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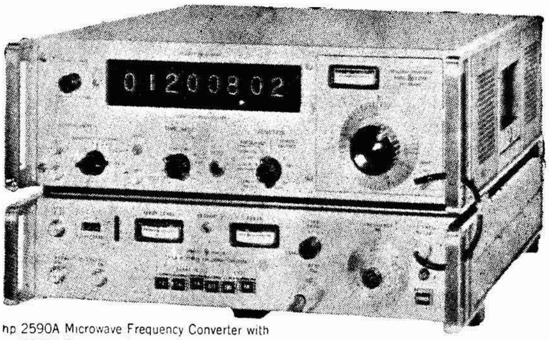

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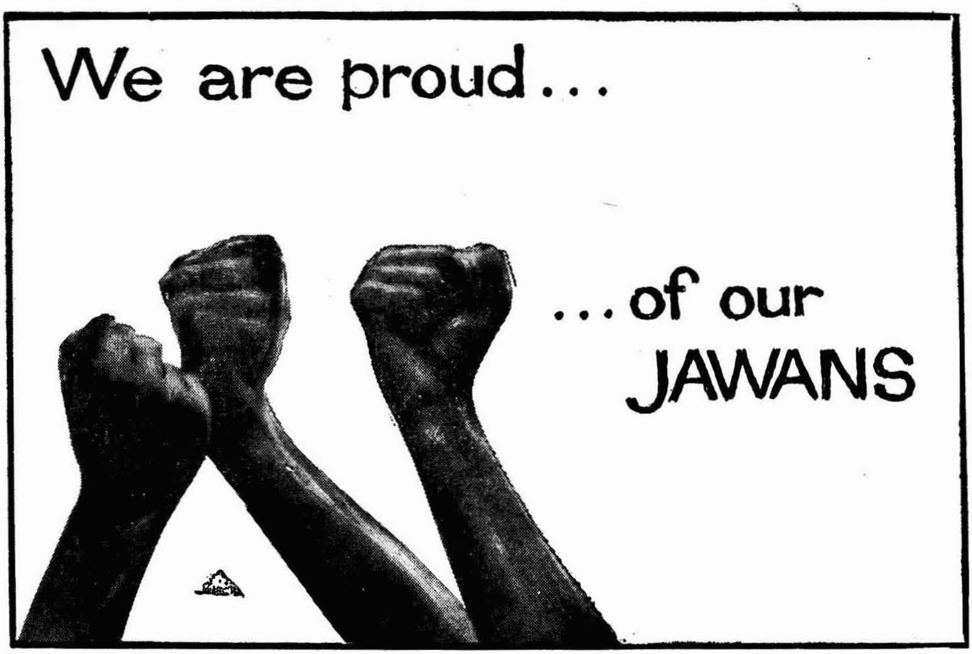
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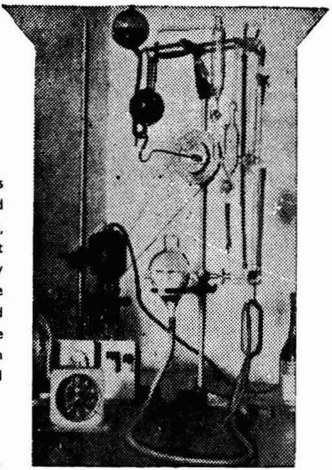

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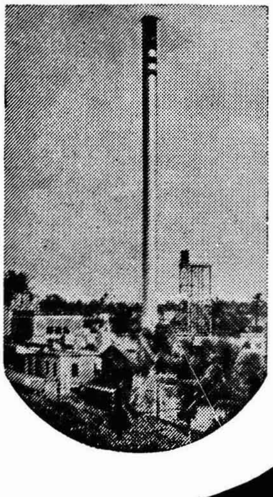

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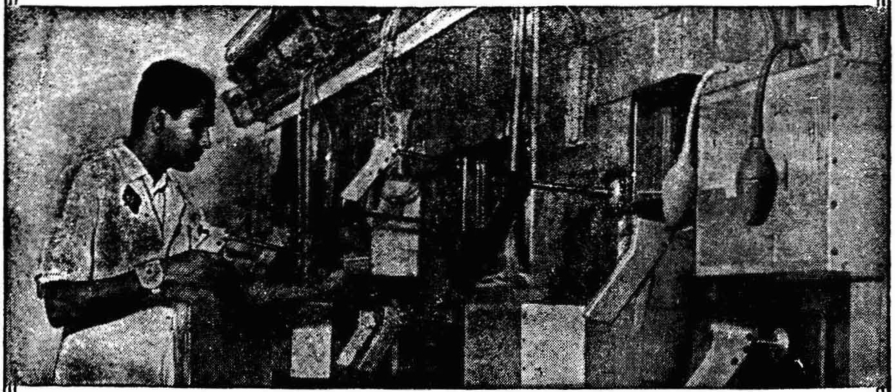

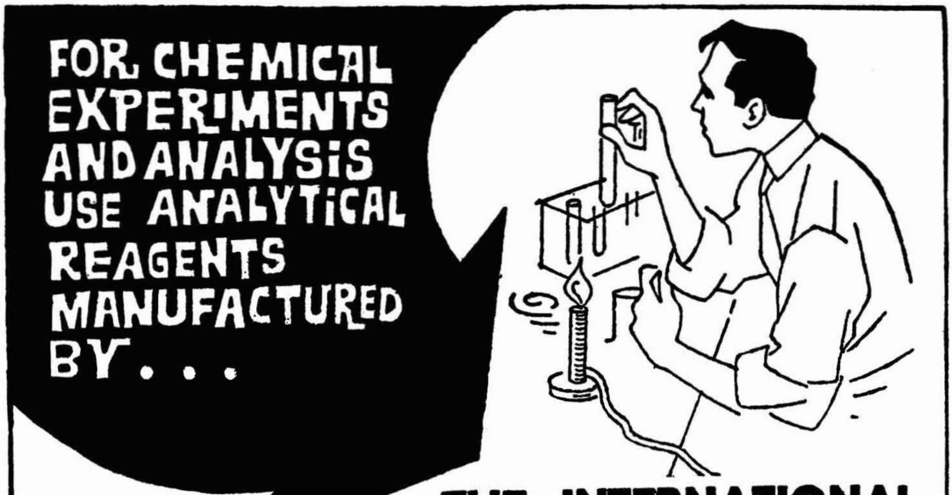
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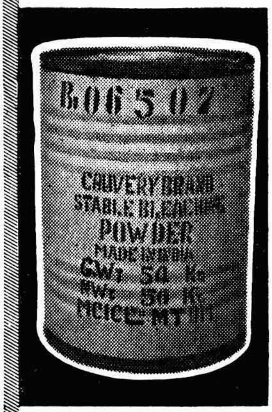
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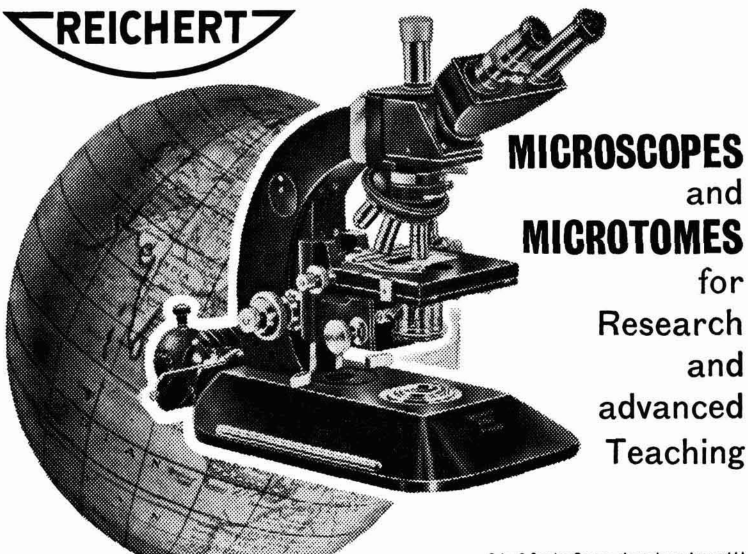
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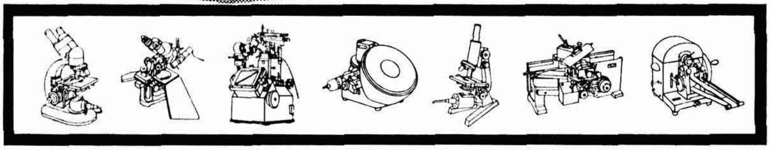

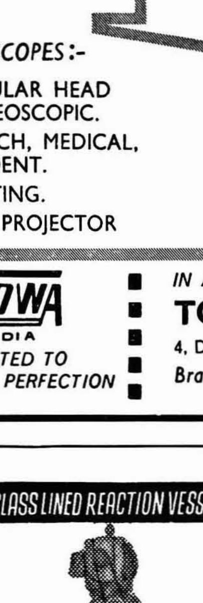

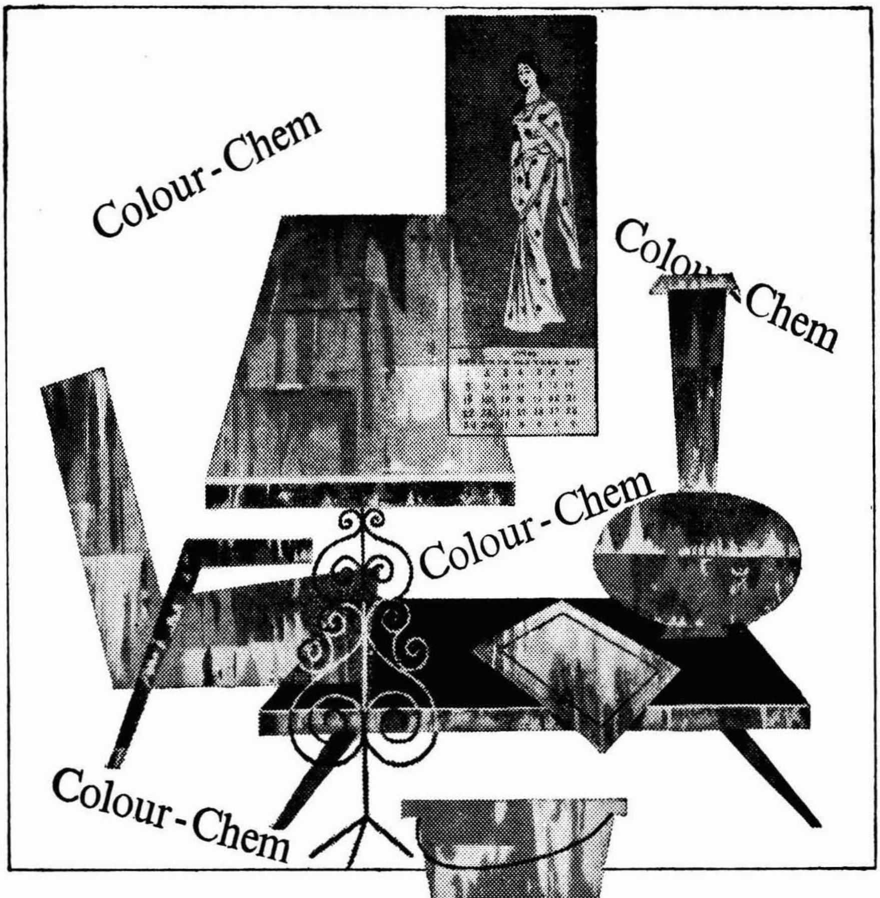
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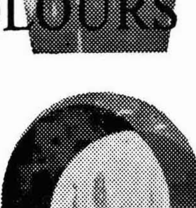

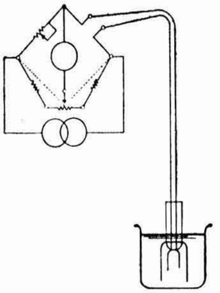

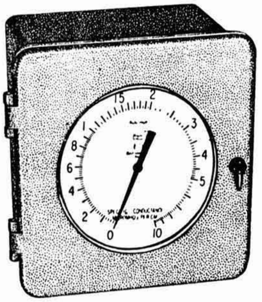

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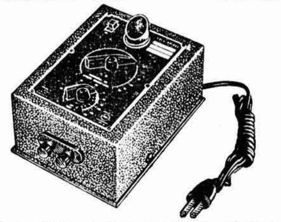

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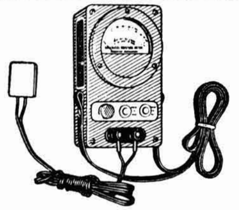

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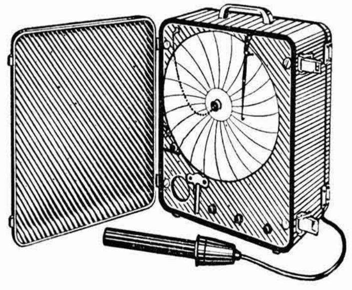

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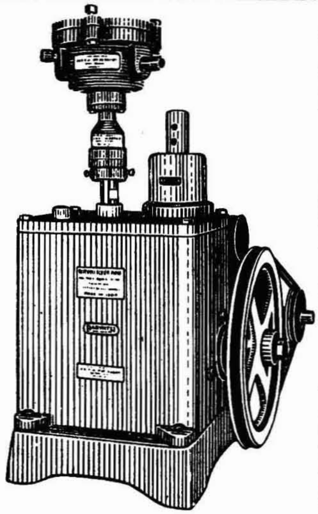

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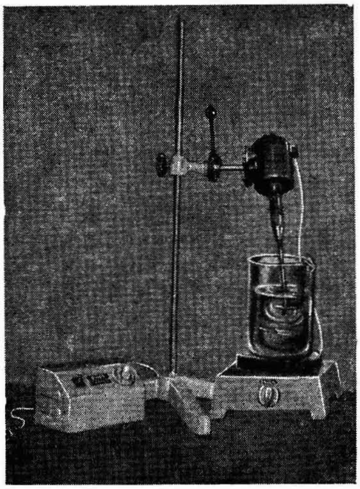

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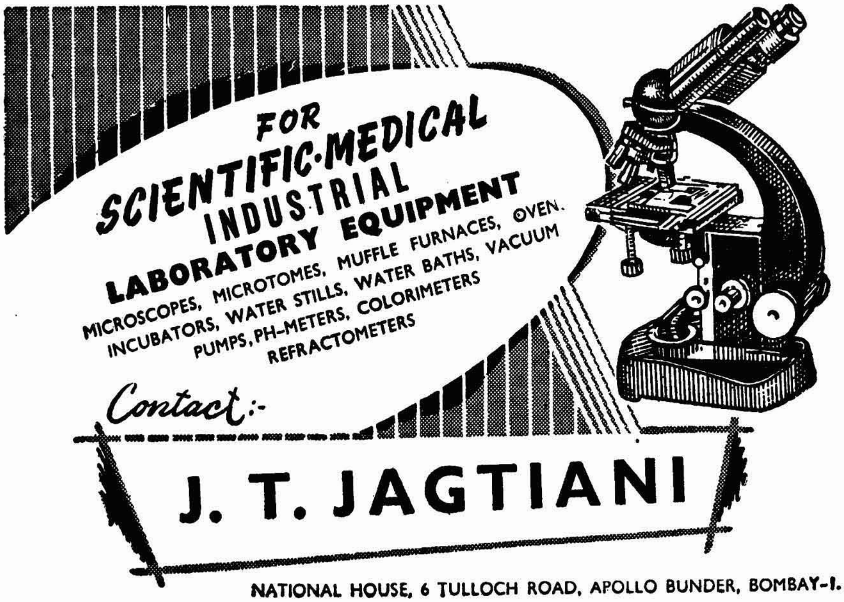

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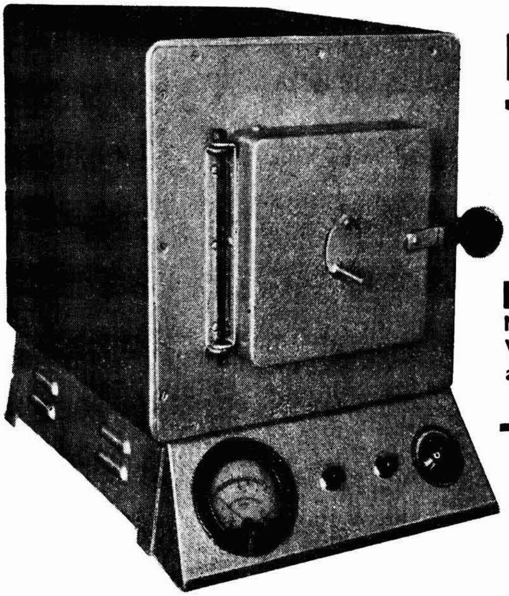

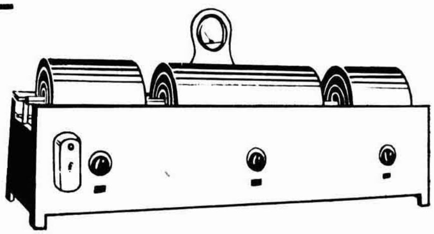

Current Topics

Research & Development Work at the Telecommunication Research Centre: An Example of Successful User Oriented Research

THE report of the committee set up under the chairmanship of Dr S. Bhagavantam, Scientific Adviser to the Ministry of Defence, to review the work and progress of the Telecommunication Research Centre (TRC), New Delhi, attached to the Posts and Telegraphs (P & T) Department, is a document meriting serious study by all those concerned with research and development work in the country. The work and achievements of the centre, as reviewed in the report, present a refreshing approach to the problem of utilization of research results, which often bristles with complex and apparently insurmountable bottlenecks. Effective and speedy utilization of research results is conditioned by the efficiency with which the following objectives are achieved: (i) identification of the problems of the user and planning of research programmes accordingly; (ii) development of suitable machinery for quick exploitation of the research results; and (iii) collaboration between the research organization and the user. It appears from the report that the work and achievements of TRC show the way as to how the above objectives can be achieved. The projects and programmes of TRC, as the committee observes, are user oriented, and it would be, therefore, of interest to examine how TRC has found the answers to speedy and effective utilization of research results.

Established in 1956, the TRC has emerged into an efficient research organization, and has added considerable resources to the development of communications and electronics industry in the country. The chief objective of the centre is to improve and expand telecommunication services in India, to the maximum extent possible, through modern technology and with the resources available in the country. Briefly the efforts of TRC are directed to (i) provision of long distance telephone circuits utilizing carrier techniques; (ii) development of carrier telegraph systems to provide large blocks of circuits; (iii) design and development of different switching circuits and exchanges; (iv) design of electronic instruments for production, installation, maintenance, fault location, general measurement, etc.; (v) design of equipment for providing power supplies to different types of telecommunication equipment; (vi) collection of data for use in planning; (vii) drawing up of broad engineering plans for expansion to serve as guide lines for development and utilization of technology; and (viii) consultant services, training and advice.

The magnitude of the task imposed on the centre can be judged from the fact that it involves design of equipment and systems, and the application of recent advances in technology, particularly in the field of electronics where the developments are many and rapid. The work also involves a major undertaking requiring considerable accumulation of experience and knowledge of all aspects of telecommunications as well as of many scientific and engineering disciplines. Finally, effective methods have to be evolved to get the designs of equipment and systems developed translated into industrial designs, and manufacture has to be established. Above all, the programme of work has to be coordinated at all stages with the planning and other branches of P & T Department in order to fit into the expansion plans of the department. In all the projects undertaken by TRC, its efforts have been well directed towards drawing up of programmes, directing of research and translating the designs developed to manufacture and getting the manufactured product into practical application — thus completing the whole cycle of a typical user oriented research programme. The programmes are drawn up taking into account modern trends and developments in various fields, and specifically to meet the requirements of the user in a given time. For this purpose, the basic studies concerning the systems, the design of the different units constituting the system, and the development of the necessary scientific and engineering disciplines are tackled in a well-directed manner and reviewed to keep them in proper perspective. The economic aspects of the programmes are kept under constant review so that the range of applications of the systems developed is as wide as possible. Since the time element is an important factor, considerable advance planning and coordination between TRC and the planning and other branches of P & T Department, and the manufacturer (usually the Indian Telephone Industries Ltd) is done. This aspect is given the greatest importance at all stages of the programme.

It would be pertinent to present some of the more important achievements of TRC. Considering the fact that the centre has been in existence for a short period of 10 years and the modest budget of Rs 16 lakhs currently available to it, its achievements are impressive and many-sided. The number of items designed by TRC and in large-scale production is considerable and the centre is able to meet the major needs of the P & T Department. The work of the centre has effected considerable savings in foreign exchange and this in turn has permitted the steady growth and expansion of the P & T Department. This has been made possible because of the ability of the centre to design the needed equipment from indigenous sources. The TRC, in addition to meeting the needs of the P & T Department, has also designed equipment for other users such as the railways where all the items for communication and signalling have been made indigenously from TRC designs. The TRC has developed a large variety of carrier telephone systems, the annual value of the equipment produced being about Rs 2·5 crores. The interstice carrier equipment designed is considered to be unique and the Indian P & T Department is among the first in the world to use carrier systems economically and reliably on interstice pairs to provide communication to small towns and rural areas along the coaxial cable route. Many important items of transmission equipment, vital for the balanced development of telephone services, have been developed and are in extensive use. The centre has carried out important studies in the field of electric traction. It has designed more than 40 items of test equipment for use by the P & T Department, Defence Services, Indian Telephone Industries Ltd, Hindustan Cables Ltd, Hindustan Teleprinter Ltd, etc. A variety of power plant systems, ranging from 24 to 50 V. supplies and higher voltages for use in different communication systems, have been developed. Microwave systems, which constitute an extremely important category of equipment for the development of telecommunications, are being designed; a system in 7 kMc/s. for providing 300 channels has been designed and its large-scale production is under way. Switching systems covering almost the entire range of equipment needed in the country have been evolved. Other designs developed include gas pressure systems for cables as well as for jointing plastic cables. The centre has also developed many techniques for developing the systems employed in carrier communication networks, VHF and microwave equipment, pulse, logic and memory devices, and power plant. The centre has also played an important role in the standardization of equipment and operational procedures, training of engineers in many specialized areas of electronic designs and communication equipment.

The impressive work and achievements of the TRC and its overall contribution to the national development should not be measured just in terms of the results achieved by the centre. What is more important is the fact that the TRC has shown that it is possible, with proper planning and direction, to design and manufacture complex equipment with indigenous resources and know-how rapidly and on a competitive basis. The collaboration between TRC and the Indian Telephone Industries Ltd in translating the designs developed by the former into large-scale manufacture is an important achievement, and has been responsible for the setting up of a large and complex industry in the country. This example could be followed with much benefit in other spheres of industrial research. The manner in which TRC has developed the expertise and know-how, and put them to practical ends to meet the increasing diversity of demands made on it is also worthy of notice. The TRC forms part of the P & T Department, which in effect sponsors the research programmes as well makes use of the end product of research, and this is an advantage. Such an overall scheme of research programming and research utilization as followed by the P & T Department could be followed with much benefit in other government departments, defence establishments, public and private sector enterprises and the cooperative research associations to achieve the same degree of success as that of TRC. Considering the excellent record of achievements of TRC, the fine tribute paid by the Reviewing Committee — . . . the centre has an extremely important and vital role to play in the development of telecommunications and of electronics in the country, and it should be treated as an institution of national importance . . . — is well merited. The recommendations of the committee in regard to the future set-up and expansion of the centre should be given effect to *in toto* in order that the centre continues to shoulder and discharge the tasks assigned to it with the same efficiency as in the past.

International Conference on Cloud Physics

BH. V. RAMANA MURTY
National Physical Laboratory, New Delhi 12

THE International Conference on Cloud Physics was held in Japan from 24 May to 1 June 1965 under the joint sponsorship of the International Association of Meteorology & Atmospheric Physics of the Union of Geodesy & Geophysics, the World Meteorological Organization, the Science Council of Japan and the Meteorological Society of Japan. About 200 delegates from 15 countries participated in the conference.

The conference consisted of two main events: Tokyo Scientific Session and Sapporo Seminar on Precipitation Physics and several associated activities. The agenda for the first series of meetings held during the 6-day session at Tokyo (24-29 May) covered 12 different topics. Following this, during the seminar held on 1 June at Hokkaido University, Sapporo, invited papers, one each on (i) the theory of ice crystal nucleation, (ii) the nucleation and growth of ice crystals, (iii) the mechanism of hailstone formation, (iv) the aerial observations of snow and rain clouds, and (v) the snowfall in the winter monsoon season of Japan, were read and discussed. An informal discussion meeting on charge generation was held on 2 June.

Movies on cloud physics which relate to 'Snow crystals', 'Icing' and 'Frost flower' taken by the late Prof. Nakaya were shown. Laboratory demonstrations of the experimental work done or in progress in the Laboratories of Snow, Ice and Meteorology at the Hokkaido University were arranged on one of the days during the conference.

The meeting offered a unique opportunity for exchange of ideas, greatly helped further elucidation of various problems currently under investigation and provided encouraging stimulus for future development of research in different aspects of the subject.

Cloud Dynamics

Features relating to cumulus convection received major attention. Model experiments conducted and actual observations made in the free atmosphere on rising thermals have pointed out that appreciable buoyant material mixes into the environment at all heights. However, in large-scale systems, theory and direct observations indicated that entrainment is of no importance.

Release of latent heat under certain conditions of environmental lapse rate is found to promote additional growth of cloud. Variations in lapse rate in time and in space make it obvious that extensive observations and advanced planning are necessary to anticipate the consequences of artificial cloud modification experiments in a given situation.

Aerosol and Air Chemistry

Organic matter of microbiological origin in sea water and bursting air bubbles at the surface of the sea have been shown to be of significant importance for interaction between the atmosphere and the ocean surface. The organic layer, on account of its high molecular weight and lack of volatility, helps retard evaporation of the droplets of salt solution—phenomenon considered responsible for the observed persistence of fogs below their humidity limits. Sea salt particles have been found to undergo chemical fractionation during the process between their supply from sea spray into the air and rainfall.

Studies on aerosols have shown that the size distribution of particles in the troposphere changes very little with altitude up to about 20,000 ft and that it is a conservative property of the geographical location more than of altitude. The most characteristic feature of the particles is that they have peak concentration around 0·2-0·3 μ diam. and that their source is in the near surface atmosphere. It has been found possible to infer the relative colloidal stability of clouds during different seasons and in different locations from a knowledge of aerosol state of the atmosphere.

Cloud Particles

The role of giant sea salt nuclei in the formation of large size droplets in clouds, the influence of wake capture and of electric fields on the collision efficiency of cloud droplets and the refinements introduced in computations on collection efficiency of small drops (less than 30 μ radius) have been considered.

The majority of large droplets in clouds which may freeze and rime while ascending in up-currents above the 0°C. level seem to originate on giant sea salt nuclei. The careful methods employed for detection of collisions in model experiments by the charge transfer technique, devised with a view to verifying computational results in the size range 30-130 μ radius, have not provided a definitive answer. Computed collision efficiencies have been considered to be approximately correct in the higher size range, but experimental verification by more accurate means has been found essential for droplets in the smaller size range. The theoretical prediction that the collection efficiency of droplets less than 19 μ radius is zero has been supported by experiments. At drop radius ratio less than 0·1, the experimental values of collection efficiency are found to be higher than the calculated values and failed to show sharp cut-off as predicted by theory. It was pointed out that theory itself might be unreliable in this region.

Some advance has been made in the understanding of the probable features aiding coalescence when droplets are charged or when set in an electric field. The electric forces may distort the liquid surfaces so that drainage of the air film and formation of liquid bridge are facilitated. The efficiency of collision between 5 μ droplets and 30 μ drops was found to increase by a factor of 10 in an electric field of 2100 V./cm.

Atmospheric Ice Nuclei

The precautions found necessary to obtain valid measurements with millipore filters, sources of origin of the ice-forming nuclei and their role in precipitation and the implication of the observed pattern of lunar influence on rainfall with latitude on the possible air-exchange mechanisms between the stratosphere and the troposphere figured prominently in this session.

One point of interest which emerged from studies using millipore filter is that the millipore filter when used in conjunction with mixing-type cloud chamber will reveal whether the ice nucleating material under question is a good sublimation or freezing nucleus.

As regards the nature of origin of the ice-forming nuclei, i.e. terrestrial or extraterrestrial, there have been evidences in support of both. Some of the investigations reported pointed out that the ice nuclei distributions are more closely related with upper air circulation (the position of jet stream) than to surface weather patterns. Ice nuclei and giant sea salt nuclei have been considered to play a combined role sometimes in the development of individual precipitation elements as, for example, when embroys of graupel pellets form as a result of interaction between supercooled drops grown on giant sea salt nuclei and ice crystals formed on ice nuclei near the tops of clouds.

Ice Nucleation and Crystal Growth

The importance of fit between the crystal lattice of ice and that of the nucleating substances, the existence of an activation process in the case of some solid particles under dry and very cold conditions which helps to initiate ice phase even after the particles have been warmed to temperatures near 0°C., and the possible interactions between water molecules and the surface structure of nucleators which appear to play vital role in the case of certain organic compounds known for their efficient ice nucleation received attention in this session.

It has not been so far fully understood what is the most important requirement for a good ice nucleator. In an interesting experiment described, it has been found that the phase which best fits the nucleator has been preferentially nucleated even though that phase has the lower stability. In the case of certain solid particles, ice once formed and retained in the capillaries has been found to be the source of their ice-forming ability — a process which does not depend on the property of the particles but only on their surface characteristics, such as low contact angle, existence of capillaries, pores, etc. In the case of organic substances, the formation of hydrogen bond between water and a polar group on the nucleating molecule appears to be the controlling factor for nucleation. It has been found possible to explain a large portion of the observed variation in the nucleating power of similar organic compounds on the basis of energy differences only without recourse to crystallographic considerations. In the case of silver iodide acting as ice nucleus, the mechanism of contact nucleation appears to play significant role.

Ice and Snow Crystals

The characteristic features of ice crystal growth in the temperature range −40° to −90°C., the probable cause for the observed dislocations in the natural snow and hoar crystals and the factors which contribute for the stability of ice crystal movement in the atmosphere were the important items considered in this session.

Entrapped aerosol particles have been shown to be mainly responsible for the observed dislocations in snow crystals. The crystal porosity has been pointed out to be one more vital factor to be considered, in addition to the parameters characterizing the value of Reynolds number, for judging the growth of ice crystals in supercooled clouds.

The famous Nakaya's Ta-S diagram regarding the temperature conditions for various crystal shapes has been verified in actual practice by direct observations on the shapes of snow crystals in clouds by the 'Snow Crystal Sonde' technique developed very recently.

Precipitation Physics

The influence of cloud structure on precipitation in middle Europe, the effect of drop disintegration on raindrop size distribution, the possible mechanisms by which ice can form in natural clouds at temperatures warmer than −10°C. figured prominently in this session.

One of the interesting features pointed out in the case of a particular type of drizzling rain from fairly low nimbo-stratus clouds with no noticeable updraft inside, popularly known in Japan as 'Saiu', has been that cloud particles, after having grown by condensation to certain size, get off immediately without growing any larger inside the cloud by collision-coalescence mechanism. Wide droplet spectra in clouds of middle Europe have been found to be associated with rain down the valley and narrow spectra with snowfall. Pre-activated nucleus mechanism and drop agitation mechanism have been provisionally considered to be relatively more important for primary ice formation in small cumulonimbus clouds.

Hail Studies

The mode of hailstone growth, its structure interpretation and the various heat transfer mechanisms operating in the course of growth history of the hailstone were the important items considered.

An examination of hailstones has revealed that they grow as three-dimensional arrays of almost completely frozen lobes separated by regions of spongy ice characterized by radial lines of bubbles. Knobs produced by the lobes on hailstone are found to serve as excellent heat loss regions. This fact combined with the results of some laboratory experiments, which showed that unfrozen water instead of being shed could be retained to give a spongy ice-water mixture, has been found to explain the growth of hailstones to a diameter of 8 cm. without becoming appreciably spongy. One of the most striking features pointed out about hailstone structure is the very short transition from large crystalline to small crystalline zones and vice versa. Characteristic air bubbles embedded in transparent ice have been considered to be a reliable sign of wet growth.

Radar Meteorology

Discussions on Signal Integrator Device, fabricated at the National Severe Storms Laboratory of the US Weather Bureau, for obtaining estimates of weather echo average power, using solid state circuitry of the type used in digital computers and monostable transistor circuits, and on 3·2 cm. pulsed Döppler radar developed at the Meteorological Research Institute, Tokyo, to measure the size distribution of raindrops at different heights in the vertical, were of considerable interest during this session.

Measurements made with a vertically pointing 5·45 cm. pulsed Doppler radar have revealed the presence of what is known as ' balance level ' where the mean Doppler velocity becomes zero on account of half the reflectivity observed having been contributed by rising particles and the remaining half by falling ones. The feature appears to be very intimately related with ' first echoes ' in convective clouds, which have been observed to develop in the upward and downward directions at roughly the same rate. One of the interesting features pointed out from study of an extratropical cyclone was that the bright band observed on the radar screen has been found lifted up by 1000 m. within a few minutes. The effect is interpreted as due to lifting up of the pre-existing melting layer by the sudden updraft brought out by the advancement of the cyclone centre over the area.

Atmospheric Electricity

This was the session in which maximum number of scientific papers were presented. The several possible charge generation mechanisms considered responsible for the observed electric state of the atmosphere, of cloud droplets and of precipitation, and the influence of thunder and lightning on the precipitation characteristics attracted attention in this session.

Two charge generation mechanisms, i.e. whenever bubbles produced by wave action break and whenever there is volcanic eruption, have been pointed out to be operating at the surface of the sea. Ejection of photoelectrons, friction, desorption of gases are some of the new processes suggested for production of electric charge on a small scale. It has been found possible to reconcile the conflicting results of most of the experiments on charge production during riming by taking into account the effect of non-uniformity of the growing hydrometeor (when ice crystals and supercooled water drops coexist in clouds, the growing hailstone becomes more rough and this feature is considered responsible for enhancement of charge) and velocity of impact.

An interesting observation reported was that addition of small quantity of ammonia to water before freezing would reduce the thermoelectric power of ice to zero or even change the sign — a feature which is of possible importance to cloud physics as it suggests a means of investigation or even control of thunderstorm activity. One very interesting phenomenon pointed out in connection with studies relating to clouds of volcanic eruption was that the clouds so formed produced rain and lightning even when they rose to only a few kilometres in altitude. The evidence suggests that the electric charges observed in the cloud have been acquired by a subterranean process and not by mechanisms acting after the affluent gases had entered the atmosphere. No one single process of charge generation known has been found to explain satisfactorily the observed electrical state of rain in the tropics.

Attempts made by chaff seeding — a novel technique which is being experimented in USA with a view to bringing about reduction in the electric fields of thunderstorms — have shown encouraging results.

Atmospheric Radioactivity

Features relating to the interaction between radioactive substances and aerosols, atmospheric washout and the radioactivity of precipitation were the main items of investigations considered during this session.

The mean life of radioactive ion is found to be inversely proportional to the concentration of condensation nuclei in the atmosphere. The ' melting zone effect ' which pointed out reduced content of fission products in the transition zone from solid to liquid precipitation has been consistently observed. The high value of the ratio of Cs-137 to Sr-90 (2·7) observed in rain-water in Japan suggested re-examination of the comparatively low value (1·7) obtained in rainfalls in UK and other countries.

Cloud Modification

Some of the more efficient cold cloud seeding techniques which have been recently developed, the comparative merits and demerits of silver iodide and solid carbon dioxide when used as seeding agents, the results of seeding experiments conducted in fogs, clouds and hail, and some of the important lessons learnt from long-term cloud seeding experiments using silver iodide, were the subjects figuring prominently during this session.

Studies on metaldehyde which is seen to possess remarkable qualities as an ice nucleator even at temperature as high as $-0{\cdot}4$°C. have opened up a new and promising field for experiments on weather modification. Use of liquid propane, which has been found to yield very large numbers of ice crystals when sprayed in supercooled clouds or in air supersaturated with respect to ice, suggested one more new line of approach in this connection. The latter method has been experimented and found effective in the dispersal of supercooled fogs. A point of extreme importance suggested as a result of 10 years of silver iodide seeding experiments in mountainous regions in France is that silver iodide might have no ice-forming action in natural clouds such as observed in cloud chambers.

The doubt has been further strengthened by the results of later experiments conducted on stationary orographic clouds both with silver iodide and liquid carbon dioxide. The results of silver iodide seeding trials by aircraft in Western Quebec, Canada, during 1959-63, which have been conducted with utmost care and all possible precautions, have indicated a slight negative effect. Experiments in progress in Japan have suggested that silver iodide seeding has been effective in increasing annual rainfall.

Cloud seeding experiments with silver iodide conducted so far have in general not been considered sufficiently sensitive to give unequivocal results. The factors pointed out as responsible for the uncertainty are: (1) silver iodide on some occasions may increase precipitation and on other occasions may as well decrease it; (2) seeding may increase the variance of rainfall in the test region, and hence extend the time necessary to achieve a significant result; and (3) cumulative effects due to seeding, if any, will make the design of the randomized experiment progressively more insensitive. The design of future experiments in this connection should be suitably improved so as to reduce or eliminate these effects. The Upper Geyser Basin area of Yellow Stone Park (7300 ft m.s.l.) in USA, where ground-based supercooled clouds form in abundance in winter from moisture from hot springs, has been considered to be one of the finest outdoor laboratories in the world for conducting studies and research related to atmospheric and other natural sciences.

In the only paper of its kind presented on hail suppression, it has been pointed out that firing of explosive rockets in Kenya does reduce the damage caused by hail, a result which has not been readily deduced from the previous experiments conducted in other parts of the world.

Micro-metallurgy—The Role of Minute Additions to Ferrous & Non-ferrous Metals & Alloys—A Symposium

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MICRO-METALLURGY, with special reference to metals and alloys, is of basic importance in the context of development of alloys and super-alloys, which depend chiefly for their metallurgical characteristics and physical properties on the minute additions of certain elements. The subject of micro-metallurgy is not new. Examples of minute additions of various substances to metals exerting harmful effects or conferring beneficial properties, particularly in the case of ferrous and non-ferrous alloys, are abundant. However, the mechanism of action of micro-additions is not yet properly understood and presents to the theoretical scientist and the metallurgist considerable scope for research and development work. With a view to focusing attention on the various aspects of micro-metallurgy, a symposium on 'Micro-metallurgy' was organized by the National Metallurgical Laboratory (NML) during 29 March to 1 April 1965. The symposium provided an international forum for discussing the role of minute additions to ferrous and non-ferrous metals and alloys, and for exchanging technical know-how, examining interrelated problems and facilitating further study and research on the subject. More than 200 delegates, including some top-ranking scientists and technologists, participated in the deliberations of the symposium. Of these, twelve were from abroad.

Welcoming the delegates, Dr B. R. Nijhawan, Director, NML, surveyed the research and development projects essential to the growth of mineral and metallurgical industries, which NML had been called upon to handle during the successive five-year plans. He observed that a prominent place has been given in the laboratory's research programmes to research in the field of micro-metallurgy.

Shri Asoka Mehta, Deputy Chairman, Planning Commission, inaugurating the symposium, observed that the subject of the symposium was of profound interest, particularly to the developing countries lacking in certain crucial metals. He congratulated Dr Nijhawan and his colleagues for organizing international symposia and for the splendid work they have done in diverse fields.

Dr Husain Zaheer, Director-General, Council of Scientific & Industrial Research, addressing the delegates, complimented NML for the valuable work done in diverse fields of metallurgy and the number of project-oriented industrial problems undertaken on behalf of industries. He referred to the tribute paid to NML by the Third Reviewing Committee headed by Sir A. Ramaswamy Mudaliar that the laboratory, with its interest in applied and basic metallurgical research, has forged close links and won the confidence of Indian mineral and metallurgical industries. The valuable suggestion made by the Reviewing Committee that NML should also focus attention on fundamental aspects of the work being carried out in the laboratory has been implemented by holding the symposium on micro-metallurgy, a subject in which the laboratory has done pioneering work.

Sir Jehangir Ghandy, Chairman, Executive Council, NML, speaking on the occasion, stated that NML has been holding an international symposium every year on subjects of fundamental and applied metallurgical interest and this is the fourteenth annual symposium to be organized under its auspices. Sir Jehangir observed that NML has undertaken important research programmes on various aspects of micro-metallurgy. These related to grain size control in steel and abnormality and strain-ageing effects in steel. Research is also being conducted in micro-additions of rare earth elements to stainless steels and aluminium-magnesium alloys, and on the ageing of aluminium alloys. In addition, studies on phase changes in relation to micro-constituents, micro-metallurgy of aluminium-silicon alloys and heat resistant alloys, and analytical techniques are being made.

Shri M. S. Rao, Chairman, Hindustan Steel Ltd, who was the Chief Guest, referred to the yeoman's service that NML has rendered to Hindustan Steel Ltd, not merely through general research studies carried out, but also by carrying out pilot plant studies, specifically for Hindustan Steel Ltd, on beneficiation of the iron ores for the three steel plants, and also studies on the sintering of Barsua iron ore for the Rourkela and the Rajhara iron ore for the Bhilai steel plants. NML is regarded as the main research centre for original studies for Hindustan Steel Ltd. Continuing, Shri Rao said that purposive research on micro-constituents in metals and alloys would put in our hands not only the ability to control or eliminate their occurrence so as to improve the speed and quality of production of metals and alloys with reference to the raw materials available in the country, but would also enable us to replace certain rare and costly metals not readily available in the country in the making of alloy steels by indigenously available metals.

Technical Sessions

Twenty-nine papers covering various facets of micro-metallurgy were presented and discussed in six technical sessions.

At the first session, five papers were presented. R. L. Craik (Bisra Laboratories, UK) presented the results of laboratory trials relating to low carbon high manganese, niobium and vanadium steels in both controlled rolled and normalized conditions. Low carbon contents in ferrite-pearlite steels have been found to improve toughness and weldability of the steels. However, in air-cooled carbon steels, low carbon contents lead to coarse ferritic grain structures which have an adverse effect on the yield strength and toughness properties of steels. Manganese lowers the transformation temperature and when present in moderate amounts improves toughness. Niobium and vanadium are excellent grain refining additions. J. M. Capus (Gillette Industries, UK) presented the results of studies on the influence of residual trace elements on the mechanical properties of constructional alloy steels. Phosphorus, arsenic, antimony and tin, in trace amounts, have been found to promote temper-brittleness of alloy steels; silicon and manganese produce the same effect when present in larger amounts. The embrittlement of quenched and tempered alloy steels around 350°C. can be promoted by nitrogen. Sulphur is a contributing element in high temperature embrittlement as well as the brittleness encountered in welding.

L. Nemethy (Atlas Steels, Canada) discussed the role of rare earth metals in stainless steel making. After the Second World War, stainless steels are being produced on a mass scale due to their numerous new applications such as automobile rims, cooking utensils, architectural appliances and food processing equipment. A number of special grade austenitic stainless steels have been developed for special applications, such as the extra low carbon austenitic stainless steels, molybdenum bearing stainless steels, special austenitic steels for cold heading and welding wire applications, etc. Despite many improvements, the processing of stainless steels presents some difficulties, particularly during the initial stage of hot working. The author critically discussed the effect of rare earth metals' addition to solve the problem of hot workability.

Techniques for the study of micro-phases and their influence on properties of materials were discussed by D. Scott [National Engineering Laboratory (NEL), UK]. In NEL, many metallographic techniques are currently in use in materials research, including electron microscopy, replica methods, thin foil techniques, fractography, dynamic electron metallography, etc. B. F. Oliver, F. Garofalo, S. Arajs and R. Preistner (Edgar C. Bain Laboratory for Fundamental Research, United States Steel Corporation, USA) contributed a paper on the purification of iron by selective purification and oxidation zone melting. Employing gas-metal oxidation reaction and zone smelting simultaneously, several high purity irons have been successfully prepared in a levitating zone melter. Iron samples ranging in purity from 99·89 to approximately 99·99 per cent with low interstitial contents have been obtained.

In the second technical session, Y. Imai (Tohoku University, Japan) presented the results of studies on the transformation of austenite to martensite based on statistical thermodynamics and crystallography using iron-nitrogen alloys and the results were compared with those obtained in the case of iron-carbon alloys. M. Tanino (Yawata Iron & Steel Co., Japan) dealt with the effect of addition of a small amount of vanadium and niobium on the macro-structures and the strength of pro-eutectoid ferrite of iron-carbon alloys. It has been found that the strength of pro-eutectoid ferrite in steels containing vanadium and niobium is generally higher than that in plain carbon steels, and the maximum strength can be obtained when the steels are cooled at the rate of 60-80°C./min. T. Saito (Technical Research Laboratory, Kawaski Steel

Corporation, Japan) dealt with the effect of minor elements on normal grain growth in singly oriented silicon iron and presented data relating to the normal grain growth of cold rolled 3 per cent silicon-iron sheet. The rate of primary grain boundary migration has been found to be strongly retarded by the existence of minute quantities of impurity elements such as silver, gold, copper, nickel, titanium, niobium, antimony, sulphur, selenium and tellurium. The value of free energy of activation for primary grain boundary migration in specimens containing sufficient addition of these elements is in close agreement with the free energy of activation for lattice self-diffusion of α-iron. Impurity atoms with a low intragranular solubility segregate preferentially at the grain boundary because they can reduce the misfit energy; then the free energy of activation for boundary migration tends towards a value approaching that characteristic of lattice self-diffusion.

T. R. S. Goel (Delco Radio Division, USA) and F. H. Vitovec (University of Wisconsin, USA) presented the results of studies on grain boundary segregation in binary iron-molybdenum alloys based on variations of grain boundary internal friction peak with increasing concentration of molybdenum in iron. The activation energy for grain boundary segregation of molybdenum in iron has been calculated to be 5300 cal./mole. The segregation of molybdenum in the test sample has been verified by X-ray microscopy using Co-K_α radiation.

In the third session, six papers were presented. Research in micro-metallurgy at the NML formed the subject of a paper by Dr B. R. Nijhawan. Almost a decade back, at one of the NML symposia, the role of micro-metallurgy in relation to alloy steels was discussed, with particular reference to some pioneering work undertaken in the field at NML. Basic and applied researches on diverse facets of micro-metallurgy have since been pursued; the problems studied include the effect of micro-additions on grain size control of steel and on abnormality, strain-ageing effects in steel in relation to residual micro-constituents, micro-additions of rare earths to stainless steels and aluminium-magnesium alloys, micro-metallurgy of liquid metals, ageing of aluminium alloys in relation to micro-constituents, micro-metallurgy of aluminium-silicon alloys and heat resistant alloys and analytical techniques for estimating the amounts of micro-constituents in alloys.

Abnormality in steels was discussed in a paper presented by B. R. Nijhawan, A. B. Chatterjea and S. S. Bhatnagar (NML). Micro-additions of aluminium and nitrogen to steels exercise significant effects on their austenitic grain growth characteristics and physical properties. The effects of micro-additions of aluminium and nitrogen in relation to the properties, isothermal transformation characteristics, MS points and grain growth characteristics of steels were discussed in a paper entitled ' Micro-metallurgy of austenitic grain size control of steels ' by A. B. Chatterjea and B. R. Nijhawan (NML). It has been established that in steels containing optimum aluminium content, the precipitation of AlN provided the requisite grain growth inhibition while its solution leads to abnormal grain growth. The agglomeration of AlN in high aluminium bearing steels causes reversion to normal grain growth behaviour.

K. B. Mehta (Foundry Forge, Heavy Engineering Corp. Ltd, Ranchi) presented the results of his studies on the effect of aluminium additions on the primary grain size of steel castings carried out with the object of determining whether a relationship exists between the lattice of the nucleating particles and that of the solidifying metal. The influence of the casting conditions, such as the state of deoxidation of the melt, casting temperature, pouring rate and turbulence of the melt during solidification on the as-cast primary structure in steel castings has been studied. The results obtained have indicated that maximum grain refinement can be achieved through combined effect of optimum aluminium additions, low casting temperatures and suitable turbulence. The effects of micro-impurities and alloying elements on zirconium and zircaloy-2 were discussed by H. C. Katiyar, P. Pande, K. B. Moorty and N. K. Rao (Atomic Energy Establishment, Trombay). L. J. Balasundaram and Rajendra Kumar (NML) discussed the distribution and function of micro-phases and micro-additions in metals and alloys and attempted correlation of the micro-additions and subtractions with the mechanical properties of steels.

At the fourth session, four papers were presented. B. Minari, H. J. Latiere and R. Michaud (Centre de Recherches Physiques, CNRS, France) presented the results of their studies on the morphology and polygonization of copper whiskers in the form of ribbons. From morphological studies it has been deduced that the ribbon-shaped whiskers are rich in dislocations. Annealing under elastic strain leads to polygonization which cannot be explained unless the presence of dislocations is assumed in the initial ribbon. The importance of micro-metallurgy in non-ferrous metals and alloys used in navy was discussed by G. Venkateswarlu (Naval Chemical & Metallurgical Laboratory, Bombay). Addition of arsenic (0·02-0·06 per cent), antimony or phosphorus inhibits the dezincification in alpha brasses used for condenser tubes. Addition of 0·03-0·45 per cent iron improves the resistance to impingement attack of cupro-nickel alloys in sea water environment. Aluminium bronzes containing small amounts of silicon, nickel or iron have been found to possess high strength and corrosion resistance. The influence of small amounts of boron and zirconium on hot working characteristics and creep rupture properties of some vacuum melted nickel base alloys was reviewed by V. N. Madhav Rao and R. V. Tamhankar (Defence Metallurgical Laboratory, Hyderabad). The combined effect of the two elements has been found to be more than additive. The permissible amount of the two elements has been found to be critical. Stress rupture strengthening brought about by micro-additions of B and Zr has been found to be accompanied by increase in total rupture ductility. K. Balaramamoorthy, B. C. Katiyar and N. K. Rao (Atomic Energy Establishment, Trombay) contributed a paper on the effect of minor additions of alloying elements on the irradiation behaviour and mechanical properties of natural uranium. Carbon and aluminium have been found to have a marked effect in minimizing volume increase during irradiation of uranium. Molybdenum also has a beneficial effect, while chromium, iron, nickel and titanium have no effect. Chromium has been found to be very effective in promoting grain refinement and increasing the strength of uranium at room temperature. High carbon contents do not counteract the beneficial effects of chromium.

Six papers were presented at the fifth session. Jatinder Mohan (NML) presented the results of a study on the effect of micro-additions of different elements on the surface tension of Swedish iron ores. It has been observed that addition of 0·05 per cent silicon, molybdenum, phosphorus, calcium, vanadium, nickel or chromium causes rise in surface tension of the iron, whereas addition of aluminium, titanium, lead, manganese, sulphur and zinc at the same concentration level lowers the surface tension. Antimony, tin and copper do not have any noticeable effect. A paper presented by M. Croutzeilles and J. Moriceau (Metallurgical Research Centre, Pechiney, France) dealt with studies on the distribution of impurities in the alloys Be-Fe, Be-Al and Be-Si and several varieties of commercial beryllium employing electron microscopy and micro-diffraction techniques. It has been observed that heat treatment of commercial beryllium does not have any influence on some of the impurities which always remain out of solution. Iron has an important role. At 800°C., beryllium can dissolve 0·25 per cent iron and ageing treatments in the range 500-700°C. precipitate the oriented phase $Be_{11}Fe$, mainly in the grain boundaries. In the presence of aluminium, the solubility of iron in beryllium falls considerably. The nature of the precipitate appearing during ageing treatment at 500-700°C. depends on the temperature of heat treatment. The precipitate appears in the boundaries and decorates the dislocations within the grains. G. P. Chatterjee, B. P. Sen and J. Bhattacharjee (Hindustan Steel Ltd, Durgapur) reviewed the results of their recent investigations on the nature of micro-constituents in metals and alloys employing the electron microprobe and by some specialized chemical techniques based on the use of X-ray diffraction. It has been shown that the ferrite banding in steel, usually attributed to microsegregation of phosphorus, may be due to some other reasons. A special heat treatment for eliminating the banding and methods developed for recovering inclusions in steel for structure study were reported.

Ved Prakash (NML) reviewed the progress made in understanding of the role of trace elements in the ageing of some aluminium base alloys. Y. N. Trehan, S. P. Bhadra, P. K. Gupte and B. R. Nijhawan (NML) presented the results of their studies on micro-additions to Al-Mg wrought alloys. The results obtained on the effects of addition of misch metal up to 3 per cent, silver up to 0·1 per cent, copper up to 0·1 per cent to Al-7 per cent Mg alloys were presented. It has been observed that additions of misch metal do not cause any significant changes in the hardness of the alloys after ageing. Addition of silver and copper improves the response to age-hardening at 250°C. Such improvement is perceptible on ageing for 24-100 hr after quenching from the solution-treatment temperature. N. G. Banerjee (NML) reviewed the recently developed methods for the analysis of gases in metals and alloys, and discussed the merits and demerits of the conventional methods in use for the determination of nitrogen and hydrogen. R. D. Naidu and M. Nirmala (Defence Metallurgical Laboratory, Hyderabad) described a spectroscopic method for the determination of micro amounts of different elements in steels. The method consists in grinding a filed flat of the specimen at one spot to form the electrode surface, to which a low voltage condensed discharge is directed from a graphite counter electrode. The spectrum is photographed and the intensity ratios of the spectral lines of the selected pairs of elements determined with the microphotometer. The photographic plates are calibrated with a group of iron lines whose relative intensities have been measured previously. The concentrations of the elements are plotted against the respective intensity ratios to obtain standard curves for the estimation of each element.

M. K. Ghosh, P. C. Debnath, Sumitra Dasgupta and B. C. Kar (NML) described some new methods developed at NML for the spectrographic analysis of micro-constituents in ferrous and non-ferrous metals and alloys. These include methods for the estimation of boron in steel; trace amounts of aluminium in steel; magnesium in nodular cast iron; copper and magnesium in zinc alloys; trace amounts of antimony in Pb-Sn solders; and impurities in tin. P. Koteswara Rao, S. L. N. Acharyulu and M. K. Joshi (Defence Metallurgical Laboratory, Hyderabad) reviewed the analytical methods in micro-metallurgy, including special methods, such as micro and ultramicro techniques.

A résumé of the symposium proceedings was given at the end of the technical sessions by Dr B. R. Nijhawan. The delegates were conducted round the various research divisions of NML and the pilot plants of the laboratory.

Some Aspects of Lubrication & Combustion Problems of Ground Vehicles at High Altitudes

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INTERNAL combustion engines of both SI and CI types are used at high altitudes. The fuels and lubricants recommended for such engines are generally suitable for sea-level conditions. With change in altitude, there is wide variation in air density as a result of variation in air pressure and temperature. This affects the combustion and lubrication efficiency of the engines. The compression ignition engines are designed to operate with excess air (air-vapour ratio, 27) at normal sea-level conditions to achieve a clear exhaust smoke. As such, the power loss with altitude is much less in CI engines as compared to SI engines. Nevertheless, there seems to be a definite advantage in using petrol engines at high altitudes for the following reasons: (i) the compression ratio of a diesel engine is around 19 : 1; that of petrol engine from roughly 6·1 to 8·5 : 1. It is easier to turn over and start the SI engine using more volatile fuel in emergency when all starting aids have failed; (ii) the basic engine weight of a diesel engine is much higher than that of a petrol engine; (iii) the 'cold-starting' behaviour of a petrol engine is superior to that of a diesel engine and can be adjusted easily by stipulating suitably volatile components of the fuel used for petrol engine; and (iv) a petrol engine generally gives a rich mixture composition.

The discussion in this article has been restricted solely to methods of improving the performance of SI engines.

General Properties and Combustion Problems of Gasolines

Considering *n*-heptane as a typical component of motor gasoline, we get for theoretically perfect combustion

$$C_7H_{16}+11O_2 = 7CO_2+8H_2O \qquad ...(1)$$

Thus, one volume of hydrocarbon vapours to 11 volumes of oxygen or assuming air to contain 20 per cent of oxygen (by vol.), one volume of hydrocarbon vapours to 55 volumes of air are needed. The theoretical mixture, therefore, contains 1/55 or 1·87 per cent of *n*-heptane (by vol.). Another method of expressing mixture strength is to state the number of parts by weight of air present for every part of hydrocarbon vapours. In the above example, this works out to 15·12 : 1 for the theoretical mixture.

The relation between the pressures in mm. of Hg and the altitude in 1000 ft as defined by the International Commission for Air Navigation (ICAN) is shown in Fig. 1 (ref. 1).

The relation between decrease in pressure and density of air with height is evident from the data presented in Table 1 (ref. 2).

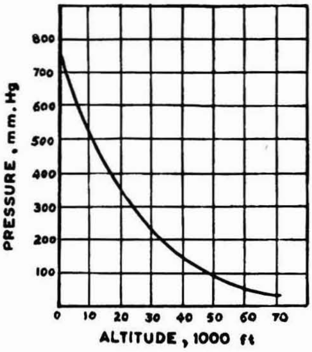

Fig. 1 — Variation of pressure with altitude

It follows that at an altitude of 15,000 ft and under ideal conditions, the theoretical mixture should contain approximately 2·49 per cent by volume of fuel. The air-fuel ratio works out to 10·08 : 1. For a typical gasoline mixture, the lower and higher inflammability limits are 1·1 and 6·6. For the same gasoline, the gross calorific value and theoretical air-fuel ratio (by wt) is respectively 20,000 B.t.u./lb. and 14·85 (ref. 3).

Thus, although under ideal conditions, the mixture composition entering the combustion chamber at an altitude of 15,000 ft may remain within the limits of inflammability, the combustion will be incomplete, resulting in incomplete release of enthalpy. The power output and efficiency of an internal combustion engine depend on the heat of combustion (enthalpy) of the fuel. Numerical calculations relating brake efficiency with calorific value are given in the Appendix. It is evident that the brake efficiency becomes less at high altitudes due to calorific value becoming less as a result of incomplete combustion.

Heimel and Dugger[4] showed that the initial mixture temperature has a direct effect on laminar flame velocity (S_L) and can be expressed by the following equation with fair degree of accuracy:

$$S_L = 10+0{\cdot}000342T_0^{2\cdot 0} \qquad ...(2)$$

where T_0 is the temperature of the working fluid.

TABLE 1 — FALL IN PRESSURE AND AIR DENSITY WITH ALTITUDE

	Altitude, ft			
	5000	10000	15000	20000
Pressure, mm. Hg	645	540	473	350
Density of air, g./m.^{3}	1070	880	770	660

At high altitudes, considerable quantity of cold air is inducted in the combustion chamber. An approximate relationship between atmospheric temperature and altitude has been given in the Appendix. Eq. (2) shows that as a result of induction of cold air and consequent lowering in temperature of the working fluid, there is possibility of flame velocity being affected which may give rise to 'knock' as a result of low temperature oxidation of the fuel.

A simple way to improve the combustion efficiency of gasoline at high altitudes seems to be incorporation of some hydrocarbon soluble liquid oxidizer which is expected to make up oxygen deficiency and increase reaction velocity. The extent of increase of reaction velocity should be such that it should not give rise to flame travel of more than 1000 ft/sec., as such fast reaction is known to cause 'knock' or detonation.

Cold-starting

Twenty revolutions are regarded as the practical limit for starting. Brown[5] found that an engine could be started in approximately seven revolutions if the 10 per cent evaporated point on the ASTM distillation curve, expressed in °F., does not exceed (engine temperature °F.+100)×1·25.

It is, however, evident that 10 per cent distillation temperature should not also be too low as this may lead to 'vapour-locking'. Brown[5] obtained the following relation for the minimum 10 per cent evaporated point on the distillation curve for which freedom from 'vapour-lock' troubles can normally be expected.

$$\text{Minimum 10 per cent evaporation temp. (°F.)} = 100 + \tfrac{1}{2}\,[\text{av. atm. temp. (°F.)}] \qquad \ldots(3)$$

The above relationship does not take into account the viscous drag offered by lubricating oils. Nevertheless, taking oil viscosity and fuel volatility into consideration, 'cold-starting' can be easily effected in a petrol engine.

Vapour and Air Release from Fuels

The solubility of air in petroleum hydrocarbon products is small when expressed on weight basis. However, up to 25 per cent by volume of air, measured at standard temperatures and pressures, can dissolve in the lighter products, such as gasoline. This dissolved air, however, affects the behaviour of gasoline at high altitudes. There are a number of different ways of expressing the solubility of a gas in a liquid under equilibrium conditions. From Henry's law of partial pressure

$$K = P_a/N_a$$

where K is the solubility coefficient; P_a, the pressure of gas A in mm. Hg; and N_a, mol. fraction of gas A in solution.

The Bunsen absorption coefficient (α) is defined as the volume of gas reduced to 0°C. and 760 mm. which is absorbed by one volume of liquid under a partial pressure of 760 mm. The other factor affecting performance is the evaporation of fuel due to reduction of altitude.

Air solubility has been exhaustively studied in the case of gasoline type fuels[6,7]. It has been shown that the release of air gives rise to problems which are insignificant compared to those arising from vapour release and fuel boiling. Air release from high vapour pressure fuels is, therefore, not dealt with in this article. The percentage loss of fuel (by wt) for altitudes 5000, 10,000 and 15,000 ft is 12·8, 15·2 and 15·0 respectively. The volumetric rate of vapour evolution on change of altitude in respect of two high vapour pressure fuel samples has been reported to be 730 and 608 cu. ft/min./100 gal. fuel. The main characteristics of the fuels are given in Table 2.

TABLE 2 — CHARACTERISTICS OF THE FUELS

	Fuel 1	Fuel 2
Sp. gr. (60°F./60°F.)	0·7220	0·7070
RVP at 100°F., lb./sq. in.	5·0	6·5
Distillation		
IBP, 0°C.	48·0	40·0
Recovery (%) at		
50°C.	—	1·0
60°C.	1·5	6·0
80°C.	24·0	33·0
100°C.	64·0	65·5
130°C.	95·5	95·0
140°C.	97·0	96·5
FBP°C.	153	147
Loss	1·5	1·5

No data concerning the extent of vapour loss at lower altitudes are available in the published literature. Nevertheless, from the data presented, it is evident that the problem of fuel loss and vapour release from volatile fuels at high altitudes is considerable and is expected to give rise to serious troubles by way of 'vapour-lock' and reduction in expected mileage. In addition, if adequate venting in the fuel line is not provided or other precautions are not taken, there is a possibility of excessive pressure build up in the fuel tanks. Two promising methods by which both the fuel weight losses and tank venting problems can be reduced seem to be a moderate degree of tank pressurization or refrigeration of the fuel on the ground.

Spark Ignition

The influence of altitude on minimum spark ignition energy required to relight a combustion chamber is appreciable. However, the mixture strength in the chamber, particularly in the region of the spark ignitor, is also an important consideration. The work of Swett[8] on minimum spark energy requirement for propane-air mixtures using a fuel-air ratio 0·08 and spark duration of 600-800 μsec. showed that the minimum spark requirement is nearly doubled for a change of altitude of 5000 ft.

Lubrication

The problem of lubrication with change in altitude is relatively simple as the effect of altitude on lubrication efficiency is solely related to lowering of temperatures and the change in air pressure has no bearing on lubrication efficiency. It is desirable to use universal oils and greases where possible to improve logistic reserve factors and simplify the

TABLE 3 — SCHEDULE OF LUBRICANTS RECOMMENDED FOR OPERATION AT HIGH ALTITUDES*

	Lubricant	Specification	Viscosity cs.	Pour point °F.	Drop point °F.
Crankcase	Detergent/dispersant oil	CS 2994	5·0 (210°F.)	−65	—
Gear (hypoid)	Extreme pressure oil	CS 3108	50000 (65°F.)	−65	—
Gear (non-hypoid)	Special formulation		5825 (−40°F.)	−65	—
	Detergent/dispersant oil	CS 2994	3·0 (210°F.)	−65	—
Steering (hydraulically operated)	Mineral lubricating oil	DTD 585	10 (130°F.)	−70	—
Water pump	Multi-purpose grease	Mil-G-10924	—	—	140
Wheel hub	do	do	—	—	140
Hydraulic brake	Hydraulic brake fluid	CS 2906 A	4-6·5 (70°F.)	−50	—

*Data based on information gathered during Vivian Fuch's Trans-Antarctic Expedition.

work of operators. Although generally the fall in temperature with altitude can be calculated on the basis of the equation presented in the Appendix, the rate of decrease of temperature with altitude is subject to considerable variations for local reasons. The fall is generally less in winter than in summer, less at night than during the day, less in plateau than on mountain and still less in planes[9]. In addition, the vehicles have usually to ply at different altitudes on a particular day. It is, therefore, necessary to provide for lubricants which should work satisfactorily at ambient temperature ranging from +120° to −50°F. A recommended schedule of lubrication under different conditions is given in Table 3.

Another way of achieving satisfactory lubrication is to dilute the oil or grease with gasoline to obtain the desired viscosity. However, this practice is not desirable and is not conducive to efficiency, as there will be loss of gasoline once the engine is sufficiently heated up resulting in frequent 'topping up' operation of lubricants with gasolines.

Summary

Some salient features of SI engines have been discussed with special reference to their use at high altitudes in preference to CI engines. The change in air-fuel ratio at altitudes of 15,000 ft has been calculated. Relation between theoretical b.h.p. and heat of combustion has been presented. It has been shown that the composition of the resulting mixture at 15,000 ft will be such that it will lead to incomplete combustion resulting in lower heat of combustion than the theoretical value and consequently lower b.h.p. Mathematical relationship linking 'cold-starting' ability of gasolines with their volatility characteristics and prevailing engine temperature has also been presented. It has been suggested that other possible major troubles to be expected at high altitudes are: (i) increase in spark energy requirements, (ii) air-vapour release resulting in 'vapour-lock', (iii) 'flame extinction', and (iv) loss of fuel.

A method suggested for improving combustion efficiency is incorporation of a liquid oxidizer. A practical means to overcome troubles arising out of air-vapour release at high altitudes has also been suggested. A schedule of lubrication suitable for use at ambient temperatures ranging from +120° to −50°F. has been included.

Acknowledgement

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References

1. DERBY, L. D. & FAULKNER, B. A., *Petroleum*, **38** (1953), 475.
2. BROOKS, C. E., *Climate in everyday life* (Everest Benn Ltd, London), 1950.
3. EVANS, E. B., *Petrol. Times*, **3** (1950), 220.
4. HEIMEL, S. & DUGGER, H., *Flame speeds of methane-air, propane-air and ethylene-air mixtures at low initial temperatures*, National Advisory Commission on Aeronautics, Technical Note No. 2642, 1952.
5. BROWN, G. G., *Engng Res. Bull., Michigan Univ. No.* 14, 1930.
6. *CRC handbook* (Cooperative Research Council of America, Washington), 1946, 222.
7. BRIDGEMAN, O. C. & ALDRICH, E. W., *J. Soc. Auto Engrs*, **27** (1930), 93.
8. SWETT (Jr), C. G., *Proc. third symposium on combustion, flame and explosion phenomenon* (Williams & Wilkins, Baltimore), 1949, 353.
9. FENN, S. B. & FOMEY, H. B., *Industr. Engng Chem.*, **43** (1951), 1663.

APPENDIX

Calculation of b.h.p.

If an engine has a fuel consumption 0·5 lb./b.h.p. hr, the overall efficiency can be calculated from the calorific value of the fuel used, e.g. 0·5 lb. fuel with a net calorific value of 20,000 B.t.u./lb. supplies 10,000 B.t.u./hr to the engine. The brake output is $(33000 \times 60)/778$ B.t.u./hr, since 1 h.p. = 33,000 ft lb./min. and 1 B.t.u. = 778 ft lb. The ideal brake efficiency is, therefore,

$$(33000 \times 60)/(778 \times 10000) = 25{\cdot}5 \text{ per cent (approx.)}$$

Calculation of Temperature

$$T_{\text{alt.}} = T_{\text{stand.}} - 0{\cdot}0035\ h$$

where $T_{\text{alt.}}$ is the environmental temperature at any altitude; $T_{\text{stand.}}$, environmental temperature at normal sea-level condition; and h, altitude in ft.

Integrated Field Intensity of Atmospherics in Relation to Radio Wave Propagation

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IN recent years, particularly during the IGY and post-IGY periods, round-the-clock observations of the integrated field intensity of atmospherics (IFIA) at different frequencies particularly in the very low frequency (v.l.f.) range have been systematically recorded in various parts of the world. The object of these investigations are mainly threefold: (1) to gather a better knowledge about the world distribution of noise power at various frequencies and to evaluate the spectral distribution of the same; (2) to study the influence of various meteorological phenomenon on the IFIA and to explore the possibility of predicting noise on a global basis; and (3) to observe the diurnal, seasonal and solar cycle variations of the IFIA besides the various transient variations and to explain these on the basis of corresponding changes in propagation conditions.

A vast amount of literature is now available on the various aspects of atmospherics' measurements. The purpose of this paper is to give a brief account of the nature of atmospherics including the historical background of investigations on atmospherics and to review the present state of knowledge particularly in respect of the last aspect of the investigations as mentioned above.

Nature of Atmospherics

Interfering noise in the form of clicks, grinders, sizzles often limit the useful sensitivity of a radio receiver. The noise may either be man-made as those generated in sparks in various types of electrical machinery or may be those generated by electrical disturbances in the atmosphere such as lightning flashes. It is the latter type which is termed as atmospheric noise, with which the present review is concerned. It is now well established that lightning flashes give rise to electromagnetic impulses. In general, these impulses last about 100 μsec. and have a spectral distribution of power with a maximum at about 10 kc/s. The corresponding electromagnetic wave when received at a distance is called an atmospheric.

The studies of atmospherics were commenced by Appleton *et al.*[1] and they found excellent correlation of atmospherics with lightning flashes. An investigation by Schonland *et al.*[2] revealed that electrostatic and electromagnetic fields are generated by a lightning discharge and it is the electromagnetic radiation field that is propagated by reflection in ionospheric layers to long distances. However, for short distances either or both of the waves, viz. ground wave and the sky wave, will be predominant. Location of the sources of atmospherics by direction finding methods have shown that the great majority of the sources are situated in the region of definite meteorological disturbances where thunderstorms would be expected and very frequently where thunderstorms are reported[3]. It has also been shown that the major sources of atmospherics lie in certain well-defined regions usually associated with equatorial continental areas and that all thunderstorms within 6000 km. of the observing station are significant as possible sources. The radiation field produced is the resultant of a large number of individual disturbances, the mean duration of the rapidly changing portion of each atmospheric being about 6 μsec. These impulses arrive in random time relationship and the ratio of peak to average value is about 4. The number of impulses received from a large distant storm centre is probably not much less than about 3000/sec. Brooks[4] estimated that 50,000 thunderstorms occur everyday throughout the globe and that on the average about 2000 storms are in progress at any moment, corresponding to at least 100 flashes per second.

A lightning flash can be regarded as an impulse generator having energy components extending over a wide range of frequencies[3]. Within any specified band the nature and intensity of atmospherics at a place will, naturally, depend on (a) the distance of the flash; (b) the power of the electromagnetic wave radiated by the flash within the specified band; (c) the waveform of the impulse generated by the flash; (d) the height of the flash, for its effect on propagation; (e) the orientation of the flash with respect to the direction of propagation; and (f) the propagation characteristics of the path for the specified frequency, time and location.

The nature and intensity of the resultant response in the receiver will depend on the magnitude of the individual disturbances, duration of each disturbance, the rate of repetition and the total duration of the discharge. It will also depend on the frequency of operation and the bandwidth of the receiver. Extensive studies of atmospherics have been made before 1940 at a number of places, though these early studies confined their attention to the frequency range 10 kc/s. to 30 Mc/s.

Since then intensive studies on various aspects are being carried out in many laboratories all over the globe covering a frequency range from 1 c/s. to 10,000 Mc/s. These studies were initiated by the pressing need for long-range navigation systems, long distance communication and worldwide frequency standards. Prompted by these needs extensive theoretical as well as experimental studies of radio propagation are, in fact, being made in recent years, employing the electromagnetic energy radiated by a continuous wave transmitter. While theoretical studies are quite comprehensive, experimental studies are handicapped by the rather limited power of such transmitters, particularly when propagation over long distances are considered. The studies based on the harnessing of the results of a study of IFIA characteristics, on the other hand, offer a distinctive advantage over the continuous method for the following reasons: (i) the power radiated by a source of lightning is enormous (of the order of 1000 kW. peak power at 10 kc/s. for a 1 kc/s. bandwidth); (ii) propagation over long distances is relatively easily detectable; and (iii) the spectrum of the source radiations extends over a very wide range of frequencies, which facilitates also the spectral studies of radio propagation.

Experimental studies employing continuous wave transmission is particularly impossible at extra low frequencies (e.l.f.). In fact, there is no transmitter in operation at e.l.f. and between 25-50 kc/s. Further, since the sources of activity are distributed over a wide area, interference effects between the ground wave and the ionospherically reflected wave are not likely to be present in the integrated field intensity and hence the variations in IFIA truly represent those of the ionospherically reflected wave alone.

Studies of atmospherics can be classified under one or the other of two well-defined topics: (a) sources of atmospheric noise in lightning discharge and (b) propagation of the electromagnetic energy from lightning discharge. Of these, topic (a) can be further subdivided into: (i) nature of lightning discharge; (ii) characteristics of an atmospheric from a single nearby lightning discharge; and (iii) directional studies of sources of atmospherics; and so far as (b) is concerned investigations were mainly concentrated to study the influence of propagation on waveforms, spectrum and the peak field intensity of the atmospherics.

Besides the two topics mentioned above, intensive studies are being made, in recent years, on the properties of integrated atmospheric radio noise for estimating or predicting the performance of a given radio system and thus provide data useful for the future design of the radio systems. During the IGY period, two aspects of the integrated atmospheric radio noise extensively studied were the world distribution of noise power and the description of noise structure in statistical terms[5,6]. Besides these measurements to establish the distribution and properties of noise, other experiments, in particular those of the diurnal variations of noise at frequencies near 27 kc/s., were also carried out with the object of studying factors affecting radio wave propagation. The study of integrated atmospheric radio noise has four distinct aspects, viz. (i) the amplitude probability distribution (APD); (ii) world distribution of noise power; (iii) integrated field intensity; and (iv) waveforms.

In early measurements of the integrated atmospheric radio noise the objective in most cases was to evaluate the noise level with a view to assessing the interfering effects in radio transmissions of various types. Moreover, the data were obtained by observations at discrete time intervals. As a result, only certain general features of atmospheric radio noise level could be ascertained while the finer structure of the variations of the radio noise was largely overlooked.

There has been no correlation between measurements made at different places and consequently it is exceedingly difficult to make comparison between the results and deductions made at one place and time with those made at another place and time. Furthermore, a variety of different methods of measurements have been employed and in the absence of any agreed standard method of measurement it is difficult and often impossible to interpret the results in terms of any known definition of noise. In most cases the significance of the bandwidth of the receiver has not been appreciated and corrections to a standard bandwidth is impossible.

It was only during the IGY that systematic studies were started with continuous round-the-clock observations. And employing a relatively large time constant in the detector recording equipment, a smooth trace, indicating directly the IFIA as a function of time, was obtained in a form which is rather easy to interpret. In certain observations, by making a discharge time constant larger than the charging time constant, the equipment was made specially suitable for the recording of sudden enhancement of atmospherics (s.e.a.) subsequent to a solar flare. Such equipments were extensively used in different countries for the radio patrol of a solar flare. The same equipment will, in fact, be highly suitable also for the recording of a s.e.a. subsequent to a high altitude nuclear detonation and also enhancements associated with certain local meteorological disturbances. It is the purpose of this paper to review the present state of knowledge in the subject of integrated field intensity of atmospherics particularly in relation to radio wave propagation.

Regular Variations of the IFIA

The IFIA at a place exhibits a diurnal, seasonal and yearly variation, which arises from the changes of either of the source activity or of propagation conditions or of both of them.

Diurnal variations — Diurnal variations in recorded atmospherics were observed by a large number of workers in different countries and the results of these investigations have been reported in literature[3]. During the IGY period, such studies were continued with special emphasis on observations of IFIA at a large number of countries[5-12]. The general diurnal variation pattern has, in fact, been subdivided in accordance with Recommendation No. 40 of the World Meteorological Organization into the following parts: A – sunrise effect, B – first minimum, C – recovery effect, D – morning minimum, E – afternoon maximum, F – late minimum, and G – night maximum[13]. A typical record of the diurnal variation showing these effects is reproduced in Fig. 1. The sunrise effect has been explained to be due to the absorption in the D-region of the ionosphere which is formed with the sunrise at the layer. Likewise, the night maximum marks the disappearance of the D-region from the propagation path[12,14,15]. The late minimum arises partly due to variation of thunderstorm activity and partly to the D-layer absorption[16]. The afternoon maximum occurs due to the increase of local sources of activity at such times, while the recovery effect

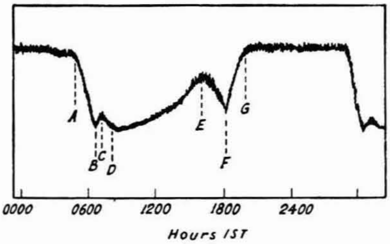

Fig. 1 — Diurnal variation of the IFIA [A, sunrise effect; B, first minimum; C, recovery effect; D, morning minimum; E, afternoon maximum; F, late minimum; and G, night maximum]

arises presumably from a transient improvement of propagation with some of the reflections from the D-layer[15]. Besides these, a sharp single or sometimes a double peak in intensity occurs just before and just after sunset and sunrise respectively. Potter[17] and Khastgir and Ali[18] have given similar explanations of the single peak. During sunset, with the gradual disappearance of the ionizing solar radiations, the electron density of the D-layer as well as that of the E-layer decreases. As a result, non-deviative absorption in the D-layer decreases, while at the same time deviative absorption in the E-layer increases. At the beginning, the increasing E-layer absorption is predominant thereby decreasing the intensity, while after sunset the decreasing D-layer absorption becomes more effective causing an increase of intensity. The single peaks near sunrise have also been explained by a similar reasoning. The double peaks sometimes observed can be explained in terms of reflection involving two layers, E and F, and the sudden increase of the height of reflection from the lower E-layer to the higher F-layer[18,19]. In fact, location of thunderstorm centres has been determined from the times of occurrence of the peaks[20]. It is worthy of note that the sunrise and the sunset effects had been previously recorded by Espenschied *et al.*[21]. The diurnal characteristics of the distant atmospherics were also studied by Khastgir[22] and Khastgir and Ray[23].

Seasonal variation — The integrated field intensity of atmospherics exhibits a seasonal variation. The noise level in the northern hemisphere is greater in summer than in winter. This arises presumably due to the greater source activity in the summer[3]. However, the summer to winter ratio of the noise level is highly variable with location as well as with frequency. In regions near to the equatorial storm centres, the seasonal effect is determined predominantly by local meteorological conditions. For instance, in India the atmospheric noise level is exceptionally high in the monsoon period[24]; local thunderstorms occurring in the premonsoon months in the north-eastern part of India give rise to unusually large atmospheric noise[25]. A typical record of the IFIA on a disturbed day is shown in Fig. 2 along with the record for an undisturbed day for comparison. The seasonal variation decreases with increasing frequency until above about 15 Mc/s. it becomes unimportant. In polar regions, the radio noise is exceptionally low in all seasons[26].

From the available data, it seems that the seasonal variations of the IFIA are, in general, dominated by variation in source activity, which is in fact highly variable and, therefore, it will be rather difficult to discern any seasonal variation of propagation conditions from these studies.

Solar cycle variation — Influence of solar activity on the IFIA is not yet clearly known. Austin[27,28] found an inverse relationship between the yearly averages of day-time noise level at 24 kc/s. and the sunspot number. However, the correlation falls markedly when the averages of less than a year were considered. Pickard has also indicated an inverse correlation of the noise level at 1·3 Mc/s. with sunspot number. The day-time noise level at 15-25 kc/s. is also subjected to a small 27-day cycle variation associated with solar rotation. The available information is too meagre. However, there is a general tendency that the day-time noise level would be decreased with sunspot activity which is likely to increase the absorption. Besides the absorption, the source activity might also be influenced by solar activity and one should be cautious about this while interpreting the results. In fact, Brooks[29] has shown that the eleven-year cycle of sunspot activity produces a variation of about 11 per cent on either side of the mean noise level. Recent measurements of the IFIA in Japan on the v.l.f. range indicated an annual variation of intensity in inverse proportion to solar activity[30]. It is likely that the inverse relation arises from propagation variations induced by solar activity. This deduction is justified by the fact that propagation in the v.l.f. range is determined predominantly

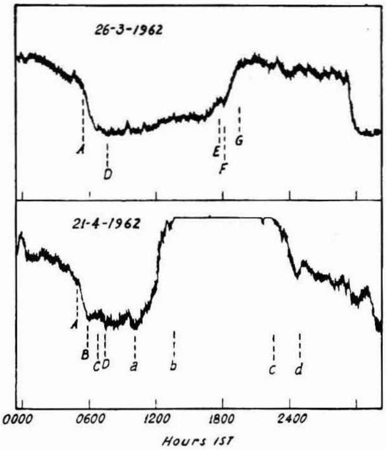

Fig. 2 — Comparison of typical records of the IFIA on a normal day with that on a disturbed day observed at Calcutta[25] [Upper record shows the usual diurnal variations as observed on a normal day. The lower record shows the gradual increase in atmospheric activity in thunderclouds prior to a nor'wester. Markings A-G indicate the same effects as in Fig. 1. (a) Rise of IFIA at 1002 hrs; (b) exceeding the range of measurement at 1330 hrs; (c) re-entering the range of measurements at 2230 hrs; and (d) attaining the normal value at 0043 hrs on the following day]

by the phase height of the lower ceiling of the D-region rather than by its electron density, which is normally sufficiently large for good propagation over long distances. Although solar activity might increase the electron density to some extent, the predominant role of the associated decrease of phase height probably becomes apparent in the integrated field intensity.

Transient Variations in the IFIA

Solar origin — Besides the regular variations described above, it is seen that IFIA, particularly in the low frequency, often exhibits a sudden enhancement associated with solar flares[31]. During the IGY period this sudden enhancement of atmospherics (s.e.a.) has, in fact, been widely used as a tool for radio patrol of solar flares[32-34]. The enhancement occurs due to better propagation condition for the low frequencies around 30 kc/s. brought about by increased ionization of the D-region of the ionosphere produced by X-rays (1-2 A.) emitted from the flare region on the sun[35]. During solar cosmic ray flares, the largest of which occurred in 23 February 1956, the v.l.f. atmospherics are usually found to decrease suddenly instead of any enhancement. This is now known to be due to increased ionization at a sufficiently low height produced by the arrival of cosmic ray particles from the sun. The effect has also been observed even on the night side of the earth[36-39]. Solar eclipse should also be expected to produce changes in the atmospheric noise arising from changes of ionization of the ionosphere brought about by cutting off of the ionizing radiations from the sun at such times[40-42]. At low frequencies the effect is an increase of atmospherics' field intensity caused by the disappearance of the D-region resulting in better reflection from the base of the E-layer. At high frequencies, on the other hand, the effect should be one of decrease of atmospherics due to the decrease of critical frequency of the E- and F-layers at such times.

Origin in high altitude nuclear explosions — Besides the abnormal changes of field intensity due to solar flares, s.e.a. in the v.l.f. and l.f. ranges have also been observed (Fig. 3) to be associated with high altitude nuclear explosions which result in increased ionization of the D-region at such times[11,43-47]. Saha *et al.*[44] observed that a s.e.a. associated with high altitude nuclear explosion has a larger amplitude at 100 kc/s. than at 27 kc/s., a fact which they pointed out to be a distinctive feature of a s.e.a. produced by a nuclear detonation. Sen[47], in addition to observing a similar effect, viz. the amplitude at 120 kc/s. being larger than that at 30 kc/s., also observed a lower amplitude at 210 kc/s. which is indicative of a peak in the frequency spectrum of the s.e.a. around 120 kc/s.

Night-time anomaly — Sachdev[9] observed severe fading having a quasi-period of about 2 hr, in the night-time records at 27 kc/s. on certain days. The phenomenon has been called night-time anomaly. The fading is believed to be associated with disturbed conditions in the ionosphere. A similar fading effect with a quasi-period of about 1-4 hr was observed[48] at 20 kc/s. in Canada when the centre of a storm passed to the north of the observatory within a range of 200-400 miles. The origin of the night-time anomaly is not yet precisely known.

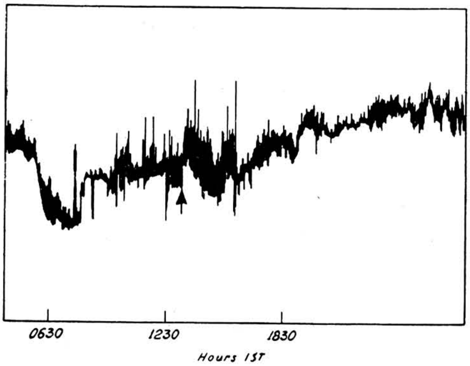

Fig. 3 — A typical record of the IFIA observed at Calcutta[11], showing the sudden enhancement of atmospherics subsequent to a high altitude nuclear explosion made by the Russians [The arrow indicates the time of start of the enhancement (1320 hrs IST); the explosion occurred at 1255 hrs IST on 4 November 1961]

Conclusion

From an analysis of the results so far obtained from studies of the IFIA during the IGY period and later, the following conclusions can be drawn. (i) Sunrise and sunset effects on the IFIA can be explained in terms of sunrise and sunset respectively at the D-layer. (ii) Seasonal effects on the IFIA are influenced predominantly by variations of sources activity; varying incidences of storms make it rather difficult to discern any seasonal effect on propagation. (iii) Variations of the IFIA with solar cycle variations originate mainly due changes in propagation condition produced by solar activity. However, variations of source activity induced by solar activity cannot be altogether neglected. (iv) Transient variations in the IFIA during sunrise and sunset originate from transient improvement of propagation during layer formation by solar ionizing-radiations. (v) Transient enhancements in the IFIA in low frequencies during a solar flare occur due to increased ionization of the D-region by X-rays emitted from the flare region on the sun. (vi) Transient decrease in the IFIA at low frequencies is a rare phenomenon and arises from increased ionization at a sufficiently low height where the density is high. (vii) Transient enhancement in the IFIA produced artificially by nuclear detonations originate presumably from increased ionization of D-region by the shock wave emanating from the detonation region. (viii) During a solar eclipse due to the temporary absence of ionizing radiations, the D-region disappears and the ionization of the other layers are also reduced. The effects observed on the IFIA under these conditions can be explained in terms of the resulting propagation changes. (ix) Long period fading with a quasi-period of several hours is observed at low frequencies on certain nights; the fading may have relation to the disturbed condition of the ionosphere.

Scope for Further Investigations

The general features of the world distribution of integrated noise power have been determined during the IGY by a network of sixteen stations distributed throughout the world[49]. However, such studies were confined to the measurement of the average noise power within a 4 hr time block. As a result, the detailed features of the integrated noise occurring within the time block would be smoothed out. Further studies are needed in the world distribution of the noise, with a network of a larger number of stations and employing, preferably, time blocks of shorter duration such as a 1 hr block, in order to explore the true nature and the origin of the latitude and longitude dependence of the integrated noise. Now that the statistical properties of the integrated atmospheric noise have been determined fairly well, the noise power could also be deduced from the integrated field intensity of atmospherics. Extensive theoretical and experimental studies have been made on the propagation of continuous wave transmissions[49-60]. At present, the world distribution of the sources of radio noise is now precisely known[61] along with the spectra of the sources. By combining the knowledge about these aspects of the noise sources with the known characteristics of propagation it would now be possible to predict radio noise on a worldwide basis. Observations regarding the dependence of the integrated noise on frequency might reveal important features of radio propagation. For instance, the spectrum of the source varies inversely as the square of the frequency above about 10 kc/s., while the propagation modified the source spectrum tending to produce an inverse frequency dependence of the integrated atmospherics. Further studies in ascertaining the true nature of these frequency dependences will be worth while. Besides this, the s.e.a. produced by a solar flare or a high altitude nuclear explosion reveal distinct features in the spectra of the enhancements. For example, the s.e.a. show a peak around 27 kc/s. when the enhancements are induced by a solar flare, while a peak at 120 kc/s. occurs when the enhancements are induced by a high altitude nuclear detonation. The difference might be due to a difference in height gradient of electron density in the D-region in the two cases and further studies in this direction would be important since they provide a successful method of detection of a high altitude nuclear explosion from a long distance[47]. The diurnal variation of IFIA has, in general, been explained in terms of variations of either of the source activity or of propagation or of both of them. However, certain important features of the diurnal variation still warrant further investigations. For instance, the duration of the sunrise effect in the v.l.f. and l.f. ranges and particularly its frequency dependence cannot be explained in terms of the existing theories of radio propagation[62]. The afternoon maximum is often characterized by a double peak of which the first one arises from propagation effect, while the second one is caused by the source variations. The first peak caused by the propagation effect indicates a variation affected by the solar cycle variation. The diurnal pattern of the variation of IFIA often exhibit unusually large enhancements associated with local meteorological disturbances. Such enhancements supplemented by directional studies of atmospherics would provide an aid to weather forecasting. For example, there are definite indications that thunderclouds produce large increases of integrated atmospherics several hours before their culmination into a thunderstorm[25]. The seasonal variation has not been studied thoroughly. However, there are indications that the seasonal variation is dominated by local meteorological conditions. The wide variation of the activity of the sources in different seasons makes it rather difficult to discern any seasonal variation of propagation. However, the seasonal variation has a potential usefulness in assessing the meteorological conditions in the neighbourhood of the observing station. So far as the solar cycle variation is concerned, although there is a general agreement in the finding of the inverse correlation with sunspot activity, the cause is not yet precisely known and further investigations would be informative.

Summary

A brief account of the nature of atmospherics including the historical background of the investigations on atmospherics is given. The advantages of the IFIA studies as compared to the continuous wave method in providing data useful for the future design of radio systems are pointed out. The results of observations made on the IFIA during the IGY period and post-IGY period at a number of places are reviewed with special emphasis on aspects which affect radio wave propagation. The nature of and causes for diurnal, seasonal and solar cycle variations, sudden enhancements and decreases originating from solar flares and high altitude nuclear explosions and long period fluctuations are discussed. The scope for further investigations on the IFIA in relation to radio wave propagation is indicated.

Acknowledgement

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References

1. Appleton, E. V., Wattson Watt, R. A. & Herd, J. F., *Proc. roy. Soc.*, **A111** (1926), 654.
2. Schonland, B. F. J., Elder, J. S., Hodges, D. B., Philips, W. E. & Vanwyk, J. W., *Proc. roy. Soc.*, **A176** (1940), 180.
3. Thomas, H. A. & Burgess, R. E., *Radio research special No.* 15 (Department of Scientific & Industrial Research, London), 1947.
4. Brooks, C. E. P., *Geophysical memoirs and professorial notes No.* 24 (Meteorological Office, London), 1925.
5. Horner, F., *Radio noise of terrestrial origin* (Elsevier Publishing Co. Inc., New York), 1962, 100.
6. Horner, F., *Advances in radio research*, Vol. 2 (Academic Press Inc., New York), 1964, 124.

7. Gerson, N. C., *Report to the U.S. National Committee of URSI for IGY* (National Bureau of Standards, Washington), 1958.
8. Kimpara, A. & Kimura, Y., *Proc. Res. Inst. Atmos. Nagoya*, **5** (1958), 21.
9. Sachdev, D. K., *J. sci. industr. Res.*, **17A** (1958), 262.
10. McKerrow, C. A., *J. geophys. Res.*, **65** (1960), 1911.
11. Das Gupta, M. K. & Sen, A. K., *J. atmos. terr. Phys.*, **24** (1962), 739.
12. Chiplonkar, M. W. & Karekar, R. N., *J. atmos. terr. phys.*, **25** (1963), 23.
13. *Final report of the working group of atmospherics* (World Meteorological Organization, Geneva), 1957.
14. Lugeon, J., *C.R. Acad. Sci., Paris*, **188** (1929), 1690.
15. Rieker, J., *Geofis. pure appl.*, **46** (1960), 241.
16. Lugeon, J., *Tirage a part de Annales de la station centrale suisse de meteorologique* (Swiss Central Meteorological Station, Zürich), 1947.
17. Potter, R. K., *Proc. Inst. Radio Engrs, N.Y.*, **19** (1931), 1731.
18. Khastgir, S. R. & Ali, M. I., *Indian J. Phys.*, **15** (1942), 399.
19. Khastgir, S. R., Das Gupta, M. K. & Ganguly, D. K., *Indian J. Phys.*, **21** (1947), 169.
20. Khastgir, S. R., Das Gupta, M. K. & Ganguly, D. K., *Nature, Lond.*, **159** (1947), 572.
21. Espenschied, L., Anderson, C. N. & Bailey, A., *Proc. Inst. Radio Engrs, N.Y.*, **14** (1926), 7.
22. Khastgir, S. R., *Sci. & Cult.*, **7** (1942), 233.
23. Khastgir, S. R. & Ray, A. K., *Sci. & Cult.*, **5** (1940), 772.
24. Chakravarti, S. P., Ghosh, P. B. & Ghosh, H., *Proc. Inst. Radio Engrs, N.Y.*, **27** (1939), 780.
25. Das Gupta, M. K. & Sen, A. K., *J. atmos. terr. Phys.*, **25** (1963), 306.
26. Gerson, N. C., *J. atmos. terr. Phys.*, **26** (1964), 531.
27. Austin, L. W., *Proc. Inst. Radio Engrs, N.Y.*, **15** (1927), 837.
28. Austin, L. W., *Proc. Inst. Radio Engrs, N.Y.*, **20** (1932), 280.
29. Brooks, C. E. P., *Roy. met. Soc. J.*, **60** (1934), 153.
30. *Progress in radio science in Japan* (Japanese National Committee for URSI, Science Council of Japan, Veno Park, Tokyo), 1963.
31. Bureau, R., *Nature, Lond.*, **139** (1937), 110.
32. Waldmeier, M., *Z. Astrophys.*, **26** (1949), 205.
33. Ellison, M. A., *Publ. R. Obs. Edinb.*, **1** (1950), 51.
34. Ellison, M. A., *J. atmos. terr. Phys.*, **4** (1953), 226.
35. Ellison, M. A., *Planet Space Sci.*, **11** (1963), 597.
36. Ellison, M. A. & Reid, J. H., *J. atmos. terr. Phys.*, **8** (1956), 291.
37. McKerrow, C. A., *Nature, Lond.*, **177** (1956), 1223.
38. Aarons, J. & Barron, W. R., *Nature, Lond.*, **178** (1956), 277.
39. Feibelman, W. A., *J. geophys. Res.*, **63** (1958), 8661.
40. Lauter, E. A., *Solar eclipse and the ionosphere*, edited by W. J. G. Beynon & G. M. Brown (Pergamon Press Ltd, London), 1956, 124.
41. Enmert, A. & Revellio, K., *Solar eclipse and the ionosphere*, edited by W. J. G. Beynon & G. M. Brown (Pergamon Press Ltd, London), 1956, 126.
42. Bost, R., *Solar eclipse and the ionosphere*, edited by W. J. G. Beynon & G. M. Brown (Pergamon Press Ltd, London), 1956, 132.
43. Kimpara, A. & Obayashi, T., *J. Geomag. Geoelect., Kyoto*, **11** (1959), 48.
44. Saha, A. K., Karabin, M. & Mahajan, K. K., *J. atmos. terr. Phys.*, **25** (1953), 212.
45. Obayashi, T., *Planet Space Sci.*, **10** (1963), 47.
46. Saha, A. K. & Mahajan, K. K., *J. atmos. terr. Phys.*, **26** (1964), 618.
47. Sen, A. K., *J. atmos. terr. Phys.*, **26** (1964), 1291.
48. Gherzi, S. J. E., *Bull. Geophys., College Jean-de-brebeuf, Montreal*, (No. 10) (1961), 3.
49. Crichlow, W. Q., *Proc. Inst. Radio Engrs, N.Y.*, **45** (1957), 778.
50. Budden, K. G., *Proc. Inst. Radio Engrs, N.Y.*, **45** (1957), 772.
51. Liebermann, L., *J. appl. Phys.*, **77** (1956), 1477.
52. Wait, J. R., *Proc. Inst. Radio Engrs, N.Y.*, **45** (1957), 760.
53. Wait, J. R., *Proc. Inst. Radio Engrs, N.Y.*, **45** (1957), 768.
54. Alpert, Ya. L., *Radiotech. Electron.*, **1** (1956), 281.
55. Heritage, J. L., Weisbrod, S. & Bickel, J. E., *Symposium on VIF radio waves, Prepublication record* (National Bureau of Standards, Boulder, Colorado), **4** (1957), 29.
56. Pierce, J. A., *Proc. Inst. Radio Engrs, N.Y.*, **43** (1955), 584.
57. Pierce, J. A., *Proc. Inst. Radio Engrs, N.Y.*, **45** (1957), 794.
58. Crombie, D. D., Allan, A. H. & Newman, M., *Proc. Instn elect. Engrs*, **B21** (1958), 301.
59. Wait, J. R., *Proc. Inst. Radio Engrs, N.Y.*, **47** (1959), 998.
60. Volland, H., *Arch. elektr. Übertr.*, **13** (1959), 443.
61. *World distribution of thunderstorm days* (World Meteorological Organization, Geneva), 1953 & 1955, Tables—Parts I & II.
62. Whitson, A. L., *SRI project No.* 3171 (Stanford Research Institute, California), 1961.

Measurement of Pressure in High & Ultrahigh Vacuum Regions Using Ionization Gauges: Part I—Hot Cathode Gauges

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THE problem of production and measurement of pressures in high and ultrahigh vacuum regions (pressure of the order of 10^{-3} to 10^{-8} mm. of mercury is referred to as high vacuum and below that as ultrahigh vacuum) has gained considerable importance in the field of vacuum technology. Applications of ultrahigh vacuum technique is indispensable in many investigations where gases of very high purity are needed, particularly in thermonuclear machines[1] and for studying the interaction[2] of electrons, ions and the atoms in a gas. Other fields where high vacuum techniques find application are in the study of the physics and chemistry of surfaces[3] and production of thin film circuit elements for microcircuitry[4], superconducting films for cryotrons[5] in logic and memory devices and vacuum evaporated ferromagnetic films used in computer memory systems. Also, the testing of electronic components under conditions simulating free space[6] will probably require pressures as low as 10^{-16} mm. of mercury.

Until 1950, devices were not available for the measurements of pressures in the ultrahigh vacuum region. Among the techniques developed for the measurement of very low pressures one is the method of measuring the partial pressures of the gases present in a system using the mass spectrographs[7]. But the total pressure is not evaluated with this method and it is only the ionization gauge in its various forms and modifications which has adequate sensitivity for the measurement of the total pressure in the regions of high and ultrahigh vacua. In 1957, Gomer *et al.*[8] succeeded in producing an ultimate vacuum estimated by them to have a pressure of the order of 10^{-17} mm. of mercury and only recently Lafferty[9] has developed a device for the accurate measurement of such low pressures.

Even though several reviews[10-17] covering the field of production and measurement of vacua have been published from time to time, many important developments have taken place in this field recently and it would be worth while to focus attention on these developments.

A survey of the literature dealing with the use of ionization gauges for vacuum measurements shows that these gauges could be divided into two classes, viz. hot cathode types and cold cathode types. The present paper reviews the recent developments in the field of the design and operation of hot cathode type gauges.

Measurement of High Vacuum

Most common devices[18] for the measurement of pressures in this range are the McLeod gauge, Knudsen gauge, Pirani gauge and the ionization gauge. McLeod gauge is an absolute gauge and is used for the measurement of pressures ranging from 1 mm. to 10^{-6} mm. of mercury. It cannot be used for the entire high vacuum range since the vapour pressure of mercury at 20°C. is relatively high ($\approx 10^{-3}$ mm. of mercury). The readings with this gauge are never very dependable below 10^{-5} mm. of mercury and in order to eliminate mercury vapours from the system it is necessary to insert a liquid air trap. The other disadvantages of this gauge are that it does not indicate the pressure of condensable gases and vapours like carbon dioxide, water vapours, etc., and does not give the continuous indications of pressure when pressure changes. In addition to the above disadvantages, it takes also appreciable time to make observations of pressure. Various modifications[19] to the original McLeod gauge have been suggested recently and as a result the accuracy of the gauge has been increased enormously in the above-mentioned ranges.

The Pirani gauge, based on the dependence of thermal conductivity of gases on pressure, cannot be used below 10^{-3} mm. of mercury, because at such low pressures the heat loss by conduction becomes negligibly small as compared to the radiation losses.

The ionization gauge[20], which covers the entire high vacuum range, consists of three electrodes (cathode, grid and ion collector) sealed in a glass bulb. Tungsten filaments used in these gauges are either bare, thoriated or oxide coated. If the potential of the grid is higher than the ionization potential of the gas molecules, there exists a finite probability that the electrons will ionize the gas molecules on collision with them. At sufficiently low pressures the collision probability is so low that anyone electron does not make more than one collision during its movement from cathode to grid. Under these conditions, the electronic space charge is small and so the number of positive ions produced will be proportional to the gas pressure and the electron emission. Consequently, the rate of production of positive ions is an indication of the gas pressure. Under the conditions discussed above, the ion current is given by

$$i_p = SPI_0 \qquad \ldots(1)$$

where S is a constant known as the sensitivity of the gauge and partly depends upon the nature of the gas. At higher pressures, of the order of 10^{-3} mm. of mercury and above, the ionization gauge does not work properly due to space charge and other considerations. The sketch of the ionization gauge designed by Dushman and Found[21] is shown in Fig. 1. Buckley[20] has suggested two different

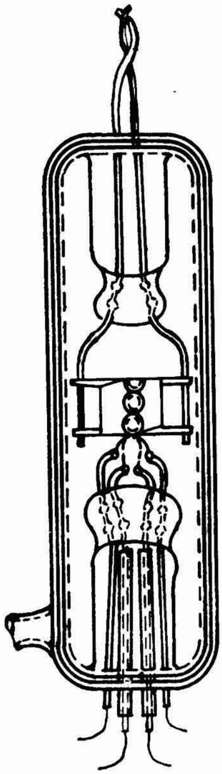

Fig. 1 — Ionization gauge designed by Dushman and Found[21]

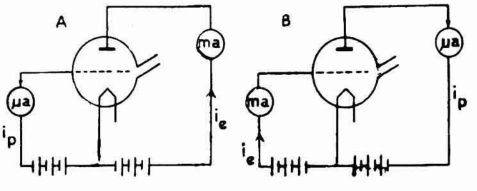

Fig. 2 — Modifications suggested by Buckley[20] for using the triode structure of an ionization gauge [A, internal control type; and B, external control type; i_p and i_e represent the positive ion and electron currents respectively]

ways of using the triode structure in the ionization gauge and these are shown in Figs. 2(A) and 2(B) and are known as internal and external control types respectively. The use of the latter type is always preferred because it gives higher sensitivity than the former under similar conditions of voltage, pressure and emission current.

The typical values of voltages and currents used in the ionization gauge are: grid voltage, + 250 V.; ion collector voltage, −22 V.; and emission current, 0·5 ma.

The above type of the ionization gauge worked properly up to about 10^{-8} mm. of mercury; at lower pressures, the ion current becomes constant, thus rendering the gauge ineffective. Efforts to extend the working range of the gauge to lower pressures are discussed in the following sections.

Measurement of Ultrahigh Vacuum

Nottingham[22] and Apker[23] observed that the conventional ionization gauges (Fig. 1) were not capable of measuring pressures below 10^{-8} mm. of mercury because the ion current measured at pressures below 10^{-8} mm. of mercury was constant and independent of pressure. This constant current was called as residual photocurrent. Nottingham[22] suggested that this residual photocurrent was produced by the impact of soft X-rays (wavelength approximately 100 A. produced at the grid due to the impact of the electrons) and ultraviolet radiations (emitted from the heated filament) on the ion collector.

Bayard-Alpert (B-A) and Lander Gauges

Design considerations of ionization gauges for the measurement of the degree of ultrahigh vacuum were first discussed by Bayard-Alpert[24] and Lander[25] who also gave independent designs for the ionization gauge which will extend the lower limit of pressure measurement. In designs suggested by them, the residual photocurrent was decreased by incorporating the following two changes in the design of the gauge: (i) minimizing the surface area of the ion collector and (ii) changing the potential distribution in the gauge in such a way that the ion collector acts efficiently.

Sketch of the ionization gauges based on these designs are shown in Figs. 3 and 4. Though the principle of working of both the high vacuum and the ultrahigh vacuum gauges is the same, the latter requires special considerations in its construction, calibration and operation, since these gauges should be bakable and must not act as a source of contamination and should retain the calibration even after baking.

In the B-A gauge (shown in Fig. 3), the positions of the filament and the ion collector are interchanged and hence it is also known as the inverted ionization gauge. The surface area of the ion collector is thus reduced to about one-hundredth of that in the conventional designs and hence the lower limit of pressure measurement is also extended by this factor. A comparison of the grid potential versus the ion collector current characteristics of the conventional as well as the inverted gauge is shown in Fig. 5. It is clear that the curve showing the relation between the ion current and grid potential for the conventional gauge is a straight line below a pressure of 10^{-8} mm. of mercury which was shown by Bayard and Alpert to be due to the photocurrent produced by the X-rays. On the other hand, in the inverted type gauge the characteristic is not a straight line even below a pressure of 4×10^{-9} mm. of mercury. These workers found that the sensitivities of the conventional and the inverted gauges were the same.

The Lander gauge (Fig. 4) has two ion collectors P_1 and P_2 which are used for measuring pressures at high and ultrahigh vacua respectively. For the latter type measurements, the effective surface area of the ion collector P_2 is reduced by keeping

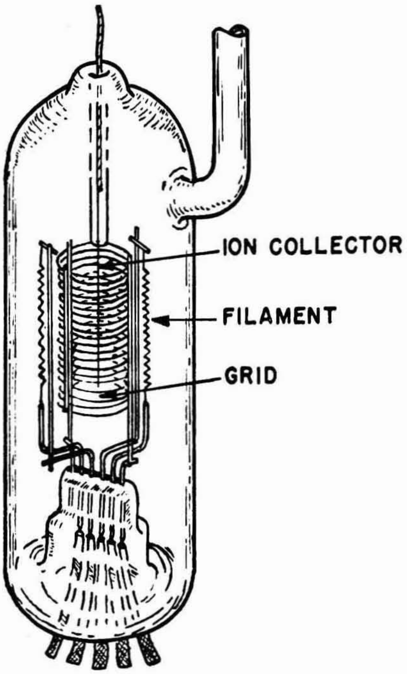

Fig. 3 — Bayard-Alpert (B-A) ionization gauge[24]

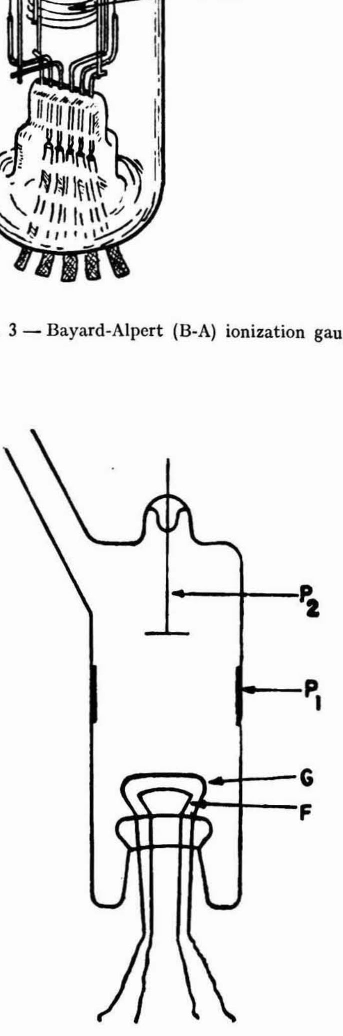

Fig. 4 — Ionization gauge designed by Lander[25] [P_1, ion collector for high vacuum measurements; P_2, ion collector for ultrahigh vacuum measurements; F, filament; and G, grid]

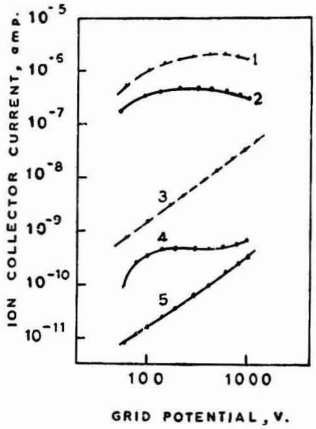

Fig. 5 — Grid potential versus the ion collector current characteristics of the ionization gauge [—, characteristics of the Bayard-Alpert gauge; and - - -, characteristics of the conventional ionization gauge. Pressures in mm. of mercury: curve 1, 10^{-5}; curve 2, 4×10^{-6}; curve 3, less than 10^{-8}; curve 4, 4×10^{-9}; and curve 5, near 5×10^{-11}]

it sufficiently away from the filament. Thus P_2 intercepts about one part in 500 of the direct radiation from the grid. But it has been observed by Lander that under normal operating conditions the ion collector collects about one-fifth of the total ion current. Thus the ratio of the photocurrent to the ion current should be lowered to one-hundredth of that corresponding to the ion collector P_1 of the conventional gauge. Using this design Lander could measure pressures of the order of 10^{-10} mm. of mercury at an ion current of about 10^{-12} amp.

In 1954, Nottingham[26] tried to increase the sensitivity of the B-A gauge for pressure ranges below 10^{-10} mm. of mercury, by introducing another electrode, called the modulator, between the grid and the ion collector (Fig. 6). Redhead[27] has explained how the range and sensitivity of this gauge is increased by introduction of the modulator. While using the gauge for measurements of pressures at ultrahigh vacua, the error caused by the photocurrent is eliminated by measuring the apparent ion current under two different conditions: first when the modulator is at grid potential and then when the modulator is at ion collector potential. Let i_1 and i_2 be the measured values of the ion currents under the above two conditions, i_r the residual photocurrent and i_p the actual ion current, then

$$i_1 = i_p + i_r \qquad \ldots(2)$$

$$i_2 = \alpha i_p + i_r \qquad \ldots(3)$$

$$i_p = (i_1 - i_2)/(1-\alpha) \qquad \ldots(4)$$

where α, called the modulation factor, represents the fraction of the total ion current collected by the ion collector when the modulator is at ion collector potential and may have values ranging

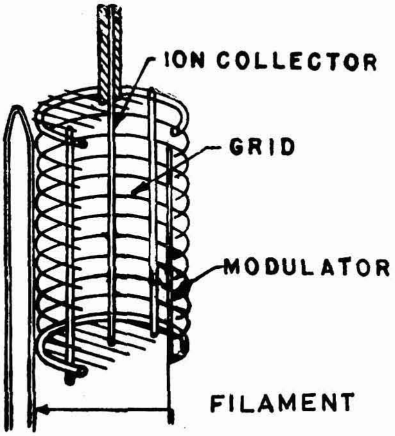

Fig. 6 — Sketch of the modified[27] Bayard-Alpert gauge

from 30 to 40 per cent. At higher pressures $i_p \gg i_r$ and so from Eqs. (2) and (3) it is seen that the value of α becomes equal to i_2/i_1. This value of α is used to determine i_p from Eq. (4) and hence the pressure in the ultrahigh vacuum region.

Orbitron Ionization Gauge

Recently, Mourad *et al.*[28] have suggested a new design of hot cathode ionization gauge, called the orbitron gauge, which has high ionization efficiency and requires low input power. A sketch of the gauge is shown in Fig. 7. In the orbitron gauge, the electrons produced by heating the filament are ejected into the electrostatic field applied between two concentric cylinders as shown in the figure. The inner cylinder is referred to as anode and is kept at a positive potential with respect to the filament which itself is kept at a lower positive potential with respect to ground and serves as an electron collector. The outer cylinder is kept at ground potential and serves as an ion collector. One of the leads of the filament has a non-emitting extension which acts as a shield so that a large portion of the electrons leaving the filament will have sufficient angular momenta with respect to the central axis to miss the anode and will follow curved paths the shape of which has been studied by Hooverman[29]. Thus a relatively long mean free path for the electrons is achieved. The gauge is operated at a very low emission current (4 μa.) which is sufficient to produce ion current of the magnitude obtained from relatively high emission current (8 ma.) in a conventional B-A gauge. The photocurrent caused by X-rays and ultraviolet radiations is very low in this type of gauge due to the fact that the ion collector is away from the main source of light and X-rays and that the emission current is also low.

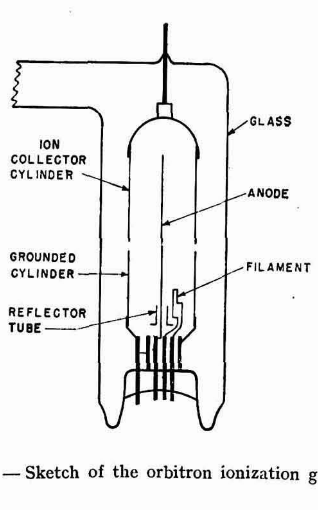

Fig. 7 — Sketch of the orbitron ionization gauge[28]

The gauge has been found to have a linear response at pressures below 1×10^{-5} mm. of mercury and has been used down to 5×10^{-11} mm. of mercury pressure. The lower limit of the pressure measurement with this gauge has yet to be determined.

Magnetron Gauge

In order to extend the lower limit of the pressure measurement with any ionization gauge, it is necessary for a given constant emission current to increase the ratio of the ion current to the X-ray photocurrent. This was done by Lafferty[30] by increasing the ion current and decreasing the electron current (which produces the X-rays and the attendant photocurrent) in the gauge. In this gauge designed by Lafferty called the magnetron gauge (Fig. 8) the ion current is increased by applying a magnetic field along the axis of the cylindrical grid. The end plates serving as ion collector and the shield are maintained at a negative potential relative to the cathode. The shield prevents the escape of the electrons. The shield, the ion collector and the grid are kept at -10 V., -45 V. and $+250$ V. respectively. The magnetron gauge is operated at a magnetic field of 250 oersteds which is more than the cut-off value of the magnetic field[31] (H_c) given by

$$H_c = 6{\cdot}74(V_p/r_p)^{\frac{1}{2}} \qquad \ldots(5)$$

where V_p is voltage of the anode and r_p the radius of the grid.

The magnetic field increases the path of the electrons several times, thereby increasing their collision probability with the gas molecules and thus increasing the ion current. This fact is obvious from Fig. 9, where the ion current and the electron current are shown plotted as a function of magnetic field at a pressure of 10^{-6} mm. of mercury. The gauge has high stability and maximum ratio of the ion current to the electron current when operated at an emission current of 10^{-7} to 10^{-9} amp. Lafferty showed that in this gauge the ion current would equal the X-ray photocurrent at a pressure of $2{\cdot}4\times10^{-14}$ mm. of mercury. Thus a pressure of at least this value can be measured by the magnetron gauge discussed above.

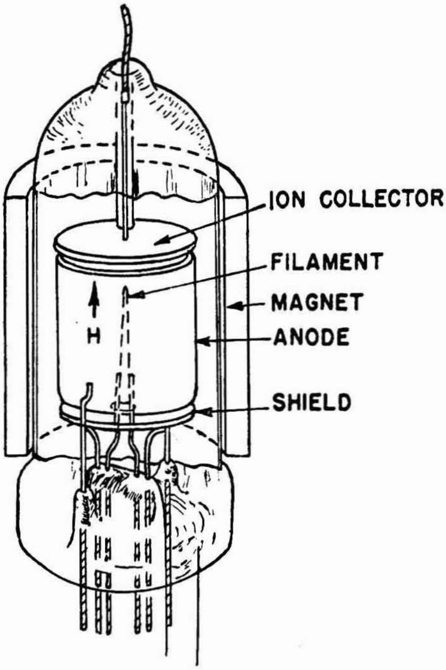

Fig. 8 — Sketch of the Lafferty's hot cathode magnetron ionization gauge[30]

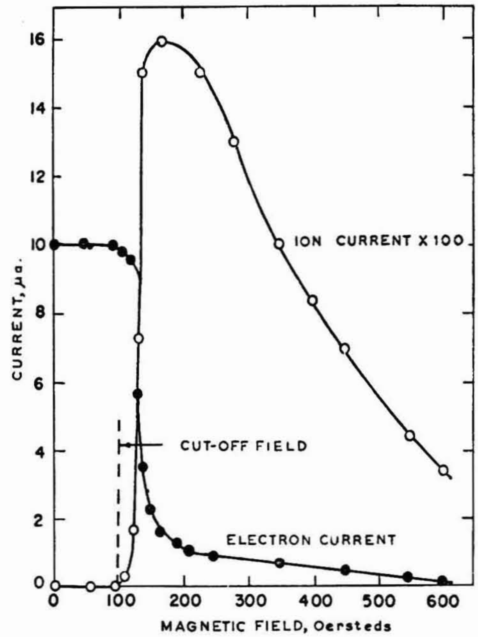

Fig. 9 — Variation of the ion current and the electron current with magnetic field at a constant emission current

Modified Magnetron Gauge

In his efforts to further increase the lower limit of pressure measurement Lafferty[32] modified the magnetron gauge by introducing an electrostatic lens system which focused the ions on the first dynode of an electron multiplier and by using a lanthanum hexaboride coated filament[33]. This filament gives appreciable emission at low temperatures (675°C.) and its vapour pressure also is very low (of the order of 10^{-16} mm. of mercury at a temperature of 825°C.). Thus the photocurrent due to ultraviolet radiations and the vapour pressure of the hot filament were both reduced still further. The gauge in this form has a linear response down to a pressure of the order of 10^{-15} mm. of mercury with an output current approaching 10^{-11} amp. Recently, Lafferty[9,34] has improved the design of the electron multiplier used with the hot cathode magnetron gauge. The new design (Fig. 10) prevents X-rays, generated at the grid from reaching the first dynode directly. The ions produced are made to pass through two narrow apertures, thereby reducing the intensity of X-rays and ultraviolet radiations reaching the first dynode. The ions are then focused on the first dynode by a combination of electrostatic lenses, thus increasing the ratio of the ion current to the photocurrent. The output current (I) of the multiplier is given by

$$I = G[i_r + \eta \Upsilon S I_0 P] \qquad \ldots(6)$$

where i_r is the residual current including photocurrent and the dark current of the multiplier; S, the sensitivity; η, the fraction of the ion current that reaches the first dynode; G, the overall gain; Υ, the number of electrons per ion; I_0, the emission current; and P, the pressure. Lafferty's measurements have shown that this device has a linear response down to a pressure of 2×10^{-17} mm. of mercury. The lower limit to which pressures can be measured with this gauge is fixed by the inherent dark current of the multiplier.

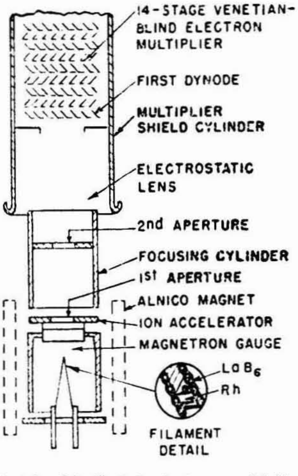

Fig. 10 — Sketch of Lafferty's electron multiplier magnetron gauge[32]

Limitations of Hot Cathode Ionization Gauges

Though the hot cathode ionization gauge measures a very wide range of pressures, its use is beset with the following disadvantages which restrict its use only for cases requiring very accurate measurements: (1) The gauge is always associated with a complicated electronic circuitry and hence special skill is needed in its operation. (2) The sensitivity of the gauge varies with the gases and vapours in the system, necessitating changes in the calibration of the gauge with different gases and vapours. (3) The filament is always susceptible to burn out if exposed to air while hot. (4) The hot filament decomposes certain gases (specially hydrocarbons). (5) Pumping action is found to be present in all types of ionization gauges specially those which employ magnetic field. This action of hot cathode type of gauges is mainly due to the interaction of chemically active gases with the hot filament and due to the ions getting adsorbed on the surface of the ion collector. (6) In spite of the various methods for overcoming the effect due to photocurrent produced in the gauge, the inherent photocurrent cannot be completely eliminated. (7) The vapour pressure of the material of the hot filament limits the use of the gauge for the measurement of pressure in the far ultrahigh vacuum regions.

Some of the above-mentioned sources of errors, namely the production of photocurrent, vapour pressure of the hot filament and additional chemical reactions with the filament, are completely avoided by the use of cold cathode ionization gauges[35]. A review article bringing out the recent developments in the design of cold cathode ionization gauge will be published later.

Summary

The recent developments and techniques used in the measurement of pressures near high and ultrahigh vacuum regions with particular reference to the use of hot cathode ionization gauges are critically reviewed. Comparative merits of the McLeod gauge, Pirani gauge and different type of ionization gauges are discussed. Limitations of even improved types of hot cathode ionization gauges are indicated and it is pointed out that the cold cathode ionization gauge is free from some of the limitations.

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References

1. Munday, G. L., *Nucl. Instrum. Methods*, **4** (1959), 367.
2. Germer, L. H., Scheibner, E. J. & Hartman, C. D., *Phil. Mag.*, **8** (1960), 222.
3. Dyke, W. P., Charbonnier, F. M., Strayer, R. W., Fley, L., Barbour, J. P. & Trolan, J. H., *J. appl. Phys.*, **31** (1960), 790.
4. Greenland, K. M., *J. sci. Instrum.*, **38** (1961), 1.
5. Caswell, H. L., *J. appl. Phys.*, **32** (1961), 105.
6. Santeler, D. J., *Transactions of the national symposium on vacuum technology*, Vol. 6 (Pergamon Press Ltd, Oxford), 1959, 129.
7. Huber, W. K., *Vacuum*, **13** (1963), 469.
8. Gomer, R., Wortman, R. & Lundy, R., *J. chem. Phys.*, **26** (1957), 1147.
9. Lafferty, J. M., *Rev. sci. Instrum.*, **34** (1963), 467.
10. Yarwood, J., *J. sci. Instrum.*, **34** (1957), 297.
11. Alpert, D., *Handbuch der phys.*, Vol. 12 (Akademische Verlags GmbH, Leipzig), 1958, 609.
12. Venema, A. & Bandringa, M., *Philips tech. Rev.*, **20** (1958), 145.
13. Redhead, P. A. & Karnelsen, E. V., *Vakuum Tech.*, **10** (1961), 31.
14. Lafferty, J. M. & Vanderslice, T. A., *Proc. Inst. Radio Engrs, N.Y.*, **49** (1961), 1136.
15. Redhead, P. A., *Advanc. electronics electron phys.*, Vol. 17 (Academic Press Inc., New York), 1962, 323.
16. Schweitzer, J., *Le Vide*, **14** (1959), 165.
17. Vanderslice, T. A., *Science*, **142** (1963), 178.
18. Dushman, S., *Scientific foundations of vacuum techniques* (John Wiley & Sons Inc., New York), 1962.
19. Carr, Paul H., *Vacuum*, **14** (1964), 37.
20. Buckley, O. E., *Proc. nat. Acad. Sci., Wash.*, **2** (1916), 683.
21. Dushman, S. & Found, G. G., *Phys. Rev.*, **17** (1921), 7.
22. Nottingham, W. B., *Proceedings of the 7th annual Massa chusetts Institute of Technology conference in physics and electronics*, 1947.
23. Apker, L., *Industr. Engng Chem.*, **40** (1948), 846.
24. Bayard, R. T. & Alpert, D., *Rev. sci. Instrum.*, **21** (1950), 571.
25. Lander, J. J., *Rev. sci. Instrum.*, **21** (1950), 672.
26. Nottingham, H., *Transactions of the national symposium on vacuum technology*, Vol. 1 (Pergamon Press Ltd, Oxford), 1954, 76.
27. Redhead, P. A., *Rev. sci. Instrum.*, **31** (1960), 343.
28. Mourad, W. G., Pauly, T. & Herb, R. G., *Rev. sci. Instrum.*, **35** (1964), 661.
29. Hooverman, R. H., *J. appl. Phys.*, **34** (1963), 3505.
30. Lafferty, J. M., *J. appl. Phys.*, **32** (1961), 424.
31. Hull, A. W., *Phys. Rev.*, **18** (1921), 31.
32. Lafferty, J. M., *Transactions of the 8th national symposium on vacuum technology* (Pergamon Press Ltd, Oxford), 1962, 460.
33. Turnbull, A. H., Barton, R. S. & Riviere, J. C., *An introduction to vacuum technique* (Newness Practical Science Books, London), 1962, 89.
34. Lafferty, J. M., *Transactions of the 9th national symposium on vacuum technology* (Pergamon Press Ltd, Oxford), 1963, 438.
35. Roberts, R. W. & Vanderslice, T. A., *Ultrahigh vacuum and its application* (Prentice Hall Inc., New York), 1963.

Concept of Complementarity in Biological Activity

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EVER since the inception of curiosity in human thinking an explanation has been sought for phenomena such as olfaction, palate and various other sensory responses. Over 2000 years ago, a simple explanation for olfaction was suggested by Leucretius, the poet[1]. According to him, every odorous substance gave off tiny 'molecules' of a particular shape, which could enter the pores of various sizes and shapes to elicit the responses of the odour depending upon the pore in which a particular molecule fitted. Since then, analogous speculations have been put forward to explain such diverse biological processes as enzyme catalysed transformation, antigen-antibody interaction, fertilization, parasite infection, olfaction, drug action, nerve impulse initiation and transmission, etc.

Macroscopically, involvement of cells is one of the common features of almost all these biological processes. This may be in the form of a cell-to-cell interaction or as an interaction of a cell with a foreign body. One of the most fundamental features of the cell function in these processes is their discriminatory capacity for admitting or excluding selectively specific physical stimuli and chemical agents. However, the mechanism of these processes are microscopic and ultimately molecular. A single molecule interacts with another single molecule in such a manner that the fundamental event occurs as a topochemical reaction, and these elementary events coordinate into the appearance of macroscopically manifest phenomena. In recent years, some of these phenomena have been interpreted in terms of interlocking of molecules of matching configuration.

Biology, by and large, has so far followed a course to rely upon direct observation of the events, mainly with the help of more and more powerful microscopes. But all these tools get exhausted no sooner than they come into operation. The obvious reason is their limited utility in the study of intact and living organism in general and microscopic phenomena such as the subcellular and molecular events in particular (due to their functional limit of operation). The description of the molecular events underlying the manifest phenomenon is, therefore, the cherished aim of molecular biologists. The present review is an endeavour to trace the evolution of the concept of structural complementarity (of surface topology and binding forces) in biological activity at the molecular level. It also embodies the applications of this concept together with some of its important implications. In spite of the fact that the authors are well aware of the applicability of the concept of complementarity in quite a few biological processes, it is obviously not possible to cover them all in a single review.

Evolution of the Concept of 'Receptor'

The modern trends in this direction may be said to have started with the classical studies of Paul Ehrlich. His early work was concerned with selective staining of living tissues with dyes, and this led to the discovery of antimalarial activity of methylene blue. The explanation of this observations, by Ehrlich, led to the discovery of a trypanocide (Trypan Red) and the development of Bayer 205 (Antrypol). This was followed by his studies in immunization which resulted in the enunciation of his 'side chain' or 'receptor' theory[2,3], in which he postulated specific points or areas of chemical affinity in antigens and antibodies and subsequently similar receptor points were brought forth to explain the parasite-drug interaction[4]. He also developed this idea in terms of 'intrinsic affinity' or, in his own[5] words, 'the primary attraction of toxins', which was elaborated to explain different responses. He also advocated the validity of anchoring a particular part of the organism and foresaw[5] that 'both kinds of substances exert their power by purely chemical means'.

A new dimension to this concept was given by Hopkins[6]. He emphasized that an essential and indispensable condition for the occurrence of a multitude of biochemical reactions was an exact coordination, in time and space, between the 'seats of chemical events' and the interacting molecules. He further pointed out that the attention of a chemist in the study of a living organism should mainly be focused on these seats of chemical events, which are intrinsically synonymous to the term 'receptor' given earlier by Ehrlich. Since then this unifying influence of chemistry in biology has been experienced increasingly, although such studies have been largely scattered. The term 'receptor' has since been retained in the functional sense and defined[7] as 'a pattern of forces of diverse origin forming a part of some biological system'. Obviously, this 'part of biological system' is considered to be the origin of molecular events.

More or less similar ideas have been used in different disciplines such as pharmacology, therapeutics, chemotherapy, enzymology, cancer research, study of olfaction and gustation, hormone action and the action of insecticides and pesticides, etc. Through the studies in these fields, attempts have been made to refine the concept of drug-receptor interaction to explain specific phenomena, and these refinements have firmly established the so-called 'key and lock' theory. The usual approach of these hypotheses has been to seek an explanation on the basis of available information and to test their predictability by further experiments. In general, they offer satisfactory models but are, more often than not, the oversimplification of the reality. The terms receptor, active site, biologically reactive site, attachment site, binding site, etc., have all been used by workers in various fields to explain, more or less, similar phenomenology and thus carry the same sense, i.e. *a part of the biological system which* *is directly involved in the interaction with a foreign molecule.* Similarly, the terms phage, antigen, hapten, drug, ligand and substrate have all been used, at one time or another, by various workers to describe the interacting foreign molecule. We shall retain the term ' ligand ' for all types of interacting foreign bodies, and the term ' receptor ' for all biological ultrastructures directly involved in the interaction, throughout the present article.

The Nature of Receptor

The receptors seem to represent only a small fraction of the total surface of the cell or the organism on which they are situated, since extremely low threshold concentrations of some ligands elicit the corresponding responses, e.g. acetylcholine and atropine are active in concentrations of 10^{-8} mM, the antidiuretic hormone[8] at 10^{-12} mM, musk and ethyl mercaptan[9] elicit their odours at about 10^{-15} mM, and some pheromones[10] are active at as low concentrations as 10^{-17} mM. These extremely low concentrations do not even permit a monomolecular spreading of the ligand over the receptor cell surface. Similarly, it has been shown that the area of the cell surface which is suitable for the attachment (and infection) by any particular type of bacteriophage is only a small fraction of the total cell surface[11].

A rather indirect, though intersting, proof of this fact was provided by the work of Janoff[12] who showed that the tetanus toxin bound only to a certain fraction of the ground rat brain cells. This immediately leads to the conclusion that the active portion of these cells (receptors) which interacts with the tetanus toxin comprises only a small fraction of them. A more direct substantiation of this fact came from the important observations of Woolley and Gommi[13]. They found that the serotonin receptors which are directly involved in the ion transport mechanism could be extracted by fat solvents and that in fractionation they behaved similar to sphingolipids or phospholipids[14,15]. Recently, Kimura[16], from a study of the interactions of various substances with acetylcholine receptors at different *p*H values, has postulated their size to be of the order of only a few Ångström units. Thus the receptors appear to be of molecular dimensions.

As already pointed out, most of the biological processes are initiated by receptor-ligand interaction. Various theories and hypotheses have been put forward to explain the specificity, selectivity, response type, efficiency and antagonism which characterize these processes and appear to be the manifestations of the ligand-receptor complementarity. The theories and hypotheses which have been put forward on the basis of the above concept can be grouped in the following representative types: (i) steric theory of olfaction and related phenomena; (ii) complementariness in immunological reactions; (iii) antibiotic activity of various naturally occurring substances; (iv) hypothesis of metabolite antagonism and related phenomena; (v) carcinogenicity of polycyclic aromatic hydrocarbons; and (vi) ' active sites ' in enzymology.

Steric Theory of Olfaction and Related Phenomena

The hypothesis of Lucretius[1] has been rejuvenated, of course, with modifications, in recent times, by quite a few workers to fit in with the needs of their specific problems. In 1938, Timmermans pointed out that the shape of the molecules having camphoraceous smell was spherical[17]. Later on he drew attention to the fact that the olfactory behaviour and the stereochemical configurations of the odorants were closely related and their shape was probably responsible for their characteristic odour[18]. Pauling compared the behaviour of antibodies with simple chemical substances (ligands) and concluded that molecular configuration was important in determining the biological activity[19]. He further maintained that the sense of odour was also based upon the molecular configuration and not on ordinary physico-chemical properties such as osmotic pressure, partition coefficients, surface tension, etc., as was believed earlier by some workers[20]. He hypothesized that a molecule having shape, for example, like camphor molecule must smell as camphor even though it might be quite unrelated to camphor chemically. But these theories did not receive much attention till 1951 when this hypothesis was reformulated in modern terms[20]. This prompted the most significant contribution to the stereochemical fit of odorous molecules and their shapes and dimensions by Amoore[21-25] who in a series of papers has outlined the so-called steric theory of olfaction. According to him, the response of seven primary odours are elicited as a result of specific fits of the odorous molecules at the selective sites. He has deduced the dimensions and shapes of the receptor sites corresponding to the seven primary odours assuming a great degree of complementarity in the ligand-receptor interaction. He has further suggested that the odours different from any of the seven primary ones are the result of mixed responses at two or more receptors due to different molecules or a single molecule having different structural features to elicit the response under question. Johnston[26], following this suggestion, has successfully synthesized many complex odours; for example, one of the complex odours resembling cedarwood has been synthesized by mixing musky, camphoraceous, floral and minty odorants. The theory has been able to explain[27-29] successfully the phenomenon of olfaction and has encountered only one exception, the odour of hydrocyanic acid[30], which according to Amoore[31] is due to some secondary reasons. In an attempt to explain the odour of musk, Beets[32] independently put forward the concept of ' profile-functional group ', which has recently been developed to explain the phenomenon of olfaction[33,34]. The broad outlines of both these theories are almost the same, but Amoore's study is more exhaustive in that he has deduced even the receptor dimensions.

The phenomenon of gustation is also a related one. Many attempts[35-39] have been made to explain the taste of a substance in terms of its chemical constitution. Although some correlations have been found, yet no unifying generalizations have been given. However, some of the recent studies seem to be quite promising. From a study of 80 compounds related to saccharin, Hamor[40] concluded that ' perhaps a lock and key fit at a receptor site is necessary for the taste '. Even earlier, Finzi and Colonna[41] had concluded from an extensive study of sweet and bitter compounds that taste depended not on any single functional group but on a particular structural feature of the molecule participating in the interaction. A study of the structural features of the naturally occurring lactones points out that the γ- and δ-lactones, having an exocyclic double bond in βγ- or γδ-positions from the alcoholic oxygen atom of the lactone ring, are bitter[42]. The structural features responsible for the bitterness in certain other types of bitters, e.g. hop bitters, cucurbitacins, etc., also appear to be isosteric[43] with the structural feature already pointed out. Similarly, Horowitz[44] deduced the structural feature responsible for bitterness in some of the flavanoids and polyphenolics, which also appears to be isosteric with the above feature. The study of the models of various bitter compounds is in progress in this laboratory and it is hoped that the measurements of the exact dimensions and shapes of these molecules may provide a clue to the receptor model and a unifying generalization about the taste-constitution correlation.

The mode of action of these gustatories appears to be through adsorption on the specific receptors and, therefore, the magnitude of the response is directly proportional to the number of sites occupied[45]. It follows that this adsorption would be competitive and a particular molecule may, by preferential adsorption, block some receptor sites. This is probably the case with gymnemic acid which gets preferentially adsorbed on both bitter and sweet-taste-receptor sites. The antagonism of the taste response by the application of a mixture of weak and strong stimulant to give a response less than that of the stronger one has also been observed[44]. These studies definitely indicate that the receptor modalities for the taste receptors could be deduced, based on the assumption that a fair degree of ligand-receptor complementarity exists.

Complementariness in Immunological Reactions

The immunological reactions are characterized by a high degree of specificity, which is one of the most important and fundamental propositions of all types of induced biological activities. However, an absolute specificity and homogeneity of the antibody forming molecule is inconceivable since a number of variables are involved in these interactions. Ever since the Ehrlich's concept of anchoring group in the haptenic body (ligand) was advanced, the mode of action and formation of antibodies has been studied through its various aspects.

The idea of antigen-antibody ' complementariness ' was suggested by various workers almost simultaneously[46-48], and was later on elaborated by Pauling[49] according to whom the chemical composition of all antibody molecules as well as of ' normal ' globulin was the same and immunological differences were the results of variations in specific spatial configurations assumed by the terminal amino acid chains of antibody proteins. This appears to have been confirmed by the studies of Porter[50] on the amino acid composition of the antibody reactive groups. Moreover, the mode of formation and action of an antibody appears to be through the formation of ' prints ' on the host compounds (e.g. globulins) which then act as attachment sites for the guest molecules (infection or parasite). An extremely interesting parallelism has been reported by Dicky[51], who has shown that silica gel formed in the presence of a certain dyestuff has, after removal of the dye, a strong adsorptive capacity for that dye. Based on these facts Beckett and Anderson[52-54] put forth the hypothesis of ' configurational footprints '. It follows that if the interacting ligand has a rigid structure, then a stereoselective adsorbent could be obtained, which may be able to distinguish even between a pair of enantiomorphs — a rather common phenomenon observed in biological processes. Similar aspects of the interactions have been covered by the ' occlusion ' theory[55] and the ' framework ' theory[56].

The forces involved in these antigen-antibody reactions are generally non-specific, weak, short-range and physical in nature, and the specificity results from the complementariness of antigen-antibody surfaces[57]. Rothen[58] postulated some novel long-range forces involved in the antigen-antibody reactions which extended over a distance of 200 A. These forces, however, were later on shown to be artefactual manifestations of the ' film '[59]. The manifestation of coulombic attraction in the so-called ' hepten inhibition constant ' has also been demonstrated[60,61] in the cases of haptens carrying some charged groups. Moreover, the extraordinary rapidity of the hepten-antibody reaction and its small activation energy indicate that little or no conformational change (rearrangement) are required within the active sites of the antibody molecules on specific bindings of the hepten[62]. The various aspects of the antigen-antibody interaction have been reviewed by Campbell and Bulman[63], and the important factors in these interactions according to them are: (i) chemical composition of the site, (ii) size and/or area of the site, (iii) total number of sites on a single antibody molecule, (iv) relative positions of the sites, (v) degree of specificity with respect to single determinant, (vi) stability of the sites and (vii) the possibility that a single molecule contains sites of different specificities.

A critical examination of the above factors led them to the conclusion that the basis of specificity is the spatial configuration of the combining site on antibody and the specific determinant on the antigen. The forces involved in the combination of antigen and antibody molecules are relatively weak and come into operation when suitable complementariness of surfaces exists.

Antibiotic Activity of various Naturally Occurring Substances

Symbiosis is observed in pairs of organisms having complementary metabolic requirements[64,65].

Parasitism may result when this complementariness is destroyed, and it may be achieved through slight changes in the metabolite or metabolic apparatus of either of the two. These changes in metabolites are discussed in the next section. The metabolic apparatus is the whole organized molecular structure of the organism and its variation appears to be the species determining or differentiating factor. Various fungi, for example, yield some molecules as the product of their metabolism which have typical antibiotic activity. In all these cases, there appears to be some common basic structural pattern complementary to the site of synthesis and to the site of action of these molecules. This makes them antimetabolites from metabolites due to slight variation in the biological ultrastructures acting as receptor and the site of synthesis respectively. The architectural profile of both of these sites and that of the ligand remains complementary enough to maintain the affinity, and so the biological activity is exhibited in the functional sense of the term. Similar factors appear to be responsible for the disease-resisting properties of the plants and animals[66].

Curiously enough, in most of the cases, only the naturally occurring isomers have the activity, which is almost absent in the synthetic ones, since the latter do not possess complementarity. These natural molecules have served as modalities in the design of potential drugs, and have dominated the line of thought in drug design for the past 20 years. The basic patterns in the biosynthetic molecules thus appear to store considerable information about their 'mould' or the site of synthesis and the site of action.

The complementarity at the molecular level has been demonstrated recently by Hershey and Burgi[67] in the case of the interacting sites at the ends of Lamda DNA molecules.

In an attempt to explain the mode of action of plant hormones, it was suggested by Skoog *et al.*[68] that an auxin must possess a special configuration which would allow it to occupy a specific place in a larger molecular aggregate (receptor), and it must also have special reactive group. Veldstra[69] developed this idea into a specific physico-chemical theory of auxin action, according to which its activity is governed by: (i) the presence in the molecule of a correct balance of hydrophilic and lipophilic groups, and (ii) the existence of a flat molecule from which an acidic group projects at an angle to the plane of the molecule. All these structural restrictions clearly emphasize the role of complementarity in this field.

Hypothesis of Metabolite Antagonism and Related Phenomena

Although Ehrlich[70] and later on Quatal and Wooldridge[71] seem to have realized the possibility of the existence of competition in the ligand-receptor interactions, yet the principle of antagonism was first conceived by Woods[72] who proved that the chemotherapeutic action of sulphanilamide was based on a competition of this drug with *p*-aminobenzoic acid for a specific enzyme. This was followed by a thesis by Fildes[73] who stated that chemotherapeutic substances might be obtained by the synthesis of compounds related to metabolites and growth factors. These synthetic molecules may antagonize the action of the metabolites by competition for or neutralization of the site of action. These potential antimetabolites have provided the basis for the design of drugs for the subsequent years.

Through its predictive value the theory of antagonism stimulated the experimental work in various fields and its success lies in that it offered, indirectly, the dimensions of the receptor sites. The concept has since been used to explain various phenomena such as competitive dualism in action, adaptation, synergistic action, drug modification, etc., on the basis of the degree of complementarity in the agonist and the antagonist with the receptor, and their mode of interaction. Although this theory is still far from complete, some of its implications are strikingly noticeable. Clark[74] tried to explain the action of acetylcholine in terms of (i) fixation of the drug on the receptor and (ii) its power to produce action after fixation. Both these factors are involved when the agonist has to produce a secondary effect and are apparent when the stimulus is competitively antagonized because then the secondary effect of the interaction is inhibited, e.g. the inhibition of the nerve impulse in neurons or chemical transformation in enzymes. The two features of the ligand differentiated above were respectively assigned the more general terms 'affinity' and 'intrinsic activity'[75,76] or 'affinity' and 'efficacy'[77]. They were also distinguished in various other types of biological activities such as drug interaction[78], cancer chemotherapy[79], enzymology[80] and vitamin activity[81].

As already pointed out the interacting ligand elicits the response only if it possesses intrinsic activity in addition to the affinity. If the ligand is a small molecule both these factors are liable to be more interdependent, and any change in one will naturally influence the other. Also, comparatively less flexibility of the smaller molecules would demand a higher degree of ligand-receptor complementarity. A critical study of the factors has been made by Ariens *et al.*[82] with special reference to mimetics and lytics. They have proposed the following three zone receptor model.

Zone I: Innermost zone where charges are located and hydrogen bonding and other physical interactions occur, which may result in the induction of stimulus.

Zone II: The attachment zone where coulombic and other comparatively long-range interactions occur. The matching in the shapes of receptor and ligand may determine the specificity in the affinity, only to a comparatively smaller extent.

Zone III: The biophase which plays a part in the penetration of the drug but does not influence the drug and the receptor.

Some of the interactions have been found to directly influence the ionic permeability of the cell membrane, for example, DDT acts through a charge transfer complex formation to inhibit the K permeability[83], and aldosterone stimulates the active transport of Na by interacting with the epithelial cells of the toad bladder[84]. This action is incidentally similar to that of the antidiuretic hormone[85]. Recently, an attempt has been made by Singh and Jain[86] to explain such permeability changes in neurons on molecular basis. Antagonism in all such cases appears to have been observed which may manifest itself in various types of secondary biological activities[87].

Local anesthetics prevent conduction along the axon either by decreasing the amount of released acetylcholine[88-90] or by blocking acetylcholine receptors[91]. Their potency will thus be proportional to their binding capacity with the specific receptor[92,93]. The acetylcholine receptors have been isolated through fractionation by Ehrenpreis and Nachmansohn[94] and they possess curare binding properties. They compared the binding strengths of the isolated protein with a great variety of tertiary bases, which are known to act as inhibitors, and mono- and diquaternary compounds related in structure to acetylcholine, and found a great difference. From this they concluded that binding of activators was poorer than that of inhibitors.

It is believed that the action of volatile anesthetics depends on physical interaction at a site which is still uncertain but may be the cell membrane of certain neuron[95]. An interesting suggestion has been made in this respect that a stabilizing effect of anesthetics, including compounds like rare gas xenon, on the hydrate microcrystals of various dimensions formed by water molecules, may be essential for their action[96]. These hydrate microcrystals might be in the organized hydration sheath over these receptors whereby the interaction might block the attack by the transmitter or any other stimulant.

Various aspects of antimetabolites and their mode of action have been discussed by Woolley[97].

Carcinogenicity of Polycyclic Aromatic Hydrocarbons

All the polynuclear aromatic compounds which are known to cause the mammary cancer are flat molecules with a system of conjugated double bonds. Their activity is dependent upon their planarity and the electron density profile[98,99], the latter being directly related to their ability to form charge transfer complexes with local receptors[100].

Recently, Yang *et al.*[101] in their studies on carcinogenesis have tried to correlate the role of steroidal hormones and carcinogens, and shown that there exists a marked sterical similarity between the two groups of molecules and that the carcinogenic activity of a molecule is directly related to its similarity to the steroids. This immediately leads one to the interesting speculation that there exists competitive antagonism between carcinogens and the steroids. The molecular models of the carcinogens can be inserted into the frame constructed from the molecular, models of the base pair (guanine-cytosine). This frame also incorporates the molecular models of progesterone, testosterone and estradiol-17β. The polynuclear carcinogens have an identical thickness (3·6 A.) to the base pairs and thus there exists a possibility of their incorporation into the nucleic acid chain. The thickness of the steroid molecule (5-6 A.), however, precludes their intercalation in the double stranded structure of nucleic acid, and thus they are not carcinogens[102]. Handdow[103] earlier pointed out that there exists some significant association between the molecular planarity of the carcinogens and the flatness of the nucleotide plates of purine: pyrimidine bonded pairs of the Crick-Watson model, which are of the same order of size. Electron transfer and geometric factors thus appear to be involved in determining the carcinogenic activity of a molecule.

Antagonism seems to have been observed in carcinogenicity; weakly active carcinogens have been reported to antagonize the carcinogenesis induced by highly active ones[104].

Concept of ' Active Site ' in Enzymology

Ever since the discovery of substrate concentration dependence of enzyme catalysed reactions[105], their kinetic aspects have been studied and an explanation of this phenomenon has been put forward which is based upon the assumed formation of an intermediate enzyme-substrate complex. Various aspects of these enzyme catalysed reactions such as reaction rate, solvent and *p*H dependence have been reviewed[106]. These enzymatic processes show antagonism and various examples of diverse types are known. Bergman *et al.*[107] studied specificity of dipeptidase action on a series of synthetic dipeptides, and postulated the structural feature responsible for the attachment over the enzymatic sites. Another case of stereospecific enzyme action is that of succinic dehydrogenase[108]. A particularly striking evidence of a thorough understanding of this phenomenon is borne out in the work of Wilson *et al.*, in their prediction and development of an effective antidote for insecticide poisoning. Cholinesterase is irreversibly phosphorylated with organophosphorus insecticides, which results in the death of the animal[109]. Wilson suggested that a suitable nucleophilic group should be able to displace the phosphoryl group specially if the former is at a proper atomic distance from the quaternary nitrogen which may promote dephosphorylation. Among a number of compounds suggested by Wilson and Ginsberg[110] pyridine-2-aldoxime methiodide (2-PAM) proved to be extremely powerful reactivator. From this study it was concluded that the basis of activity was molecular complementariness between PAM and phosphorylated esterase[111]. Similarly, Bernhard and Gutfreund[106] concluded from their study that the binding of molecules to the enzymatic site is always dependent on the extent of stereochemical complementarity between enzyme and substrate.

These active sites which directly interact with the substrate are the small portions of the large molecules which come in direct contact with the substrate molecules. They are functionally the same as the receptor sites. They can be described as constituted of functional groups, peptide linkages and hydrophobic regions of the protein structure and these structures are directly involved in the construction of transition state for the chemical transformation catalysed by the enzyme[112,113]. Slight conformational changes might result in the loss of activity. For example, the activity of renin is lost within 30 min. in 4·6M urea solution at 37°C. — a comparatively too mild condition to denature most of the proteins. Such a loss of activity can be attributed only to a minimal change in molecular configuration[114].

At these sites transformation takes place through actual contact. The selectivity and the specificity, the manifestations of complementarity, determine the efficiency of the contact or the complex formation. The sites in these cases also have solvation sheath and a certain degree of internal association and hydrogen bonding. These factors influence the rate, the activation energy and the transition state energy profile of the transformation. In these processes low activation energy is involved as in chelation and inclusion and clatherate complex formation, which is further reduced by reorientation of the hydrogen bonds present in the free enzyme[115]. The close contact of the substrate and the enzyme has the further advantage that for the whole process such a mechanism can be concerted and the local concentration and electrostatic effects may reduce the activation energy, and the electron transfer may occur easily through conjugated structure or through secondary structure of the macromolecule[116]. The distortion of the active site (by bond stretching, bending, etc.) is expected to activate the enzyme, perhaps by releasing its strain energy in causing the substrate to react. But for overall cooperative reaction a rigid active site skeleton appears to be a prerequisite. An induced fit accompanied with conformational changes may be thermodynamically less favourable. These systems thus offer very satisfactory models for the study of more complex biological phenomena.

The foregoing study leads to the conviction that the specificity and antagonism are the consequences of complementarity, which is also the guiding force in the ligand-receptor interactions. The mode of interaction not only determines the response type duration and efficiency of the overall process, but is also one of the prerequisites for the evaluation of the degree of complementarity. It is evident that there does exist the complementarity of surface topology of the gross macromolecular skeleton and that of the electronic charge profile. Although both of these are interdependent, yet during interaction one may overweigh the other since the forces governing the interaction are determined by the proximity to which the complementary topological surfaces and the charges can be brought. This in turn may govern a part of the permissible free energy changes — mostly changes in the entropy of the system. Moreover, some of these forces have limited range in which they are operable. Thus the permissible variations in the dimension and relative configuration without any appreciable loss of activity will also be determined by the operable limiting conditions. The dose-response relationship, of course, will be determined by the mode of interaction and is thus also a manifestation of complementarity.

These interactions may be of one of the following types.

Interactions through Non-specific Short-range Physical Forces

(i) *Dispersion forces*[117] — These can arise from induced electronic dipole moment. Two molecules which can bring large portions of their surfaces into close contact (about 10^{-7} cm. apart) will in general show much stronger mutual attraction than molecules with less extensive complementarity of the surface topology. Obviously, a difference of a few Ångströms at certain points in complementary profiles shall not altogether destroy the forces of interaction and hence the activity.

(ii) *Hydrogen bonding* — Hydrogen bonding with the polar groups of the macromolecular structure or the solvation sheath may lead to binding of approximately 4-8 kcal. strength[118]. The complementarity of the surface topology is not as important as the orientation of the polar groups since the bond is spatially directional[119].

(iii) *Coulombic attractions* — They require the complementarity of the electronic charge profile, are not strongly directional and permit separation over a considerable distance.

(iv) *Ion-dipole interactions* — Ions and polar groups as well as non-polar groups interact with water. These groups modify the structure of water (and so the solvation sheath). The range of influence of ions has been estimated experimentally (it is approximately 5 A. for alkyl ammonium ion[120]). Non-polar groups cause water molecules near them to become more strongly hydrogen bonded to one another than in pure water giving rise to abnormally high heat capacity[121]. Therefore, the charged and also the non-polar groups can induce changes in the cybotactic region resulting from the organized water structure[122]. The role of water may be further important in the rate processes by diffusion control.

(v) *Charge fluctuation interactions* — When the large molecules in solution have many ionized groups such as COO^-, NH_4^+. At any instance when only a fraction of these groups are fully ionized (over a time average, each group may be partially ionized) the protons move in a more or less random way from one group to another and the dipole moment of the entire molecule fluctuates. This fluctuation induces dipoles in the neighbouring molecules and leads to an attractive interaction[123]. The fluctuation frequency is 10^7 cycles per second and it is a short-range interaction.

Chemical Forces

These forces are involved when atoms are at very small distances. In order to bring two atoms close together from the equilibrium distance governed by the dispersion forces, it is necessary for the electronic orbitals to interpenetrate. In this region of separation of two atomic nuclei there is large coulombic repulsion. Hence a comparatively large 'activation energy' is required to attain the proper distance and the critical orientation for the formation of stable chemical bonds. Thus when large changes in the binding stability are encountered in the interaction of a series of structurally related ligands with the receptor, then the formation of a chemical bond is implicated.

However, in pi-pi interaction and charge transfer complex formation the energy barrier is not high. The complementarity of the electronic profile along with that of the surface topology appears to be important in chemical interactions.

Based on the above study, the following propositions conducive to the concept of complementarity, with particular reference to the conceptual and functional model of the receptor, are put forward.

Primary structure: (i) Skeletal profile — It is due to the primary macromolecular structure which is extremely rigid and no change is possible in it without making or breaking of some covalent bond. Such changes are expected to result in the irreversible denaturation and deactivation of the system. This retains the proper orientation and rigidity of the structure. (ii) Electron density profile — It is manifested in the form of conventional functional groups, which may or may not be in contact to translate the electronic effects by conjugation, polarization, etc. It is disturbed when the interaction, which is accompanied by charge transfer, covalent bond formation, pi-pi interaction, coordination and coulombic interaction, takes place. The dependence of the biological activity on *p*H is probably due to the change induced in this profile and this in turn may also effect the secondary receptor structure.

Secondary structure — (i) The structural profile arising due to secondary, tertiary and quaternary macromolecular structures which determine the degree of internal association and the shape of the overall structure, as well as the initiation of the train of events leading to the response, in cooperation with other structural features. (ii) Solvation profile — The distribution, orientation and relative conformations of various functional groups determine the extent and stability of the solvation sheath, and consequently the dimensions of the receptor cavity. The short-range physical forces are operable in this region. The receptor is enveloped with the so-called ' biophase ' which determines the pharmacodynamic properties of the ligand.

Summary

The concept of ligand-receptor complementarity at molecular level has been advanced as a unified explanation for many diverse biological processes. Some important manifestations of this concept such as specificity, efficiency, antagonism, etc., as observed in these processes have been discussed at length and their implications brought home.

Importance of surface topology and binding forces of various types in determining the mode of ligand-receptor interactions has been emphasized and explained on the basis of existing knowledge of intermolecular forces.

A model of the receptor, inherent in the concept of complementarity, has been proposed which can account for the pharmacodynamic behaviour of ligands, their mode of interaction, response type and the various types of antagonisms typifying the biological processes.

References

1. Latham, R. E., *Lucretius on the nature of universe* (Penguin Books Ltd, Harmondsworth, England), 1951.
2. Ehrlich, P., *Proc. roy. Soc.*, **66** (1900), 424.
3. Ehrlich, P., *Lancet*, (1913), 445.
4. *The collected papers of Paul Ehrlich*, Vol. **2**, edited by F. Himmelweit (Pergamon Press Ltd, Oxford), 1956, 596.
5. Ehrlich, P., *Ber. dtsch. chem. Ges.*, **42** (1909), 17.
6. Hopkins, G., *Glukestein memorial lecture* (Institute of Chemistry, London), 1932.
7. Schueler, F. W., *Chemobiodynamics of drug design* (McGraw-Hill Book Co. Inc., New York), 1960, 140.
8. Clark, A. J., *Handbuch der experimentellen pharmacologie*, Vol. 4 (Springer Verlag, Berlin), 1937.
9. Lorus, J. M. & Milne, M., *The senses of animals and men* (Andre Deutsh & Co., London), 1963, 123.
10. Butenandt, A. & Hecker, E., *Angew. Chem.*, **73** (1961), 349.
11. Weidel, W., *Annu. Rev. Microbiol.*, **12** (1958), 27.
12. Janoff, A., *Nature, Lond.*, **202** (1964), 193.
13. Woolley, D. W. & Gommi, B. W., *Nature, Lond.*, **202** (1964), 1074.
14. Wooley, D. W., *Proc. nat. Acad. Sci., Wash.*, **44** (1958), 197.
15. Woolley, D. W., *Proc. nat. Acad. Sci., Wash.*, **44** (1958), 1202.
16. Kimura, M., *Chem. Pharm. Bull., Tokyo*, **13** (1965), 1.
17. Timmermans, J., *J. chem. Phys.*, **35** (1938), 331.
18. Timmermans, J., *Nature, Lond.*, **174** (1954), 235.
19. Pauling, L., *Chem. Engng News*, **24** (1946), 1064.
20. Moncrieff, R. W., *The chemical sense* (Leonard Hill Ltd, London), 1951.
21. Amoore, J. E., *Perfum. essent. Oil Rec.*, **43** (1952), 321.
22. Amoore, J. E., *Proc. Sci. Sect. Toilet Goods Ass.* (Suppl.), **37** (1962), 13.
23. Amoore, J. E., *Proc. Sci. Sect. Toilet Goods Ass.* (Suppl.), **37** (1962), 1.
24. Amoore, J. E., *Nature, Lond.*, **198** (1963), 271.
25. Amoore, J. E., *Ann. N.Y. Acad. Sci.*, **116** (1964), 457.
26. Johnston, J. E., *Georgetown med. Bull.*, **17** (1963), 40.
27. Johnston, J. W. & Sandoval, A., *Proc. Sci. Sect. Toilet Goods Ass.*, **33** (1960), 3.
28. Saunders, H. C., *Proc. Sci. Sect. Toilet Goods Ass.* (Suppl.), **37** (1962), 246.
29. Rubin, M., Apotheker, D. & Lutmer, R., *Proc. Sci. Sect. Toilet Goods Ass.* (Suppl.), **37** (1962), 24.
30. Fullman, B., *Nature, Lond.*, **199** (1963), 912.
31. Amoore, J. E., *Nature, Lond.*, **198** (1963), 271.
32. Beets, M. C. J., cited in *Molecular structure and organoleptic quality* (Society of Chemical Industry, London), 1957, 59.
33. Beets, M. C. J., *Molecular pharmacology*, Vol. **2** (Academic Press Inc., New York), 1964.
34. Beets, M. C. J., *Amer. Perfumer Aromat.*, **76** (1961), 54.
35. Taylor, N. W., *Protoplasma*, **4** (1929), 1.
36. Paris, R., *Ann. Pharm., franc.*, **42** (1946), 207.
37. Korte, F., *Arch. Pharm.*, **286** (1953), 257.
38. Bose, P. K., *J. Indian chem. Soc.*, **37** (1960), 653.
39. Courtney, J. L., *Rev. pure appl. Chem.* (*Aust.*), **11** (1961), 118.
40. Hamor, G. H., *Science*, **134** (1961), 1416.
41. Finzi, C. & Colonna, M., *Gazz. Chim. ital.*, **68** (1938), 132.
42. Jain, M. K., *Bitterness and chemical constitution*, paper presented at the Symposium B at the First Annual Convention of Indian Chemical Society, Bombay, 1963.
43. Jain, M. K., *Bitterness and chemical constitution*, paper presented at the Symposium B at the Second Annual Convention of Indian Chemical Society, Allahabad, 1964.
44. Horowitz, R. M., cited in *Biochemistry of phenolic compounds* (Academic Press Inc., New York), 1964, 545.
45. Beidler, L. M., *Progr. Biophys. Biochem.*, **12** (1962), 109.
46. Breiml, F. & Horowitz, F., *Z. Physiol. Chem.*, **192** (1930), 45.
47. Mudd, M., *J. Immunol.*, **23** (1932), 423.
48. Alexander, J., *Protoplasma*, **14** (1931), 296.
49. Pauling, L., *J. Amer. chem. Soc.*, **62** (1940), 2643.
50. Porter, R. R., *Biochem. J.*, (1950), 473, 479.

51. Dicky, F. H., cited by J. F. Brown, *Sci. Amer.*, **207** (1962), 82.
52. Beckett, A. H. & Anderson, P., *Nature, Lond.*, **179** (1957), 1074.
53. Beckett, A. H. & Anderson, P., *J. Pharm. Pharmacol.*, **11** (1959), 258 T.
54. Beckett, A. H. & Anderson, P., *J. Pharm. Pharmacol.*, **12** (1960), 228 T.
55. Boyd, W. C., *J. exp. Med.*, **75** (1942), 407.
56. Pauling, L., Pressman, D. & Campbell, D. H., *J. Amer. chem. Soc.*, **66** (1944), 330.
57. Pauling, L., Campbell, D. H. & Pressman, D., *Physiol. Rev.*, **23** (1943), 203.
58. Rothen, A., *J. biol. Chem.*, **168** (1947), 75; *J. Amer. chem. Soc.*, **70** (1948), 2732.
59. Singer, S. J., *J. biol. Chem.*, **182** (1950), 189.
60. Pressman, D., Grossberg, A. L., Pense, L. H. & Pauling, L., *J. Amer. chem. Soc.*, **68** (1946), 250.
61 Pressman, D., Nisonoff, A. & Radzinski, G., *J. Immunol.*, **86** (1961), 35.
62. Sturtevant, J. M., Wofsy, L. & Singer, S. J., paper presented to the Autumn Meeting of National Academy of Sciences, Washington, October 1961 (LaJolla and Los Angeles).
63. Campbell, D. H. & Bulman, N., cited in *Progress in the chemistry of organic natural products*, Vol. 9, by L. Zechmeister (Springer Verlag, Berlin), 1952, 443.
64. Kogl, F. & Fries, N., *Hoppe-Seyl Z.*, **249** (1937), 93.
65. Fries, N., *Nature, Lond.*, **152** (1943), 105.
66. Virtanen, A. I., *Angew. Chem.*, **70** (1958), 544.
67. Hershey, A. D. & Burgi, E., *Proc. nat. Acad. Sci., Wash.*, **53** (1965), 325.
68. Skoog, F., Schneider, C. L. & Malan, P., *Amer. J. Bot.*, **29** (1942), 568.
69. Veldstra, H., *Enzymologia*, **11** (1944), 97, 137.
70. Ehrlich, P., *Experimental researches on specific therapeutics*, Harben Lectures of 1907 (Paul B. Hoebner, New York), 1909.
71. Quatal, J. H. & Wooldridge, W. R., *Biochem. J.*, **22** (1928), 689.
72. Woods, D. D., *Brit. J. exp. Pathol.*, **21** (1940), 74.
73. Fildes, P., *Lancet*, **i** (1940), 955.
74. Clark, A. J., *Quart. J. exp. Physiol.*, **26** (1937), 374.
75. Ariens, E. J., *Arch. intern. pharmacodyn.*, **99** (1954), 32.
76. Ariens, E. J., van Rossum, J. M. & Simonis, A. M., *Arzneimittel-Forsch.*, **6** (1956), 282.
77. Stephenson, R. P., *Brit. J. Pharmacol.*, **11** (1956), 379.
78. Cavallini, G., Massarani, E., Nardi, D. & Mauri, L., *Gazz. Mal. Infett.*, **13** (1961), 155.
79. Ross, W. C. J., *Biological alkylating agents* (Butterworths Scientific Publications, London), 1962.
80. Koshland, D. E., *Advances in enzymology*, **22** (1960), 45.
81. Martius, C. & Nitz-Litzow, D., *Biochem. Z.*, **327** (1960), 1.
82. Ariens, E. J., Simonis, A. M. & van Rossum, J. M., cited in *Molecular pharmacology*, Vol. 1, edited by E. J. Ariens (Academic Press Inc., New York), 1964, 176.
83. O'Brien, R. D. & Matsumura, F., *Science*, **146** (1964), 657.
84. Crabbe, J., *Nature, Lond.*, **200** (1963), 787.
85. Frazer, H. S., Dampsey, E. F. & Leaf, A., *J. gen. Physiol.*, **45** (1955), 433.
86. Singh, H. & Jain, M. K., *Indian J. Chem.*, **3** (1965), in press.
87. Beckett, A. H. & Casy, A. F., *J. Pharm. Pharmacol.*, **7** (1963), 433.
88. Harvey, A. M., *Johns Hopkins Hosp. Med. Bull.*, **65** (1939), 223.
89. Watson, P. J., *J. Pharm., Lond.*, **12** (1960), 257.
90. Straugham, D. W., *J. Pharm., Lond.*, **13** (1961), 49.
91. Schoffeniels, E. & Nachmansohn, D., *Biochim. biophys. Acta*, **26** (1957), 1.
92. Rosenberg, P. & Higman, H., *Biochim. biophys. Acta*, **45** (1960), 348.
93. Ehrenpreis, S. & Kellock, M. G., *Biochem. Biophys. Res. Commun.*, **2** (1960), 322.
94. Ehrenpreis, S. & Nachmansohn, D., *Science*, **134** (1961), 1962.
95. Featherstone, R. M. & Muchlbaecher, C. A., *Pharmacol. Rev.*, **15** (1963), 97.
96. Pauling, L., *Science*, **134** (1961), 15.
97. Woolley, D. W., *A study of antimetabolites* (John Wiley & Sons Inc., New York), 1952.
98. Arcos, M. & Arcos, J. C., *Arzneimittel-Forsch.*, **8** (1958), 643.
99. Buu-Hoil, Ng. Ph., *Arzneimittel-Forsch.*, **6** (1956), 251.
100. Szent-Gyorgyi, A., Isenberg, I. & Baird (Jr), S. L., *Proc. nat. Acad. Sci., Wash.*, **46** (1960), 1444.
101. Yang, N. C., Castra, A. J., Lewis, M. & Ting-Wa Wong, *Science*, **134** (1961), 386.
102. Hyggins, C. & Yang, N. C., *Science*, **137** (1962), 257.
103. Handdow, A., cited in *Proceedings, Canadian cancer research conference*, edited by R. W. Begg (Academic Press Inc., New York), 1957, 361.
104. Butanandt, A. & Hecker, E., *Angew. Chem.*, **73** (1961), 349.
105. Michaelis, L. & Menten, M. L., *Biochem. Z.*, **49** (1913), 333.
106. Bernhard, S. A. & Gutfreund, H., *Progr. Biophys. biophys. Chem.*, **10** (1960), 115.
107. Bergman, M., Zervas, L., Fruton, J. S., Schneider, F. & Schlejich, H., *J. biol. Chem.*, **109** (1935), 325.
108. Potter, V. R. & Dubois, K. P., *J. gen. Physiol.*, **26** (1943), 391.
109. Wilson, I. B., *J. biol. Chem.*, **199** (1952), 113.
110. Wilson, I. B. & Ginsberg, S., *Biochem. biophys. Acta*, **18** (1955), 168.
111. Wilson, I. B., Ginsberg, S. & Quan, C., *Arch. Biochem. Biophys.*, **77** (1958), 286.
112. Kosower, R. M., *Molecular biochemistry* (McGraw-Hill Book Co. Inc., New York), 1962.
113. van Rossum, J. M., cited in *Molecular pharmacology*, Vol. 2, edited by E. J. Ariens (Academic Press Inc., New York), 1964.
114. Cheeseman, G. C., *Nature, Lond.*, **205** (1965), 1011.
115. Westheimer, F. H. & Ingrahem, L. L., *J. phys. Chem.*, **60** (1956), 1668.
116. Sebara, D. K. & Taube, H., *J. Amer. chem. Soc.*, **83** (1961), 1785.
117. London, F., *Z. Physik.*, **63** (1930), 245.
118. Huggins, M. L., *J. org. Chem.*, **1** (1936), 407.
119. Pimentel, G. C. & McClellan, A. L., *The hydrogen bond* (W. H. Freeman & Co., London), 1960.
120. Evertt, D. H., *Disc. Faraday Soc.*, **24** (1957), 220.
121. Frank, H. S. & Wen, W. Y., *Disc. Faraday Soc.*, **24** (1957), 133.
122. Kosower, E. M., *J. Amer. chem. Soc.*, **80** (1958), 3253.
123. Kirkwood, J. G. & Schumaker, J. B., *Proc. nat. Acad. Sci., Wash.*, **38** (1952), 855.

The Photochemical Stage of Photosynthesis

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THE three aspects of photosynthesis, viz. air improvement (i.e. oxygen liberation), energy storage and organic synthesis, are associated with three distinct stages of the overall process. This tripartite nature of photosynthesis is concerned with three stages: (1) production of oxygen molecules by the removal of hydrogen (atoms) from water, (2) the transfer of hydrogen atoms from an intermediate in stage 1 to an intermediate in stage 3, and (3) the conversion of carbon dioxide to a carbohydrate. All these reactions occur within tiny cell organelles called chloroplasts[1]. Stage 1 is the least known part of photosynthesis. It occurs by a non-photochemical reaction and requires at least one manganese-containing enzyme[2,3]. The third stage includes a series of enzymatic reactions. It is the best known part of the overall process — mainly due to the pioneering and extensive studies with the carbon isotope tracer ^{14}C by Benson, Bassham and Calvin (*see* Bassham[4]). The present article deals mainly with the second stage — the energy storage part — the photochemical stage of photosynthesis. This stage is now beginning to yield some of its secrets to biophysical and biochemical research. This is the part of photosynthesis of greatest concern to photochemists and photobiologists because in it the power station function of photosynthesis is fulfilled.

Photosynthesis : An Oxidation-Reduction Reaction

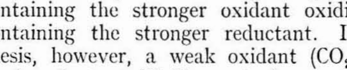
That the photochemical part of photosynthesis is an oxidation-reduction reaction was first recognized by Van Niel[5]. These are reactions in which hydrogen atoms (or electrons) are transferred from a donor (reductant), which is thus oxidized, to an acceptor (oxidant), which is thus reduced. The transfer of hydrogen atom may be replaced by that of an electron. An electron transfer, combined with acquisition or loss of an H^+ ion from the aqueous medium, can become equivalent to the transfer of H-atom. Some stages in a complex redox reaction chain — such as those involved in photosynthesis — may be electron transfers; others, hydrogen atom transfers.

In photosynthesis, hydrogen atoms (or electrons) are moved uphill against the chemical potential with the help of light energy. Light energy is stored in the form of chemical energy. Chloroplasts (the microscopic chlorophyll-bearing particles in photosynthesizing plant cells) act as chemical pumping stations; they can also be described as ' savings banks ' of life energy.

A measure of chemical energy stored in the transfer of hydrogen atoms (or electrons) from a certain donor to a certain acceptor is the difference of their oxidation-reduction (or redox) potentials (ΔE_0). The higher (more positive) the E_0 value, the stronger is the oxidant; vice versa, a low (negative) redox potential indicates a strong reductant. (Note that a redox potential always belongs not to an oxidant — or a reductant — as such, but to a certain oxidation-reduction couple; thus, oxygen has a potential of +0·81 eV. when it is reduced to H_2O, but only +0·27 eV. when it is reduced to H_2O_2.)

In ordinary chemistry, when two oxidation-reduction couples are brought together, the one containing the stronger oxidant oxidizes the one containing the stronger reductant. In photosynthesis, however, a weak oxidant (CO_2) oxidizes a weak reductant (H_2O), producing a strong oxidant (O_2) and a strong reductant $(CH_2O)_n$; this energy-consuming reaction is made possible by the massive investment of light energy.

The amount of energy stored in photosynthesis is determined by the difference between the redox potentials of the couple O_2/H_2O (+0·8 eV.) and $CO_2/(CH_2O)$ (−0·4 eV.). In the transfer of a single electron (or H-atom) from water to carbon dioxide, the amount of energy stored is $+0{\cdot}8-(-0{\cdot}4) = 1{\cdot}2$ eV. Now, four electrons (or four H-atoms) are needed to reduce one molecule of CO_2 to a carbohydrate (*see* equation below); the total energy of their transfer is $1{\cdot}2\times4 = 4{\cdot}8$ eV. Energy conversion tables tell us that 1 eV. is equivalent to 23 kcal./mole; therefore, the energy stored in the redox stage of photosynthesis can be also expressed as $4{\cdot}8\times23 = 110$ kcal. (per mole of reduced CO_2). We can thus write the equation



$$O{=}C{=}O + 2H_2O \rightarrow \underset{}{\overset{H}{O}} - \underset{H}{\overset{H}{C}} - \overset{H}{O} + O_2$$

$$[\rightarrow (CH_2O) + H_2O] + O_2 + 110 \text{ kcal.} \quad \ldots(1)$$

[That the hydrogenation product, $CH_2(OH)_2$, loses a molecule of water and becomes $(CH_2O)+H_2O$ is not important for the energy balance.]

To sum up, the energy-storing stage of photosynthesis is an oxidation-reduction reaction in which about 110 kcal. are stored per four hydrogen atoms transferred from an intermediate (which we shall call ZH) in stage 1 to an intermediate (which we shall call X) in stage 3.

Robert Hill discovered (*see* Hill & Scarisbrick[6]) that upon destruction of the cell, releasing a suspension of whole or fragmented chloroplasts, the capacity of the cell for photo-oxidation of water remains, while its capacity for the photoreduction of carbon dioxide is lost. Substitute oxidants (a ferric salt, a quinone or a dye) have to be supplied to the chloroplast suspension to liberate oxygen in light (so-called Hill reaction). The capacity to reduce CO_2 can be regained, as shown by Thomas and coworkers[7], by adding certain enzymes and cofactors; but even after such reconstruction, the actually observed carbon dioxide-reducing capacity of the chloroplast preparation is only a few per cent of that of the intact cell.

The photochemical process in photosynthesis is, according to our belief, not a 'photolysis of water' (H_2O + light $\rightarrow$ [OH] + [H]) — now a widely used formulation; nor is it a 'decomposition of carbon dioxide' (CO_2 + light $\rightarrow$ C + O_2) as has been often assumed in the past; rather, it is an energy-storing step (or steps) in the transfer of hydrogen atoms (or electrons) from H_2O to CO_2.

The Primary Photochemical Products

The nature of the primary donor (ZH) and primary acceptor (X) and thus also of the primary photochemical products, Z and XH, is not definitely known. There is a great deal of evidence suggesting that X may be that well-known cellular catalyst, NADP (nicotinamide adenine dinucleotide phosphate; formerly called TPN (Triphosphopyridine nucleotide); and that the reduced form of this compound, NADPH, feeds hydrogen into the CO_2-reducing enzymatic reaction sequence. The redox potential of the couple NADP/NADPH ($E_0 = -0{\cdot}32$ V.) is not sufficiently negative to reduce the couple $CO_2 \Big/ \frac{1}{n}(CH_2O)_n$ (E_0 = about $-0{\cdot}4$ eV.). However, light is known[8,9] to produce in chloroplasts adenosine triphosphate (ATP) — an ubiquitous cellular energy carrier, able to release about 8 kcal./mole when it is hydrolysed. With the help of ATP as a booster, NADPH can overcome its insufficient reducing power, and initiate the reduction of carbon dioxide; the now widely accepted scheme of photosynthesis suggests that this is what actually happens. Calvin's investigations of the reaction sequence leading from CO_2 to (CH_2O) in photosynthesis suggested that ATP is needed not only in this reduction step, but also in the phosphorylation of ribulose monophosphate to ribulose diphosphate. Whether the yield of ATP-production in light by chloroplasts is high enough to supply the ATP molecules needed according to this reaction scheme is an open question.

Recent evidence has indicated that the first reduced product in photosynthesis may not be NADPH, but a certain iron protein ('ferredoxin') with a somewhat more negative potential ($E_0 = -0{\cdot}42$ V.), which then reduces NADP by a secondary, dark reaction[10-12]. Recently, Kok[13] has suggested that 'X' may be a compound with an E_0 value as low as about $-0{\cdot}6$ eV.

The Two Photochemical Steps

We now ask: What is known about the process by which hydrogen atoms (or electrons) are moved, with the help of light, from the donor, ZH, to the acceptor, X?

An important new development in this field is the finding that this process apparently includes two successive photochemical steps; and that cytochromes (a type of iron-porphyrin-protein complexes well known from their catalytic role in respiration) are the likely intermediates between them.

That two light quanta may be used to move one hydrogen atom in photosynthesis was first suggested by Franck and Herzfeld[14] and elaborated by Rabinowitch[15]; it was then merely a hypothesis, based on Emerson's quantum yield measurements of photosynthesis, which indicated that eight may be the minimum number of light quanta required to transfer four hydrogen atoms needed to reduce one molecule of CO_2 to (CH_2O).

This hypothesis has since received experimental confirmation from several sides.

Red Drop and Emerson Enhancement Effect in Photosynthesis

The first set of these observations pertains to the so-called 'enhancement effect'[16]. Since the measurements of Emerson and Lewis[17], it has been known that the quantum yield of photosynthesis (the number of oxygen molecules evolved per quantum of light absorbed) is approximately constant throughout the spectral region of chlorophyll absorption — except for the far red and the blue end of the spectrum, where it declines. The latter is easily interpreted by the low efficiency of carotenoids as sensitizers for photosynthesis; the red drop is more difficult to explain. In green plants and green algae, this red drop takes place at wavelengths longer than 680 mμ[16,17]. This red drop is clearly seen in the action spectrum of photosynthesis, which is the plot of the quantum yield of a light-produced change as function of the wavelength of light. The red drop occurs in the region where light is absorbed only in chlorophyll *a* and not in chlorophyll *b*. Red marine algae contain only chlorophyll *a*; in addition, they contain a red, water-soluble pigment, called phycoerythrin, which absorbs in the green part of the spectrum; and (in a smaller amount) a blue pigment, called phycocyanin, which absorbs in the orange and red. In red algae, the red drop begins at 650 mμ, that is, in the region where absorption by phycocyanin ends and chlorophyll *a* becomes the only absorbing pigment[18]. It thus appears as if in both cases chlorophyll *a* were an 'inefficient' (or totally ineffective) pigment in photosynthesis — a strange conclusion to make in the face of the fact that chlorophyll *a* is the one common pigment of all photosynthesizing plants!

Emerson and coworkers[16,18-21] made an important discovery. They found that photosynthesis in the region of the red drop can be brought up to full efficiency (i.e. to a quantum yield of the order of $\frac{1}{8}$) by simultaneous illumination with light of a shorter wavelength. For example, the quantum yield of photosynthesis in *Chlorella* in pure 700 mμ light is only 0·06, while that in pure 650 mμ light is 0·12; when the two light beams are given simultaneously, the quantum yield becomes 0·12 for the total light. This has become known as the 'Emerson effect'[21,22].

This observation led Emerson[19] and Emerson and Chalmers[20] to the suggestion that photosynthesis comprises two photochemical processes, of which only one can be brought about by light absorption in chlorophyll *a*, while the other requires light absorption in another pigment — chlorophyll *b* in green algae, phycocyanin or phycoerythrin in red algae, etc. Further development of this point of view led to the generalization that photosynthesizing cells contain two pigment systems, both of which have to be excited by light absorption for efficient photosynthesis. In the largest part of the visible spectrum, pigments belonging to both systems participate in light absorption, thus making efficient photosynthesis possible; but in the far red, above 680 mμ in green cells, and above 650 mμ in red cells — absorption is limited to one pigment system, and this causes the red drop.

This hypothesis called for a systematic study of the yield of photosynthesis in various combinations of monochromatic light beams. Such studies were begun by Emerson and coworkers[20,21]. A constant beam in the region of the red drop (e.g. at 700 mμ) was combined with a second beam of variable wavelength, and the rate of oxygen liberation was measured, first in each beam separately and then in two of them together. In this way, the action spectrum of the Emerson effect could be determined. In each of the four types of algae studied — red, green, blue-green and brown — the action spectrum of the enhancement effect showed peaks in the region where one or the other of the accessory pigments absorbed most strongly.

The conclusion seemed close at hand that of the two postulated pigment systems, one contains chlorophyll *a*, and the other includes all other pigments — which were previously dismissed as accessory, implying their relative unimportance for photosynthesis!

This conclusion was not only startling; it also ran into contradiction with conclusions derived from the study of the fluorescence of plant pigments *in vivo*[23,24]. These studies showed that the fluorescence of photosynthesizing cells is always essentially that of chlorophyll *a*, even when the exciting light is first absorbed by another pigment. Observations of this sensitized chlorophyll *a* fluorescence (i.e. the emission by chlorophyll *a* of light energy first absorbed by another pigment) showed convincingly that light quanta absorbed by chlorophyll *b* are transferred to chlorophyll *a* with practically 100 per cent efficiency; that for phycoerythrin and phycocyanin, the transfer efficiency is only slightly less — of the order of 90 per cent; that for fucoxanthol in diatoms, it is of the order of 80 per cent, etc. We are thus driven to an implausible conclusion that for photosynthesis, the cells need one quantum of light to be absorbed directly in chlorophyll *a*, and one quantum to be absorbed by an accessory pigment, and then transferred, by resonance, to chlorophyll *a*! How should chlorophyll *a* distinguish between quanta received by direct absorption and quanta received by resonance transfer, and require one of each kind to bring about photosynthesis?

Two sets of observations helped to clarify this paradox. One was due to the studies by Govindjee and coworkers[22,25-27] and by French and coworkers[28], of the action spectra of the Emerson effect. It was found that this action spectrum contains, in addition to peaks corresponding to the accessory pigments, also a peak or a shoulder at 670 mμ, within the absorption band of chlorophyll *a in vivo*. (This band extends roughly from 660 to 690 mμ.)

This finding suggested that there are two kinds of chlorophyll *a* in green cells — one with an absorption band at 670 mμ, and one absorbing at longer waves. The first form — which was called Chl *a* 670 — must be associated in a common pigment system with the accessory pigments; this is the form that collects excitation energy transferred to chlorophyll *a* by resonance from the accessory pigments, and is the source of sensitized chlorophyll *a* fluorescence. The other form of chlorophyll *a*, absorbing at the longer wavelength, in the region of the red drop belongs to another pigment system (for analysis of absorption bands, *see* Brown and French[29] and Cederstrand[30]).

Since, upon extraction of plant cells, only one chlorophyll *a* is found, the two chlorophyll *a* forms *in vivo* must differ not in their chemical composition, but either in their state of aggregation, or in their association with different partners — proteins, lipoids or other pigments. Which of the factors is most essential remains a controversial subject.

Be this as it may, the new observations suggest that what is needed for photosynthesis is excitation of two types of chlorophyll *a* molecules. One of them can be excited either directly or by resonance transfer of energy from an accessory pigment; while the other has to be excited directly.

This is a much more plausible hypothesis than Emerson's original suggestion that what is needed for photosynthesis is excitation of chlorophyll *a* and of one of the accessory pigments!

According to this picture, a 'balanced' excitation of the two pigment systems

System I — chlorophyll *a* absorbing in green cells maximally at 680-690 mμ
System II — chlorophyll *a* absorbing in green cells maximally at 670 mμ and accessory pigments (e.g. phycobilins, chlorophyll *b*, etc.)

is needed for effective photosynthesis. According to this hypothesis, monochromatic light should produce photosynthesis with a quantum yield dependent on how well balanced is the excitation of the two systems. The yield should be highest where both systems participate equally in the absorption and dip down whenever one or the other of them receives too much (and the other too little energy); an extreme case of such imbalance is found in the region of the red drop. This hypothesis is generally labelled separate package model[31-33]. This should cause a fine structure of the action spectrum of photosynthesis, which remains to be confirmed and analysed. The dip of the curve at 660 mμ in the action spectrum of photosynthesis in *Chlorella* is one example of such fine structure. An alternative to this hypothesis exists: It postulates resonance energy transfer from pigment system II to pigment system I (but not vice versa!), leading to automatic balancing of excitation between the two systems whenever too much energy is absorbed in system II. This hypothesis is usually labelled spill-over model[31-33]. It would be simpler if this hypothesis were not needed; one could then postulate a spatial separation of the two pigment systems in the chloroplasts.

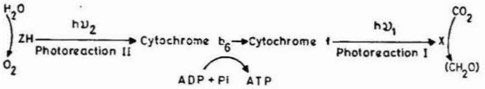
The Role of Cytochromes

The above-described measurements led to the postulation of two photochemical reactions in photosynthesis, brought about by excitation of two forms of chlorophyll *a*; but nothing was said about the nature of these two reactions. Here, a second set of experiments is of great importance, experiments dealing with the transformation of cytochromes in photosynthesis.

Robert Hill and coworkers (*see* Hill[34]) had discovered two types of cytochromes in chloroplasts. One they called cytochrome *f*; it belongs to the type of cytochrome *c* known in respiration. What is most important for us is that it has a positive redox potential, $E_0 = +0{\cdot}42$ eV. The other cytochrome, found in chloroplasts and designated by Hill as cytochrome b_6, belongs to the cytochrome *b* type, and has a potential close to 0·0 eV.

Duysens[35] observed that in illuminated (and, presumably, photosynthesizing) suspensions of algal cells, absorption bands belonging to reduced cytochromes disappear, and bands belonging to oxidized cytochromes appear instead. Upon return to darkness, the change is reversed.

Hill and Bendell[36] made the ingenious suggestion that the two cytochromes, b_6 and *f*, play the role of intermediate carriers in the 'bucket brigade', carrying hydrogen atoms (or electrons) from ZH to X in a two-step mechanism. The following diagram is a modified version of Hill-Bendell hypothesis:



One photochemical reaction (reaction II) takes a hydrogen atom (or electron) from ZH and transfers it to cytochrome b_6; thus reduced cytochrome b_6 then reacts, in a dark, 'downhill' reaction, with oxidized cytochrome *f*, reducing the latter. Another photochemical reaction moves the electron from reduced cytochrome *f* to X. The $h\nu_2$ and $h\nu_1$ in the diagram refer to light quanta absorbed in systems II and I respectively. In the downhill part, one ATP molecule can be formed from ADP (adenosine diphosphate) and Pi (inorganic phosphate), storing the released energy, in the same way in which this happens in respiration.

The oxidized Z evolves O_2 from H_2O by a dark reaction (*see* left side of the diagram) and reduced X feeds hydrogen atoms (or electrons) into the 'Calvin sequence', ultimately reducing CO_2 to the reduction level of a carbohydrate (CH_2O).

This hypothesis was supported by the findings by Duysens *et al.*[37] that in red algae, only light quanta absorbed in 'pigment system II' (i.e. in phycoerythrin) cause reduction of the cytochrome, while quanta absorbed in system I (i.e. in the longer wave components of chlorophyll *a*) cause its oxidation. The pigment system II can be thus assigned the role of energy supplier for the transfer of hydrogen atoms (or electrons) from ZH to cytochrome b_6. The pigment system I can be similarly assigned the function of sensitizing the hydrogen (or electron) transfer from reduced cytochrome *f* to the acceptor X.

According to this scheme, light absorption in system II must cause a reduction, and light absorption in system I, an oxidation, of all intermediates in the reaction sequence connecting the two photochemical steps.

Duysens and Amesz[38] concluded, from quantitative studies of these phenomena, that the several pigments are not neatly divided between the two pigment systems; rather, some chlorophyll *a* is present also in system II, and some accessory pigments (particularly, phycoerythrin in red algae) in system I. This problem as well as the earlier mentioned one of possible excitation energy transfer by resonance from system II into system I are now under intensive study in several laboratories. The role of cytochrome b_6 has not been clearly established.

Photosynthetic Units and P700

Twenty or more enzyme molecules are likely to be involved in photosynthesis. Each is a protein with a molecular weight of 10^5-10^6, and requires a volume of the order of 10^{-18} to 10^{-19} cm.^{3}. That means that a total volume of about 10^{-17} cm.^{3} may be required to accommodate a single set of photosynthetic enzymes. A typical chloroplast has a total volume of the order of 5×10^{-11} cm.^{3}; thus, even if it were tightly packed with nothing but photosynthetic enzymes (which it is not!), it could not hold more than, say, 5×10^6 such sets. On the other hand, a chloroplast may contain — in fact, it must contain, in order to absorb significant amounts of light! — as much as 10^9 chlorophyll molecules. Obviously, several hundred pigment. molecules must share a single set of enzymes — a common enzymatic 'conveyor belt'. This calculation provides an *a priori* justification of the hypothesis of a 'photosynthetic unit'. This concept was proposed by Gaffron and Wohl[39] to explain the results of Emerson and Arnold[40,41] on the maximum yield of photosynthesis in intense light flashes. This yield was found to be about one O_2 molecule per flash per 2400 chlorophyll molecules, meaning that one H-atom (or electron) could be transferred from ZH to X per flash per 600 chlorophyll molecules (since four H-atoms are involved in the release of one O_2 molecule). This figure could be interpreted as measure of the content in chloroplasts of a 'yield-limiting' enzyme — an enzyme that can be put to work only once during the practically instantaneous flash. (Other experiments suggested that this enzyme requires about 10 millisec. to complete its action and become available for the next flash). One molecule of this enzyme must be present (at least in normal green cells) per 600 chlorophyll molecules. If two pigment systems of equal size are postulated, one molecule of the limiting enzyme must be associated with 300 pigment molecules.

Since then, much evidence has accumulated, confirming the existence in chloroplasts of units of about 300 chlorophyll molecules, somehow associated with a single molecule of an enzyme (or rather, with the entrance to a single enzymatic conveyor belt). The pigment molecules belonging to a unit are packed so densely that excitation of anyone of them by light is easily transferred, by resonance, to its neighbour — the picture reminding one of a pinball table on which a steel ball is running about, lighting one electric light after another. The energy can thus migrate through the unit, until it arrives at an enzymatic centre. This energy migration is a quantum-mechanical phenomenon; this means that the excitation energy cannot be divided between two or several molecules, as in the case of resonating mechanical vibrators — bells or tuning forks. Rather, what diffuses through the unit is the probability of finding the energy quantum as a whole in different pigment molecules. When the probability of finding it at the entrance to an enzymatic conveyor belt becomes significant, the quantum is in fact trapped there, and utilized to inject an H-atom (or an electron) on to this belt (or to unload an H-atom or an electron from it).

The pigment molecules immediately adjoining the enzymatic centre can be expected to differ somewhat from those in the bulk of the unit, since they are the only ones likely to participate chemically in the oxidation-reduction process (all others serving as merely physical 'energy suppliers' for the centre).

Kok[42] found evidence that 'pigment system I' contains a minor component with an absorption band at 700 mμ (he called it 'pigment 700', or P700), which, similar to the cytochromes, shows evidence of reversible oxidation and reduction in photosynthesis. The absorption band of P700 lies on the long-wave side of that of the bulk of chlorophyll *a* in system I (680-690 mμ); i.e. its excitation energy quantum is slightly smaller: this makes P700 suitable to act as a trap, catching the energy quanta migrating through the unit. The concentration of P700 (about 1/300 of that of chlorophyll *a*) was also found to be 'just right' for the purpose assigned to it — it corresponds to one molecule of P700 per unit. (Incidentally, the same is roughly correct also for the number of cytochrome *f* molecules present!) Kok[43] was able to determine also the oxidation-reduction potential of P700, and found $E_0 = +0{\cdot}45$ eV. — slightly above that of cytochrome *f*; this, too, is just right for a pigment that is supposed to recover the electron (or H-atom), which it had lost by transfer to the acceptor (X) in the primary photochemical step, from cytochrome *f*. We are thus justified in placing P700 in the key position assigned to it.

The situation is less clear in pigment system II, containing accessory pigments and Chl *a* 670. One is tempted to search there, too, for a small proportion of a special form of chlorophyll *a*, with an absorption band at slightly longer wavelengths than that of bulk (perhaps, in the neighbourhood of 680 mμ), which could serve as a trap for migrating energy; one would expect this component to be reversibly reducible and oxidizable, so as to be able, after having received an H-atom (or electron) from ZH in a photochemical reaction, to transfer it to cytochrome b_6 or some other intermediate by a dark, enzymatic reaction. We may call this hypothetical energy trap 'pigment 680' or P680. So far, no convincing evidence has been found for the existence of such a component in system II in algae. Krey and Govindjee[44] have observed a new fluorescence band in red algae at 693 mμ upon excitation with saturating light absorbed primarily in system II. This band may arise from our hypothetical P680.

Two other interesting components have been found in chloroplasts—one called plastoquinone[45], a naphthaquinone related to vitamin K, and one called plastocyanin, a copper-protein complex[46]. Both are redox catalysts with potentials close to those of cytochromes b_6 and *f* respectively; they are also present in concentrations of the order of 1/300 of that of chlorophyll — suggesting that they, too, may be intermediate catalysts in the photochemical reaction chain. Recent experiments[47,48] have implicated that both plastoquinone and plastocyanin play an important role in the electron transfer in photosynthesis.

Nothing in the suggested scheme of the photochemical reaction in photosynthesis is established beyond doubt; it is merely an attempt to penetrate analytically into the inner sanctum of photosynthesis — its primary light reaction sequence (as contrasted to the enzymatic follow-up reactions).

We have already mentioned two alternatives — either spatially separate pigment packages, containing pigment systems I and II respectively, or a close association of units of two kinds, permitting energy transfer from system II to system I (but not vice versa!) by resonance (so-called spill-over model).

Another alternative was proposed by Franck and Rosenberg[49]. They suggested that the two photochemical redox steps may take place in one and the same reaction centre or energy trap, containing a chlorophyll *a* and a cytochrome molecule. In one light reaction, the cytochrome is reduced by electron transfer from ZH to the cytochrome; in another light reaction, the same cytochrome molecule is oxidized, giving its extra electron to an acceptor (X). The salient point in Franck's theory is that one photochemical step is brought about by chlorophyll *a* in the singlet, short-lived state (the state in which the valence electrons have opposite spins; lifetime, 10^{-8} sec.), because the cytochrome is associated with the reaction centre and available for immediate reaction; while the other step involves the reduction of a free-swimming acceptor molecule X, and therefore occurs after a delay, during which the excited chlorophyll *a* molecule is transferred into a metastable triplet state (with the two electrons having parallel spins; lifetime, several milliseconds or more). The experimental foundation of this picture is the approximate doubling of the fluorescence yield of chlorophyll upon light saturation of photosynthesis; this was interpreted by Franck as suggesting that of the two steps in photosynthesis one competes with fluorescence — i.e. occurs in the singlet excited state — and the other does not — i.e. occurs in the triplet excited state.

We cannot discuss here in more detail the relative advantages of the two pictures, and the possibility of combining them. What seems significant is the considerable degree of agreement between them, particularly in the assumption of two successive photochemical oxidation-reduction steps.

Many workers in photosynthesis have been now brought to this picture by their own observations[50-52]; it is unlikely that it should not contain some elements of truth.

References

1. Thomas, J. B., *Endeavour*, **17** (1958), 156.
2. Kessler, E., in *Research in photosynthesis*, edited by H. Gaffron (Interscience Publishers Inc., New York), 1957, 243.
3. Pirson, A., *Annu. Rev. Pl. Physiol.*, **6** (1955), 71.
4. Bassham, J. A., *Sci. Amer.*, **206** (No. 6) (1962), 88.
5. Van Niel, C. B., *Advanc. Enzymol.*, **1** (1941), 263.
6. Hill, R. & Scarisbrick, R., *Proc. roy. Soc.* **129B** (1940), 238.
7. Thomas, J. B., Haans, A. J. M., Vander Leun, A. A. J. & Koning, J., *Biochim. biophys. Acta*, **25** (1957), 453.
8. Frenkel, A. W., in *Research in photosynthesis*, edited by H. Gaffron (Interscience Publishers Inc., New York), 1957, 303.
9. Arnon, D. I., Whatley, F. R. & Allen, M. B., *J. Amer. chem. Soc.*, **76** (1954), 6324.
10. Arnon, D. I., in *Photosynthetic mechanisms of green plants*, edited by B. Kok & A. T. Jagendorf (National Academy of Sciences — National Research Council, Washington DC), 1963, 195.
11. Davenport, H. E., in *Photosynthetic mechanisms of green plants*, edited by B. Kok & A. T. Jagendorf (National Academy of Sciences — National Research Council, Washington DC), 1963, 278.
12. Fry, K. T. & San Pietro, A., in *Photosynthetic mechanisms of green plants*, edited by B. Kok & A. T. Jagendorf (National Academy of Sciences — National Research Council, Washington DC), 1963, 252.
13. Kok, B., *Reducing power generated in photosynthesis*, paper presented at the 49th annual meeting of the Federation of American Societies for Experimental Biology, Atlantic City, New Jersey, 9-14 April 1965.
14. Franck, J. & Herzfeld, K. F., *J. phys. Chem.*, **45** (1941), 978.
15. Rabinowitch, E., *Sci. Amer.*, **179** (No. 2) (1948), 24; *Photosynthesis and related processes* (Interscience Publishers Inc., New York), 1945, 162.
16. Emerson, R., Chalmers, R. V. & Cederstrand, C. N., *Proc. nat. Acad. Sci., Wash.*, **43** (1957), 133.
17. Emerson, R. & Lewis, C. M., *Amer. J. Bot.*, **30** (1943), 165.
18. Brody, M. & Emerson, R., *J. gen. Physiol.*, **43** (1959), 251.
19. Emerson, R., *Annu. Rev. Pl. Physiol.*, **9** (1958), 1.
20. Emerson, R. & Chalmers, R. V., *Phycol. Soc. Amer. News Bull.*, **11** (1958), 51.
21. Emerson, R. & Rabinowitch, E., *Pl. Physiol.*, **35** (1960), 477.
22. Govindjee & Rabinowitch, E., *Biophys. J.*, **1** (1960), 73.
23. Duysens, L. N. M., *Transfer of excitation energy in photosynthesis*, Ph.D. thesis, University of Utrecht, The Netherlands, 1952.
24. Dutton, H. J., Manning, W. M. & Duggar, B. B., *J. phys. Chem.*, **47** (1943), 308.
25. Govindjee, in *Photosynthetic mechanisms of green plants*, edited by B. Kok & A. T. Jagendorf (National Academy of Sciences — National Research Council, Washington DC), 1963, 318.
26. Govindjee, *Effect of combining two wavelengths of light on the photosynthesis of algae*, Ph.D. thesis, University of Illinois, USA, 1960.
27. Govindjee, R. & Rabinowitch, E., *Biophys. J.*, **1** (1961), 377.
28. French, C. S., Myers, J. & McLeod, G. C., in *Comparative biochemistry of photoreactive systems*, edited by M. B. Allen (Academic Press Inc., New York), 1960, 311.
29. Brown, J. S. & French, C. S., *Pl. Physiol.*, **34** (1959), 305.
30. Cederstrand, C. N., *Spectrophotometric and spectrofluorometric characterization of the two pigment systems in photosynthesis*, Ph.D. thesis, University of Illinois, 1965.
31. Myers, J. & Graham, Jo-Ruth, *Pl. Physiol.*, **38** (1963), 105.
32. Bannister, T. T. & Vrooman, M. J., *Pl. Physiol.*, **39** (1964), 622.
33. Govindjee & Govindjee, R., *Photochem. Photobiol.*, **4** (1965), 401.
34. Hill, R., *Annu. Rev. Pl. Physiol.*, **4** (1953), 115.
35. Duysens, L. N. M., *Annu. Rev. Pl. Physiol.*, **7** (1956), 25.
36. Hill, R. & Bendell, *Nature, Lond.*, **186** (1960), 136.
37. Duysens, L. N. M., Amesz, J. & Kamp, B. M., *Nature, Lond.*, **190** (1961), 510.
38. Duysens, L. N. M. & Amesz, J., *Biochem. biophys. Acta*, **64** (1962).
39. Gaffron, H. & Wohl, K., *Naturwissenschaften*, **24** (1936), 81, 103.
40. Emerson, R. & Arnold, W., *J. gen. Physiol.*, **15** (1932), 391.
41. Emerson, R. & Arnold, W., *J. gen. Physiol.*, **16** (1932), 191.
42. Kok, B., *Acta botan. Neerl.*, **6** (1957), 316.
43. Kok, R., *Biochem. biophys. Acta*, **48** (1961), 527.
44. Krey, A. & Govindjee, *Proc. nat. Acad. Sci., Wash.*, **52** (1964), 1568.
45. Crane, F. L., *Amer. J. Bot.*, **34** (1959), 128.
46. Katoh, S., *Nature, Lond.*, **186** (1960), 533.
47. Klingenberg, M., Müller, A., Schmidt-Mende, P. & Witt, H. T., *Nature, Lond.*, **194** (1962), 379.
48. de Kouchkovsky, Y. & Fork, D. C., *Proc. nat. Acad. Sci., Wash.*, **52** (1964), 232.
49. Franck, J. & Rosenberg, J. L., *J. theor. Biol.*, **7** (1964), 276.
50. Govindjee, *Sci. & Cult.*, 1965 (in press).
51. Rabinowitch, E. & Govindjee, *Sci. Amer.*, **213** (No. 1) (1965), 74.
52. *Currents in photosynthesis*, edited by J. B. Thomas & J. H. C. Goedheer (Ad Donker, Rotterdam, The Netherlands), 1965.

REVIEWS

THE ATOMIC NUCLEUS by M. Korsunsky; translated from the Russian by G. Yankovsky (Gordon & Breach Science Publishers Inc., New York), 1965. Pp. 454. Price $ 12.50

This is the English translation of a Russian monograph, with essentially the same title. The volume is intended as a text-book, but as there is no preface, it is perhaps meant as a survey of the characteristics of the nucleus for the student as well as the scientific reader who is interested in the general structure of the nucleus.

The approach is descriptive rather than mathematical and physical concepts are emphasized with illustrations that are quite relevant and helpful.

The subject matter has been carefully selected and dealt with systematically in 14 chapters. The presentation is factual and objective and the treatment is at a uniform level throughout. After introductory chapters concerned briefly with the discovery and properties of radioactive material, there are chapters on the discovery of the positron, artificial radioactivity, mesons, the neutrino, structure of the atomic nuclei and nuclear fission. The last 3 chapters furnish an excellent and up-to-date survey of the nuclear chain reaction, the peaceful uses of atomic energy and thermonuclear reactions and a valuable appendix of 45 diagrams.

This book is a very welcome addition to the literature on atomic nucleus, bringing together compactly most of the recent advances and should prove a valuable addition to all libraries — schools, colleges and public.

H. S. VENKATARAMAN

LATTICE DEFECTS IN QUENCHED METALS edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson & M. Meshii (Academic Press Inc., New York), 1965. Pp. xxii+807. Price $ 22.00

This book is a collection of twenty-eight papers that were presented and the discussions that followed them at a conference at the Argonne National Laboratory in 1964. In this conference volume, all aspects of the field of lattice defects in quenched metals are covered although particular attention has been given to quenched-in vacancies, vacancy clusters and their interaction with impurity atoms. The topic of activation energy is given much emphasis. Detailed consideration is given to precise experimental determination of migration and binding energies and experiments which allow different types of defects to be distinguished. Most of the papers include an account of the authors' recent researches, a critical review of earlier related work and suggestions for future work. This volume thus presents a complete and up-to-date review in this field.

It is remarkable how the study of defects in quenched metals and alloys has transformed itself, over the last decade from a theoretical science into experimental one. It was first proposed by Frankel in the mid 1920's, that vacant lattice sites and interstitial atoms are formed in solids with densities dependent on temperature. This followed the work of Schottky and Wagner who worked out detailed models of defects and carried out experiments successfully with ionic solids. Unfortunately, these experimental methods were not applicable to metals and alloys and so the detailed nature of the thermally induced defects in such materials remained a matter of speculation and controversy for nearly thirty years. However, during this period several observations intensified the interest in detailed nature of defects in individual metals. Then quite suddenly everything changed, the pioneering experiments of Kauffman and Koehler inspired a systematic study of lattice defects in quenched metals and several methods of observations of defects appeared. The conference served the purpose of centralizing diverse theories and bringing some order to the mild state of confusion into which it had fallen due to immense advancement and development of diverse experimental methods, and no doubt this volume will form a basis for future development and research in this field. Some of the papers could be mentioned below.

Koehler and Lund in their paper entitled ' Non-equilibrium situation involving vacancies in gold ' discussed the question of vacancy generation in pure and alloyed gold, particularly in the case of pulse heating. Seeger and Schumacher described different techniques of studying quenched-in defects and outlined the processes of analysis to obtain correct and accurate values of activation and interaction energies for different types of defects. In two papers Balluffi *et al.* reported the results of investigations on the relationship between sink structure and annealing rate of quenched gold and worked out the method of analysing complex quenching experiments.

Cost recommended the Zener relaxation studies of quenched alloys as a powerful method to study annealing even under conditions of small supersaturation and under-saturation, and thus to eliminate spurious annealing effects due to multiple vacancies, variable sink concentrations and quenching stresses.

In three papers by Kuhlmann-Wilsdorf, Cotterill and Doyama dealing with divacancy and vacancy cluster formations in quenched pure and impure metals, a large number of models of vacancy clusters of growing sizes were given and their formation and migration energies were investigated both theoretically and experimentally. Federighi in his paper worked out the resistometric method fully which will be very helpful to intending future workers in this field.

Two papers, one by Schultz on tungsten and the the other by Meakin, Lawley and Koo on molybdenum, have opened up new hopes of further work in the case of quenched b.c.c. metals, attempts on which so far proved unsuccessful.

This volume can be unreservedly recommended to solid state physicist and metallurgist interested in the theoretical as well as experimental study of quenched metals and alloys. They will be encouraged to work in this field by the delightful combination of experiment and theory it offers and which is so well brought out in this volume by eminent scientists and authorities in this field.

M. A. Quader

Fundamentals of Engineering Mechanics by L. Vevinson; translated from the Russian (Gordon & Breach Science Publishers Inc., New York), 1965. Pp. 333. Price $ 10.50

This is a very elementary book on mechanics with an engineering bias. Both higher secondary students and those studying in polytechnics can benefit from it. The style is simple and direct and emphasis is laid on fundamentals and clarity. Very little knowledge of mathematics is assumed: not even the elements of calculus are needed.

The book is divided into two parts — the first part includes statics, kinematics and dynamics and covers 14 chapters. In the second part, the theory of machines and the fundamentals of strength of materials are treated. This covers 11 chapters. Neat figures and illustrative examples are in abundance and help to understand the principles involved. A number of oral exercises and review type questions along with their answers are also given.

The book has all the strong and weak points of the classical treatment. No modern concepts are introduced. Even though it is stated that absolute rest does not exist, statics has not been derived as a particular case of the dynamical treatment.

B. R. Seth

Materials Data Nomographs by Robert L. Peters (Reinhold Publishing Corp., New York), 1965. Pp. 224. Price $ 16.50

The book contains about 250 nomographs on the strength, modulus, hardness, density, electric and magnetic properties, heat parameters, atomic, nuclear, radiation and other properties of materials. A wide range of engineering materials is covered, including common metals, ferrous and non-ferrous alloys, plastics of various types, glass, graphite, etc. The material codes and the classification of the type of materials are also systematically drawn. In the type code, the materials are even differentiated as low, medium or high density, low, medium or high heat resistant and in the case of plastic materials, whether they are extrusion grade or molding grade, whether the material is compression molded or injection molded or whether a foam is of rigid or flexible type. It is only natural that in a work of this nature, a few materials are not coded, though their properties are given in the chart or a few materials are left out from the list.

The charts provided give the conversion of the units of properties from one system to the other. This is one of the important aspects of the book, of particular interest to Indian engineers, in view of the adoption of metric system in the country.

Detailed instructions for the use of the nomographs with examples wherever necessary make the use of the charts simple and easy.

The book will be very useful to all engineers connected with the utilization of engineering materials given in this unique and highly useful collection of nomographic charts and explanatory data.

K. S. Chari

Nucleic Acids: Structure, Biosynthesis and Function (Council of Scientific & Industrial Research, New Delhi), 1965. Pp. xi+360. Price Rs 20.00; 40s.; $ 6.00

The exponential growth of interest in nucleic acids evidenced from the unending spate of publications of symposia, seminars, reviews, etc., is a phenomenon to which the already bewildered research worker has reconciled himself in a spirit of utter self-surrender. Any meaningful retrieval of information on nucleic acids currently getting into print in scientific journals and books requires tackling by the methodology of operational research.

The belated publication of the volume in the hands of the reviewer trumpets our entry into the fashionable era of international meets of scientific luminaries for the ostensible purpose of exchange of information and to seek clues for the ' break-through ' of problems challenging solution in the field of the biosynthesis and function of nucleic acids. In January 1964, with the blessings of the Council of Scientific & Industrial Research and generous financial support from the Wellcome Trust, London, and other charitable institutions, the Regional Research Laboratory, Hyderabad, played host to 34 invited participants from USA, UK, Israel, Japan, Germany and India and over a hundred observers who were thrown together for six days reviewing some aspects of the structure, biosynthesis and function of nucleic acids. Thirty-three papers were presented at this symposium and of these thirty-one have found place in the volume under review, about a year and half subsequent to the holding of the symposium.

The papers presented in this volume embody the utterances of some of the high priests of the cult of molecular biology on the magic of the genetic code, and its translation and transcription. These are sufficiently awe-inspiring ! Scattered here and there are pedestrian and, to the bench workers' relief, more familiar accounts of isolation of nucleic acids and description of enzyme systems from bacterial, plant and animal tissues that mediate the synthesis of nucleic acids. One looks in vain for a connecting thread or a basic philosophy of outlook in this assembly of papers. Perhaps that was not one of the objectives of the sponsors of the symposium. Admittedly it is safer to be pragmatic in such an exciting field as nucleic acid research ! This line is not written, however, to belittle the stimulating nature of the articles included in the present volume.

The possibility that long homopolymeric sequences could occur in nature is illustrated by Edmonds and Abrams in their report on thymus nuclear enzymes which elaborate polyadenylate. The intriguing role of histones as regulators of nucleic acid synthesis and breakdown is discussed independently in two papers by Butler and coworkers and Mirsky and coworkers from either side of the Atlantic. The collinearity problem of transcription is illuminated by Crick with his usual clarity and forcefulness of style. The use of purine pyrimidine antagonists in chemotherapy and their mode of incorporation is discussed by Heidelberger. The nature of ribosomal RNA and the origin of ribosomes have been dealt with in five papers. The capacity of tissue RNA to carry the genetic code is demonstrated by *in vitro* experiments on the induction of tissue specific enzymes and species specific haemoglobin.

Eleven papers dealing with hepatic cells in the study of nucleic acid turnover, isolation of infectious DNA from vaccinia virus, role of hormones in the synthesis of RNA, nutritional status and RNA biosynthesis in liver, orotic acid metabolism and liver degeneration, chromosome mapping, a theoretical approach to genetic crossover, polynucleotide phosphorylase of *A. vinelandii*, induction of enzymes in *L. plantarium*, polynucleotide synthesis in chloroplasts and DNA synthesis in liver constitute the indigenous contribution to this international symposium.

The reviewer gathers from one of the invited participants of the symposium that the discussion following the papers was of a high order. The decision of the convener of the symposium not to include these discussions in the present volume is, therefore, to be highly regretted. It is a safe assumption to make that a symposium of this nature is seldom the venue for announcing new discoveries or break-throughs! However, during the course of discussion, very often, valuable suggestions are made not necessarily by the authors of papers. One sorely misses these silent sparks in the present volume.

The reviewer has no complaint against the get-up of the book. The picture on the front dust cover reminds him, however, of the valiant but futile efforts of the neo-Picassos who claim to shock the senses but only stir the on-lookers' pity! One does not see why a conventional double helical could not have been used as the motif! The book is eminently free from printing mistakes. The sponsors of the symposium, according to the prefatory remarks of the convener, had the stimulation of nucleic acid research in India as one of their aims in organizing this symposium. It will be presumptuous to believe that the publication of this book in its present form alone would achieve that objective. The reviewer, however, can only wish that young minds in the postgraduate departments of our universities and medical colleges will be stimulated by exposure to the contents of this book to go deeper into the fascinating story of nucleic acids.

C. R. KRISHNA MURTI

BIOLOGICAL CONTROL OF INSECT PESTS AND WEEDS edited by Paul DeBach & Evert I. Schlinger (Reinhold Publishing Corp., New York), 1964. Pp. xxiv+844. Price $ 22.50

This book is the outcome of the collective efforts of 16 eminent research workers among whom (as the editor, Dr Paul DeBach, says in the preface) 'over 200 man-years of specialization in biological control is represented'. In spite of this multiplicity of authors the entire book is a cohesive whole. The treatment of the subject is in a refreshingly lucid style and the approach is incisive and analytical throughout.

The plan of the book merits a brief description. The book is divided into eight sections and twenty-four chapters, covering every aspect of the theory and practice of biological control. Section I: Introductory, comprises two chapters, viz. The Scope of Biological Control (Paul DeBach) and The Historical Development of Biological Control (R. L. Doutt). Section II: The Ecological Basis of Biological Control, consists of three chapters, viz. Population Ecology — Historical Development (C. B. Huffaker & P. S. Messenger), The Concept and Significance of Natural Control (C. B. Huffaker & P. S. Messenger) and Some Biological Control Concepts and Questions (R. L. Doutt & Paul DeBach). Section III: Biology and Systematics, has three chapters — Biological Characteristics of Entomophagous Adults (R. L. Doutt), Development Stages of Parasites (K. S. Hagen) and Systematics in Relation to Biological Control (E. I. Schlinger & R. L. Doutt). Section IV: The Introduction, Culture and Establishment Programme, comprises six chapters, viz. Foreign Exploration for Beneficial Organisms (B. R. Bartlett & R. Van den Bosch), Quarantine Handling of Entomophagous Insects (T. W. Fisher), Culture of Entomophagous Insects and Their Hosts (G. L. Finney & T. W. Fisher), Nutrition of Entomophagous Insects and Their Hosts (K. S. Hagen), Insectary Facilities and Equipment (T. W. Fisher & G. L. Finney) and Methods of Colonization, Recovery and Evaluation (Paul DeBach & B. R. Bartlett). Section V deals with the Conservation and Augmentation of Natural Enemies and comprises three chapters, viz. Manipulation of Entomophagous Species (Paul DeBach & K. S. Hagen), Environmental Modification and Biological Control (R. Van den Bosch & A. D. Telford) and Integration of Chemical and Biological Control (B. R. Bartlett). Section VI deals with Insect Pathology and comprises four chapters: Microbial Diseases of Insects (E. A. Steinhaus), Epizootiology of Insect Diseases (Y. Tanada), Mass Production of Insect Pathogens (M. E. Martignoni) and Use of Microorganisms in Biological Control (I. M. Hall). Section VII, dealing with Biological Control of Weeds, has two chapters, viz. Fundamentals of Biological Weed Control (C. B. Huffaker) and Projects in Biological Control of Weeds (J. K. Holloway). The last part of the book (Section VIII) — Conclusion, has one chapter, Successes, Trends and Future Possibilities (Paul DeBach), and is broadly a summing-up and includes two comprehensive lists (Tables 12 and 13) of successes, complete or partial, achieved in the biological control of insect pests in different parts of the world.

Thus, the book follows an orderly pattern beginning from the more fundamental and theoretical aspects and then touching upon the various aspects of applied biological control. Because of this, it can very well serve as a text-book in colleges and universities and thus it fulfils a long-felt need. While all the twenty-four chapters are of interest to any advanced student of the science of biological control, the six chapters of Section IV (The Introduction, Culture and Establishment Programme) are of special interest for applied work on biological control.

There is a useful bibliography consisting of over 3000 references, and an index to scientific names. But there is no index to authors' names; while such an index is not very essential, it is certainly useful. Also, the table of contents, where the chapters are listed, does not mention the names of the authors of the different chapters and one has, therefore, to turn to the actual chapters to know them.

For certain reasons, Indian work is rather incompletely touched upon in this book. While the successful control of the pea aphid *Acyrthosiphon pisi* (Harris) (=*Macrosiphum pisi* Kaltenbach) in California by the imported Indian parasite *Aphidius smithi* Sharma & Subba Rao has been mentioned, the introduction into USA of another Indian parasite *Dusmetia sangwani* Subba Rao has been omitted. The latter has been playing an important role in controlling its host *Antonina graminis* (Maskell) in large areas of USA. The successful laboratory culturing of *Apanteles angaleti* Muesebeck, an Indian parasite of the pink bollworm, on a factitious host (*Corcyra cephalonica* Stainton) does not find mention either in the text of Chapter II (Culture of Entomophagous Insects and Their Hosts) or in the table entitled 'Selected listing of mass-produced entomophagous insects' on page 354.

The book should find a place on the shelf of every entomologist, particularly those who are especially working in the fields of insect parasitology and biological control. The book will certainly prove of immense use to teachers and students alike. The authors have made a noble gesture in deciding to send the royalties from this book to the Harry S. Smith Memorial Fund, University of California, set up to honour a great teacher and a very eminent worker in the field of biological control, the late Prof. H. S. Smith.

S. PRADHAN

STRUCTURE AND FUNCTION IN BIOLOGICAL MEMBRANES: Vol. 2, by J. Lee Kavanan (Holden Day Inc., San Francisco), 1965. Pp. x+760. Price $ 14.75

This volume and the preceding one of the series is an attempt by the author to present a comprehensive account of the current concepts on the interrelationship of structure and function in biological membranes. In the volume under review, the following topics are dealt with in detail: protoplasmic streaming, coalescence between membranes, amoeboid locomotion, effect of physical factors on protoplasm, transport and diffusion mechanism across membranes and electron optical evidence for the existence of membrane structure. The properties of micelles, monolayers and water-solute interactions in the biophase are described on the basis of advanced physico-chemical theories. The existence of both closed and open configuration of membranes is assumed to explain ion transport and enzymic reaction mediated by lipoprotein membranes. The aid of the ubiquitous feedback control is invoked to provide theoretical support to the assumption of a nebulous state of equilibrium between closed and open configuration of membranes. The electron optical evidence for the existence of double membrane system in bacterial and yeast protoplasts, mitochondrial and erythrocyte membranes is presented in a number of electron micrographs. The remarkable resemblance between an artificially prepared lecithin-cholesterol complex when visualized under an electron beam after exposure to saponin and a similarly treated preparation of spinal cord homogenate indicates how fruitful it is to have experimental models of biomembranes.

The author is to be warmly complimented for having performed a rather neat feat of assembling a formidable mass of data and concepts and theories on biomembrane from the standpoint of structure-function relationship. For this he deserves the gratitude of workers whose interest are currently converging towards the discovery of a molecular basis for membrane function.

C. R. KRISHNA MURTI

ISTA BULLETIN: Vol. 1 (Nos. 1-4), 1964-65, published by the Indian Scientific Translators Association, c/o Insdoc, New Delhi 12

Scanning through the first four issues of the new quarterly (published October, January, April and July) started as the organ of the Indian Scientific Translators Association (ISTA), one is convinced of the need for such a journal. Apart from serving as a forum for the scientific translators in India, the journal will be useful to all those interested in linguistics. The ISTA was formed with the object of promoting the facilities for scientific translation and for improving the status and service conditions of translators. In his presidential message to the first issue, Prof. M. S. Thacker has stressed the importance of scientific translation to any developing country.

The contents of the issues so far published include articles on general linguistics, special problems encountered in technical translation and notes on languages, which will be of practical use for practising translators. An account of the proceedings of the Second Seminar on Scientific Translations organized by the ISTA during 15-17 April 1965 has been reported in the July 1965 issue. Even though the circulation of this mimeographed bulletin is confined to members of ISTA at present, perhaps due to economic considerations, the ISTA's plans to print this bulletin with a view to wider circulation is to be welcomed. With a wider circulation, the value of the bulletin will be better appreciated by all those concerned with the teaching of languages and linguistic research, in addition to those connected with translation work.

K. S. RANGARAJAN

APPLICATION OF METALLURGICAL MICROSCOPY by Handrickson & Iannone (Baush & Lomb, New York), 1965. Pp. 28

This unpriced publication gives a brief account of all the important principles of metallography and can serve as a text-book for a short course in this field. The text which is accompanied by photomicrographs is divided into the following sections: Microstructure and the properties of metals; Metallographic laboratory practice; Photographic aspects of metallography; Measurements with a metallograph; Types of illumination; Research techniques; and Examples of outstanding metallo graphy.

KULDIP CHAND

STATISTICAL ANALYSIS IN BIOLOGY by Kenneth Mather (Methuen & Co. Ltd, London), 1965. Pp. 267. Price 12*s*. 6*d*.

Statistical analysis is a basic technique used in many branches of science for a proper analysis and correct interpretation of research data. It is becoming increasingly necessary to present the basic principles of this essential scientific tool to meet the needs of a particular branch of science by eliminating the drudgery of long and complicated mathematical proofs and pinpointing its applied aspects. This book meets this need and the present paperback form of the original edition published in 1943 enlarges its accessibility to a wider circle of users in view of the lower price. The book should prove very useful to research workers engaged in biological research and help them to correctly imbibe the elementary concepts of statistical analysis. The good number of well-chosen examples from the field of biology should assist the user in applying the analysis to his own data.

D. S. R. MURTY

PUBLICATIONS RECEIVED

METHODS IN CARBOHYDRATE CHEMISTRY: Vol. 5 — GENERAL POLYSACCHARIDES edited by R. L. Whistler (Academic Press Inc., New York), 1965. Pp. xxii+463. Price $ 16.50

OPTICAL CIRCULAR DICHROISM — PRINCIPLES, MEASUREMENTS AND APPLICATIONS by J. Velluz, M. Legrand & M. Grosjean (Academic Press Inc., New York), 1965. Pp. xii+247. Price $ 10.00

EVALUATION OF DRUG ACTIVITIES: PHARMACOMETRICS: Vol. 2, edited by D. R. Laurence & A. L. Bacharach (Academic Press Inc., New York), 1965. Pp. vii+459-900. Price $ 14.00

INTEGRATED CIRCUITS: DESIGN PRINCIPLES AND FABRICATION edited by Raymond M. Warner & James N. Fordemwalt (McGraw-Hill Book Co. Inc., New York), 1965. Pp. xxix+385. Price $ 12.50

JET AIRCRAFT POWER SYSTEMS by Jack V. Casamassa & Ralph D. Bent (McGraw-Hill Book Co. Inc., New York), Third Edition, 1965. Pp. vii+408

RECENT PUBLICATIONS

NEWER METHODS OF NUTRITIONAL BIOCHEMISTRY: Vol. 2, edited by Anthony A. Albanese (Academic Press Inc., New York), 1965. Pp. 480. Price $ 17.50 (approx.)

PRINCIPLES OF SENSORY EVALUATION OF FOOD by Maynard A. Amerine, Pangborn, Rose Marie & Edward B. Roessler (Academic Press Inc., New York), 1965. Pp. 600. Price $ 22.00 (approx.)

ENERGY METABOLISM edited by K. L. Blaxter (Academic Press Inc., New York), 1965. Pp. 450. Price $ 15.00; 95*s*.

THE ANATOMY OF THE LABORATORY MOUSE by Margaret J. Cook (Academic Press Inc., New York), 1965. Pp. 150. Price $ 6.00; 35*s*.

FUNDAMENTALS OF CARBANION CHEMISTRY by Donald J. Cram (Academic Press Inc., New York), 1965. Pp. 270. Price $ 9.50 (approx.)

METABOLISM OF STEROID HORMONES by Ralph I. Dorfman & Frank Ungar (Academic Press Inc., New York), 1965. Pp. 716. Price $ 24.00

OPTICAL PHYSICS by M. Garbuny (Academic Press Inc., New York), 1965. Pp. 466. Price $ 14.50

STRUCTURE AND MECHANISM IN ORGANO-PHOSPHORUS CHEMISTRY by R. F. Hudson (Academic Press Inc., New York), 1965. Pp. 320 (approx.)

COURSE 31: QUANTUM ELECTRONICS AND COHERENT LIGHT (Academic Press Inc., New York), 1965. Pp. 370. Price $ 16.00

PHYSICO-CHEMICAL APPROACH TO THE DENATURATION OF PROTEIN by M. Joly (Academic Press Inc., New York), 1965. Pp. 150 (approx.)

MECHANISMS OF HORMONE ACTION edited by P. Karlson (Academic Press Inc., New York), 1965. Pp. 276. Price $ 14.50

INTERPRETATION OF ORGANIC SPECTRA edited by D. W. Mathieson (Academic Press Inc., New York), 1965. Pp. 180

BIOCHEMISTRY OF QUINONES edited by R. A. Morton (Academic Press Inc., New York), 1965. Pp. 585. Price $ 18.00

MOLECULAR BIOPHYSICS edited by Bernard Pullman & Mitchell Weissbluth (Academic Press Inc., New York), 1965. Pp. 540. Price $ 18.00 (approx.)

CHEMICAL OCEANOGRAPHY: Vols. 1 & 2, edited by J. P. Riley & G. Skirrow (Academic Press Inc., New York), 1965. Vol. 1: Pp. 712. Price $ 25.00; Vol. 2: Pp. 500 (approx.)

THE BIOCHEMISTRY OF ANIMAL DEVELOPMENT: Vol. 1 — DESCRIPTIVE BIOCHEMISTRY OF ANIMAL DEVELOPMENT edited by Rudolf Weber (Academic Press Inc., New York), 1965. Pp. 610 (approx.)

STARCH: CHEMISTRY AND TECHNOLOGY: Vol. 1 — FUNDAMENTAL ASPECTS edited by Roy L. Whistler & Eugene F. Paschall (Academic Press Inc., New York), 1965. Pp. 530 (approx.). Price $ 22.00

SYMMETRIES IN ELEMENTARY PARTICLE PHYSICS edited by A. Zichichi (Academic Press Inc., New York), 1965. Pp. 440 (approx.)

NOTES & NEWS

New theory on comet break-up

The spectacular break-up of comets is considered for long to be caused only by close encounters with the sun or the planets. A new theory in this respect was put forward recently by Dr Fred L. Whipple and Mr Robert Stefanik of the Smithsonian Astrophysical and Harvard College Observatories in a paper read at the Thirteenth International Astrophysical Symposium on the Nature and Origin of Comets held in July 1965 at the University of Liège, Belgium. This theory suggests that the break-up could result from the comet's own structural defects. Studies conducted at the observatory show that the decay of radioactive material at the comet's core may weaken the body's structure so that it breaks apart upon entering the warmer region of the planets after a long orbital ride through the colder regions of the outer solar system beyond the planets.

The new theory is a development of Dr Whipple's early work describing comets as conglomerations of ice and particles of extraterrestrial material.

It is believed that the comets were created in and beyond the region of the giant planets, Jupiter, Saturn and Uranus, nearly 4·5 billion years ago, about the same time as other bodies in the solar system. As the huge cloud congealed to form the sun and planets, the comets collected as balls of cosmic debris held together by ' ices ' of water, ammonia and methanol.

Further, the extraterrestrial material in the comet's body is thought to be similar to the material found in meteorites, thus containing a small amount of radioactive matter. Radioactive material begins to decay as soon as it is created, thereby producing heat and energy. The heat generated by the decaying process in the comet would cause the more volatile ices at the centre of the comet to sublime into their gaseous state. The gases would seep toward the outside of the comet's body where they would immediately refreeze and form a hard crust or shell around the fluffy and partially decomposed centre.

Structurally strong and relatively hard-packed when originally kicked into deep space, the comets return billions of years later crystallized to the point where the solar heat in the region of the inner planets causes a thermal shock that splits them into two or more comets.

This theory would explain why several groups of comets have similar orbits. All these groups may have been parts of the same body which broke up into related sister-comets wandering together through the solar system.

Rotation of Mercury

Radar observations made on the planet Mercury at the Arecibo Sonospheric Observatory, Puerto Rico, have indicated that, contrary to the current belief, this planet does not rotate with the same side always facing the sun. This observation clears up a long-standing puzzle, namely the apparent uniformity of surface temperature of the planet in spite of there being no atmosphere which would equalize the temperature difference between the faces facing the sun and the opposite side, assuming that the planet is revolving around the sun with the same face towards it.

Apart from being unexpected, this observation has interesting theoretical implications. It indicates that either the planet has not been in its present orbit for the full period of geological time or the effect of the tidal forces acting to slow the initial rotation has not been correctly interpreted in previous computations of the motion of the planet. The observations were made by sending 500 μsec. pulses (at 430 Mc/s. and a transmitted power of 2 MW) from a radar system having sufficient sensitivity to detect echoes not only from the nearest part of the planetary disk but also from regions further distant up to 0·06 of the planet's radius. Since the source of the delayed echoes can quite reliably be associated with a known area of the planetary surface, the magnitude of the apparent planetary rotation can be inferred from the measured spectral dispersion through a simple geometrical relationship and the actual rotation period can be evaluated by applying corrections for the relative motion of the observer and the target planet. Observed values of the apparent rotation of the planet were used to compute the most likely value of intrinsic planetary rotation, using a procedure developed by Dr Irwin Shapiro of the Lincoln Laboratory, Massachusetts Institute of Technology. If the direction of rotation of mercury is direct (i.e. of the same direction as that of the earth), the computed value of the period of rotation is 59±5 days while for retrograde rotation the period is 46±5 days. Radar observations support the presumption of a direct rotation period of 59±5 days. Assuming the orbit to be circular, the difference between the computed rotation period and the orbital period around the sun (88 days) could mean that the planet has been in its present orbit for not more than 400 million years. Otherwise the planet's spin would have relaxed from any original value to one that is of the type similar to the motion of the Moon around the earth. However, in case the orbit has substantial eccentricity, the tidal torque at perihelion will exceed that at other times, and the angular velocity of the planet will thus settle at a value greater than the mean orbital angular velocity at perihelion. Under these conditions, for mercury (eccentricity, 0·2) a spin with a sidereal period lying between 56 and 88 days may be expected.

A more precise calculation may be made based on the consideration that the final angular velocity of the planet will be such that the time average of the tidal torque around the orbit is zero. No further change in the planet's spin will then occur except on the much longer time scale on which other orbital elements can be influenced by tidal friction effects which probably are unimportant in the age of the solar system. The precise calculation of the angular velocity to fit this condition can be made without a quantitative description of the dissipation properties of the planet, but involving certain assumptions. Such calculations indicate that Mercury is indeed in its final state of spin, and that its present rotation reflects very accurately certain characteristics of the dissipation process. The above assumptions are based on the supposition that the solar torque exerted on the tidal bulge exceeds that exerted on any permanent deformation from axial symmetry. In the converse case a period of 88 days for the rotation would result. This may imply that Mercury has not much permanent rigidity. The high surface temperature may be partly responsible for this. The solar system thus provides examples for each of the final states of rotation that tidal friction can bring about — the Moon which has locked into synchronous rotation, and Mercury which has come to the rotation that is enforced in the absence of any permanent asymmetry of the body [*Nature, Lond.*, **206** (1965), 1240; *Sci. Newslett., Wash.*, **87** (1965), 277].

Pure K-meson beam

A 'beam' of separated negative K-mesons possessing more momentum than what has been achieved earlier has been obtained at the European Organization for Nuclear Research (CERN), Geneva. K-mesons are obtained when a suitable target is bombarded with a stream of high energy protons. Other particles like neutrons, antiprotons and other types of mesons also formed along with the K-mesons are to be separated to get the beam of K-mesons only. In the conventional method the separation was effected by a steady electric field in which the particles deflected by different amounts according to their mass. In the CERN experiment, an alternating electromagnetic field was used.

Particles of equal momentum are introduced into a tube 3 m. long in which an electromagnetic wave is travelling. Particles having a velocity equal to that of the wave will get deflected through an angle that depends on their location with respect to the crest of the wave. On leaving this first r.f. tube, the particles are focused to a second tube 50 m. away. At this distance, small differences in mass — and, therefore, in velocity, for the same momentum — will appear as differences in arrival time. By suitable arrangement, the pi-mesons can be made to arrive at the second tube half a wavelength behind K-mesons with the result that these two beams are deflected through equal but opposite angles. Further, it can be ensured by proper synchronization of the two cavities that K-mesons will always be deflected by equal and opposite amounts in turn, thus emerging along the axis of the instrument, while pi-mesons are deflected successively further from the axis by the two cavities. In this way, bursts of about 10 negative K-mesons of energy 10 GeV. were obtained [*New Scientist*, **26** (1965), 178].

Laser excitation by chemical reaction

The feasibility of exciting laser action in the infrared region by the energy of a chemical reaction has been demonstrated for the first time by Jerome V. V. Kasper and Dr George C. Pimental at the University of California, Berkeley. This achievement of the first operating laser based on the excitation by a chemical reaction, viz. $H+Cl_2 \rightarrow HCl^*+Cl$, confirms the earlier prediction made by Dr J. C. Polyani of the University of Toronto, that the vibrationally excited hydrogen chloride formed in this reaction would show stimulated emission. This development also indicated a new way to determine energy distribution in this as well as other chemical reactions. The wavelength, intensity and lifetime of the laser emission also give valuable information about the nature of the excited species. In the operation of the laser a mixture containing one volume of chlorine and two volumes of hydrogen in a laser tube is exposed to the flash from a xenon-filled quartz flash tube. The resulting laser emission is centred about the 3·8 μ region. A chemical laser converts the free energy change of a chemical reaction into a specific excitation of some product species leading to critical population inversion (i.e. excess populations of electronically, vibrationally and rotationally excited atoms or molecules) and thus to laser action. This is in contrast to the well-known successfully operating present-day lasers such as the ruby or helium-neon laser whose energy comes from outside sources such as light and electric discharges.

Chemical lasers of a different type have also been developed earlier and though pumped by the energy of the chemical reaction, they required an external source (such as photons, gamma rays, electrons, etc.) as the initiator of the chemical reaction. Three types of such lasers are in operation. The first type is the photodissociation laser (also developed by Kasper and Pimental) in which photons initiate a chemical reaction that produces excited atoms. For example, in the first laser of this type laser action is observed during flash photolysis of gaseous CF_3I and gaseous CH_3I molecules. The stimulated emission is due to the $2P_{1/2} \rightarrow 2P_{3/2}$ transition of atomic iodine in the 1·315 μ region. The second type of laser operates due to an electrical discharge which breaks up water vapour into hydrogen atoms and rotationally excited OH radicals. The third type of lasers operate due to the passage of electric discharge through carbon monoxide at very low pressure [*Chem. Engng News*, **43** (No. 6) (1965), 38].

Nekoflavin, a new flavin compound

A new flavin compound, nekoflavin, has been isolated from the choroid and tepetum of cat's eyes at the Laboratories of the Research Institute of Atomic Energy, Osaka University. Nekoflavin, like flavin, has a yellow colour and yellowish-green fluorescence in aqueous solution and can be reversibly reduced and oxidized. Its absorption spectrum resembles that of riboflavin, indicating that it is a flavin. It differs from riboflavin, its derivatives and photodecomposition products by its behaviour on paper chromatography. But the similar absorption spectra of nekoflavin and riboflavin suggest the presence of isoalloxazine ring in nekoflavin. The difference in the R_f values of the two must be due to differences in their side chains. Nekoflavin, therefore, seems to be a new flavin compound differing from riboflavin in its side chain.

The trichloroacetic acid extract (80 ml.) from 94 g. of choroid was passed through a Florisil column (2·5×15 cm.) which was washed successively with 1 litre of 5 per cent trichloroacetic acid, 1 litre of water and 30 ml. of 0·5 per cent aqueous pyridine. The flavins were then eluted with 5 per cent aqueous pyridine. The yellowish-green fluorescent fraction (500 ml.) was collected and extracted four times with 200 ml. aliquots of chloroform to remove pyridine, and then concentrated to 6 ml. *in vacuo*. The concentrate was filtered and saturated with ammonium sulphate. The flavins were extracted into three 2 ml. aliquots of liquid phenol. The extracts were combined and mixed with 10 ml. of water and 250 ml. of ether. The water layer was extracted three times with 100 ml. aliquots of ether and then dried *in vacuo*. The residue was dissolved in 5 ml. of an *n*-butanol-formic acid-water mixture and chromatographed on a cellulose column. The first fraction contained riboflavin and the second fraction nekoflavin [*J. Biochem., Tokyo*, **57** (1965), 201].

An improved disc electrophoresis apparatus

An improved, simple and robust apparatus for disc electrophoresis has been designed by L. J. Rogers, University College of Wales, Aberystwyth (Great Britain). The apparatus has many constructional advantages over the existing ones. Besides being inexpensive to construct, all the breakable parts of the apparatus can be readily replaced. The apparatus can be used with any suitable power supply. Also, vertical position of the gel tubes during electrophoretic run is assured, and very high resolution of protein mixtures can be achieved in a very short run.

The apparatus, which functions as a single unit when assembled, consists of two parts — the lower, a pyrex beaker and the upper, a photographic developing tank; in between the two, a perspex disc of 5 in. diam. and thickness 0·375 in. rests. The gel tubes pass from cathode to anode compartment through six holes drilled at equal intervals along the circumference, 1·375 in. from the centre in the bottom of the devoloping tank. These holes are alternately 0·406 in. and 0·5 in. in diam. and hold rubber grommets. Into these grommets fit the electrophoresis tubes in a vertical position. The arrangement provides a water-tight connection between the compartments.

The tubes of staining as well as destaining also fit the grommets and holes. The arrangement of holes, grommets and tubes can be altered to suit personal requirements. All the exposed bolts, nuts and other parts of the apparatus are well covered [*Biochem. biophys. Acta*, **94** (1965), 324].

An improved method for moisture analysis

Moisture content of materials like leather, paper, grains, etc., can be easily and quickly determined with an apparatus recently designed at the US National Bureau of Standards Institute for Materials Research. The apparatus applies the principle of the carbide reaction technique, namely that when a specimen is mixed with calcium carbide and heated to drive away the water, the volume of the acetylene generated by the reaction of water with calcium carbide is a measure of the moisture content of the specimen. The apparatus consists of a reaction flask, a calcium carbide flask communicating with the reaction flask, and provision for measuring the volume of acetylene liberated and for heating and magnetically stirring the contents of the reaction flask. While conducting a test, the specimens are placed in the reaction flask which is connected to a system of inverted burettes filled with mercury as well as to a flask containing calcium carbide. The calcium carbide is emptied into the reaction chamber which is then immersed in a heating bath and stirred. Acetylene liberated depresses the mercury level in the burettes and a coupled open tube of mercury and adjustable reservoir facilitate the precise determination of the volume of acetylene formed. The moisture content of the specimen can be evaluated with an overall experimental error of less than 2 per cent. Moisture contents of several compounds determined with this apparatus have been found to show excellent agreement with values determined from the known chemical compositions [*Tech. News Bull. U.S. Bur. Stand.*, **49** (1965), 45].

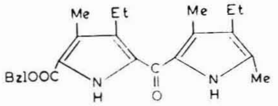
Stereochromatography

The use of three-dimensional paper pulp blocks for preparative chemical isolation and identification has formed the basis of a new chromatographic technique — stereochromatography — which may be of immense value in biochemical research. The feasibility of stereochromatography has been demonstrated by three-dimensional separation of indicator dyes in simple ascending chromatography. The blocks are fabricated by compressing 3-4 per cent paper pulp at 3000 lb./in.^{2} in a metal sieve box by means of a hydraulic press. After compression the blocks are dried for 36 hr at 70°C. The aqueous solute mixture containing mg. quantities of bromocresol green, bromothymol blue and eosine blue is injected at the centre of the base of a 25×20×7·5 cm. compressed paper block. The block is then placed on the bottom of a large closed jar containing 0·5 in. of solvent and exposed for 3 hr. The block is removed from the jar and serially cut into sections by an electric band-saw. It is necessary to section the wet blocks, for prolonged drying might facilitate zone migration. The vertical and lateral migrations of the solute zones are determined on each section by means of a metric calibrated, transparent, plastic grid. The vertical migration (R_f) values are calculated in the conventional manner. The lateral migration, or spreading factor (R_s), of the solute zones is determined by calculating the ratio of the lateral spread of the solute from the central axis of the block to the vertical migration of the solvent front. It is found that zone resolution is adequate to isolate and identify constituents of a mixture.

This technique is suitable for preparative chromatography where large amounts of solutes are to be resolved and, therefore, useful in biological and industrial purifications. The spreading factor R_s offers an additional parameter for differentiating chemical constituents especially useful in the case of compounds with similar partition coefficients and R_f values (e.g. leucine and isoleucine, valine and nor-valine). The only disadvantage in the present method is that it requires the use of an electric band-saw, and the paper blocks, though simple to fabricate, are not commercially available [*Nature, Lond.*, **205** (1965), 1003].

Two new porphyrin syntheses

The syntheses of porphyrins known so far generally depend on final coupling of two dipyrrolic units. Two new syntheses of porphyrins, now reported, proceed through crystalline tetrapyrrolic intermediates, each of which is stabilized by an internuclear carbonyl group [*J. Amer. chem. Soc.*, **87** (1965), 676]. This approach offers great advantages in the synthesis of diversely substituted porphyrins. The synthesis of mesoporphyrin described below may be taken as a typical example.



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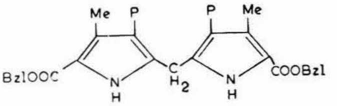

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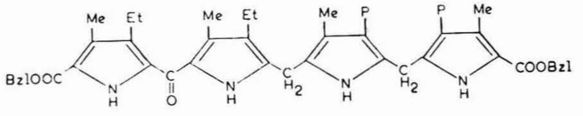

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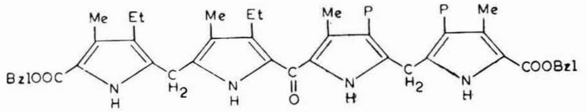


IV

Chlorination of the pyrroketone (I) in methylene chloride-HCl by *t*-butylhypochloride in tetrahydrofuran-ether (1:1) at 3° yields the chloro derivative. The chloro derivative is next coupled as its pyridinium derivative with the lithium salt of (II) to yield 44 per cent of the tetrapyrrolic ketone (III). The carbonyl group in (III) is reduced by diborane in tetrahydrofuran-ethyl acetate (1:1) to a methylene group. The bilane dicarboxylic acid resulting from hydrogenolysis is dehydrogenated to principally the bilene-*b* hydrochloride by *t*-butylhypochlorite in ether. The bilene-*b* hydrochloride on cyclization with methyl orthoformate-trichloroacetic acid (1:3) in methylene chloride, followed by aeration, gives mesoporphyrin dimethyl ester as the only porphyrinic product in an overall yield of 25 per cent from (III).

The second synthesis involves coupling of the pyrromethane amide as its phosphoryl chloride complex with the pyrromethane in methylene chloride to an imine salt. The latter is hydrolysed by aqueous sodium carbonate to give the tetrapyrrolic ketone (IV). Hydrogenation of (IV) yields the dicarboxylic acid which is decarboxylated at 185° to an oil. The latter is cyclized with methyl orthoformate and boron trifluoride etherate in methylene chloride and after aeration in the presence of triethylamine, the blue 'β-hydroxyporphyrin' is formed. Acetylation of the latter gives β-acetoxymesoporphyrin dimethyl ester. Reduction of 'β-hydroxyporphyrin' by sodium amalgam in methanol-acetic acid gives directly mesoporphyrin.

Progress Reports

Food Preservation Research in Australia

The annual report of the Division of Food Preservation, Commonwealth Scientific & Industrial Research Organization (CSIRO), Australia, for the period 1962-64 (77 pages) gives an account of the research activities of the Division in the fields of food chemistry, plant physiology, microbiology, meat research, and packaging and preservation of foods.

A laboratory scale vacuum freeze-drying unit designed to permit continuous recording of the sample weight and temperatures at selected points within the sample has been constructed to aid in the study of sublimation processes from high protein foods. From results obtained with this apparatus, a new system of freeze-drying has been evolved which gives higher quality products in a shorter time than the usual process.

A new phospholipid, tentatively named 'mitolipine', has been isolated from pigeon breast muscle; it comprises nearly 20 per cent of the total phospholipid present in this muscle; a method for the determination of both nitrogen and phosphorus in a Kjeldahl digest of phospholipid has been evolved.

Studies of induced respiration in pumpkin mesocarp and celery petiole showed no significant changes between the characteristics of induced respiration in these tissues and in the underground storage organ.

New methods have been devised for the extraction, isolation and identification of phosphorylated compounds from tobacco callus tissue and from washed disks of pumpkin, carrot and turnip storage tissues.

An enzyme, named oxalate thiokinase, catalysing the activation of oxalate has been isolated from pea seed extracts.

Studies on the mechanism of inhibition of bacterial growth on carcasses by carbon dioxide have shown that carbon dioxide inhibits the oxidation and utilization of several organic acids of the citric acid cycle. Some of the associated enzymes responsible for the oxidations have also been found to be inhibited by carbon dioxide at a concentration of 10 per cent.

Central Building Research Institute, Roorkee

Production of good bricks from inferior soils, utilization of fly ash for the production of puzzolanic cements, development of lift slab technique suitable for multi-storeyed construction and a portable scaffolding suitable for quick erection are some of the important achievements reported in the Annual Report of the Central Building Research Institute, Roorkee, for 1964-65.

During studies on the role of sulphate present in raw clay on its tendency to effloresce in the fired products a complex salt, apthitalite, has been identified in briquettes containing sulphates and fired to 1000-1060°C. Soils containing less than 5 per cent calcium sulphate do not give rise to efflorescence if they are fired to a temperature higher than 1000°C. Good quality bricks have been developed from inferior soils of Hyderabad, Ahmedabad and Bombay. Studies on the corrosion of reinforcement in brick structures have shown that epoxy resin when applied as a coating on the bars resists corrosion appreciably. A semi-mechanized plant having a double shafted mixer and a deairing pug-mill has been developed which is capable of producing up to 20,000 bricks per day. An open top, coal fired, zigzag brick kiln operating on fan draught which is as efficient as the modern Hoffman kiln although less than half as costly as the latter has been developed. Investigations have shown that Indian fly ash can be efficiently used in all sorts of concrete leading to a saving of up to 20 per cent cement. A simple and accurate method for the determination of rate dependent parameters required for the estimation of the quantity of calcium hydroxide in hydrated cement has been found out. The specific rate constant (K) at any temperature T can be represented by the equation

$$K = \frac{(A/m_0)^{n-1}(-dx/dt)}{(A-a)^n}$$

where $-dx/dt$ is weight loss during any specific period t; A, the total area under differential thermogravimetric curve for the complete reaction; a, the area up to time t; m_0, the initial mole fraction of the reactant; and n, the order of the reaction with respect to the reactant.

Experiments on hydration of Portland cement have revealed that the position of Fermi level in the Portland cement clinker minerals controls their rate of hydration. The rate of hydration is found to follow direct logarithmic law. Studies on adhesion in set Portland cement have indicated that the potential of mild steel and stones with respect to set cement increases with time while that of aluminium, copper and brass decreases and that the adhesive bond in set Portland cement and aggregation is a donor type bond. The addition of silica in colloid form in floor polishes has been found to make floors less slippery. The addition of 10 and 15 per cent colloidal silica causes a rise of the coefficient of friction by 18 and 50 per cent respectively without reducing the gloss of the polish. A tough and hard-wearing waterproofing plastic coating based on CNSL-formaldehyde synthetic resin has been developed for building boards, concrete roofs, etc. An attempt to evolve a simple, quick and efficient method of pile testing has resulted in the introduction of a new method called 'Method of equilibrium'. An apparatus has been fabricated to apply different vertical pressures on the soil surrounding a pile. The use of a small amount of bentonite slurry during boring operations has been found to prevent sand boiling in casing pipes. Model studies conducted in the laboratory to test the nature of correlation existing between static and dynamic cone penetration values have shown that the relation is linear in loose soils and exponential in dense soils. A soil pressure cell of the diaphragm type has been designed and fabricated. A simple method applicable to both single barrels and long multiple shells has been developed to analyse prestressed cylindrical shells. Design tables have been prepared for folded plates of various shapes and spans. A simple and quick method for the determination of transient thermal response of building elements from frequency response data has been worked out.

An equation of the type $L_\theta = L_m \operatorname{cosec} (\theta+\alpha-15)$ which gives the sky luminance of the sky opposite to the sun and beyond 60° on either sides, where L_θ is the luminance at an altitude θ; L_m, the observed minimum luminance; and α, the solar altitude, has been derived.

A portable high gain chopper amplifier has been designed for field measurement of temperature. A portable and collapsible unit frame scaffolding and a double deck scaffolding both made of steel have been developed.

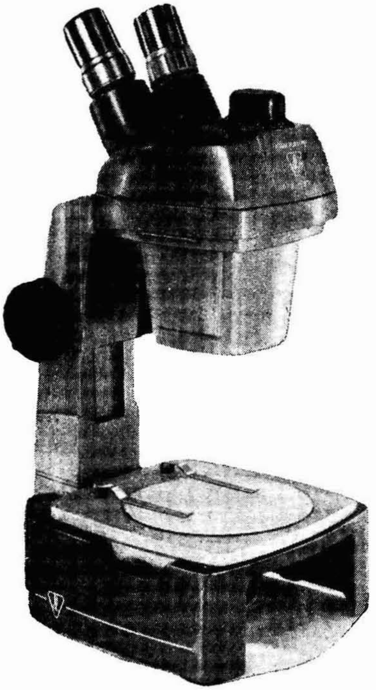
New Periodicals

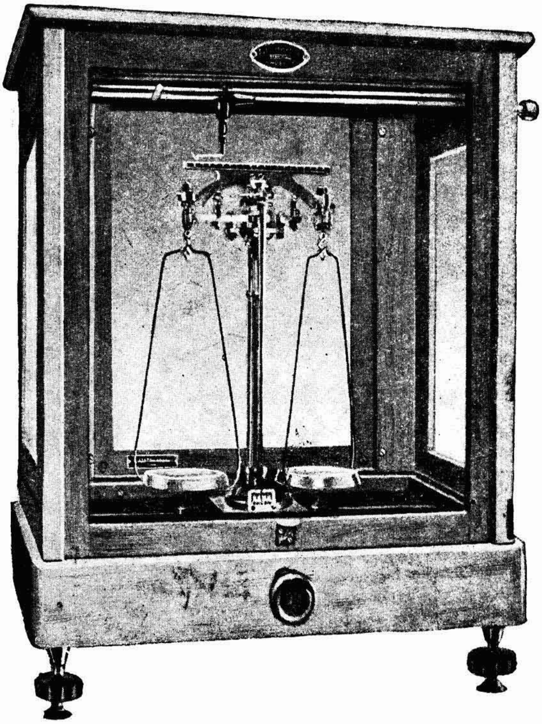
Molecular Crystals

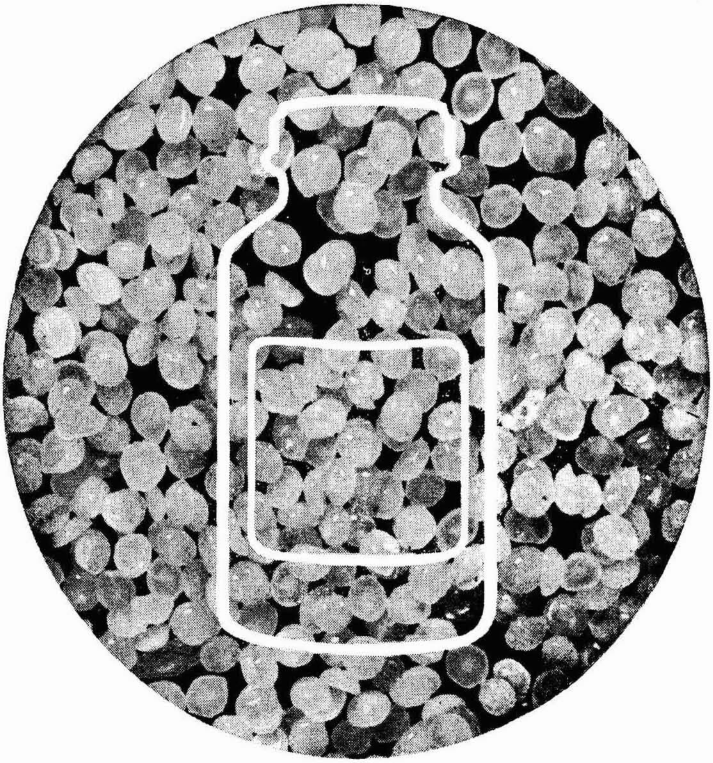
This new quarterly journal to be published by Gordon & Breach Science Publishers, New York, will commence publication from January 1966. The journal will carry original research papers dealing with molecular crystals and related topics such as crystallinity in polymers, liquid and plastic crystals and systems of biological interest. The topics to be covered include energy and charge transfer processes, photo and radiation effects, optical properties, magnetic properties, band structure and bonding, diffusivity and solubility, surface phenomena, crystal growth and structure. The annual subscription for the journal will be $ 20.00 per year; for individuals the rate of subscription will be $ 9.50.

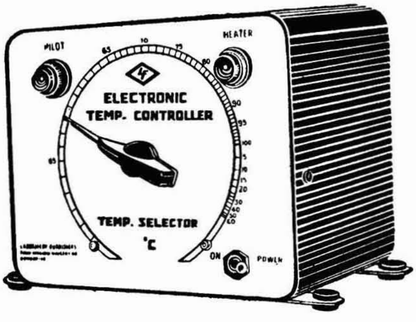
Nuclear Data

Academic Press, New York, are shortly starting this new journal, to be devoted to compilations and evaluations of experimental and theoretical results in nuclear physics. The journal will cover experimental and theoretical work on the basic properties of atomic nuclei, such as cross-sections, magnetic moments, energy levels, radioactivity, masses, transition probabilities and gamma-ray conversion. The journal, to be released irregularly, will have two sections — Section A to be devoted to data on cross-sections, binding energies, lifetimes, magnetic moments and related topics; and Section B to nuclear data sheets. Each volume will be priced $ 15.00.





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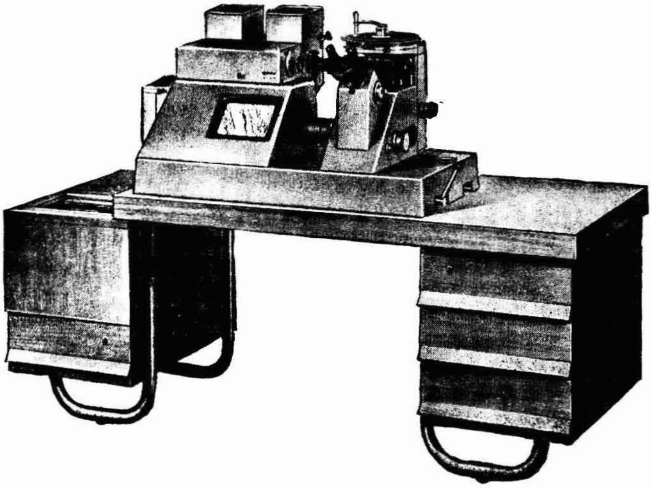

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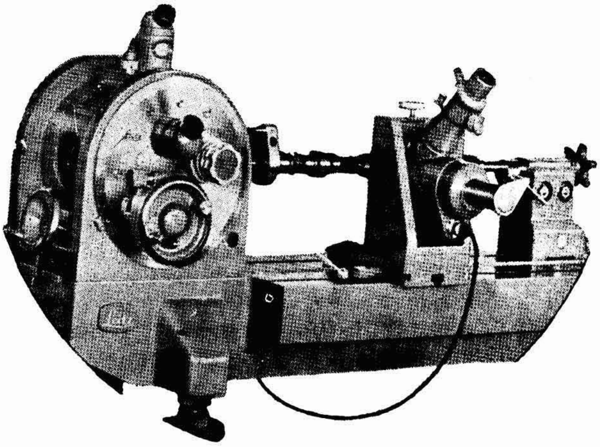

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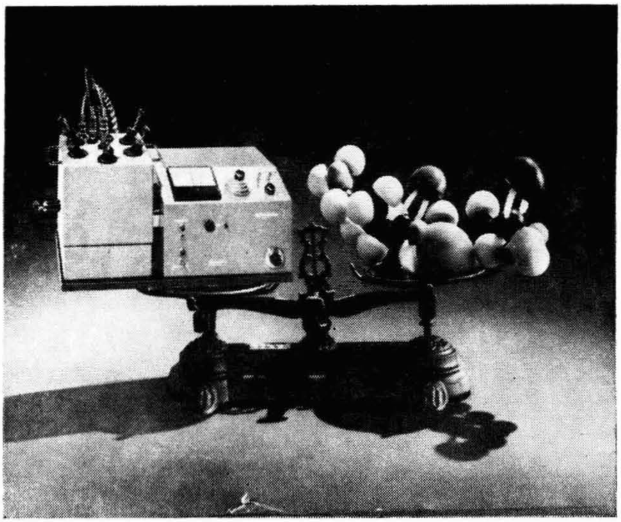

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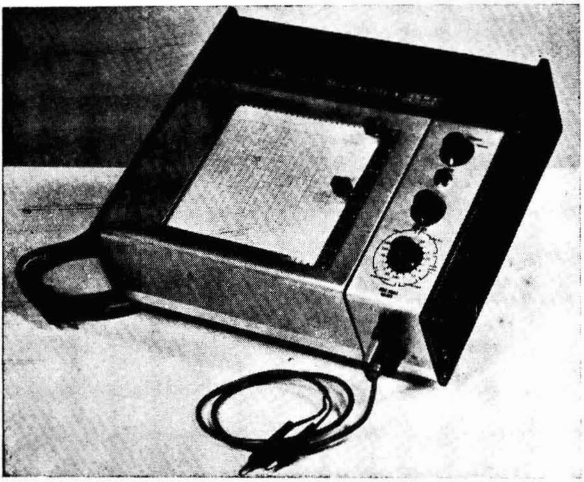

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