10^{-3} eV. at 8000 oersteds, at low temperature. This also leads to a dependence of n on magnetic field — the average variation being as shown in Fig. 15. Thus, by superimposing on a steady field an alternating component simulating the modulating wave, n can be varied and hence modulation achieved through the use of varying impurity ionization. For

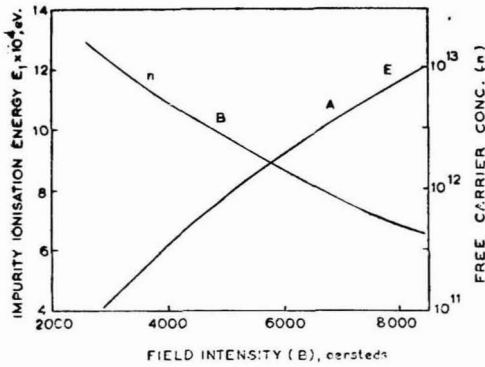


Fig. 15 — Variation of impurity ionization energy and carrier density with magnetic field in *n*-InSb at low temperature

appreciable depth of modulation with the sample mentioned above the alternating field should be 100 oersteds. This puts a fresh limit to the value of the highest usable modulation frequency, the power required for a field of this magnitude even in the Mc. range being of the kVA. order. The other limit arises out of the relaxation time of the majority carriers which is usually much less than τ_p . The success of the method, therefore, depends upon the possibility of having the required magnetic field at high frequencies without appreciable requirement of power.

Interband transition variation — An entirely different type of carrier absorption modulator may be derived by making use of the multiplicity of bands. The valence band in Ge, for example, is actually a complicated structure consisting of a collection of several bands whose relative disposition with regard to energy depends on the momentum vector k . The effective mass of free carriers occupying these different bands are different. Two of these bands are separated from each other by an energy 0.29 eV. in the vicinity of $k = 0$, the separation being largely independent of temperature (Fig. 16). Transition of a carrier between these two bands causes absorption of photon⁶⁶ in the range 3.4 μ . The absorption coefficient for the process is at least 10 times that of ordinary free carrier absorption. The extent of absorption also depends on the relative population of holes in the two bands, and this, in turn, depends upon temperature through the so-called distribution function of the free holes. Now, the temperature may be varied by making the carrier 'hot', as mentioned earlier, with the help of an appropriate electric field. Brown and Paige⁶⁷ have studied this possibility using *p*-type Ge at low temperature. Fig. 17 shows the trend of results obtained by these authors, for a lattice temperature 93°K. the maximum error in δT_n being ± 15 per cent. It is seen that for a 20° change in temperature the field required is no more than 250 V./cm. and that the δT_n - E relation is not badly non-linear in this region. A modulation depth of 10 per cent should, therefore, be obtainable with a modest expenditure of modulating power.

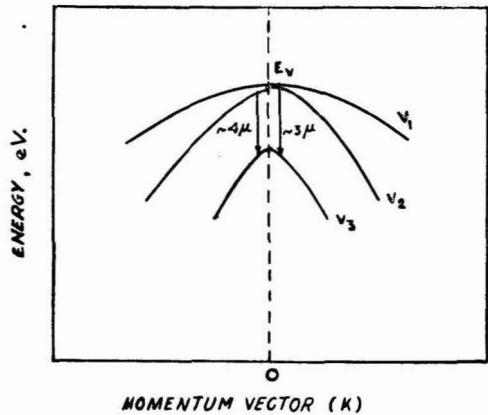


Fig. 16 — Multiplicity of valence band in Ge and the associated absorption

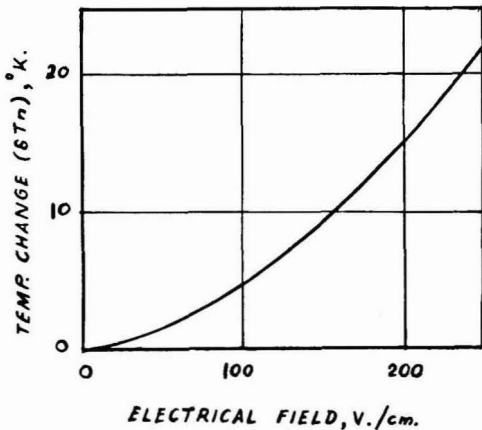


Fig. 17 — Hole temperature versus electric field strength in Ge at 93°K. (after Brown and Paige⁶⁷)

The response time of the device should be limited by the energy relaxation time of the free holes which has been estimated to be 10^{-11} and 10^{-10} sec. at 300° and 93°K. respectively. Thus the permissible modulation frequency extends up to the microwave range.

The main drawback of the method is the restricted wave band over which the effect can be observed. Only development of materials with the multiple bands separated by a wide range of energy values can overcome this limitation of a potentially powerful method of modulation.

Intrinsic Absorption

A beam of light passing through a thin slab of intrinsic semiconductor may create hole-electron pairs and get partially absorbed. The extent of absorption could be varied if it were possible to vary the intrinsic absorption coefficient. Such a variation may be realized by restricting operation near the absorption edge, where k varies sharply

with λ , and varying the edge itself through the application of a pressure or an electric field. The way a high pressure might affect the absorption edge is illustrated by the dotted curve in Fig. 6. It is seen that large pressure is required for the purpose. A varying pressure of such a magnitude is difficult to obtain at any reasonably high value of frequency. Very powerful ultrasonic generators may, in principle, extend its operation up to that band of frequency. But this cannot be considered to be a reasonable limit of performance for a practical modulator.

A different method, requiring small modulating power, is possible by utilizing the shift in absorption edge due to an electric field^{68,69}. Franz⁶⁸ has shown that for an absorption edge obeying the transmission law

$$A = A_0 \exp \alpha_1(\omega - \omega_0) \quad \dots(51)$$

ω_0 being the threshold angular frequency and α_1 a constant for a given material, an electric field E should result in a shift in ω_0 by an amount

$$\Delta\omega_0 = \frac{q\alpha_1^2 E^2}{12m^* \hbar} \quad \dots(52)$$

Moss⁷⁰ has experimentally obtained evidence for such a shift in highly resistive GaAs. For this material $\alpha_1 \approx 10^{-13}$ sec. and the energy equivalent (eV.) to $\Delta\omega_0$ is given by

$$\Delta E = 8.5 \times 10^{-16} E^2 \quad \dots(53)$$

E being in m.k.s. unit.

Fig. 18 shows the variation of transmitted signal intensity as a function of applied voltage obtained by Moss for a particular specimen of GaAs at the wavelength of optimum effect. The result clearly indicates possibilities of modulation^{55,71}.

Assuming the transmitted intensity to vary as per Eq. (51) and the field to be composed of a steady part E_0 and a varying part ΔE ($\Delta E \ll E_0$) we can, by using the method already indicated, obtain for GaAs

$$\eta \approx |j9.6 \times 10^{-13} E_0 \Delta E| \quad \dots(54a)$$

$$m = \frac{\Delta J}{J_0} \approx 2.4 \times 10^{-13} E_0 \Delta E \quad \dots(54b)$$

$$J'_0 \propto \exp(\sim 10^{-13} E_0^2) \quad \dots(54c)$$

A field strength of 10^7 V./m. is seen to be required for good modulation. Racette⁷² realized this with a small voltage using the depletion region of a reverse-biased p - n junction and obtained 3 per cent modulation of 9000 A. wave at 100 kc/s. The need for a high resistivity material was also thereby avoided. The same technique has also been used by Frova and Handler [Frova, A. J. & Handler, P., *Appl. Phys. Lett.*, 5 (1964), 11] to obtain modulation with reverse-biased Ge diode.

In spite of the high field required for modulation the power consumption is moderate since the carrier density in the GaAs used may not be more than $10^{17}/\text{cm}^3$ corresponding to a resistivity of 16^8 ohm cm. The fundamental response time may be 10^{-14} sec. In practice the capacitance of the specimen used would be a more stringent limiting factor. Nevertheless, as Moss has indicated, with a

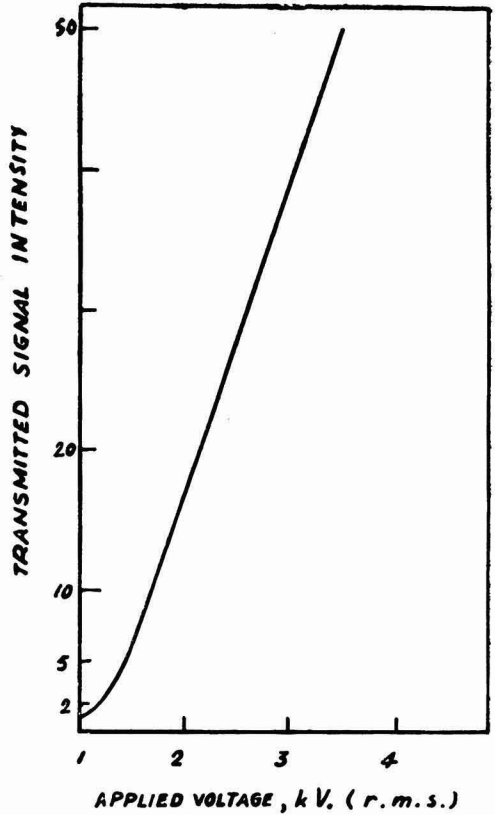


Fig. 18 — Transmitted intensity versus electric field strength in GaAs (after Moss⁷⁰)

specimen of 100 μ thickness and 1 cm.² area the limiting frequency may be as high as 3000 Mc/s.

With bulk materials the required high resistivity for low power consumption imposes a limit to the minimum band gap permissible. A value less than 1 eV. is unlikely to be of use and as such satisfactory operation should be possible with λ_0 value below the 1.2 μ limit. From this point of view Si, GaP, SiC are the other materials suitable for this type of modulators. Use of reverse-biased diode, of course, obviates the band gap limitation to some extent.

Extrinsic Absorption

As stated earlier, a magnetic field of sufficient strength may vary the impurity ionization energy in a material like n -InSb. Eq. (30) shows that extrinsic absorption varies directly as the coefficient of absorption. The latter depends upon the value of E_I . The nature of dependence is rather complex. Using the hydrogen model approximation, Lax and Burstein *et al.* have shown that near the extrinsic absorption edge the relationship between E_I and k is of the form⁴²

$$k = Q E_I^{5/3} / \nu^{8/3} \quad \dots(55)$$

Q being a constant.

Fig. 15 shows the type of variation obtained from the results given by Putley⁴³ for n -InSb over 10-1.8°K. This and Eq. (55) clearly establish the possibility of modulation. For appreciable modulation an a.c. field of about 100 oersteds may be required. Such a field at ultra-high frequency and microwave region may not be realizable owing to the high power requirement. Special circuit elements providing local concentration of energy density should serve well with thin samples. Operation at low temperature constitutes a hazard of the method. Owing to small value of E_I the extrinsic absorption method would be suitable for radiation in the mm. and sub-mm. wave band.

Landau splitting of energy levels in the conduction band might also occur due to the d.c. bias field making Eq. (55) invalid. In such an event modulation might still be possible because of the fact that absorption-wavelength curve has the form of a hump whose peak may be shifted by means of a varying magnetic field (Fig. 11).

A deep impurity level⁷³ and variation of E_I through an electric field as in intrinsic absorption permits realization of an extrinsic absorption type modulator free from the above limitations. Nevertheless, applicability of the hydrogen model to such impurities appears to be rather doubtful.

R'-Modulators

Eq. (2) giving the relation for R' does not permit us to visualize any ready method of variation of the parameter. A variation in k will certainly promote k -modulator action and a practicable method of varying ϵ is difficult to be realized (ref. 74). A different approach would be to make use of a surface space charge layer and change the electrical state of the layer without affecting the bulk. A surface layer (thickness $\sim 10^{-4}$ cm.) contains excess of carriers lodged in the surface states and is more readily formed in a specimen of higher resistivity. A beam of light traversing the specimen and incident at the boundary face at an angle greater than the critical value cannot undergo total reflection owing to the absorption due to these carriers. Such 'frustrated total internal reflection' lowers the value of R' from unity. It is possible to enhance the effect by using a long slab in which the ray is allowed to undergo a number of successive 'frustrated reflections' at the boundaries. Harrick⁷⁵ has utilized the method to study the problem of surface states in Si over the wavelength range 1.5-4 μ . In this experiment the so-called field effect mobility was varied by means of a bias voltage applied across the layer. Seraphin and Orton⁷⁶ have used the same technique to devise an optical modulator. The field effect mobility is defined as

$$\mu_E = \frac{d(\Delta G_0)}{d\Delta S} \quad \dots(56)$$

ΔG_0 being the conductance and ΔS the charge per unit surface area.

Now, ΔG_0 is given by

$$\Delta G_0 = q(\mu_p \Delta p + \mu_n \Delta n) \quad \dots(57)$$

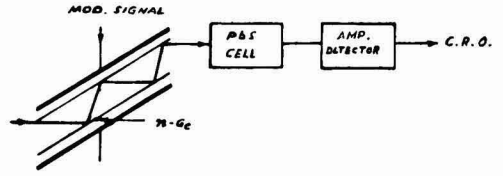


Fig. 19 — Arrangement in a modulator using frustrated total reflection (after Seraphin and Orton⁷⁶)

and

$$\Delta S = CV \quad \dots(58)$$

Δp and Δn being the excess hole and electron per unit area of the layer; C , the capacitance per unit area; and V , the voltage across the layer.

If the ray travels from interior towards the surface to meet it at an angle θ (Fig. 19) then, since it traverses the surface twice, we should have

$$J_0 = J'_0 \exp \left[-\frac{2}{\cos \theta} (\alpha_p \Delta p + \alpha_n \Delta n) \right] \quad \dots(59)$$

If the absorption coefficient $(\alpha_p \Delta p + \alpha_n \Delta n)$ is small, then

$$\frac{\Delta J}{J_0} = \frac{2}{\cos \theta} (\alpha_p \Delta p + \alpha_n \Delta n) \quad \dots(60)$$

Using Eqs. (57)-(60) and putting $\mu_p \sim \mu_n = \mu$, $\alpha_p \sim \alpha_n = \alpha_0$

$$\eta = \left| \frac{8j\alpha_0 C}{q\mu \cos \theta} \mu_E \Delta V \right| \quad \dots(61a)$$

and

$$m = \frac{2\alpha_0 C}{q\mu \cos \theta} \mu_E \Delta V \quad \dots(61b)$$

With a 30 ohm cm. sample having a dimension permitting four internal reflections and an arrangement shown in Fig. 19, Seraphin and Orton could modulate the light from a tungsten lamp (2.5 μ) at 85 c/s., the depth of modulation rising linearly with modulating voltage attaining about 4 per cent at 225 V. peak for an accumulation layer. Second harmonic distortion was also observed. In particular, the modulation was predominantly at the second harmonic frequency at the stage when the surface layer changed from n - to p -type. The speed of operation was limited by the minority carrier lifetime for a depletion and majority carrier relaxation time for an accumulation type layer. Hence, with the latter type of layer the method is capable of giving modulation up to the microwave frequency range — provided relation (56) holds at those frequencies. As regards power drainage, the field developed was 3×10^5 V./cm. and with a 30 ohm cm. sample of 1×0.1 cm. face and 200 V. signal the V.-amp. required can run into the kVA. order. It is also claimed that the small modulation depth obtained may be amplified to a considerable extent through the use of interferometric technique in a properly matched multilayer arrangement⁷⁷. Experimental realization of a high frequency and high depth of modulation following up these ideas

should make this method of R' -modulation a powerful technique in the far infrared and sub-mm. wave ranges.

π -Modulators

If the principal planes of the polarizer and the analyser (Fig. 12) are set at 45° , the intensity of the beam coming out of the system in the absence of a field would be half of that emerging out of the sample. A modulated transmitted intensity would, however, result if the plane of polarization is rotated by means of a field while passing through the sample. Such a rotation is obtained in Faraday effect due to a magnetic field. This is observed whenever the right- and the left-handed circular components of a plane polarized beam have different phase constants in the material of the sample. The effect has been studied in elemental and compound semiconductors and may arise out of both the free carriers and the intrinsic material⁷⁸⁻⁸⁰.

Free Carrier Modulator

For this case, when the condition $\omega\tau \gg 1$ is satisfied, and the applied magnetic induction is not large the rotation per unit distance is given by

$$\theta = \frac{1}{2}\mu Bk \quad \dots(62)$$

where k is the free carrier absorption coefficient. A propagating wave evidently suffers absorption due to free carriers unless k is low. Thus, for good rotation with small absorption, μ must be the maximum possible for a given field. n -InSb having $\mu = 7 \text{ m}^2/\text{V. sec.}$, therefore, should be the most desirable material. As m^* is also very low, Eq. (37) would show that an overall substantial margin of excellence in respect of the product μk is expected.

Generally μ increases with decrease in temperature but not so much the product μk . More detailed theoretical consideration⁷⁸ has shown that for acoustical phonon scattering θ in Ge increases on cooling up to nearly the liquid N_2 temperature. A subsidiary disturbing effect is, however, that the beam also tends to become elliptically polarized on account of the attenuation constant for the right- and the left-handed components, being slightly different; the ellipticity also tends to increase with lowering of temperature. With n -Ge (Fig. 20) ellipticity is zero for a field giving maximum θ ; but apart from the quite large field required for realization of such a condition, this also makes $d\theta/dB \approx 0$. In any event, a field of the order 10^3 oersteds is required to give a reasonably good modulation with a sample of manageable length. Realization of such high fields even over short distances is a problem at high frequencies and this limits good performance at such frequencies even though the fundamental process itself has sufficient speed of response to ensure good operation up to the microwave range. Thus Moss⁵⁵ points out that even with InSb at 77°K. and 1 MW. power at 10 cm. flowing down a waveguide the maximum modulation expected is 20 per cent.

Intrinsic Rotation Modulation

The vexed problem of background absorption is avoided through the use of intrinsic Faraday rota-

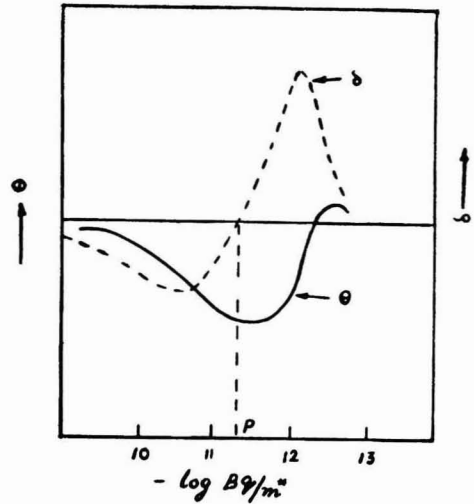


Fig. 20 - Variation of Faraday rotation and ellipticity with magnetic field in Ge (after Donovan and Webster⁷⁹)

tion due to an undoped sample of semiconductor. Pronounced rotation of this type is obtainable near the absorption edge λ_0 of the material⁷⁹. According to classical treatment the rotation θ for the intrinsic case is given by

$$\theta = \frac{q}{m^*c\lambda^2} \frac{dn'}{d(1/\lambda^2)} B \quad \dots(63)$$

n' being the refractive index. To avoid absorption λ must be larger than the threshold value λ_0 . For such a wavelength region $dn'/d(1/\lambda^2)$ has been found to be a constant for Ge and hence a much stronger effect will be observed at shorter wavelengths⁸⁰. The optimum effect has been found in the 2-2.5 μ region at 300°K. giving a $20^\circ/\text{cm.}$ rotation for 10^4 oersteds. The value rises to $25^\circ/\text{cm.}$ and the optimum wavelength increases to 3-3.5 μ at 77 K. As the question of absorption is of secondary importance rotation can, in principle, be made large for a given B by increasing the length of the region over which B is active. In the high frequency range, however, maintenance of an appreciably large value of field over a long path is a difficult problem. Speed of response is again limited by the difficulty in obtaining high fields at high frequencies.

It may be noted that the transmitted intensity at high values of θ should vary as $(1 - \sin 2\theta)$. Hence, if θ could be made large to ensure adequate modulation depth, the problem of distortion will tend to complicate matters to an increasing extent.

Other Methods

Quite a number of modulators which differ in details from the types described above are known^{81,82}. All the modulators described above work external to the source generating the radiation. As opposed to these there may be internal modulators which act directly on the generators themselves.

Some of these modulators will be mentioned in the section on 'Generation'.

Apart from amplitude modulation one can also think of frequency modulation or phase modulation. Such modulations are also best effected internally.

Polarization Modulation

In a recent publication a system of communication involving polarization modulation has been discussed⁸³. A polarization modulated wave can be obtained with the help of a suitable semiconductor immersed in a magnetic field. As stated above, Faraday rotation of a plane carrier in Ge has been shown, in general, to be accompanied by a transformation of the wave to an elliptically polarized one⁷⁸, the sense of rotation of the ellipse changing with change in the sign of B . For high frequencies and weak field the ellipticity δ is linearly related to the field B and its length l , and increases with lowering of temperature. It has been shown that with $B \approx 1000-3000$ oersteds, $|\delta|$ might be as high as 0.8 at 200°K. A biasing field of this order and modulating signal of 100 oersteds should give good modulation. This obviously would restrict the highest frequency of modulation. The attendant background absorption and Faraday rotation modulation also make things complicated. Use of a bias value for which Faraday rotation is zero is of little help as, with such values, the δ - B curve tends to pass through a maximum implying $d\delta/dB = 0$. It appears that a value for which $\delta = 0$ is occupied by a maximum of Faraday rotation curve. This latter condition (point P in Fig. 20) of operation would give a solution of the problem provided the detector is sensitive to the sense of rotation of the elliptically polarized beam. The field required for good modulation at such a point is, however, excessive.

Thus a number of possibilities exist for use of semiconducting materials as low frequency modulator of optical and sub-mm. waves. At least two methods are also available for modulation up to the microwave frequencies. But low depth of modulation seems to be a common feature of all the various schemes. Polarization modulation may also be possible using some of the available semiconductors.

GENERATION

The primary requisite for any communication system is a means of generation of a coherent carrier wave. It is, therefore, important to examine the possibilities semiconducting materials and devices offer in the generation of such waves over the optical and sub-mm. wave bands. A perusal of the literature shows that such possibilities are indeed quite many and may be broadly classified under three heads: conventional junction and point contact devices, plasma and negative resistance devices using bulk materials, and lasers using both junction devices and bulk materials.

Conventional devices like parametric and tunnel diodes of new design are steadily extending the range of operation beyond the cm. wave band. Such operations have been achieved in the mm.

wave region⁸⁴ and it is likely that in the coming years the frontier of sub-mm. wave band will have been crossed. The basic theory of operation of these devices has been discussed in a number of books and we shall not go into any further consideration of these here.

Most of the negative resistance type of devices are still in the realm of theoretical possibility. Various ways for realizing negative resistance have been suggested in the literature, e.g. the negative mass device⁸⁵, the impact ionization devices^{86,87}, the crossfield⁸⁸ and the transfer electron devices⁸⁹. Some of these require operation at extremely low temperature. Devices involving purely plasma and phonon interaction type oscillations in semiconductors have either certain technical difficulties which remain to be overcome⁹⁰ or yet to be extended to the wave band under discussion⁹¹. The last category, viz. laser, has made some remarkable headway towards practical realization^{92,93} and the remaining portion of the paper may be devoted solely to a discussion of such devices and to subsidiary techniques based on their use.

Semiconductor Lasers

Quite a few ideas have been advanced regarding the achievement of laser action using semiconducting materials^{94,95}. The basic principles involved in these methods may be classified as transitions involving (i) Landau levels and (ii) recombination radiation. No satisfactory experimental technique has yet been found for a practical laser of the first type; however, experimental work on some members of the second type using junction diode as the laser element has been quite substantial in recent years^{96,97}.

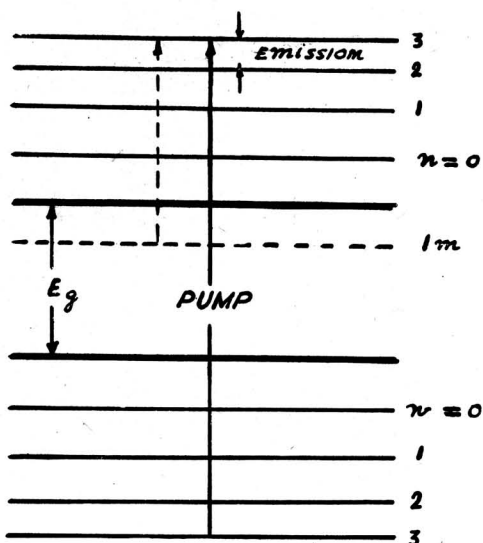
It is known that an ordinary laser using gas or crystal-like ruby depends for its operation on an 'inverted population' having a larger number of particles in the higher of the two states between which the desired transition occurs. A laser based on transitions involving Landau levels also works in the same fashion. Such a picture is not, however, immediately obvious in the recombination radiation type lasers. Operations of these are more easily stated in terms of a negative absorption coefficient or a negative temperature.

Landau Levels and Cyclotron Frequency Lasers

As stated earlier, with sufficiently low temperature and a steady magnetic field the energy levels in the valence and the conduction bands of a semiconductor may be quantized. Quantization occurs in a direction normal to the direction z of the field, the Landau levels (Fig. 21) in the simplest case being given by⁹⁸

$$\left. \begin{aligned} E_{cn} &= (n + \frac{1}{2})\hbar\omega_c + \frac{\hbar^2 k_{cz}^2}{2m_e^*} + E_g \\ E_{vn} &= (n + \frac{1}{2})\hbar\omega_h + \frac{\hbar^2 k_{vz}^2}{2m_h^*} \end{aligned} \right\} \dots (64)$$

where m_e^* , m_h^* are the electron and hole effective masses; ω_c , ω_h , the corresponding cyclotron frequencies (B^q/m_e^* , B^q/m_h^*); k_{cz} , k_{vz} , the z -components



$$n > \frac{Ah\lambda}{16\pi^2\mu^*\tau Q_L} \dots(64a)$$

Fig. 21 — Principle of operation of a cyclotron resonance laser

of the wave vector for the conduction and valence bands, the energies being measured from the valence band edge. Transitions between consecutive levels which are spaced $\hbar\omega_c$ in the conduction band should, therefore, lead to emission or absorption of radiation having the frequency ω_c . Band to band transitions are governed by the rule $\Delta n'' = 0, \Delta k = 0$. For Ge, Si, InSb and similar semiconductors the complexities in energy bands, however, make the Landau levels non-equidistant, the spacing decreasing with increasing n'' -values. The energy level diagram should, therefore, be as shown in Fig. 21. With an optical pump having energy $E_{c3} + E_{v3}$ valence band electrons may be excited to level 3 in the conduction band in sufficient number to make its electron population higher or inverted with respect to level 2. If the sample is placed in a resonator tuned to the frequency $(E_{c3} - E_{c2})/h$, a small signal at the frequency should promote stimulated transition from level 3 to 2 as shown in Fig. 21 causing release of energy in phase with itself. Upward transition through absorption is, of course, prevented by the non-equidistant level spacing mentioned above. The frequency of the emitted line depends upon the magnitude of the applied magnetic field. In order that the spectral line is well defined and its width not made appreciable by the energy of thermal motion, i.e. KT_0/h , the field should be high and the temperature low. For Ge the values desirable are 10^5 oersteds at $4^\circ K$. With such conditions satisfied, cyclotron frequency radiation can be generated if the gain through stimulated emission makes up for the losses in the resonator. In terms of the loaded resonator quality factor Q_L , the relaxation time τ , the electric dipole moment μ^* , and the wavelength λ the requirement on this account is

A being the area of the resonator end plates. The most severe requirement arises out of τ which in the present case $\approx 10^{-12}$ sec. and μ^* is also $\approx 10^{-15}$ e.s.u. Only a Q_L of sufficiently high value can overcome this difficulty to some extent. Current developments in generation of high magnetic fields permit operation of a cyclotron frequency laser up to the 100μ region using a material like InSb having a small effective carrier mass. At such wavelengths a Fabry-Perot type resonator could be used⁹⁹. In the mm. wave range such resonators have been designed¹⁰⁰ to have Q_L value up to 10^5 . This trend of resonator design and the development of extremely powerful optical masers suitable as pumps should widen considerably the prospects of a practical cyclotron frequency laser, the requirements of which have been outlined by Lax⁹⁸.

Cyclotron frequency laser involving impurity levels — In principle it is also possible to obtain laser action with a doped sample having a rather deep impurity level (I_m in Fig. 21) and a pump that promotes transition from this level to one of the higher Landau levels — the consequent population inversion and the stimulated emission being obtained through the same mechanism as above. These should obviously be the laser analogue of the tunable detector mentioned earlier. The limitation due to low relaxation time will also affect such a laser. Further, as the available impurity centres are much less than the valence band electrons, pumping requirement would be more stringent unless a sufficiently rapid process is available for recombination of the electron in the lower laser level with the impurity centres. This requires a low carrier lifetime.

Recombination Radiation Laser

Operation of this class of laser depends upon processes inverse of those involved in intrinsic and extrinsic photoconduction. Recombination of a pair of free electron and hole by a process results in emission of a photon of energy identical with that of the photon required to be absorbed for creation of the pair by the same process taking place in the reverse sequence.

The simplest of the processes involves a direct union resulting from a conduction band to valence band transition. In such a case the frequency of the emitted radiation is given by E_g/h and the momental vector k is zero for both the relevant bands such that $\Delta k = 0$. The more well-known semiconductors do not, however, have the valence band maximum and conduction band minimum at the same point in the k space (Fig. 22). For these photo effect may be possible for $h\nu$ less than the direct band gap energy (which is 0.8 eV. for Ge) provided an additional partner participates in the process to conserve the k -value. This may be a phonon provided by the semiconductor lattice itself, giving rise to an indirect band to band transition assisted by a phonon, and for this the recombination radiation emitted will be shifted towards longer wavelength tending ultimately to the value

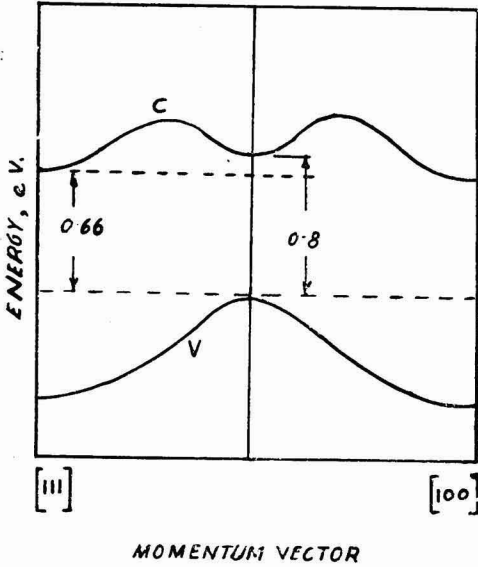


Fig. 22 — Details of band edges in Ge showing the energy associated with direct and indirect transitions

of the energy gap between the valence band maximum and the conduction band minimum. The phonon itself can disturb the energy only to a very small extent.

An electron and hole, owing to the Coulomb force of attraction, form a hydrogen-like combination and exist in the so-called 'exciton state'. Indirect recombination is, therefore, possible after the pair has formed an exciton state. Recombination involving an intermediate impurity or trap level is also possible. In one such case an electron settles down on a trap and awaits the arrival of a hole to undergo recombination. Evidently $h\nu < E_g$ for such a process. Recombination radiation had been observed in many semiconductors for both the direct and the indirect type of reactions^{101,102}. In principle, laser action is, therefore, possible through anyone of the recombination mechanisms^{103,104}.

Direct band to band transition — Let us consider a semiconductor device in which the free electrons and holes are characterized by Fermi levels F_n and F_p respectively, the corresponding Fermi distribution functions being f_c^k and f_v^k and the transitions occurring when there is a radiation field $h\nu$ having a density $\rho(\nu)$. Under this condition photon emission and absorption processes contend with each other. The time rate of photon absorption A_a is proportional to the product of the probabilities that a hole state is occupied and an electron state is vacant and to the available density $\rho(\nu)$, i.e. to

$$f_v^k (1 - f_c^k) \rho(\nu)$$

Similarly, the time rate of emission induced, A_e , is proportional to

$$(1 - f_v^k) f_c^k \rho(\nu)$$

It may be shown that the constants of proportionality are equal. For laser action the net absorption coefficient should be negative, implying thereby that emission must dominate absorption and hence

$$(1 - f_v^k) f_c^k > f_v^k (1 - f_c^k)$$

As f is of the form $1/[1 + \exp(E^k - F)/KT_0]$ and

$$E_c^k - E_v^k = E_g = h\nu \quad \dots(65)$$

the above inequality requires

$$F_n - F_p > h\nu \quad \dots(66)$$

E_c^k and E_v^k being respectively the energy values for the conduction and valence band states between which transition promoted by radiation takes place.

Now, for non-degenerate materials Fermi levels are both within the band gap while for degenerate ones at least one of these lies within a band. In view of this and the fact that for direct photo effect $h\nu \geq E_g$, condition (66) implies that a laser involving the direct process can be realized if degeneracy exists in respect of either electron or holes or both¹⁰³. The situation can be realized with a *p-n* junction¹⁰³ diode with at least one region composed of degenerate material (Fig. 23). [It has been argued that Eq. (66) is not quite valid at high injection density making the requirement conditional¹⁰⁶. With carrier injection thermal equilibrium is disturbed and F_n and F_p are then treated as the so-called quasi-Fermi levels.] Now degeneracy is more readily obtained in materials having a low effective carrier mass. As such InSb or InAs should be very convenient materials for a laser diode. For these, as Table 1 shows, emission should be in the 5 and 3 μ regions. Recombination with photon emission occurs profusely when the diode is forward-biased at high injection density. This, of course, also means a greater loss of radiation on account of free carrier absorption. Collisional broadening of the spectral width of the emitted radiation also occurs when the carrier density is high. Hence laser action is generally obtained at sufficiently low temperature. It is to be noted that condition (66) is necessary but not sufficient for generation of sustained oscillations unless the inequality has been satisfied to an extent so as to make up for losses inherent in the system. This is determined by the Q_L -value of the cavity and may be made up only through adequate cooling and injection current density¹⁰⁷. A relation

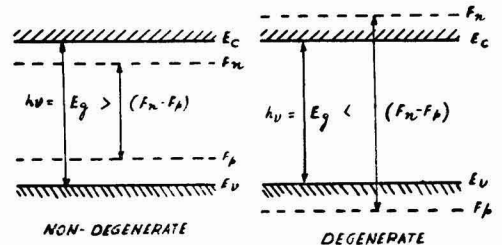


Fig. 23 — Laser diode requirement for direct band to band transition

proposed for the threshold current density required with a Fabry-Perot type cavity of length l is¹⁰⁸

$$J\tau = \frac{qn'(1/R')}{\beta l} + \frac{\alpha''}{\beta} \quad \dots(67)$$

where the index α'' is the loss, and β is related to gain G as

$$G = \beta J\tau \quad \dots(68)$$

Working on the ideas detailed above quite a number of successful junction lasers had been developed. In all these, cavities were the junctions themselves which had been cut and polished to proper dimensions with the end walls silvered so as to be resonant at the frequency of the expected radiation. Technical information¹⁰⁹⁻²⁵ with regard to a few typical members of such lasers are given in Table 3.

It may be noted that there appears to be an optimum range of injection current for good laser action; heating at too high a value affects the performance¹²⁶. Efficiency appears to be quite high (60 per cent at 20°K.) for diodes of good design¹²⁷.

Stimulated emission has also been observed in a tunnel diode¹²⁸. A particularly interesting suggestion, in this connection, is the use of simultaneous tunnelling of electrons to conduction band and injection of holes to achieve laser action in a composite junction structure which should permit independent amplitude and frequency modulation of the generated radiation¹²⁹.

The devices under discussion also hold the promise of being tunable over a finite range. Laser radiation from InSb diodes have been found to shift to shorter wavelength with a strong applied magnetic field^{130,131}. This is to be expected in view of the magneto-optical shift in band edges. A simultaneous decrease in the threshold current has also been noticed¹³². Hydrostatic pressure has also been found to shift the wavelength for coherent emission. The observed shift at 200°K., however, appears to be smaller than the expected shift in band gap¹³³.

Internal modulation of output — The radiant output of a junction laser of the type discussed above can, in principle, be modulated internally in a number of ways. The field and the pressure dependences of band gap¹³¹ constitute two possible methods of frequency modulation of the output of a GaAs laser. The former should cover a wider band. But it has to be remembered that the material is now a highly doped one and any appreciable depth of modulation would, therefore, require much larger power. A magnetic method may be used to obtain frequency modulated output from an InSb and InAs laser¹³². The frequency deviation with the magnetic method is not expected to be high. For larger deviation the cavity, which happens to be the junction itself, must be designed to have an adequate bandwidth.

The dependence of the luminous output on the injected current provides a ready method for amplitude modulation. The highest frequency of operation

TABLE 3 — CHARACTERISTICS OF SOME SEMICONDUCTOR JUNCTION LASERS

Material	Temperature °K.	Pump current	λ A.	$\Delta\lambda$ A.	Power output W.	Remarks	Ref.
GaAs	77	10 ⁴ amp./cm. ²	8500 (Si doped n-region) 8420 (Te doped n-region)	10-15	—	—	109, 110
	77	Pulsed 100 amp. at 50 μ sec.	8460	—	20	Harmonic power 10 μ W.	111
	20	—	—	—	3	Sum and harmonic frequencies also detected	112
	4.2	1100 amp./cm. ²	8326	0.5	—	Allowed S to diffuse in Zn doped material	113
	2 (continuous wave operation) 78 (Pulsed operation)	—	—	4175	—	1.6 $\times 10^{-13}$ Second harmonic. Fundamental power 5 $\times 10^{-3}$ W.	114
InSb	4.2	2.15 $\times 10^4$ amp./cm. ²	—	—	—	—	115
InAs	77	—	31500	35	—	—	116
InP	77-42	80 amp./cm. ²	9030	1	—	—	117, 118
			9100	—	—	—	
InP _{1-x} As _x	77	6.3 $\times 10^3$ amp./cm. ²	—	—	—	50 per cent molar conc. of phosphide	119
(In _x Ga _{1-x})As	—	—	20700 17700	—	—	—	120
SiC	—	120 amp./cm. ²	4560	5	—	Validity questioned by Hall	121, 122
GaAs	298	10 times that required at 77°K.	—	25	—	Room temperature operation. At 77°K. $\Delta\lambda$ reduced to 1.5 A.	123
GaP	—	10 ma. at 2 V.	7000	—	Very intense	Coherence not reported. Specially fabricated polycrystalline wafer used	124
Ga(As _{1-x} P _x)	77	—	6470	—	—	—	125

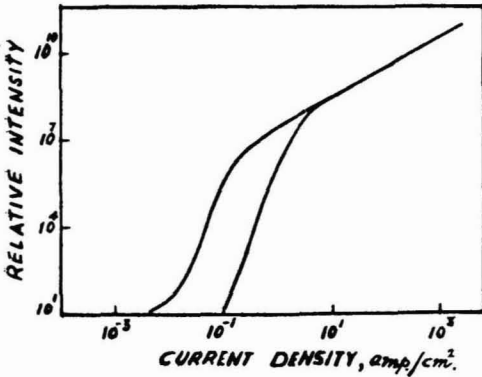


Fig. 24 — Luminous output versus injected current in GaP diode (after Grimmeiss and Scholz¹³⁷)

is determined by the reciprocal of the radiative recombination lifetime of hole-electron pairs and this, fortunately, is extremely low. For GaAs at least a linear output-current relation does not appear to be realized over a wide range¹³⁴⁻³⁶. Compensation of second harmonic distortion has, however, been shown to be possible¹³⁶. Further, as stated above, coherence is also affected beyond a limited range of current densities¹²⁴. Development of properly doped and alloyed diodes may, however, help to improve the situation, as has been reported recently for GaP diode¹³⁷ (Fig. 24). One drawback is the high level of current densities normally required for laser action in many cases. Any useful depth of modulation will, therefore, require a correspondingly high modulation power density. Goldstein and Welch¹³⁸ have recently reported successful modulation of GaAs laser output at 2 Gc/s., the modulation depth achieved being 7 per cent.

Indirect band to band transition — As stated earlier, light emission at wavelengths larger than the threshold value corresponding to the direct band gap of the semiconductor may be possible if the recombination of a hole-electron pair takes place indirectly through the assistance of a third body. The latter may be a phonon, an exciton state or any impurity state. Laser action can, in principle, occur for each one of the three processes^{139,140}. The conditions under which laser action may be obtained in such devices are discussed below.

Phonon assisted transition — Emission or absorption of a photon in such a transition is accompanied by emission or absorption of a phonon. At low temperatures phonon density is extremely low and hence an indirect absorption process becomes very rare. Under such conditions emission might outweigh absorption giving an effectively negative absorption coefficient or a negative temperature. The problem may be analysed in the same manner as in the case of direct transition, except that $h\nu \leq E_g$ and for electron and hole coming from the band edges,

$$h\nu = E_g - h\nu_p \quad \dots(69)$$

ν_p being the phonon frequency. Condition (66) has,

therefore, to be replaced by

$$F_n - F_p > E_g - h\nu_p \quad \dots(70)$$

which is a somewhat less stringent condition. Fig. 22 shows that laser action for such a case should be obtained with non-degenerate semiconductors as well. Nevertheless, it has been argued that with degenerate materials alone can an indirect band gap semiconductor yield laser action. Calculations show¹³⁷ that for Ge and Si condition (70) should be fulfilled below 10°K. Practical consideration dictates overfulfilment of condition (70) in order to make up for the various losses. Assuming that the only loss is due to free carrier absorption, Basov *et al.*¹³⁹ gave the following requirement for laser action:

$$Q > \frac{16\pi KT_0 \alpha_e \tau_R (n_0 + p_0)}{k \tau_p h \lambda^2 y^2 \exp(-y)} \quad \dots(71)$$

where Q is the excitation density given by the incident quantum flux; k , the absorption coefficient of the exciting radiation; α_e , the cross-section for photon absorption by free electron; $y = (h\nu_p + h\nu - E_g)/KT_0$; τ_R , the lifetime for indirect radiative transition; and τ_p , the unbalanced carrier lifetime. For Ge at 4°K., $\lambda = 1 \mu$, $\tau_p \approx 10^{-4}$ sec. the condition is shown to be $Q > 5 \times 10^{16}$ quanta/cm.² sec. In terms of Q_L of the cavity, the condition required for non-degenerate bands with single phonon participation has been shown to be⁹⁴

$$n\dot{p} > \frac{2\pi\sqrt{\epsilon} m_0 p_0}{Q_L k_c \exp(-h\nu/KT_0)} \quad \dots(72)$$

k_c being the coefficient of band to band absorption. Basov *et al.* pointed out that at high excitation rate τ_p may become considerably smaller than the value ordinarily encountered. The required rate of excitation is, therefore, likely to be much higher than the value estimated above, making cooling of the sample a difficult problem.

Indirect transitions involving exciton states — Indirect transition via an exciton state might also lead to laser action. Basov *et al.* have also examined this case and shown that the necessary condition for this is

$$n\dot{p} > n_0 p_0 \exp[-(h\nu_p + e' - E_g)/KT_0] \quad \dots(73)$$

e' being the exciton energy. This, it may be shown, is practically the same as condition (70). The condition when the loss is due only to absorption leading to ionization of exciton leads to the requirement

$$\alpha_i < \frac{\lambda^2}{8\pi\epsilon\Delta\nu\tau_e} \quad \dots(74)$$

where α_i is the cross-section of photoionization; $\Delta\nu$, the width of the exciton radiation; and τ_e , the exciton lifetime for radiative decay. For Si the condition has been shown to be realizable. For losses arising out of lattice and impurity absorption the condition becomes

$$n_e > \frac{8\pi\epsilon\Delta\nu\tau_e k_e}{\lambda^2} \quad \dots(75)$$

in which n_e is the exciton density and k_e the effective coefficient of absorption of the emitted radiation by the lattice and the impurity centres. Cooling helps to reduce $\Delta\nu$ and hence makes the realization

of conditions (74) and (75) easier. Further $\tau_e \ll \tau_R$. Hence, the exciton mechanism should require a lower excitation rate and a consequently easier cooling [Eq. (71)].

Transition involving impurity states—The most general mode of recombination of a hole-electron pair is the three-body process via an impurity state. A two-step process in which an electron settles on an impurity before recombining with a hole also leads to emission in the range $h\nu < E_g$. For an acceptor-like impurity capturing a free electron, radiation having any energy between $E_{g/2} - E_g$ should be obtainable. Such recombinations are indeed quite plentiful in Ge and Si at low temperatures and promise a small $\Delta\lambda$ as the captured electron and hole become immobilized and devoid of thermal motion. The necessary condition for laser action through this process is of the same form as Eq. (69). For oscillations to be obtained with a cavity the condition takes the form

$$n > \frac{2\pi\nu\tau_i\rho_0\Delta\nu}{Q_L} \quad \dots(76)$$

where ρ_0 is the density of modes of resonance and τ_i the lifetime of a carrier until radiative capture by an impurity atom. Condition (76) is more readily realized with smaller value of $\Delta\nu$ and τ_i . For the latter to be small, the density of impurity atoms should be high. In principle, the effect may be realized with non-degenerate semiconductors.

Aigrain¹⁰² had obtained laser action in a *p-n-i-p* junction device using indirect transitions. Pumping used was sufficient for creation of 10^{17} hole-electron pairs per second. Evidence for exciton recombination radiation in a GaAs junction with injected current exceeding 0.1 amp./cm.^2 has also been obtained by Wilson¹⁴¹. A class of composite junction structure has been used for successful indirect type of lasers¹⁴². It is likely that indirect transitions, e.g. those involving donor levels¹³¹, had contributed somewhat to many of the laser actions reported so far with junction devices. Nevertheless, experimental evidence for purely indirect transition type laser is still largely lacking in view of the fact that degeneracy of materials and near equality of the emitted radiation energy with the band gap value had been a common feature with almost all the successful semiconductor lasers reported so far.

Subsidiary Techniques of Generation Using Laser

Apart from its direct use as laser material, a semiconductor may also find use as subsidiary material in the generation of radiation of new wavelength, using the output of other types of lasers. Mention has been made earlier of the heterodyne type of optical detectors using such materials. The non-linear property which makes such a device possible may be utilized in mixing the outputs of two lasers to obtain oscillations at a different frequency. The technique would be suitable for generation of sub-mm. waves. Semiconductor lasers like the GaAs diode have also been applied as a pump source for other types of laser and this constitutes another significant utility of such devices in the generation of waves over new frequency bands¹⁴³.

Oscillations at lower frequencies can also be generated through parametric action. A non-linear dielectric material is a suitable medium for this purpose¹⁴⁴. Crystals like KDP and ADP have been mentioned in literature as good materials for parametric devices in the optical frequency range. Existence of such non-linearity in GaAs made possible the generation of second^{74,114} harmonic radiation, as reported in Table 3. The amount of harmonic power obtained showed that as a non-linear dielectric material GaAs may serve this purpose even better than KDP¹¹⁴. For the degenerate mode of operation, another laser of adequate power operating at double the desired frequency will be required as the pump and the sample of material so fabricated as to be simultaneously resonant with two frequencies. The pump frequency must, of course, be remote from any of the characteristic absorption frequency of the material promoting photoionization.

To summarize we note that the direct radiative transition type of semiconductor lasers are promising as generators of coherent radiation from near violet (SiC) to about 5μ (InSb) range. The Landau level type, on the other hand, holds promise for radiation from the sub-mm. to about 100μ range. The latter, however, depends on the availability of a powerful optical pump at the right frequency. For the region between 5 and 100μ the indirect transition type of devices could be used if successfully developed. The mixer and parametric types of generators are likely to be of use over longer bands of wavelength. Prospects of realizing recombination laser action in indirect band gap materials appear to be rather meagre unless extremely heavy doping is made use of^{145,146}. Many of the semiconductor lasers reported so far are inferior to other types of lasers in respect of purity of spectrum and power output. Much, of course, remains to be achieved in these directions.

SUMMARY

A critical account is given of the major experimental and theoretical considerations of the application of crystalline semiconducting materials for detection, modulation and generation of radiation from the sub-millimetre to the optical wave band. Simple expressions are given for the responsivity, frequency response and sensitivity of the various types of thermal and optical detectors and the relative merits of the more well-known semiconductor materials for detection. The performances of the different types of detectors are compared. It is pointed out that the thermal detector using Si and Ge at low temperature and 'self-cooling' can, in principle, have a fast response and hence a wider frequency limit of operation than achieved hitherto. Modulators are classified from the standpoint of basic physical principles involved. Analytical expressions are given for the modulator efficiency and the depth of modulation for most of the types of these devices. The problem of frequency response is also considered. It is pointed out that modulation may also be carried out through transitions involving impurity levels. The possibility of polarization modulation using Ge is examined. The principles of operation of the different types of

semiconductor laser are outlined and the conditions under which these should operate discussed. Methods of internal modulation and generation of new radiation through mixing and parametric action are also indicated.

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Some Aspects of the Electrochemistry of Passivating Systems*

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SEVERAL electrochemical studies on passivating systems have been in progress at this Institute.

The studies relate to the behaviour of corroding systems, potentials of corroding metals, the mechanism of passivity and inhibition, growth of passivating films on metals, etc. In this review, the results of work carried out are presented and discussed with particular reference to the contributions of other workers in the field and areas for future study have been indicated.

Potential of Corroding Metal

The potential of a reversible electrode has been interpreted in terms of the kinetics of the processes taking place at the electrode-solution interface. Nernst¹ discussed this in terms of the solution pressure at the electrode and the osmotic pressure of the ions in solution. Butler² interpreted it in terms of the rate at which metal ions left the metal lattice and entered the solution and vice versa. Gurney and Fowler³ enlarged Butler's kinetic interpretation using the methods of quantum mechanics. Subsequently, Glasstone *et al.*^{4,5} and Kimball⁶ applied the theory of absolute reaction rates to the interpretation of the potential of a reversible electrode. According to this theory, if the reversible electrode potential is established by a reaction such as $M^+ + e \rightleftharpoons M$, the rate of forward reaction (the discharge process)

$$\text{rate} = a + k_1 e^{-zV/FRT} \quad \dots(1)$$

and the rate of the reverse reaction

$$\text{rate} = k_2 e^{(1-\alpha)V/FRT} \quad \dots(2)$$

where $k_1 = kT/h \cdot e^{-\Delta F_1^\ddagger/RT}$ and $k_2 = kT/h \cdot e^{-\Delta F_2^\ddagger/RT}$ and ΔF_1^\ddagger and ΔF_2^\ddagger are the corresponding free energies of activation in the absence of an external factor like the electrode potential, α is the fraction of the electrode potential difference V which is favouring (or hindering) the forward reaction and $(1-\alpha)$ is the fraction which is hindering (or favouring) the backward reaction, a is the activity of the ions in the bulk of the solution (activity of the ions in the metal is taken as unity) and the other symbols have the usual meaning (Fig. 1). At equilibrium, the rates are equal, and 1 and 2 can be equated to get the well-known Nernst equation

$$V_c = V_0 + RT/nF \ln a_M$$

where V_c and V_0 are the equilibrium and standard electrode potentials.

If two or more statistically independent electrode reactions take place on the same metal surface, a steady state is reached when the sum of the rates of the anodic reactions are equal to the sum of the

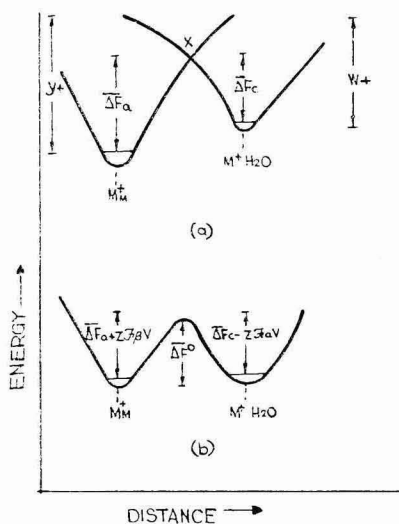


Fig. 1 — Schematic potential energy-distance relations for the ions in metal and in solution [(a) On immediate immersion; (and b) after ionic equilibrium establishment]

rates of the cathodic reactions. The electrode potential has now a different meaning as compared to the reversible electrode potential where a balance of electrical charges is obtained without any change in chemical composition. When more than one reaction takes place at the same electrode, though electrical balance may be obtained, the chemical composition of the system gradually changes. The potential of such an electrode is designated as the mixed potential⁷⁻¹⁰ and the electrode is considered as a poly-electrode. Frumkin and Kolotyrkin¹¹ and Kolotyrkin¹² applied this concept to the dissolution of lead and nickel in acids and iron in alkalies; Wagner and Traud⁷ to hydrogen evolution reaction between zinc amalgam and acid; Petrocelli^{9,13} to the dissolution of aluminium in acid and alkaline solutions; and more recently Stern¹⁴ to the corrosion rate of iron in acid solutions.

Evans¹⁵, Brown and Mears¹⁶, Akimov and others^{17,18} and Evans and Hoar¹⁹ have suggested that corrosion takes place by the existence of short-circuited cells on the metal surface similar to the commonly known voltaic cell. Accordingly, the measured potential is considered as the compromise potential of a couple formed by the different regions of the metal surface having different metal-solution potentials to start with. When current flows, these regions having different metal-solution potentials get polarized. This is represented in Evans diagram (Fig. 2). The potential corresponding to the intersection point of the two polarization curves has

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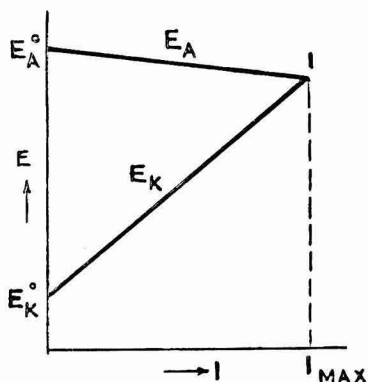


Fig. 2 — Evans diagram [E_A^0 , open circuit potential of the anode; E_K^0 , open circuit potential of the cathode; and E_A and E_K , anodic and cathodic polarization]

been designated as the 'corrosion potential' (the word 'polarization' refers to the change in potential of an electrode which results from current flow to or from the metal surface and a plot of potential against current is called 'polarization curve'). Evans and Hoar¹⁹ demonstrated the existence of a cell between the upper and the lower portions of steel vertically immersed in sodium chloride solution. Evans and Agar²⁰ mapped out regions of different potentials on zinc in sodium chloride solution. Brown and Mears²¹ using scratched aluminium showed that scratched and unscratched portions had different potentials and have summarized²² the various factors which give rise to differences in potential on the same metal surface. De La Rive's²³ early work on the decrease in corrosion rate in acid solutions with increasing purity of zinc as well as similar observations on other metals by others²⁴⁻²⁶ also appear to indicate that microcells are set up in acid solutions. This is known as the 'local cell theory of corrosion', according to which the net cathodic current of all local cells is equal to the net anodic current. The local cell theory of corrosion could explain the non-uniformity of corrosion processes such as pitting, intergranular corrosion, stress corrosion cracking, crevice corrosion, etc. Rajagopalan and Doss²⁷ and Takahashi²⁸ pointed out that any interpretation of the potential of a corroding metal must take the above factor into account.

By applying the theory of absolute reaction rates, Rajagopalan²⁹ showed that the potential of a corroding metal is given by

$$-\phi = \frac{RT}{\gamma F} \cdot \ln \frac{A_a X_2^1}{A_c X_1^1}$$

where $X_2^1 = \frac{\gamma_2^1}{1} (a_i^1) K_2^1$ and $X_1^1 = \frac{\gamma_1^1}{1} (a_i^1) K_1^1$

and A_a total anodic area in centimetre square, A_c total cathodic area in cm^2 , γ product of concentration terms, K_1^1 specific velocity of the reduction

reaction in cathodic areas, K_2^1 specific velocity of the anodic reaction in anodic areas and

$$\gamma = n_1 \alpha_1 + n_2 (1 - \alpha_2)$$

From the above equation, the significance of the corrosion potential is shown to be as follows: (i) it is governed by the ratio between the anodic and cathodic areas on the one hand and the velocity factors on the other; (ii) the corrosion potential will be shifted in the positive direction if $A_c X_1^1$ increases or $A_a X_2^1$ decreases; (iii) the corrosion potential will be shifted in the negative direction if $A_c X_1^1$ decreases or $A_a X_2^1$ increases; (iv) the potential will remain unchanged if both $A_c X_1^1$ and $A_a X_2^1$ decrease or increase to the same extent (a decrease of A_c should result in passivation and an increase in A_a should result in increased corrosion). Thus the corrosion potential ϕ_c is related to the areas A_c and A_a in the same manner as the equilibrium potential of a single electrode reaction is related to the concentrations of the oxidant and reductant. Subsequently, Rajagopalan and Rangarajan³⁰ showed that (i) $d\phi/dA_c$ is minimum when $A_c = A_a$, (ii) a maximum of i is obtained when the value of $A_c = \beta A_1$ where $\beta = n_2(1 - \alpha_2) / [n_1 \alpha_1 + n_2(1 - \alpha_2)]$, (iii) two values of A_c can satisfy a particular value of $d\phi/di$. It was emphasized that in view of (iii) in order to find out if a change in the slope means an increase or decrease in A_c , the corrosion potentials must first be compared (Fig. 3).

Potential-Time Measurements

Potential and potential-time measurements have been made use of in understanding the behaviour of corroding systems³¹⁻³³. It is found that in the presence of passivators like sodium chromate, sodium nitrite and other agents, the metal-solution potential becomes more noble in the case of several metals. This ennoblement of corrosion potential has been explained in terms of the Evans diagram as due to increase in anodic polarization by increase in resistance of the anode or by the decrease in anodic area. A fall of potential in the negative direction, e.g. on addition of chloride, sulphate, etc., was attributed to the decrease in anodic polarization brought about by more of the metal surface coming into contact with the solution. However, instances³⁴⁻³⁸ have been reported where it has been shown that the corrosion potential in itself cannot always furnish information regarding the passive or active nature of the surface, e.g. aluminium has a more negative potential compared to steel though it corrodes much less. The equation derived above shows how the potential can vary in either direction depending upon whether the cathodic area or anodic area or both are affected. The initial potential of aluminium pretreated by MBV, Pylumin and Alrok processes (Fig. 4) is more negative than that of untreated aluminium²⁹. But the rate of corrosion of the treated aluminium in 3 per cent sodium chloride solution is negligible compared to untreated aluminium. This can be explained on the basis that the effective cathodic area is reduced as a result of the treatment; this conclusion is supported by polarization data. The negligible shift in potential as a result of chromate passivation

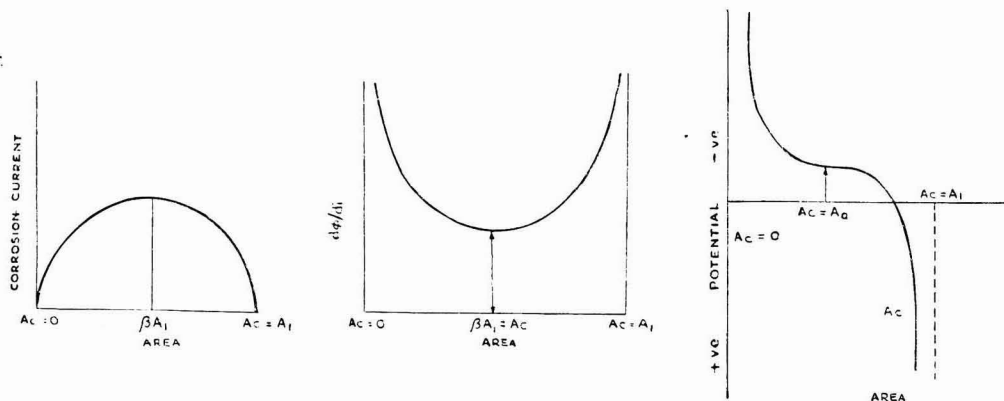


Fig. 3 — Influence of the ratio of anodic and cathodic area on corrosion current, slope and corrosion potential [A_c , cathodic area; and A_a , anodic area]

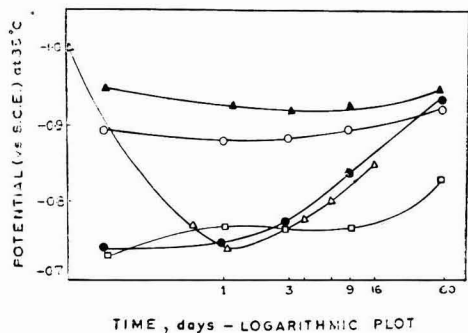


Fig. 4 — Potential of aluminium in 3 per cent NaCl solution treated by different pretreatment processes: ●, Untreated Al; □, EW process; ▲, Alrok process; ○, Pyllumin process; and Δ, MBV process]

of zinc is similarly explained as due to reduction of both anodic and cathodic areas to the same extent³⁹. This is again confirmed by the increase in slope of the anodic and cathodic polarization curves of passivated zinc. The change in potential in the positive direction in the case of addition of sodium chromate to distilled water or salt solution in which metals like steel and zinc are immersed can similarly be explained on the basis of reduction in the anodic area. It was reported by Cohen⁴⁰ that with increase in concentration of passivators like sodium chromate and sodium nitrite, the rest potential became more negative and he attributed this to the film formed in dilute solution being more perfect. A better explanation would be to say that at high inhibitor concentration, not only the anodic area but also the cathodic area gets reduced. In fact, the asymptotic nature of the potential-time curve³⁹ for zinc in chromate solutions can also be understood in terms of the inhibitor, first making itself felt on the anodic area by adsorption and subsequently modifying the cathodic area by reduction of the inhibitor and simultaneous formation of an insoluble non-conducting film on the cathode.

Polarization Studies

Of the various theories of passivity, the electrochemical mechanism of passivity and inhibition put forward by Mears⁴¹ is of particular interest to electrochemists. According to this approach based on the local cell theory of corrosion, since corrosion takes place by a flow of current between different areas on the metal surface, the potentials of the different areas are polarized. At the steady state

$$E_r = E_a + E_c + E_{R_M} + E'_{R_S}$$

where E_r is e.m.f. of the local cell, E_a the anode polarization, E_c the cathode polarization, and E_R and E'_R the potential drops caused by resistances of the metallic and solution paths. If passivity is interpreted as reduction in corrosion rate by changes on the metal surface*, it can be produced by rendering E_r smaller, e.g. by increasing the purity of the metal and by increasing E_a and E_c . The polarization term may be split into three terms

$$\eta = \eta_a + \eta_{\text{conc.}} + \eta_K$$

where η refers to the whole of the polarization, η_a the activation overvoltage brought about by the irreversibility of the electrode process at appreciable current flow which relates to a change in the activation energy required for the reaction to occur, $\eta_{\text{conc.}}$ the concentration overpotential, and η_K the potential drop caused at the electrode when insoluble products are formed. Tafel gave the following empirical relationship

$$\eta_a = a + b \log i$$

where η_a is the activation overvoltage at current density i , and a and b are constants. This equation has now been satisfactorily interpreted in terms of the theory of rate processes and the significance of the constants is adequately understood¹⁰. $\eta_{\text{conc.}}$ the concentration polarization is given by

$$\eta_{\text{conc.}} = \frac{RT}{nF} \ln \left| \frac{i_r}{(i_L - i)} \right|$$

*The equation $E_r = E_a + E_c + E_{R_M} + E'_{R_S}$ can be expressed in the form $i_{\text{corr}} = \frac{E_r - (E'_a + E'_c)}{R_M + R_S}$, where R_M and R_S are the resistances in the metallic and solution paths.

where i_L is the limiting diffusion current, i is the observed current, and n is the number of electrons taking part in the electrode reaction. This polarization is observed if the concentration of the reducible species in solution is low or if as a result of formation of passivating films, the reducible species cannot arrive at the surface as fast as in the absence of the film. This can also be observed if the metal ions cannot get away from the surface as fast as they are produced. The changes in the polarization behaviour of the local cell as a result of passivating treatments have been studied with the help of polarization curves obtained by external application of current⁴²⁻⁴⁷. But the attempts made in this direction by various workers suffer from the serious limitation that these do not take into account a factor which plays a determining part in regard to the slopes of the polarization curves, viz. the unknown area relationship between the anode and cathode of the local cells. As long as cathodic and anodic polarization behaviour are obtained by plotting potential against current, assuming the whole area to which current is applied to be anodic or cathodic, the true polarization behaviour will not be obtained. In fact, in order to reproduce the naturally formed corrosion cell in the laboratory not only the ratio of the two areas must be known but the geometry of distribution of the anodic and cathodic areas must also be maintained. This is hardly possible. Two other ways of making use of polarization data have, therefore, been explored^{48,49}. It has been suggested that the discussion of the behaviour of a corroding metal may be confined to reactions taking place on the metal surface and assumptions made that each of the reactions can take place at all points on the metal-solution interface. At potentials appreciably removed from the corrosion potential on the negative side, only the cathodic reaction may be expected to occur. The η_c - i curve may, therefore, be obtained for this reaction. Similarly, at potentials much more positive than the corrosion potential, the η_a - i curve for the anodic reaction may be obtained. In the absence of concentration and resistance polarization, two straight lines will be obtained on plotting η_c and η_a against $\log i$, if the experimental conditions are satisfactory (Fig. 5). These two straight lines may be extrapolated and the intersection gives the corrosion potential as well as the corrosion current. When passivity is obtained, the current corresponding to the intersection point is much less than before.

Stern has suggested that the η - i plots within a few mV. of the corrosion potential, where disturbing concentration effects are not likely to be observed, as in the above method, can also give valuable information on the reduction in corrosion rate. It is predicted from the theory that the anodic and cathodic slopes are identical in this region and inversely proportional to the corrosion rate. This ideal relationship would not be observed if films having different ionic and electronic conductivities are present on the metal surface and if at the corrosion potential the processes are diffusion controlled. This is made known by the fact that it is only in the case of very few systems that it has

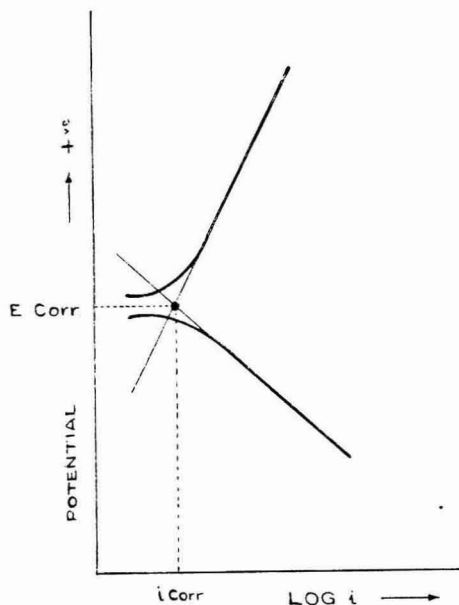


Fig. 5—Tafel plots of anodic and cathodic reactions indicating corrosion current and corrosion potential

been reported that anodic and cathodic slopes close to the corrosion potential are the same. In view of these difficulties in dealing with polarization phenomena in terms of the individual over-voltages, a somewhat simpler approach was adopted in our interpretation of polarization measurements on passivating systems. It was explained earlier that corrosion potential is a function of the ratios of the anodic and cathodic areas as well as the velocity factors. Under identical environmental conditions it may be expected that the changes in these two factors will be made known by polarization measurements as follows.

When a given value of anodic or cathodic current is passed through an electrode surface having a known apparent area, the true current density will depend upon the true area over which this current can pass. Changes in potential brought about by any of the factors mentioned earlier are a function of the current density. If the area available for the anodic or cathodic reactions is reduced then the current density will increase for a given value of applied current. The changes in the slope of ϕ - I curve (I is the applied current) would give indication as to whether the anodic or cathodic area has increased or decreased. If these measurements are made sufficiently close to the corrosion potential, then significant disturbances in the surface condition or in the medium adjacent to the surface would be avoided. Proceeding in this way, it was shown that MBV treatment of aluminium reduces the cathodic area far more than the anodic area (Fig. 6). Chromate treatment of zinc brings about a large reduction in both anodic and cathodic areas and wash primer treatment is more effective in reducing anodic and cathodic areas than

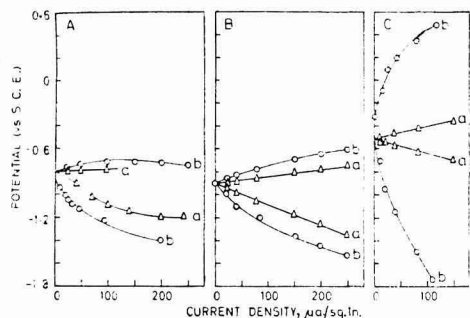


Fig. 6 — Polarization curves [A. Aluminium in 3 per cent NaCl — (a) untreated and (b) aluminium treated in MBV solution; B. zinc in 0.001 per cent NaCl — (a) untreated and (b) chromate treated; and C. steel in 0.001 per cent NaCl — (a) phosphate treated and (b) wash primer treated]

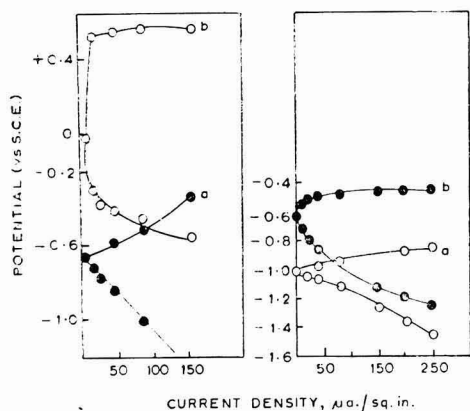


Fig. 7 — Polarization curves [(i) Steel in 0.001 per cent NaCl — (a) without inhibitor and (b) with 0.1 per cent nitrite as inhibitor; and (ii) zinc in 0.001 per cent NaCl — (a) without inhibitor and (b) with 500 p.p.m. of chromate as inhibitor]

phosphate treatment^{50,51} (Figs. 6B, 6C). Though this interpretation of polarization measurements may appear to have only qualitative significance, it is free from the limitations of the other methods referred to earlier and at the same time it is very effective in giving some insight into the manner in which surface treatment modifies the electrochemical behaviour of the metal. Further, the information that cathodic area is reduced in the case of MBV treated aluminium suggests that the pitting tendency of aluminium is likely to be minimized by this treatment. This is what has been observed in field studies. It was also shown that inhibitors like sodium nitrite and sodium chromate passivate steel and zinc surfaces by interfering with both anodic and cathodic reactions^{52,53} (Fig. 7).

Galvanostatic Studies on Passivating Systems

In a cell of the type Fe sheet (anode)/sulphuric acid/platinum (cathode), there would at the first sight appear to be no limit to the corrosion rate obtainable on the anode by an external e.m.f. which if sufficiently high can force a huge dissolu-

tion current through the anode. But this does not happen. Above a certain current, the current is mainly employed in the evolution of oxygen which would indicate that the dissolution reaction has practically ceased and the metal has become passive. Muller⁵⁴ found that anodes of iron, zinc, cadmium and copper ultimately became passive even if the liquid used was sulphuric acid.

The general picture of anodic passivation of metals on the application of a constant current was first put forward by Muller⁵⁴ and Hedges⁵⁵. According to them saturation of the solution with the metal ion takes place in the first instance and when the solubility product of salts formed with ions in solution is exceeded, film formation at the metal-solution interface takes place accompanied by a sharp rise in the metal-solution potential. This is aided by hydrogen ion migration away from the anode when the film formed is a hydroxide, oxide or basic salt. The general potential-current relationship observed at constant current⁵⁶ is shown in Fig. 8. At current density around B , with a galvanostatic system, the time lapse (τ) required before passivation sets in decreases with increase of current density and is governed by the relation

$$(i - i_L)\tau^{1/2} = \text{constant}$$

where i is current density and i_L is limiting current density below which passivation does not occur. The above relationship is likely to be observed when some of the anodically produced material leaves the vicinity of the anode before passivation sets in, i.e. for values of τ above 2 sec. When diffusion away from the anode is not significant and no replenishment of required solution — material such as salt-forming anions occurs and τ is less than 2 sec., $i\tau = \text{constant}$.

Forester⁵⁷ found that in the case of iron powder which has been exposed to air on anodic polarization in 2.4N KOH the potential jumped rapidly to passive values. Kabanov and collaborators⁵⁸ showed that on anodic polarization of film-free massive iron electrode under galvanostatic conditions two arrests were observed corresponding to the formation of $\text{Fe}(\text{OH})_2$ from Fe and of Fe_2O_3 from $\text{Fe}(\text{OH})_2$ (Fig. 9). They further observed that the potential of the massive electrode rose smoothly to

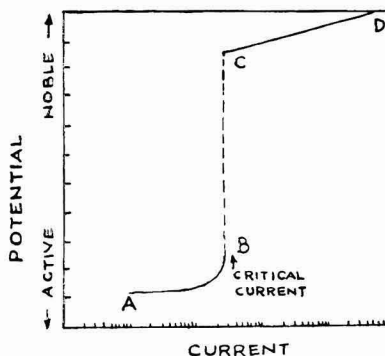


Fig. 8 — Schematic representation of polarization curve under galvanostatic condition

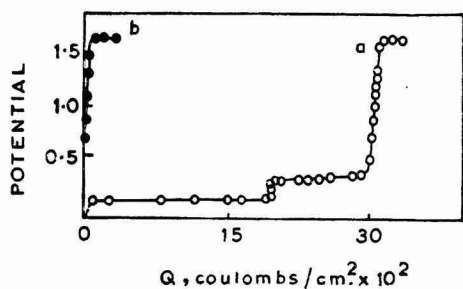


Fig. 9 — Dependence of the potential of iron electrode in 1.2N KOH on the quantity of electricity passed upon anodic polarization at constant current [(a) Outgassed iron and (b) after absorption of oxygen molecules]

oxygen evolution without arrests if adsorption of oxygen or oxide film formed by exposure to air had taken place earlier. They also showed that on anodic polarization of iron in alkaline solution containing a high concentration of chloride, the potential first rises to positive values and then falls off to lower positive values. Mayne and Menter⁵⁹ observed similar *E-t* curves for iron in NaOH solutions, and later Hancock and Mayne⁶⁰ suggested that the anodic polarization behaviour of iron could be made use of as a rapid method of finding out whether a given solution is corrosive or inhibitive. They have suggested that the inhibitive property of a given solution can be found from anodic polarization curves at a fixed current density chosen in the range of 15-100 $\mu\text{a./cm}^2$. Solutions showing a sharp potential rise to +0.3 V. (against saturated calomel electrode) on the application of a fixed current density of 10 $\mu\text{a./cm}^2$ have been characterized by them as inhibitive, and those which do not show this rise as corrosive. They have studied by this method a large number of systems, e.g. NaOH-NaCl, $\text{C}_6\text{H}_5\text{COONa-Na}_2\text{SO}_4$, and Na_2CrO_4 -NaCl, containing inhibitive and corrosive constituents. In a later paper Hancock and Mayne⁶¹ have shown that different solutions require different current densities to polarize steel specimens to the same potential. It is, therefore, not clear how studies made at a fixed current density can reflect the behaviour of a system as suggested by them.

A more elegant and sensitive method based on anodic polarization measurements was reported by Rajagopalan *et al.*⁶². In this method, when the current required to reach the passivation potential is plotted against the concentration of the corrosive constituent, an S-shaped curve is obtained for both +0.3 V. and +0.6 V., the range of potential over which the passivation of metal surface is likely to take place (Fig. 10). The curve shows that beyond a particular chloride concentration there is a sudden jump on the current needed to passivate the surface. The chloride concentration and current density corresponding to the middle point appears to divide the solutions as well as the current densities into two broadly distinguishable groups, one in which the current density required is low and the other in which the current density required is very much higher.

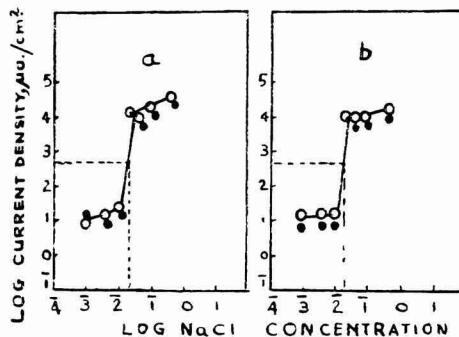


Fig. 10 — Applied current density versus sodium chloride concentration [(a) Immediately after immersion of specimen to attain a potential of +0.3 V. (●—●) and +0.6 V. (○—○) versus SCE and (b) 48 hr after immersion of specimen to attain the above potentials]

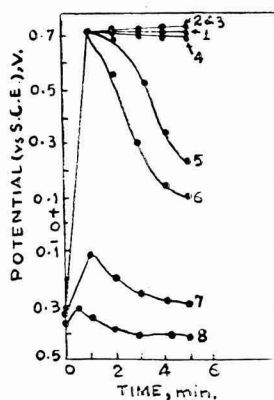


Fig. 11 — Potential-time curves of mild steel in 0.04N NaOH containing 1, 0.001; 2, 0.005; 3, 0.01; 4, 0.02; 5, 0.03; 6, 0.05; 7, 0.1; and 8, 0.5 per cent NaCl when anodically polarized at 210 $\mu\text{a./cm}^2$

It is interesting to note that the application of a constant current density of 290 $\mu\text{a./cm}^2$ corresponding to the middle point of the curve brings out, in unambiguous manner, the behaviour of the NaOH-NaCl system (Fig. 11). It is seen from the figure that on application of this current, the potential rises and remains constant at a positive value for the solutions below the concentration corresponding to the middle point of the curve and either first rises and then falls off to a negative value or does not rise for the solutions above the concentration corresponding to it indicating that Fe cannot be passivated in the latter solutions. Direct corrosion tests also confirmed this result when it was shown that rusting takes place in these solutions. It was concluded from galvanostatic measurements and corrosion tests that if OH:Cl ratio exceeds¹⁰, the solution becomes corrosive.

Potentiostatic Studies

A potentiostat, as the name implies, maintains the electrode potential at a preset value with respect to a reference electrode. If the potential drifts from this value the error signal is amplified and is fed into the output stage which provides a change in current passing through the circuit to correct this error (Fig. 12). The output change

can either be electronically or mechanically controlled, the choice resting solely on the amount of current required and the response time desired of the instrument. The first reported potentiostat circuit was described by Hickling⁶³. Since that time, circuitry has been developed⁶⁴⁻⁶⁹ to meet the different requirements of analysis, organic oxidation and reduction, study of electrochemical kinetics and corrosion processes. It is obvious that the potentiostatic technique is particularly useful for the investigation of the anodic behaviour of metals which show active dissolution and passivity at different potentials. A typical $E-I$ curve obtained with a metal which shows both active and passive behaviour is shown in Fig. 13. It is seen from the figure that there is a region where the rate of dissolution increases as the potential becomes more positive which is known as the 'active region'. The current or corrosion rate sharply decreases to a low value at a potential which is often referred to as Flade potential^{70,71}. Over a potential range above this the passive region is observed in which the current flowing across the metal solution interface is only a tiny fraction of the maximum current in the dissolution range. After the passive region, the so-called 'transpassive' region is observed in the case of some metals and is associated with the dissolution of a high oxidation state of the metal and finally, at the most positive potential, gas evolution takes place. The behaviour of iron, chromium, nickel, titanium and other metals has been studied in sulphuric acid, by this method and the potential at which the change-over from active to passive

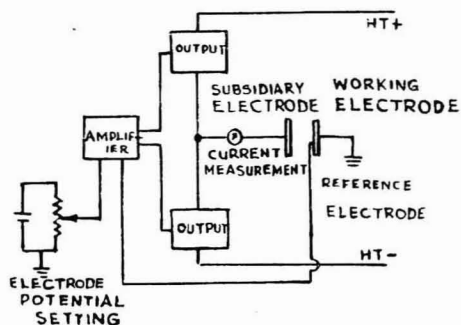


Fig. 12—Block diagram of the potentiostat circuit

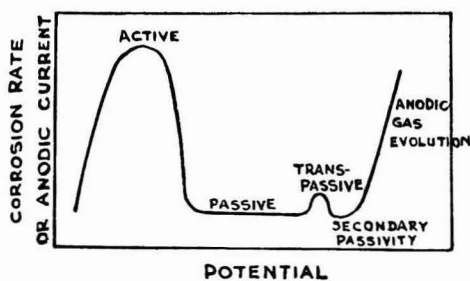


Fig. 13—Typical $E-I$ curve under potentiostatic conditions (a case of transitional metal)

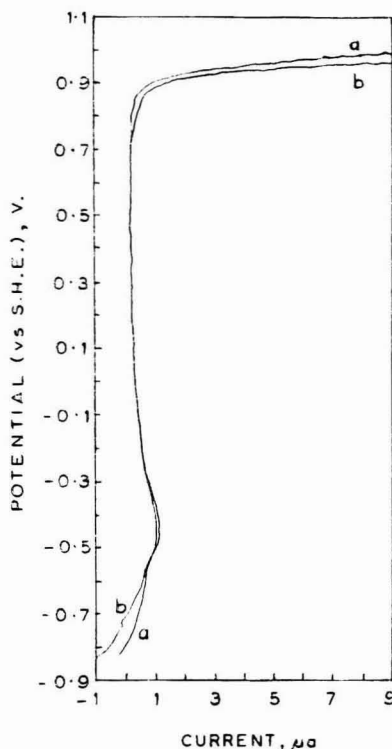


Fig. 14— $E-I$ curve for (a) iron in $N/10$ NaOH and (b) mild steel

state takes place as well as the passivation current have been determined⁷²⁻⁷⁶. The effect of the alloying constituents on the active-passive behaviour of stainless steel has been studied using this method⁷⁷.

Two methods of getting $E-I$ curves using the potentiostat are employed, namely step-wise change of potential and continuous change of potential with time, known as potentiokinetic method^{78,79}.

Venu *et al.*⁸⁰ have studied the anodic behaviour of iron in $N/10$ and $N/100$ NaOH solutions in the presence of chloride and sulphate ions. Anodic passivation of iron in NaOH is revealed by the fall in anodic current after reaching a maximum value (Fig. 14). A large passivation current is recorded. The passivating film appears to be having considerable thickness. The behaviour in solution containing chloride ions is similar to that obtained in NaOH solution up to a chloride:OH ratio of 1:1. When the chloride concentration exceeds this ratio anodic passivation is still observed but the passivation current increases. Breakdown of passivity is observed only at much higher chloride concentrations. This explains why pitting is observed in solutions containing both NaOH and NaCl at borderline concentrations and general attack observed only if the Cl:OH ratio is very high (Fig. 15). SO_4^{2-} ions do not appear to effect any change in the passivation behaviour of iron in $N/10$ NaOH up to the highest ratio studied (Fig. 16).

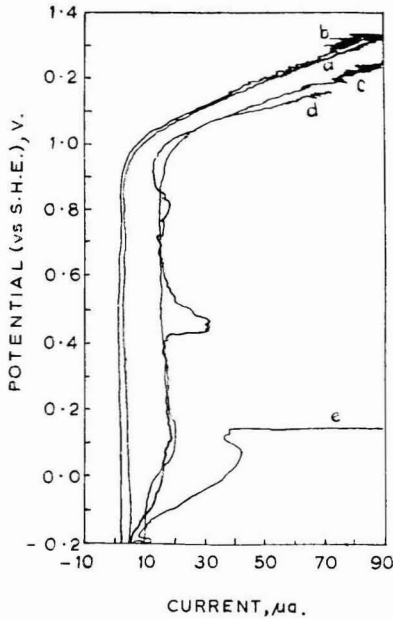


Fig. 15 — *E-I* curve for iron in *N/10* NaOH solution containing (a) *N/100*, (b) *N/10*, (c) *1N*, (d) *2N*, and (e) *4N* NaCl

Kinetics of Growth of Passivating Films on Metal Surfaces

Fleischmann and Thirsk⁸¹ have shown that the very initial stage of formation of anodic films takes place by the nucleation of discrete centres on the metal surface which grow and subsequently envelope the metal surface. There appear to be three situations of interest, namely (i) the rate of dissolution of metal into electrolyte is the slowest process and controls the rate of film formation; (ii) the rate of growth of nuclei is the slowest process; and (iii) the flow of current in the bulk of the electrolyte solution or in the external circuit controls the current⁸². The current-time relationships in the three cases are shown in Fig. 17. Rajagopalan and collaborators have observed that in the formation of phosphate film on iron surface the current reaches a maximum and then falls (Fig. 18) (Rajagopalan, K. S., Dandapani, B. & Jayaraman, A., unpublished results). This would, therefore, indicate that this is also an example of the rate of growth of nuclei being the slowest process, as in the case of many systems studied by Fleischmann, Thirsk and their coworkers.

Processes in which film growth is controlled are of particular interest as in these instances, from a study of the time dependence of current, valuable information can be obtained as regards the geometry of film growth. Fleischmann and Thirsk⁸³ have pointed out that when the nuclei are growing independently of each other six *i-t* relationships have to be considered depending upon whether the nuclei are formed instantaneously or progressive nucleation is observed and whether the nuclei is

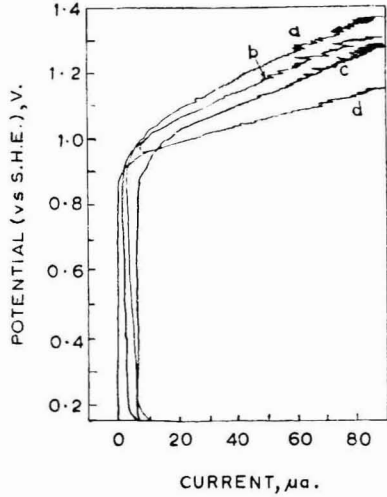


Fig. 16 — *E-I* curve for iron in *N/10* NaOH solution containing (a) *N/100*, (b) *N/10*, (c) *1N*, and (d) *2N* sodium sulphate

one-dimensional, two-dimensional or three-dimensional. The initial portion of the current-time transients can be examined for these different relationships and information obtained as to whether the growth is two-dimensional or three-dimensional. It can easily be imagined that during the process of growth of the first formed nuclei a stage would come when the area available for lateral growth would become restricted. The current will, therefore, reach a maximum and then decrease because of the overlapping of the growing centres. The particular geometry of growth which is more significant for passivation is the growth of cylinders of monomolecular height growing laterally in two dimensions. In this case the current should decrease to zero or a low value when one monolayer has been completed provided no fresh nuclei are formed in the first formed monolayer. If, however, this happens then a new current-time transient in the form of a peak can be obtained and this can be repeated. The number of peaks should give the number of monolayers that are formed before passivation. It has been shown that if the nucleation is completely random and follows a first order law the growth of each layer can be expected to follow the relationship

$$i = \frac{ZF\pi hMAk^2t^2}{\rho} \dots \exp \left[-\frac{\pi M^2 Ak^2t^3}{3\rho^2} \right]$$

where *h* is the height of the monolayer, *M* the molecular weight of the film-forming material, *A*

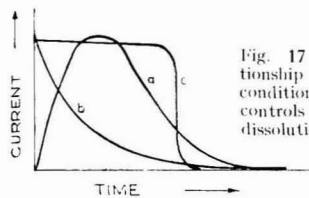


Fig. 17 — Current-time relationship under potentiostatic condition when (a) film growth controls the rate, (b) metal dissolution controls the rate, and (c) the rate is not controlled by electrode processes.

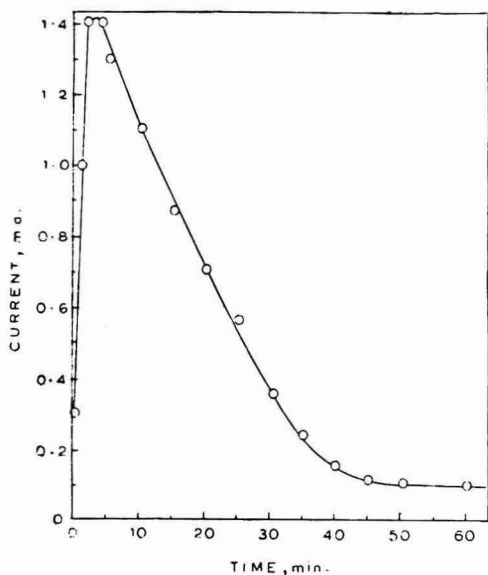


Fig. 18 — Current variation during phosphate film formation

the nucleation constant expressed in nuclei/cm.²/sec., k the growth rate constant expressed in moles/cm.²/sec., t the time in sec. and ρ the density. The above conditions may be obtained on a structureless surface like that of mercury or an amalgam. This can be illustrated in the case of passivation of cadmium amalgam in NaOH solution⁸⁴.

The current-time transients for the formation of cadmium hydroxide on cadmium amalgam is shown in Fig. 19 and for the three overpotentials for one amalgam and for one solution. At low overpotentials the current shows two maxima which differ considerably in height and time scale. As the overpotential is increased the difference between the first and the second maxima diminishes and a shoulder develops after the second peak. The area under the first peak is constant and is somewhat larger than that calculated for 001 plane of cadmium hydroxide, about 230 μ c. The area under the second peak together with that of the shoulder is somewhat larger (roughly $2\frac{1}{2}$ monolayers) than that corresponding to two layers of this orientation. In all cases the reaction stops after the shoulder and the amalgam is passivated.

If the rate of nucleation is known or the number of nuclei are kept constant by preformation at a higher potential or the nucleation constant is independent of overpotential, the growth rate constant k expressed in moles/cm.²/sec. can be obtained from the relationship between i and t . By studying the dependence of k on pH , metal ion concentration and potential, the mechanism of film formation can be elucidated. With regard to the formation of cadmium hydroxide on cadmium amalgam, the most probable mechanism is a rate determining rearrangement of two discharged OH ions with the two-layer planes separating the cadmium ions.

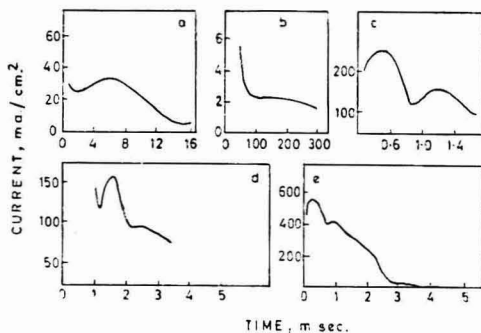


Fig. 19 — Variation of current with time for the formation of cadmium hydroxide on 1 per cent cadmium amalgam in 1N sodium hydroxide [(a) First layer at an overpotential of 20 mV., (b) second layer at an overpotential of 20 mV., (c) first and second layers at an overpotential of 80 mV., (d) second and third layers at an overpotential of 80 mV., and (e) first, second and third layers at an overpotential of 170 mV.]

Summary

The significance of the potential of a corroding metal is discussed. It is shown that the corrosion potential can be satisfactorily interpreted in terms of Glasstone, Laidler and Eyring theory of rate processes. According to the equation derived by one of the authors, changes in potential following passivation treatments and potential-time data can be satisfactorily understood in terms of changes in the anode to cathode area ratio as well as changes in the ratio of the velocities of the anodic and cathodic reactions. It is also shown that it is necessary and reasonable to interpret changes in polarization behaviour brought about by passivating conditions taking into account the area changes on the metal surface. Reviewing studies on anodic passivation of metals at constant current, the authors describe a satisfactory method based on application of a constant current to distinguish between corrosive and inhibitive solutions.

The applications of the potentiostat in the study of passivation phenomena are discussed. It is pointed out, citing the example of the NaOH-NaCl system, that the potentiokinetic technique provides a powerful tool for the study of the active-passive behaviour of metals. The theory of electrocrystallization of anodic films is discussed. It is observed that the particular geometry of growth which is of the greatest interest from the point of view of metal passivation is the growth of cylinders of monomolecular height growing laterally in two dimensions. Analysis of the current-time transient for the formation of cadmium hydroxide on cadmium amalgam shows that passivation takes place after the formation of three monolayers.

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Department of Chemistry, King's College, New Castle-upon-Tyne, quoted in this paper.

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REVIEWS

INTERPRETED INFRARED SPECTRA: Vol. I, by Herman A. Szymanski (Plenum Press Inc., New York), 1964. Pp. vii+293. Price \$ 10.75

The present book is the first volume of a series planned by the author to collect and present all the available data on the infrared spectra of organic molecules. This volume relates to the alkanes, benzene ring compounds, cyclopropane derivatives, cyclobutane derivatives, cyclopentane derivatives and cyclohexane derivatives. Each such group of allied molecules is dealt with under the following heads: vibrational analysis, correlation tables, discussion of spectra and interpreted spectra.

Taking a typical case like benzene ring compounds, the infrared frequencies along with Raman frequencies are tabulated and their individual assignments presented under vibrational analysis. This is done for benzene and its various substituted compounds like $C_6H_6-C_6H_5$, C_6H_5F and $C_6H_5CH_3$.

Another series of tables gives the aromatic ring frequencies for various typical frequencies like CH stretch occurring usually as several peaks in the region 3080-3030 cm^{-1} , with intensity estimates. This is followed by a discussion of the spectra as presented in the above tables. An atlas of these spectra with full markings of the frequencies is also given.

The aim of this kind of presentation is mainly to enable the identification of an unknown spectrum. References to the existing literature from which the data are collected are detailed. This series of volumes is likely to be useful not only for analytical purposes but also as a reference for those interested in the analysis of individual spectra of molecules. The book is a useful addition to any library catering to the needs of molecular spectroscopists.

V. RAMAKRISHNA RAO

ORGANIC CHEMISTRY by Hans Beyer; translated by E. B. Knott from the Tenth Edition of the German text *Lehrbuch der Organischen Chemie* (Asia Publishing House, Bombay), 1963. Pp. 947-2053. Price Rs 26.00

The present text is an English translation of the tenth edition of the *Lehrbuch der Organischen Chemie* by Prof. Hans Beyer. As is evident from the preface and the general treatment of the subject, the text is intended for the students who are at an early stage of their acquaintance with the subject. The text has succeeded in its objective as far as presentation of factual information about a large number of important organic compounds is concerned. In fact the information provided about various types of organic compounds is quite up to date though at many places perfunctory.

Shortcomings of the present edition arise of necessity because of the fact that a text-book, intended for students studying for their first degree, is attempted in a volume of about 750 pages only and a text which initially gave classical treatment of the subject has been adapted to include modern

approach of physical organic chemistry. Thus the treatment of physical organic concepts is either patchy, incoherent or otherwise unsatisfactory. For example, the phenomenon of optical isomerism, the theoretical principles underlying it and the variety of systems with respect to which it has been studied have been treated rather casually and the material presented is far less than adequate and scattered at a number of places with the result that a unified picture is missing and the student cannot form any satisfactory basic notions about this subject. The same is more or less true of the treatment of the topics like resonance, inductive and electromeric effects, theories of substitution reactions, etc. What in fact is expected of a first degree text-book is that it should help the student to form clear-cut basic notions about the subject without getting lost into intricacies and less clearly defined situations. As far as physical organic chemical principles are concerned, this desideratum is not fulfilled.

The treatment of the subject in the sections on polymers, fermentation, enzymes, carbohydrates, alicyclic compounds, radical reactions and on many other conventional topics is excellent, compact and up to date. Chapters on terpenes and steroids catalogue a large number of compounds without giving substantial details about their chemistry. No doubt, in a general text-book of this type, there are severe limitations of space, yet certain basic information about general chemistry and typical synthesis is expected at least with respect to the more common compounds. The text is very readable and yet not quite free from the usual defects of translation. At places the diction is laboured and usages grotesque. For example, on page 280 'lachrymatory odour' and on page 279 'mercuric thiocyanate is characterized by increasing enormously in volume on ignition'. References to the literature include only the work of German workers even when superior work by other national is on record. This is, indeed, deplorable and at variance with the usual scientific practice.

On the whole the text-book is a laudable attempt at bringing in as much factual information as possible in limited space. However, it fails to give due attention to many physical concepts and theories which are current in organic chemistry.

R. H. SAHASRABUDHEY

MOLECULAR REARRANGEMENTS: Part 2, edited by Paul de Mayo (John Wiley & Sons Inc., New York), 1964. Pp. 535. Price \$ 20.00

The second part of this two-volume monograph deals exclusively with rearrangements observed in natural products. The chapters included are: Terpenoid rearrangements; Rearrangements and isomerizations in carbohydrate chemistry; Rearrangements in the chemistry of alkaloids; Rearrangements in the chemistry of amino acids and peptides; Rearrangements in steroids.

In the words of Dr Warnhoff, who has written an exceedingly interesting section on alkaloid rearrangements, the contents of the entire volume may be described thus: "structural evidence for starting material (except for very well-known compounds) and product is presented briefly, since the certainty of these is the only guarantee of rearrangement. There follows a discussion of the probable or possible mechanism(s), including evidence or analogies for the favoured path." Unlike the chapters of Part 1, the part under review has little to say on the energetics, mechanistic intermediates or the transition states of the rearrangements nor is it tied down by classification according to mechanistic types. This partly is the strength of the book. The freedom from mechanistic classification has allowed the incorporation of rearrangements even under dehydrogenation conditions where 'especially little is known what actually happens'. The wealth of information thus made available and the interesting variety of skeletal ramifications provide many hours of mental exercise and stimulus for further investigations in a number of instances. Every one of the chapters is presented in an authoritative and captivating manner. Graduate students would find the book highly valuable as it affords opportunities for many useful hours to be spent in working out mechanisms for many unclassified rearrangements.

The high cost of the two volumes (\$ 25.00 and \$ 20.00 for Parts 1 and 2) would certainly keep the book exclusively in the shelves of libraries. The two parts richly deserve to find a place in the personal collections of teachers and graduate students. This alone must be a convincing argument for a cheaper edition of the two volumes. The reviewer would strongly recommend such a step to the publishers.

B. S. THYAGARAJAN

MECHANICAL WORKING OF METALS by F. A. A. Crane (Introductory Monographs in Materials Science; General Editor: A. R. Bailey) (Macmillan & Co. Ltd, London), 1964. Pp. ix+81. Price 13s. 6d. This short monograph gives a simplified and basic study into a few mechanical processes with certain factors in common. It begins with a survey of some common processes and the basic principles of rolling, tube manufacture and deep-drawing are covered and the criterion for drawability examined. An elementary analysis of stress and strain is presented next and this leads on to an introduction to plasticity and the effect of this on working methods. Approximations to the stress-strain curve and yield criteria of Tresca and Von Mises are explained. The remaining four chapters give in greater detail the mechanics of certain of the working processes considered in Chapter I. Stretching and forging processes are examined and the author considers the limitations to this with the onset of plastic instability. The case of stretch forming as well as an approximate analysis of plain strain compression are covered next. The stress distribution involved in the rolling process is studied with the assumption of plain strain. This is a vast field for research and some of the theories of hot rolling are

given. An analysis of wire-drawing and the importance of the three major contributory factors to this, namely useful deformation, friction and redundant deformation, are lucidly explained. The final chapter consists of an analysis of the extrusion process.

The monograph is very well brought out and extremely readable. Mathematical equations have been kept to a minimum and the aim has been to stress on the fundamental reasoning that goes towards explaining various processes rather than confuse the issue with a very mathematical approach. A valuable list of references is also provided. The editor in his forward states that "The object of the present series of monographs is to present concise accounts of important topics, modern in outlook and sufficient in scope to give a working introduction that can be taken further if desired", and the book under review succeeds admirably in this.

A. N. KUMAR

ELECTRODEPOSITION AND CORROSION PROCESSES by J. M. West (D. Van Nostrand Co. Ltd, London), 1965. Pp. xii+189. Price 27s. 6d.

This concise volume presents the modern aspects of electrodeposition and corrosion processes. The object is "... to present electrodeposition and metallic corrosion as alternative aspects of ionic transfer through the double layer which exists at a metal/electrolyte interface".

There are seven chapters in the book: metals in equilibrium, departures from equilibrium, electrochemical corrosion, surface films, electropolishing and bright electrodeposition, corrosion prevention, and the influence of stress. Beginning with the necessary introduction to theoretical electrochemistry, the author deals with polarization phenomena in the second chapter. Electrochemical corrosion is outlined in the next chapter, and the fourth chapter covers surface films including passivity and stainless steels. Electropolishing and bright deposition are discussed next. Corrosion prevention methods have been covered in the sixth chapter and include inhibitors, anodic protection, alloying and cathodic protection. The last chapter deals with stress-corrosion cracking, and it is good to find that a separate chapter has been devoted to this important topic.

The subject matter has been presented in an excellent manner from the theoretical viewpoint. There are problems and references at the end of each chapter. Two appendices on elementary valency theory and metal deformation are included in the end, together with the author and subject index. The book serves admirably the purpose for which it has been written. It is strongly recommended for the postgraduate students, electrochemists and metallurgists, and all those interested in the theory of electrodeposition and corrosion phenomena.

T. L. RAMACHAR

BIOCHEMISTRY OF PHENOLIC COMPOUNDS by J. B. Harborne (Academic Press Inc., London), 1964. Pp. x+618. Price 126s.

Current interest in plant phenolics is shown by the organization of plant phenolics groups in several

countries and the appearance of a number of books on the subject. The present volume is outstanding in its choice of authors, the clarity, critical and comprehensive character of the treatment, and the convincing evidence which has been provided to demonstrate the important functions of phenolic compounds in living systems. Following four excellent chapters on the chemistry (R. H. Thomson), isolation and identification (Margaret Seikel) and natural distribution (J. B. Harborne and N. W. Simmonds) of phenolics are the remaining ten chapters devoted entirely to biochemical and physiological aspects. R. E. Alston discusses the genetics of phenolic compounds and their metabolism in higher plants; microorganisms and animals is discussed by G. H. N. Towers and R. T. Williams. The best account of phenolic biosynthesis which has yet appeared is given in a series of four chapters: Major pathways of biosynthesis of phenols (A. C. Neish), Lignin and tannin biosynthesis (S. A. Brown), Enzymology of phenolic biosynthesis (E. E. Conn), and Physiological studies on phenolic biosynthesis (H. W. Siegelman). The physiology and pharmacology of phenolic compounds in animals (P. W. Ramwell, H. S. A. Sherratt and B. E. Leonard) and the pathological function of phenolic compounds in plants (I. A. M. Cruickshank and D. R. Perrin) are discussed in the next two chapters. A new and interesting aspect of phenolic glycosides, their taste in relation to structure, is discussed by R. M. Horowitz. In addition to the usual author and subject indexes there is a very useful index of genera and species. The book makes fascinating reading from cover to cover, and the reviewer is indebted to the Editor of *Journal of Scientific & Industrial Research* for enabling him to save about a hundred rupees of hard-earned money, because he should have been compelled to purchase a personal copy if he had not received it for review. J. B. Harborne has obviously carried out his work as the editor much more efficiently than editors of most multi-author books, because there are numerous cross references in the various chapters, and there is a uniformity of purpose and treatment and an unusual absence of duplication. There are minor omissions, and suggestions can of course be made for fuller treatment in a new edition of areas in which one or other reader may be interested. The tocopherols have not been mentioned and the ubiquinones only casually. The extremely interesting chapters on biosynthesis have perhaps not given adequate attention to terpenoid derivatives of phenols and to tissue culture techniques for the study of biosynthesis; but the treatment as a whole is extraordinarily stimulating; one can glance through any page of the book and find exciting problems for investigation.

K.V.

IMPERFECTIONS AND ACTIVE CENTRES IN SEMICONDUCTORS by R. G. Rhodes (Pergamon Press Ltd, Oxford), 1964. Pp. xii+373. Price 90s. The subject matter covered by this book is very much in the limelight these days specially with the development of semiconductor devices for use in other branches of physics notably solid state radiation

detectors, ultra-fast switching diodes and transistors. The knowledge of imperfections and active centres in semiconductors will help one to understand the effect of radiation on semiconductor material (including their semiconducting films).

The present book deals mainly with silicon and germanium which are most widely used semiconductors. The subject has been treated from an experimentalist point of view with detailed illustrations of a number of experiments and the analytical interpretation of their results. Chapters include physical description of different kinds of dislocations along with the standard methods for detection of the defects. The technique of growth and distribution of impurities in single crystals is discussed in some detail and their chemical and physical behaviours are outlined. A separate chapter is devoted to the study of defects and semiconducting properties of germanium and silicon. The description of etching processes and formation of etch-pits will be useful to many experimentors who use these materials to make their own semiconducting devices.

Physical concepts on dislocation are well explained and on the whole the book has a strikingly simple language. However, at a few places, e.g. pages 6, 7 and 12, the term 'diamond-lattice' is used to denote the structure and should be avoided. The book can be recommended to a student who is planning to study the properties of semiconductors with a limited background of semiconductor physics. It may not be suitable as a text-book because of rather limited approach made to explain the facts theoretically. A clear explanation is given about the essential properties of semiconducting materials when these are doped in a control manner. The effect of irradiation on minority carrier lifetime and the recombination of carriers at dislocations are clearly expressed. A fairly extensive list of references is available which should greatly help a research investigator working on related problems not otherwise well covered in this book.

A. R. VERMA

PLASMA SPECTROSCOPY by Hans R. Griem (McGraw-Hill Book Co. Inc., New York), 1964. Pp. xi+580. Price \$ 18.50

This is the first book which is entirely devoted to this modern branch of spectroscopy known as plasma spectroscopy that has acquired tremendous importance in recent years. It is well known that increasing attention is being devoted at present to the study of the physical properties of plasmas, inspired, no doubt, by the potential applications in technology and thermonuclear power. Spectroscopic methods constitute a powerful tool for the study of such properties. Incidentally, such studies also provide precise values for a number of atomic parameters (e.g. oscillator strengths) which are very useful for quantum theoretical calculations. The book covers the basic theory, numerical results, experimental techniques and applications of spectroscopy to measurements of plasma and atomic parameters.

The book is divided into 15 chapters. Classical and quantum theories of radiation are well summarized in the first two chapters. These are applied to the

calculation of three important quantities, viz. line oscillator strengths, line broadening, and intensities of continua, that are necessary for the explanation of the broad features of spectra emitted by plasmas. The equilibrium composition of plasmas is taken up in the next chapter, and the Saha equation and its developments applied to the calculation of the relative concentrations of atomic and ionic species. The next chapter deals with radiation losses — bremsstrahlung and cyclotron radiation.

The experimental aspects of the subject are next dealt with; plasma light sources of the stabilized arc and shock tube varieties are considered. The characteristics of the spectrographs useful for such studies, and the radiation detectors employed to cover the optical vacuum ultraviolet and soft X-ray regions considered in the next chapter.

The next two chapters deal with the experimental measurements of the two fundamental plasma parameters — temperature and density. Temperature measurements by relative intensities of lines from the same element in different degrees of ionization, and by relative line-to-continuum and relative continuum intensities are considered in detail, as also Doppler profile measurements. The refractivity and Stark profile methods for density measurements are well treated. The last chapter deals with measurements of atomic parameters — atomic oscillator strengths, continuum absorption measurements and line broadening parameters. The calculation of these and other spectroscopic parameters is facilitated by an exhaustive list of tables of *Recah* coefficients, oscillator strengths, etc., covering about 150 pages of the book.

At the end of each chapter are given some problems which are designed as a guide to quantitative analysis of the methods and applications of plasma spectroscopy. The solutions for these problems are given at the end of the book. References are also given at the end of each chapter. More than 200 symbols appear in the book and these are listed with their meanings at the end of the book.

The book has been well written. The printing and the get-up of the book are exceedingly good. It serves as an invaluable source of reference for spectroscopic research in experimental plasma physics and the physics of stellar atmosphere. In order to follow the book by postgraduate students, it is necessary for them to be familiar with the theory of atomic spectra, quantum-mechanical perturbation theory and statistical mechanics. The book can also serve as a good reference book for students taking spectroscopy as a special subject for the Master's degree course.

R. S. KRISHNAN

EXPLODING WIRES: Vol. 3, edited by William G. Chace & Howard K. Moore (Plenum Press Inc., New York), 1964. Pp. ix+410. Price \$ 17.50
This volume, the third in a series of exploding wires, contains the Proceedings of the Third Conference on the Exploding Wire Phenomenon held at Boston in March 1964. The exploding wire phenomenon (EWP) has passed from the initial exploratory stage to one of practical utility and this is evidenced by the papers on exploding bridge wires which are specially

important as these are used extensively in missiles and satellites, and represent the largest single application of exploding wires. Equally interesting is the paper on the elegant application of the EWP to the synthesis of chemical compounds. There are papers on theory, on shock waves and on apparatus and instrumentation which show the advances, the refinement and sophistication in the state of the art in each of these fields. Useful references are given at the end of each paper.

This third volume, like its predecessors, will provide the workers in the field with a single information source on the subject.

K. GOPALAKRISHNAN

SOVIET RESEARCHES ON LUMINESCENCE edited by D. V. Skobel'tsyn; authorized translation from the Russian (Consultants Bureau Enterprises Inc., New York), 1964. Pp. 152. Price \$ 27.00

The book gives a complete account of the soviet researches on electroluminescence and cathodoluminescence, carried out at the Luminescence Laboratories of the P. N. Lebedev Physics Institute.

After a very short historical introduction clearly bringing out the fundamentals of luminescence and its practical applications, the theoretical discussion of the general problems of electroluminescent crystals, i.e. ionization by the electric field, impact ionization and the concentration of the electric field in electroluminescence which is of great interest for the practical use of electroluminescent crystals, and the various causes which can lead to the concentration of the electric field, are given. The conditions for crystal phosphors to be good electroluminophors are also discussed with examples.

In Chapter II, a short discussion of the electroluminescence of zinc blende and its properties on varying the activator and coactivator and their concentrations, together with the electroluminescent properties of mixed crystals and their preparation is given. The construction of the electroluminescing condenser, the method of exciting and registering electroluminescence, the measurement of the energy consumed, etc., and the interpretation of the experimental results are, however, discussed in great detail both theoretically and experimentally.

In the second part of the book the cathodoluminescence of ZnS and certain other cathodoluminophors are considered in detail. The various types of excitation energy losses, the energy losses due to the thermal stabilization of the electrons and holes and their effect on the luminescence efficiency are theoretically shown to reduce it by a factor of 2.5. The dependence of the electron penetration depth on the voltage, the energy losses at different electron penetration depths in the luminophor layer are analysed in detail. The dependence of the spectral composition, brightness and luminescence energy yield on the current, density, etc., in a number of ZnS and phosphate luminophors (with suitable apparatus which are also described) is dealt with in detail. The luminescence decay of various types of cathodoluminophors to 0.1, 0.01 and 0.001 of the original brightness has been investigated and some interesting results which emerged from these studies are also given.

A complete bibliography of work performed in the Luminescence Laboratories between 1934 and 1961 is given at the end of the work.

This book will be an asset for research workers in the luminescence field and also for the industry connected with luminescent materials.

R. S. KRISHNAN

OPTICAL ILLUSIONS by S. Tolansky (Pergamon Press Ltd, Oxford), 1964. Pp. ix+155. Price 35s.

This book deals with the geometrical optical illusions. The subject though actively studied during the 19th century by several well-known scientists has almost been neglected in the present century. Prof. Tolansky revives interest in this fascinating field and has addressed this book to the layman, to the artist and to the scientist. The book has several illustrations, many of which have been specially designed and drawn. It is a delightful book and "there is amusement as well as serious instruction in the study of optical illusions". The book is written in a lucid style so characteristic of Prof. Tolansky and is very readable.

A. R. VERMA

SPACE AGE ACRONYMS by Reta C. Moser (Plenum Press Inc., New York), 1964. Pp. 427. Price \$ 17.50

How important is knowing the definition of an acronym? We agree with the editor of the volume under review when he says, "It is as important as the time lost searching for or the consequence of not finding it".

The primary aim of this book has been to offer to those in space and defence industry a central acronymic reference source that is up to date. The volume contains the largest number of acronyms ever compiled, and one is amazed at the variety of acronyms and their total number, which easily exceeds 10,000. The editor is still full of regrets (we do not regret) that he could cover only the technical and industrial acronyms and not those used by professional and other international organizations.

The reviewer honestly feels that the utility of this book will be confined mainly to industrial and military personnel associated with ANNA (Army-Navy-NASA-Air force) in the USA and its usefulness to scientific workers, including space scientists, is very limited. The book is recommended to libraries overflowing with funds.

K. S. VISWANATHAN

MICROWAVE CIRCUITS by Jerome L. Altman (D. Van Nostrand Book Co., London), 1964. Pp. xxi+462. Price \$ 15.00

The subject of the book deals with the area of passive microwave circuits and components, particularly of the non-reciprocal type. The reciprocal multiport junction type microwave components are discussed at great length in a unified way using the scattering matrix theory.

Starting in Chapter I with the introduction of circuit elements, as derived from the field expressions for guided microwaves, the author goes on to the description of the scattering matrix concept as applied

to the microwave circuits in the second chapter. This concept is used repeatedly in Chapters III-VI for analysing microwave components such as Tee and Y junctions of E and H type, waveguide directional couplers of almost all varieties, one- and two-port microwave cavities, hybrids, phase shifters, attenuators, Butterworth and Techebycheff type microwave filters using cavities, etc. A brief description of the ferrite type circuits is given in Chapter IV. Chapter VII deals with the general properties of periodically loaded transmission lines and the derivation of pass and stop band characteristics from the equivalent Y and Z parameters of the periodic discontinuities. The concluding chapter VIII describes the various applications of these components in modulators, phase detectors and other functional blocks of the systems. The book includes nineteen appendices where mathematics and details of several concepts used in the text are given.

The book presents in a lucid and comprehensive manner a rather limited part of the area of microwave circuits. Inclusion of coaxial and stripline components and the microwave circuits involving active components would have made the book more complete in its scope. The book has left out the currently active and interesting area of tunnel diode and varactor circuits untouched.

A novel feature of the book is to demonstrate the power of the scattering matrix concept in analysing the microwave circuits by its repeated use. As such, it should find wide acceptance by workers active in the area. It should also prove a useful reference material for classroom purposes.

O. P. GANDHI

ANALYSIS BY GAS CHROMATOGRAPHY by P. G. Jeffery & P. J. Kipping (Pergamon Press Ltd, Oxford), 1964. Pp. xi+203. Price 70s.

The book has been divided into three parts. Part I describes detectors, apparatus used for gas analysis, techniques for transfer of samples and the column materials. Part II deals with the determination of individual gases, giving at appropriate places details of the operation. Part III describes some complete analyses using specific mixtures, determination of gases in solid and liquid sample materials and methods of gas sampling. In all 216 references to original works are listed.

Chapters 4 and 5 (Part I) give a critical account of the construction, working and applicability of the important types of detectors. However, some recent developments in microthermal conductivity cells and microcoulometric methods of detection are not dealt with. Electronic circuit diagram for thermal conductivity detectors has been included.

The authors in the preface state that the scope of the book is limited to the analysis of "those compounds that are normally transferred to a gas chromatogram in the gaseous state". Theoretical treatment is deliberately omitted. It is implied that the readers possess some theoretical background.

The only organic compounds included are the hydrocarbons in the C_5 range. With this limitation the book is not of much interest to organic chemists.

It is certainly of greater interest to industrial chemists interested in the analysis of flue gases, atmospheric gases, exhaust gases, etc.

S. S. CHIBBER

AN INTRODUCTION TO RADIATION CHEMISTRY by J. W. T. Spinks & R. J. Woods (John Wiley & Sons Inc., New York), 1964. Pp. xi+477. Price \$ 12.75

Radiation chemistry which had its origin in the very discovery of X-rays in 1895 and of radioactivity in the following year has grown enormously during the last two decades. Some excellent books have appeared on specific aspects of the subject, such as Allen's *Radiation chemistry of water and aqueous solutions*, Charlesby's *Atomic radiation and polymers*, and the series of publications, *Actions chimiques et biologiques des radiations*, edited by Haissinsky. However, the present work is the first and so far the only single unified text-book on the subject.

As radiation chemistry derives support from a number of disciplines in physics and chemistry, a work of this kind must be very broad-based. The book rightly devotes, therefore, the first six chapters, nearly half the text, to a consideration of radiation sources, the physical principles of radiation interaction, radiation dosimetry, excitation and ionization of molecules, and free radical chemistry. Discussion of the actual effects of irradiation in chemical systems follows, Chapters 7-10 dealing with gases, water and aqueous solutions, aliphatic and aromatic compounds. The final chapters cover briefly irradiation effects in polymers and solids, and the industrial applications of radiation. The book is adequately illustrated with graphs and figures, and data, such as on radiolysis products and their yields, are extensively tabulated. Suggested reaction mechanisms are clearly described in most cases. Each chapter of the book has many literature references up to 1963. There are appendices which include a list of various useful physical quantities and several worked numerical problems which aim to illustrate the main types of calculation involved in radiation chemical work.

The book presents a lucid exposition of the whole field of radiation chemistry. A drawback is that irradiation effects in polymers and solids have not received their due share of attention. With this single qualification, the book may be recommended as a text for postgraduate courses in radiation chemistry and as an introduction to the subject for those interested.

S. R. MOHANTY

PROCESS CONTROL by Peter Harriott (McGraw-Hill Book Co. Inc., New York), 1964. Pp. xvii+374. Price \$ 13.50

Process control by Prof. Harriott comes at a time when the importance of this subject is being increasingly felt and the dynamic behaviour of processes and processing equipment is taught at almost every centre

of chemical engineering in Europe and USA. This book is remarkable in that emphasis is not placed on the mechanical features of instruments and controllers but on the dynamic behaviour of processes. There are in India very few institutions which offer courses in process control. This book is, therefore, to be greatly welcomed since it not only caters to the needs of the student but is also suitable for self-study by practising engineers.

The book is divided into 16 chapters. Starting with a historical review of control, the use of block diagrams, and close-loop and open-loop control systems, the author proceeds systematically to cover the entire basic aspects of the dynamic behaviour of processes and equipment. The most important single mathematical concept in these studies is the Laplace transform, and a full chapter is devoted to the explanation of this concept. Included in the book are chapters on frequency response of controllers, the dynamics and control of heat exchangers, the dynamics and control of distillation columns, flow control, level control, control valves and transmission lines, and the stability and control of chemical reactors. Each of the chapters is written very clearly; the average chemical engineer should find no difficulty in following this book since the level of calculus assumed should normally be within his grasp, particularly as the chief mathematical instrument, viz. the Laplace transform, has been fully explained.

It is hoped that courses in process control will be introduced in every chemical engineering school in this country, and *Process control* by Harriott is an ideal starting point both for instruction and self-study. I have no hesitation at all in recommending this book strongly to every chemical engineering school.

L. K. DORAISWAMY

ROAD RESEARCH SPECIAL REPORT No. 1 (Central Road Research Institute of India, Okhla, Delhi), 1964. Pp. viii+290. Price Rs 13.00

The Central Road Research Institute (CRRI) has published its first special report entitled 'Puzzolanic clays of India, their industrial exploitation and use in engineering works'. Part I of the report deals with an all-India survey conducted by the survey team of the Institute for locating major puzzolanic clay deposits. A total of 338 deposits were visited and of these 210 were found to yield satisfactory material, 70 of them being usable for manufacturing very reactive *surkhis* for civil engineering work.

The manufacturing aspects of puzzolana products such as puzzolana cement, reactive *surkhi* and lime-reactive *surkhi* mixtures are discussed in Part 2. Besides a few papers on clay puzzolanas of the Institute, a comprehensive bibliography covering the literature on puzzolanas and their use (1925-65) is included in Part 3.

Experimental evidence for coherent matter waves in superfluids

Recent researches made by Drs Paul L. Richards and Philip W. Anderson of the Bell Telephone Laboratories have provided strong experimental evidence that the atoms of superfluid liquid helium behave like coherent waves and interact in such a way that the viscosity of the fluid becomes zero. This has confirmed the validity of the recent theories that superfluidity and superconductivity are related and explainable by the quantum mechanics concept that matter has the properties of waves as well as particles. Theorists, in an attempt to find a relationship between superfluidity and superconductivity, have attributed the wave nature of matter as the basis for both the waves playing a role on a large scale and in a new way in the case of superfluidity. The most recent theories have proposed that the wave fields of pairs of electrons (in a superconductor) and of atoms (in a superfluid) are coherent. That is, like light waves in a laser beam, they have the same frequency, amplitude, direction, and phase relationship. To test this coherence aspect of superfluidity, a simple and direct experiment, analogous to one on superconductivity suggested by B. D. Josephson of Cambridge University (called the 'alternating current Josephson effect'), was devised.

In the experimental set-up (Fig. 1), there are two reservoirs of liquid helium filled to different levels or heads. According to the theory, matter waves in each reservoir oscillate at frequencies whose difference is proportional to the difference in heads. If the reservoirs are connected by a pinhole orifice, the superfluid tends to flow from the high level reservoir, through the orifice, to the low level reservoir, equalizing the head difference. Theory predicts that because the matter waves in each reservoir are oscillating at different frequencies there will also be, in addition to the direct flow through the orifice, an alternating flow at a frequency related to the difference in the heads.

To observe whether this alternating current actually exists, a

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small ultrasonic transducer is placed near the orifice in the low head reservoir. The vibration of the transducer generated another alternating flow of liquid helium through the orifice.

It was reasoned that the natural oscillation of liquid helium would attempt to synchronize with the impressed oscillations. That is, the liquid levels would tend to move together until the frequency of matter waves (determined by the difference in level) is the same as, or a simple multiple of, the transducer frequency. When this occurs the steady flow through the orifice will be stopped and the movement of the levels will hesitate briefly.

In the experiment the levels did, indeed, tend to 'stick' at

certain values of head difference as predicted by the theory. It is believed that these 'steps' in the changing levels can be explained only by the existence of an a.c. effect in superfluid helium analogous to the a.c. Josephson effect in a superconductor. This effect in turn demonstrates directly that the wave fields in the two reservoirs are coupled in phase and, therefore, must be coherent [News from Bell Telephone Laboratories, 7 April 1965].

Chemical reaction by two-photon effect with laser light

For the first time the two-photon effect achieved with light from a laser has been used to cause a specific chemical reaction at the Bell Telephone Laboratories, New York. When a sample of distilled styrene monomer was irradiated with light from a pulsed ruby laser, polystyrene was found to be produced. The polymerization was caused by the simultaneous absorption of two photons by the monomer molecule.

The success of these experiments may open a potentially vast area of molecular phenomena that can be explored with the laser's highly intense and monochromatic beam of light. The experiments are believed to have demonstrated a general phenomenon inducing possibly many other multiphoton photochemical reactions.

In these experiments freshly distilled styrene monomer was subjected to a succession of some 20 laser pulses. The sample was kept at liquid nitrogen temperature to stabilize free radicals released during the two-photon process. Following the irradiation, the sample was warmed to room temperature and the polymer was precipitated. An infrared spectrum analysis showed that the precipitate was identical to that of polystyrene.

The monochromatic light from a ruby laser occurs at a wavelength of 6940 Å. Photons at this wavelength have an energy equivalent

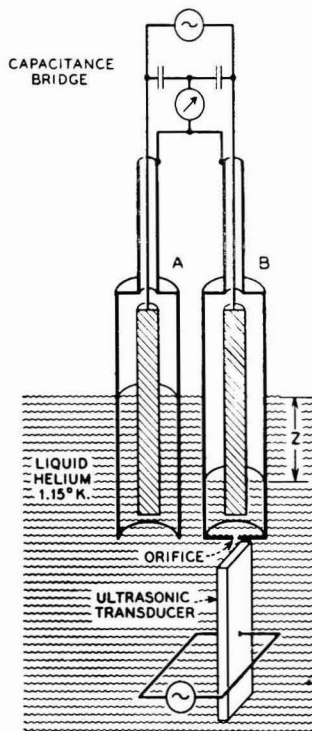


Fig. 1 — Experimental set-up for observing coherent matter waves in superfluid helium [A, coaxial capacitor; B, capacitor with a pinhole orifice; and Z, the liquid head difference]

of 1.8 eV. Styrene monomer, however, cannot absorb such light, and—even if it could—this energy would not be sufficient to induce a chemical reaction. However, in the interaction of the intense laser beam with the molecular system, there is a process by which two photons are absorbed almost simultaneously to excite the monomer by 3.6 eV. This, in turn, causes the formation of free radicals and induces polymerization.

The two-photon effect can be described as a process that proceeds from an initial state to a final state by way of intermediate states. These intermediate states are called virtual states because the transition to any one of them involves absorption of a 1.8 eV. photon and excitation of the molecular system by an energy either greater or less than 1.8 eV. The lifetimes of such virtual states are of the order of 10^{-13} or 10^{-14} sec. These states are significant only when the incident photon flux is so high that transitions from these to the final state may be induced.

When another 1.8 eV. photon is absorbed, the molecular excitation is again not equal to 1.8 eV. The sum of the two excitations, however, is equal to 3.6 eV. or equivalent to the energy of the two photons absorbed.

Estimation of radiation dose on finger tips

The Atomic Energy Establishment (AEE) of UK has evolved a new technique for measuring the radiation dose received by the fingers of persons handling radioactive materials. The technique is based on the effect of radiation on thermoluminescent properties of lithium fluoride.

The measurement of finger tip doses by means of conventional photographic film dosimeters, which hitherto presented special difficulties, is now facilitated by the use of a dosimeter using lithium fluoride powder.

A small quantity (30 mg.) of lithium fluoride powder contained in a specially designed polyvinyl chloride satchel is attached to the finger tip. The exposed lithium fluoride is removed from the satchel and heated under controlled conditions. Measurement

of the light output emitted by the powder in proportion to the radiation dose received by it provides an accurate measure of the radiation dose received by the satchel and hence by the finger tip. The lithium fluoride can be used again.

The new technique, which is in use at the AEE, UK, will also find application in hospitals to measure dose to the finger tip of the staff dealing with radioactive sources [*Atom*, (No. 101) (1965), 61].

An integrated theory of stress corrosion

An integrated theory which provides a more favourable basis for the development of an overall model for stress corrosion has been proposed by K. C. Thomas and R. J. Allio of the Atomic Power Division, Westinghouse Electric Corporation, Pittsburgh, Penn. (USA). This theory is an improvement over the currently favoured electrochemical-mechanical theory in that it may be possible to predict the effect of cations in solution and other environmental factors on the susceptibility to stress-corrosion cracking of alloys and stainless steels. According to the new theory proposed, the chloride stress-corrosion susceptibility is controlled both by dislocation of the substructure and by the chloride migration capacity of the oxide film. The concentration of chloride at regions of high stress will result in conditions conducive to stress-corrosion failure. The differences in the sizes of the chloride and iron ions and in the bond energies of Fe-O, FeCl₂ and NiO and NiCl₂ are the factors that affect the migration. The application of the new theory is being extended to studies on the determination of the migration rates of chloride ions in the oxide film which will be governed by the cations in contact with the oxide film and the cations in the film, and for developing techniques for examining the stress-corrosion failure involving the hydroxyl ion [*Nature*, 206 (1965), 82].

A new allotrope of boron

A new crystalline allotrope of boron has been prepared by research workers at the Central Electric Research Laboratory,

Schenectady, New York, employing a high pressure and high temperature technique. Low temperature modifications (β -rhombohedral and 'amorphous') of purified boron mixed with silicon powder or magnesium oxide are subjected to a pressure of 100-150 kb. in a tube, made of tantalum or titanium, and electrically heated to a temperature of 1500-2000°C. for a period of about 6 min.; later, the system is cooled and the pressure brought down to the normal. A dark pitchlike solid, denser than all the hitherto known forms of boron [d 2.52 g./cm.³], is obtained. The new allotrope of boron exhibits high electrical resistivity (10^6 ohm cm.) and both β -type and n -type semiconductivity. Periods exceeding 6 min. and pressures above 100 kb. do not materially alter the properties of the product. Debye-Scherrer patterns of the product obtained under various conditions differ from those of the other varieties and also rule out the possibility of a compound of boron with titanium or tantalum [*Science*, 147 (1965), 49].

Application of fluorography to thin layer chromatography

A new technique of applying fluorography to thin layer chromatography of tritium-labelled compounds has been developed at the Institute of Pharmacology, University of Zurich.

Autoradiographic methods have not so far found application to thin layer chromatography of tritium-labelled compounds because of the low tritium energy [$E_{max.} = 18.5$ keV.; $E_{mean} = 5.7$ keV.]. The surface density of a 250 μ thin layer of silica gel G is 5.5 mg./cm.², about 20 times the tritium range of 0.28 mg./cm.² in a layer of sodium alginate, which means a self-absorption loss of radiation of more than 95 per cent. If the thin layer material is mixed with an adequate scintillator the tritium radiation can be made visible by the fluorescence induced in the scintillator, provided the scintillator molecules are within the range of the tritium β -particles and the thin layer is transparent. The new method takes advantage of four properties of anthracene as scintillator: its

high fluorescence efficiency; the temperature dependence of its fluorescence intensity; its low solubility in most of the common solvents; and its low chemical reactivity. Solid anthracene is finely ground in a ball mill with equal amounts of silica gel G (gypsum content 13 per cent) to a crystal size of 1.5 μ . The diameters of these crystals will thus be just one-third of the range of a tritium β -particle which is calculated to be 12.7 μ . Thirty g. of this mixture are added to 80 ml. of 96 per cent ethanol. After thorough shaking, the suspension is evenly spread over glass plates with a special distribution apparatus and dried at room temperature. Thirty g. are sufficient for ten thin layer plates (20×10 m.²) 250 μ thick, their surface density being 5.5 mg./cm.². The chromatographic properties are the same as those of pure silica gel except for slightly prolonged travelling times. Chromatograms of tritium-labelled compounds are covered with X-ray films ('Kodirex' Kodak) and exposed over dry ice at -70°C .; 0.08 μC . of tritium can be detected after exposure for one day. Control experiments have to be carried out with unlabelled compound.— Low temperature during exposure is essential. A tritium-induced fluorograph is 30 times as intense at -70°C . than at $+4^{\circ}\text{C}$. Further lowering the temperature to -200°C . does not increase the film blackening. The temperature variation of the scintillator response seems to be correlated with the vibrational freedom of the molecules. The application of the above technique to ¹⁴C-labelled compounds shows no advantage over the ordinary contact autoradiography. Because of its high β -energy—about 10 times that of ³H—¹⁴C is more likely to react with the photographic emulsion than with the microcrystals of the thin layer.

The method could be improved by raising the anthracene/silica gel ratio. The amplification of tritium-induced fluorescence on pure anthracene is about 15 times higher than on mixtures containing 50 per cent anthracene. Anthracene layers are easily prepared with 10 per cent gypsum or small amounts of detergents like sodium

laurylsulphonate [*Nature, Lond.*, **205** (1965), 1190].

Mechanism of induction and formation of histidase

The current theories of protein synthesis envisage the transcription of the information necessary for the synthesis of a protein from DNA to an unstable m-RNA. The latter attaches itself to a ribosome and acts as a template for the formation of the protein molecule. Moreover, considerable evidence has been accumulated in support of the model proposed by F. Jacob and J. Monod [*J. mol. Biol.*, **3** (1961), 318] that the inducer of an enzyme acts by stimulating the accumulation of m-RNA. Recently, L. H. Hartwell and B. Magasanik [*J. mol. Biol.*, **7** (1963), 401] have studied the various steps involved in the induction of histidase by histidine in *B. subtilis* and the mechanism by which histidine induces the enzyme histidase [*J. mol. Biol.*, **10** (1964), 278]. The first step involved in the induction of histidase is the uptake of histidine by *B. subtilis*. The uptake was facilitated by a constitutive permease and the concentration necessary for the induction process was reached within 0.5 min. Kinetic studies indicated that a precursor of the enzyme histidase is formed first in 2 min. after the addition of the inducer which is converted to the active enzyme in the course of another 2 min. The conversion process does not require a protein synthesizing machinery or energy. The precursor was found to be heat labile and susceptible to sulphhydryl inhibitors, whereas the active enzyme is stable up to 80°C . and not inactivated by sulphhydryl inhibitors. Probably, the conversion of the precursor to the active enzyme may involve the formation of disulphide bonds or conformational changes resulting in the protection of sulphhydryl groups.

Histidine may induce the enzyme histidase either by preventing the destruction or increasing the synthesis of the histidase-specific m-RNA. Either of these possibilities requires the neutralization of the cytoplasmic repressor by the inducer. The cytoplasmic repressor, unless neutralized by the inducer, could decrease this level either by interacting specifically with the

histidase segment of DNA to prevent the synthesis of histidase m-RNA or by interacting with the histidase m-RNA thereby bringing about its destruction.

The finding of Hartwell and Magasanik indicates that the induction is not due to the stabilization of the m-RNA already present, but due to the stimulation of m-RNA synthesis as suggested by Jacob and Monod.— (Miss) D. E. LEELAVATHI

In vitro formation of a DNA ribosome complex

The physical connection between the two biochemically linked steps of the transfer of genetic information, transcription and translation is not yet known. However, three possibilities may be conceived: (a) completely uncoupled, (b) completely coupled, and (c) transiently coupled.

In higher organisms, it is mainly completely uncoupled. Here RNA (complementary RNA) synthesized on the nuclear DNA template is transferred on to the cytoplasmic ribosomes through the nuclear membrane with possibly the ribonucleoprotein particles acting as carriers. However, in calf thymus nuclei, protein is synthesized on the nuclear ribosome itself and is, therefore, a completely coupled process. In bacteria, where there is no distinct nuclear membrane, the transfer of message may be explained as a transiently coupled process, although other possibilities exist.

Recently, R. Byrne, J. G. Levin, H. A. Bladen and M. W. Nirenberg [*Proc. nat. Acad. Sci., Wash.*, **52** (1964), 140] have obtained evidence for the assumption that DNA-RNA-ribosome complexes are formed as intermediates during protein synthesis in *Esch. coli*:

(i) Sucrose density gradient sedimentation studies showed that the DNA that is actively engaged in nucleic acid synthesis sediments at a faster rate than the one which has lost its template activity. This faster sedimentation is probably due to the formation of DNA-RNA-ribosome complexes. The complex formation seems to be independent of protein synthesizing capacity.

(ii) Removal of RNA and DNA by RNase and DNase treatments

respectively decreased the sedimentation rates of the complex; and finally,

(iii) Electron micrographs showed clusters of particles attached to strands, with short connecting branches. The interpretation given is that the 'particles' represent 70s ribosomes, 'strands' represent DNA and the 'branches' are c-RNA.

The presence of DNA-RNA-ribosome complex may mean that the *in vitro* protein synthesis in this bacterial system is a completely coupled process, but the observed existence of polyribosomes with nascent protein leads to the conclusion that it is only transiently coupled.

From these evidences, the process of protein synthesis in this system has been pictured as follows: the ribosome goes and attaches itself to the cRNA, sometimes after the onset of the synthesis of the latter on the DNA template. This may signal the beginning of polypeptide synthesis on the ribosome. It may then be followed by the attachment of other ribosomes and this cluster of polyribosomes will be liberated from the DNA template which could still continue protein synthesis.

How far this observation helps in explaining the already existing concepts like the stabilization of cRNA, coupled regulation, etc., has been discussed by these authors. They agree that c-RNA which is very unstable could be degraded by the nucleases present in cytoplasm. Attachment of ribosomes to c-RNA will not only protect the latter from degradation but also prevent any other cytoplasmic components from getting attached to it. The ribosomes in bacterial systems may be analogous to the 'carrier' ribonucleoprotein particles of higher organisms involved in c-RNA transport.

The DNA-RNA-ribosome complex formation provides physical basis for the formation of polarity mutants with cistron sequence proposed by Ames and Hartman. If protein synthesis were to start before the synthesis of cRNA is completed on DNA template, proteins coded by the cistrons at the beginning of the operon may be synthesized earlier. Any delay either in the further synthesis of cRNA or its release from the template would result in the accumulation of proteins specified

by the initial cistrons and not by later ones.

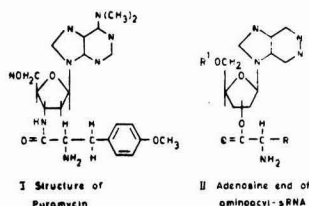
The observation that the specific enzyme synthesis is always accompanied by an alteration in the corresponding cRNA level can be explained in the light of these results. The DNA-RNA-ribosome complex represents the physical link between transcription and translation and any factor operating at this level would alter the levels of both cRNA as well as the enzyme protein.

The generality of the complex formation may be unique to the *in vitro* systems, and may be one of the factors that can differentiate the *in vitro* systems from the *in vivo*.— (Miss) J. AMRUTAVALLI

Puromycin inhibition of protein synthesis

Puromycin, an antibiotic which does not have much clinical demand due to its nephrotoxicity, has been of great value in biochemical work. It has been found to be a specific, reversible inhibitor of protein synthesis. In growing bacteria, the overall rate of protein synthesis is markedly reduced by puromycin, but RNA and DNA syntheses continue at a normal level. Removal of the drug restores the protein synthesis.

Baker [*J. Amer. chem. Soc.*, **77** (1955), 12] by degradative and synthetic studies established the structure of puromycin as a 3'-amino-nucleoside of dimethyladenosine with L-O-methyl tyrosine linked via an amide bond to the 3'-amino group. Yarmoluisky and de la Haba [*Proc. nat. Acad. Sci., Wash.*, **45** (1959), 1729] first started the studies on the mechanism of inhibition and related the structure of the antibiotic to that of an intermediate in protein synthesis, namely aminoacyl-s-RNA. They further proposed that the antibiotic inhibits protein synthesis by acting as structural analogue of esterified s-RNA.



The fact that 2'-isomer of puromycin has no inhibitory activity shows that the active form of aminoacyl-s-RNA is a 3'- rather than a 2'-adenosine ester. Daniel Nathans [*Nature, Lond.*, **147** (1963), 1076] tried different analogues of puromycin and found that the nature of the amino acid in the side chain has considerable influence on the activity of the analogue. Aromatic amino acid analogues were far more active than the others, although leucine analogue had also some activity. Nathans also showed that the particular amino acid substituted does not confer specificity for the inhibition of that particular amino acid.

Though puromycin inhibits the transfer of amino acids from s-RNA into the acid-precipitable polypeptides, amino acids continue to be lost from s-RNA and appear in acid- or alcohol-soluble products, which have been identified as peptides and free amino acids. This suggests that puromycin causes premature release of incomplete peptide chains from the ribosome template RNA complex. A possible mechanism for this release is the direct substitution of puromycin as an acceptor of the carboxyl activated peptide bond to the template.

In order to establish this mechanism, it was desirable to show unequivocally that puromycin gets linked to peptide being synthesized via a peptide bond in the course of protein synthesis. Nathans used synthetic puromycin labelled with tritium and the $-\text{OCH}_3$ group of the amino acid and added to growing cultures of *Esch. coli* and determined the radioactivity in an acid-precipitable fraction. From this, by means of chemical and enzymic treatment, radioactive O-methyl tyrosine or puromycin were recovered.— B. P. SANI

Progress Reports

Building Research in UK

Among the achievements recorded in the annual report of the Building Research Station, UK, for the year 1963, the most significant are those relating to new framework designs based on investigation of redistribution of bending moments resulting from the plasticities of mild steel when

subjected to overstress. For simple structures, a saving of about 25 per cent of steel has been made possible. Considerable progress has been made in studies on the buckling of columns restrained by beams, offering a possible saving of 15-25 per cent steel.

The station has made significant contribution in the preparation of the code dealing with the design of rigid frame multi-storey buildings for no-sway conditions, including devising simple but comprehensive and accurate design charts for the BRS method. The development of 'Humper', a universal handling machine for unloading and carrying different types of materials on building sites, has been completed. An artificial sky developed for use in daylighting studies consists of a luminous ceiling surrounded by plane mirrors of special glass, which reflect the image of the luminous ceiling to infinity, giving a true horizon. The errors inherent in the conventional hemispherical vault type artificial sky are eliminated in the new sky. Comparison has been made of the errors involved in X-ray and microscopic methods for determining the quantities of the two calcium silicates in Portland cement. The standard deviation in microscopic paint-counting has been found to be about one-third of that in X-ray diffractometry. As a part of study on the hydration products formed during the setting and hardening of cement, the equilibria in the system $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4\text{-H}_2\text{O}$ at 25°C. have been investigated. It has been observed that calcium monosulphoaluminate hydrate and tetra-calciumaluminate hydrate form a limited series of solutions of $\text{CaSO}_4/\text{Al}_2\text{O}_3$ molar ratio from 1.0 to 0.50, the longest basal spacing in the X-ray pattern changing from 8.96 to 8.77 Å. Direct X-ray examinations carried out on thin specimens of cement paste kept in a humid atmosphere showed that the hydrates were present in their fully hydrated condition. Traces of carbon dioxide, such as could be present in cement as received, can affect the hydration reactions markedly. It has been shown that in some cements the normal X-ray pattern of tricalcium aluminate appears with some of the characteristic lines doubled as a sodium calcium aluminate is present in it.

An earth pressure cell has been developed for inserting in a mass of soil. The cell has an identical stiff diaphragm on each face, each diaphragm being fitted with vibrating wire transducers. This has overcome a number of problems found in other designs.

Ore Dressing Laboratory, Melbourne

The main activities of the laboratory in the year 1963-64 covered the following areas: chemistry of flotation pulps; ore grindability; gold recovery from complex gold-sulphide concentrates; contamination of sulphide copper concentrates by nickel from grinding balls; gravity concentration; high tension separation; chemical analysis; silica products; and copper and gold ores. Some of the significant results obtained are summarized below:

Gold recovery from complex sulphide concentrates—Some promising results were obtained by roasting the concentrates, followed by cyanidation in a brine solution; however, major variations were observed in gold recovery due to minor mineralogical differences in the concentrates investigated. Silver is found to be more 'roast sensitive' than gold. Best results have been obtained by a four-stage process, consisting of cyanidation of concentrates, roasting the residue, acid brine leaching and final cyanidation. Comparative yields are: direct cyanidation, 70 and 40; cyanidation after roasting, 80 and 30; and four-stage process, 93 and 80 per cent of gold and silver respectively.

Contamination of sulphide copper concentrates by nickel from grinding balls—Contamination of copper concentrates by nickel can lead to difficulty in copper refining. Studies were conducted on the amount of nickel abstracted from Ni-hard grinding balls in the flotation concentrates. It has been observed that only about 5 per cent of the abraded Ni-hard floats, increasing the nickel content of the concentrate by 6-50 p.p.m., depending upon the amount of Ni-hard abraded during grinding, the copper content of the ore, the grade of the concentrate, and the flotation reagents used. In all ores examined there was some inherent nickel, which varied both in amount

and in distribution between the gangue minerals, the pyrite and the copper minerals. The nickel content of the pyrite, and the amount of pyrite reporting in the copper concentrate were important factors in determining the gold and nickel content of the copper concentrate.

Chemical analysis—In the estimation of tin by the cathode ray polarograph it was found that tungsten gave a distinct peak at 0.2 V. more negative than tin. A linear relationship has been found to exist between peak height and concentration of tungsten in a 5M hydrochloric acid solution.

Investigations for industry: Silica products—In attempts made to reduce the iron content of a silica sand to less than 0.02 per cent, a combination of heavy liquid and Frantz magnetic separation, with acid leaching was found to give a product containing 0.022 per cent iron. From flotation tailings, a high grade silica flour could be obtained by selective flotation and quartz whitening. Amine flotation in acid circuit removes a large proportion of the dark slate originally present. Further amine flotation in alkaline circuit gives a quartz product which is cleaned once. In plant trials, iron was dissolved during acid flotation, precipitated in alkaline circuit and interfered with the quartz float. This difficulty could be overcome by (a) floating the quartz immediately after the slate without adding alkali and cleaning the concentrate in alkaline circuit; (b) floating the quartz with a fatty acid in a circuit made highly alkaline by lime, and (c) decanting the pulp liquor after the acid float and using fresh water for subsequent alkaline quartz float. Quartz thus made gives a fairly white flour on heating and grinding. Addition of 0.2 per cent of sodium concentrate before heating is beneficial. Iron content is 0.03 per cent.

Division of Building Research, CSIRO, Australia

The main activities of the division during 1963-64 related to architectural, acoustics, bituminous materials, clay and clay products, concrete, gypsum, plaster, mortar joints, structural design and testing, paints, thermal aspects, tropical building and other studies. The establishment of a new section for

building operations and economics to undertake research on problems of the industry relating to management, organization and economics, the initiation of two new series of publications, entitled *Tropical building research notes* and *Ready research references*, and the installation of reverberation and transmission chambers for comparing the efficiency of various coverings in reducing footstep noise are some of the significant events.

To evaluate the noise level to be expected from a highway, taking into account the effects due to barriers such as trees and shrubs and other relevant influences, the noise levels and the duration of noise for different types of vehicles at varying speeds and distances from the road have been measured. Calculations of the total noise caused by a number of vehicles in random pattern (all within earshot at one moment) have been found to agree well with the observations of noise from a considerable flow of traffic. The study is expected to help in the planning of highways offering minimum discomfort to residents near the highways. A new method for studying the characteristics of absorption materials has been developed and employed for studying the performance of absorbing wedges for anechoic rooms. Studies on the performance of bituminous waterproofing membranes have shown that the best way of avoiding repture of a bituminous membrane laid over a joint in the deck where relative movement of the parts of the deck can occur, is to 'loose lay' rather than 'solid stick' the membrane in the neighbourhood of the joint. A survey of Australian ceramic resources and studies on the local raw materials in different regions, their fired products and the reactions involved in production processes have been conducted. In order to separate the triphormic and mixed layer minerals from the kaolinite and other minerals present in the Permian clays, an improvised electrophoretic cell capable of eliminating quartz completely and reducing the kaolinite content to a low level from the deposit, in just two cycles of treatment, has been designed.

Studies of the structure of opals have revealed that the water in opals is held mainly in the pores rather than as bonded (OH) groups and that all opals tend to form flaky particles when finely comminuted. Two major projects which have resulted in the accumulation of large amount of data useful to the industry are the studies connected with the light weight ceramic products and light weight concrete. A sponsored project, directed towards devising methods for the maintenance of colour on the surface of concrete roofing tiles, has shown that the loss of colour is most frequently due to the very slow dissolution of the binding material of the surface by rain water. Two parallel approaches have been adopted in an attempt to remedy this, one requiring improved curing of the tiles by fog or steam and the other seeking to protect the pigmented surface with a sprayed form of plastic film. Studies on the shrinkage of concrete in structures after prolonged mixing showed that the shrinkage of concrete mixed for 90 min. is nearly twice that of concrete mixed for 4 min. A thorough study of the characteristics of gypsum has been undertaken in view of the importance of gypsum to the building industry and observations on the physical and chemical properties of gypsum and special gypsum products have been made. The results of this study are expected to be of help in making plasters having special properties such as high water requirement or increased smoothness. Detailed recommendations have been drawn up, as a result of a series of tests on materials and methods for sealing joints in the exterior walls of a building to prevent rain penetration to the interior. An investigation directed towards developing a mould-resistant paint has indicated that paints containing zinc oxide will meet the requirement.

Announcements

■ *The Third Congress of the International Council for Building Research* will be held during 23-28 August 1965 in Copenhagen.

About 169 papers are to be presented and discussed. The congress is open to all those interested, members as well as non-members. Details may be had from DIS Congress Service, 19 Sankt Peders Straede, Copenhagen K, Denmark.

■ *A Symposium on Regulatory Mechanisms* will be held in the Department of Biochemistry, All-India Institute of Medical Sciences, New Delhi, on 28 and 29 December 1965 under the auspices of the Society of Biological Chemists, India. The following subjects will be covered: Regulatory mechanisms at body level, Regulatory mechanisms at cellular level, and Molecular mechanisms.

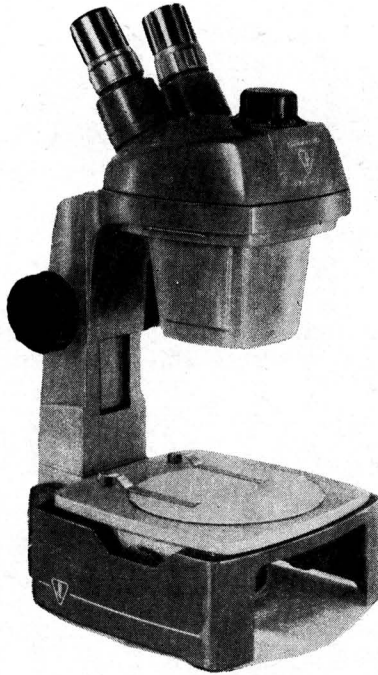
Those interested in the programme may please write to the Hon. Secretaries at Bangalore or to the organizer of the symposium, Dr G. P. Talwar, Department of Biochemistry, All-India Institute of Medical Sciences, New Delhi 16, with an abstract, not exceeding 200 words, before 15 October 1965.

■ *Amir Chand Prizes for Medical Research* — The Indian Council of Medical Research has invited applications for the award of four Shakuntala Amir Chand Prizes of the value of Rs 300.00 each for best published research work in any subject in the field of medical science including clinical research.

The prizes are open to medical and non-medical graduates who are Indian nationals and not above 40 years of age on 1 January 1965. The research paper submitted for consideration must have been published in Indian or foreign journals in the calendar year 1964, on work done in institutions in India only. Papers published on work started in India but completed abroad will not be acceptable. The person who applies for the prize should clearly indicate his/her role in the work presented in the paper.

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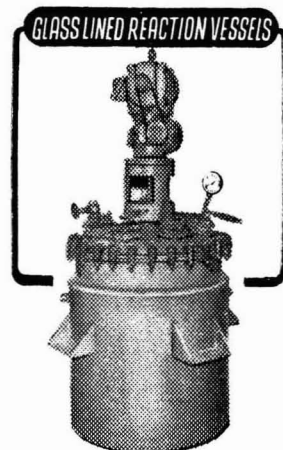
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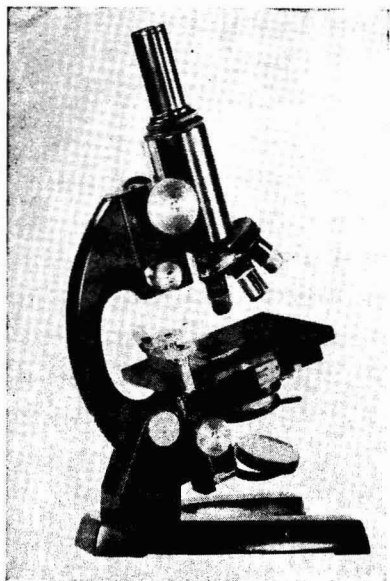
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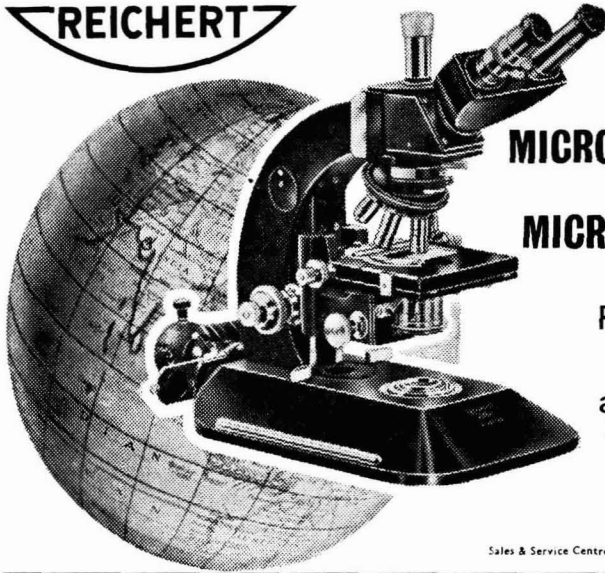
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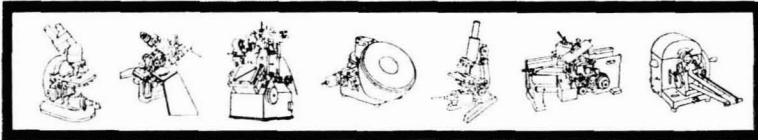
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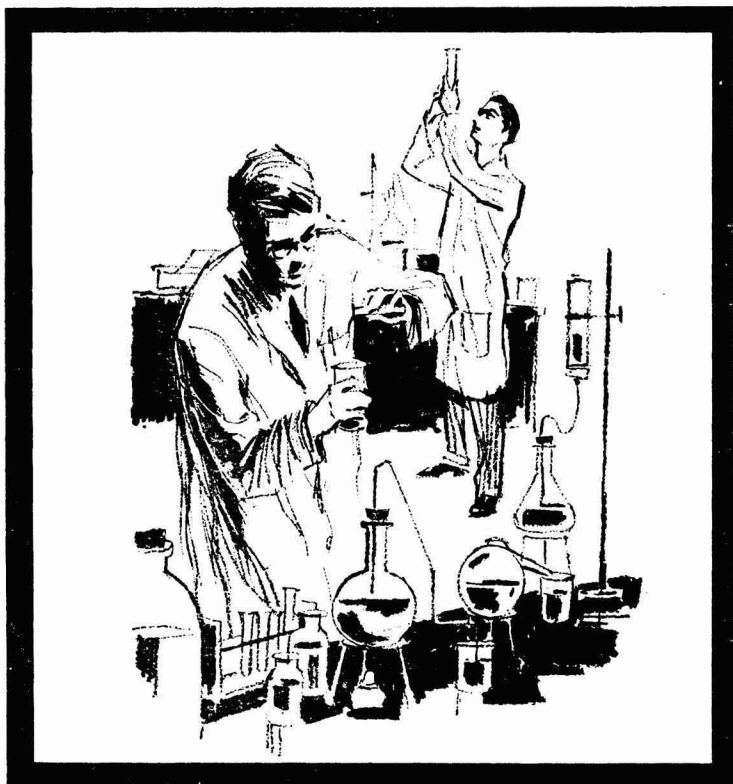
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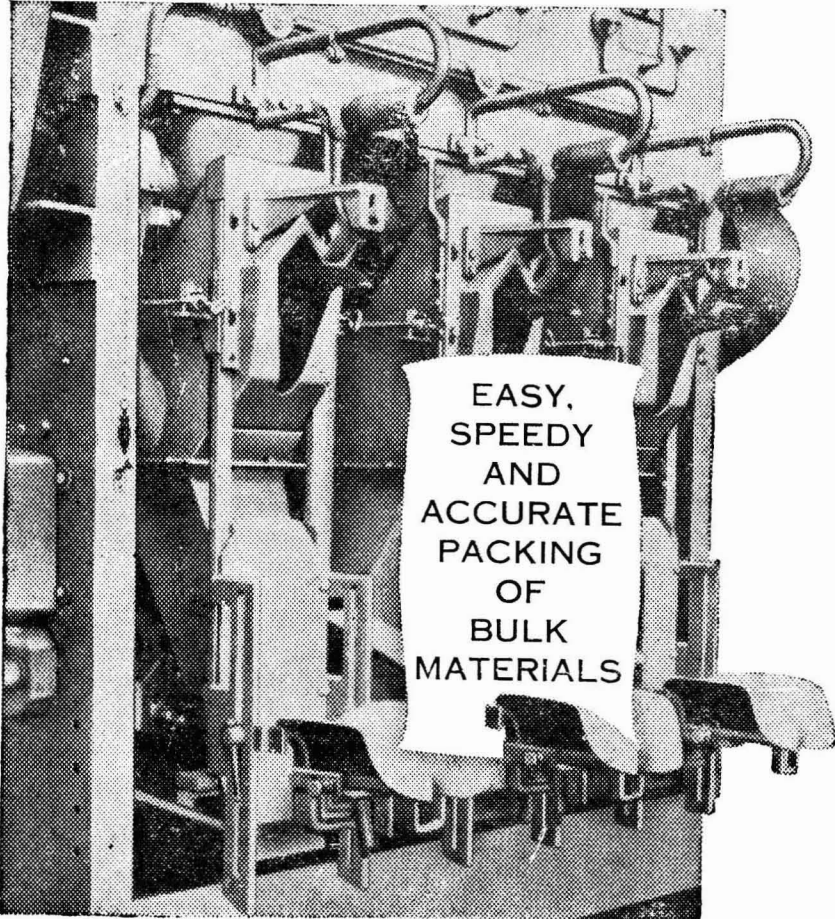
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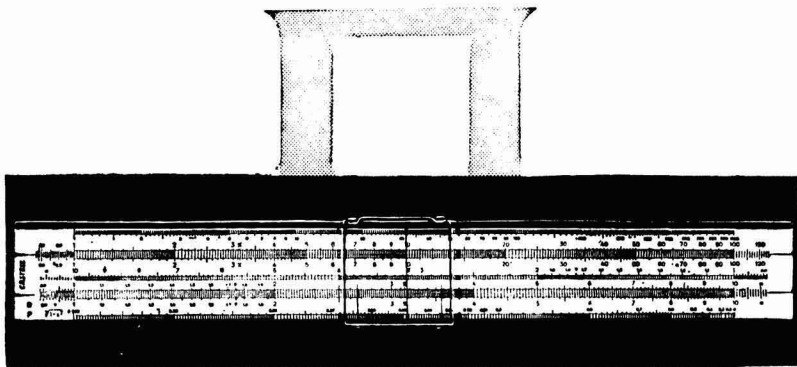
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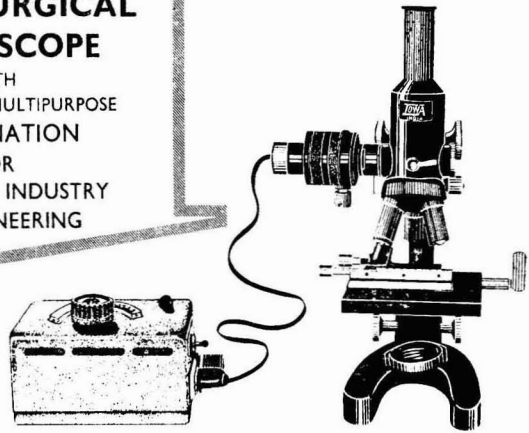
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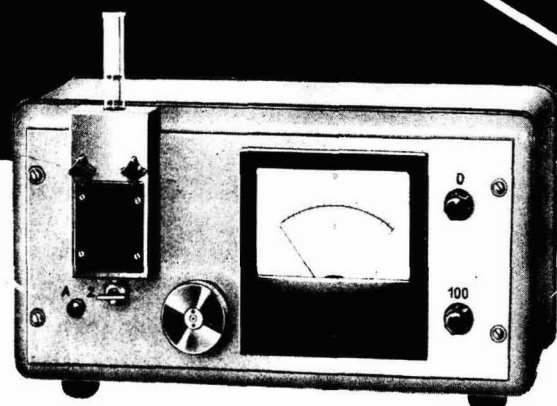
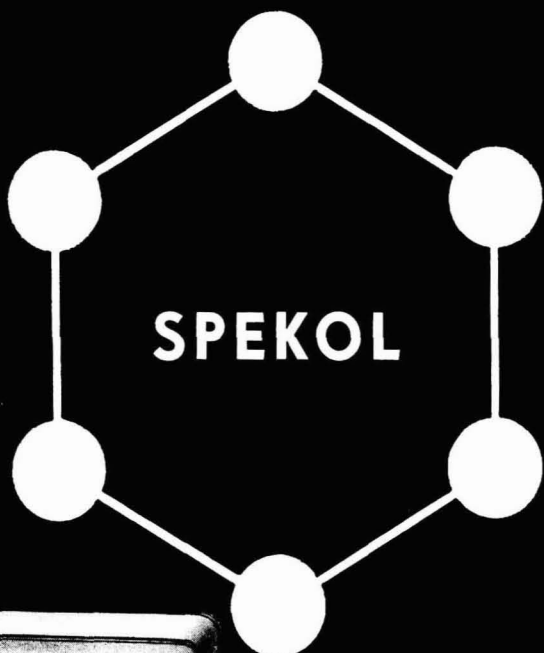
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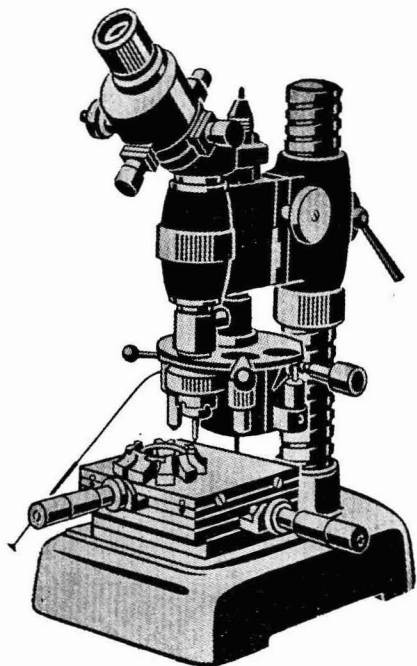
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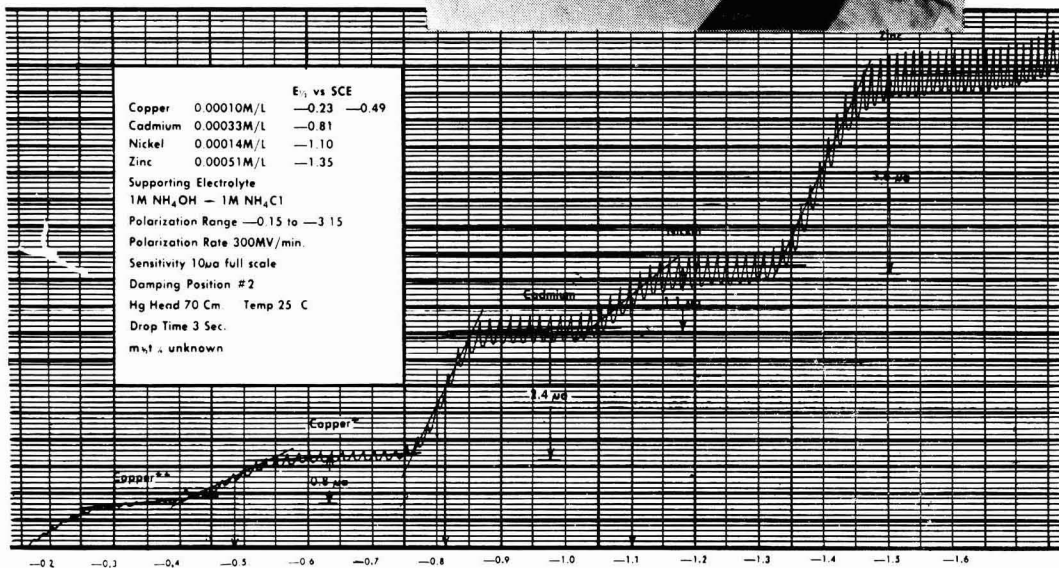
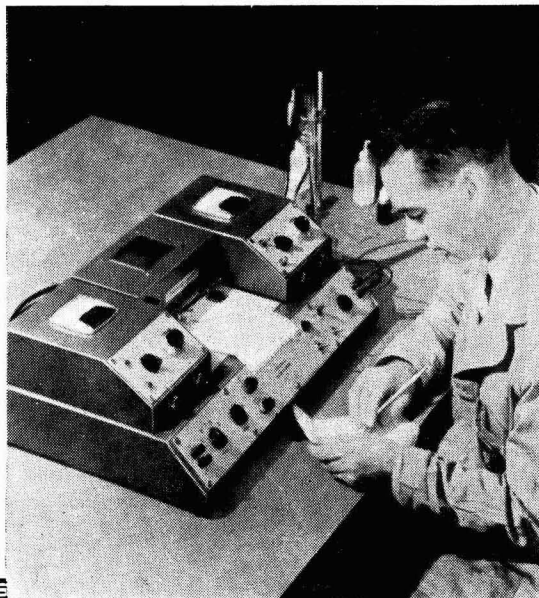
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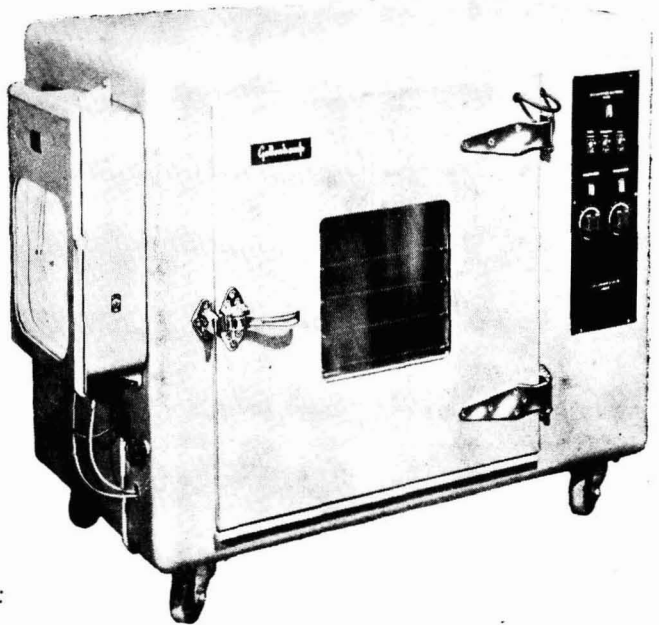
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