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CONTENTS

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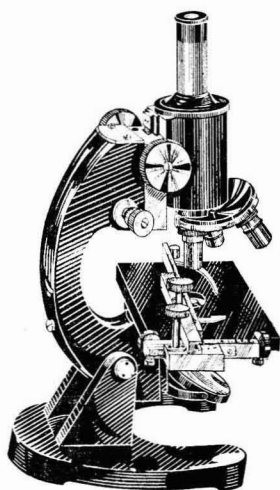
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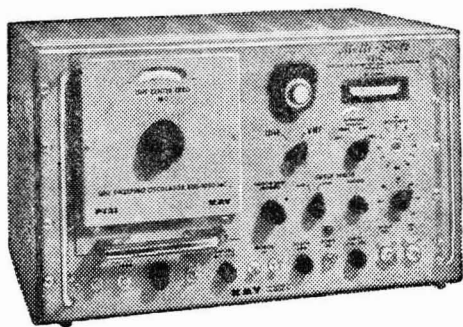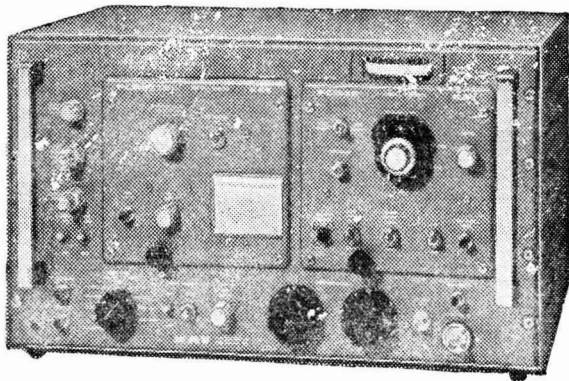
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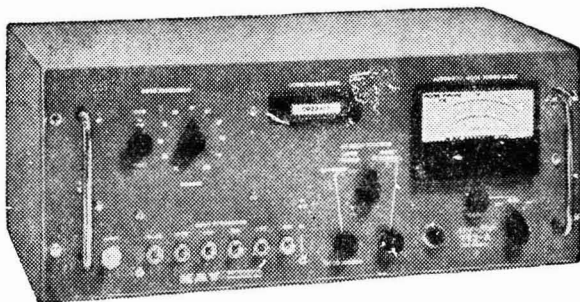
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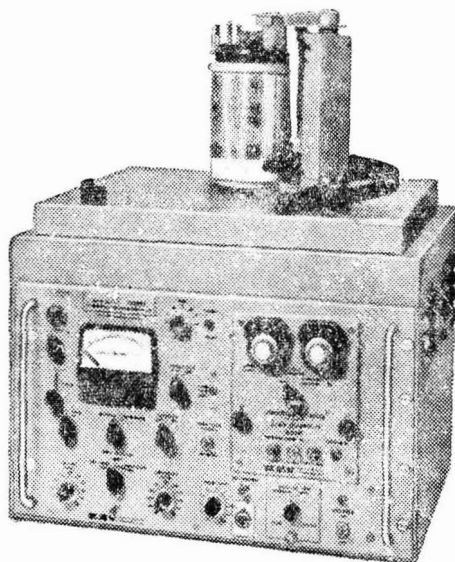
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Current Topics

Pasteur Institute, Coonoor — Diamond Jubilee

THE Pasteur Institute, Coonoor, celebrated its Diamond Jubilee on 6 September 1968, marking the completion of its 60 years' pioneering research work on rabies and other viral diseases in India. The inauguration of the Diamond Jubilee celebrations by Dr Zakir Husain, President of India, underlines the signal services the Institute has rendered the country.

A souvenir issued on the occasion highlights the numerous and varied contributions of the Institute in tackling the problems connected with the control of rabies and other viral diseases, malaria, kala-azar and typhoid. Started in 1907 with the limited objectives of making available effective means of preventing the occurrence of rabies, spreading the knowledge of such means among the public and undertaking research work on rabies, the Institute has diversified and expanded its activities over the years. The Institute is now internationally recognized as an important centre for rabies research; it is also serving as the International Reference Centre on Rabies of the WHO. Besides being the main laboratory for work on influenza in the country, it functions as the Government of India Influenza Centre. An important activity of the Institute has been the provision of training facilities in bacteriology and virology.

Notable among the Institute's contributions in the fields of viral diseases are: the development of an improved antirabies vaccine with which both the duration of treatment and the dosage of vaccine for human treatment could be reduced; a single dose antirabies vaccine containing live rabies grown in tissue culture for the prophylactic immunization of dogs; a vaccine against influenza virus grown in tissue culture, expected to be of help in controlling the future epidemics of influenza; a smallpox vaccine containing vaccinia virus grown in tissue culture; and a live oral poliovaccine.

A simple and elegant method developed for the cultivation of influenza virus using a medium containing sodium pyruvate, glycine, sodium molybdate, folic acid and glycerol has the advantage of making it possible to grow different strains of influenza virus in large quantities in a short time. The method also enables the production of good complement fixing antigens for diagnostic purposes.

A welcome addition to the research programmes of the Institute since its Golden Jubilee in 1957 has been its work on intestinal viruses. Valuable investigational work has been done in the epidemics of encephalitis among children in Delhi, Nagpur, Palghat, Coimbatore and Dhalavoipuram. Useful basic data have been collected on the epidemiology of poliomyelitis in Southern India; these data form the basis of a large-scale programme of immunization of children against poliomyelitis. The Institute has been chosen as a centre for the production of live poliovaccine for the protection of about 50 million susceptible children in the country and is now actively engaged in this work.

Among the major activities of the Institute, its work on the preparation and supply of antirabies vaccine itself during the last 60 years has been of gigantic magnitude. Besides supplying vaccine for the treatment of about a million human beings and about a lakh of animals, the Institute has maintained and conducted a critical analysis of case records of a majority of the patients treated; this has led to the important finding that among the different types of vaccines used at the Institute during the last 60 years, the best results are obtained with carbolized 5 per cent vaccine prepared from the brain of sheep inoculated with the Paris strain of rabies fixed virus. A finding of even greater significance has been that on pooling the vaccines prepared from different sheep, the antigenic value of the pooled vaccine is superior to that of the reference vaccine as well as the individual batches. On the basis of this finding, the Institute has been producing pooled vaccines for the past few years and this method is now being adopted by other institutions in the country and abroad.

The Institute can justifiably be proud of its achievements. Its impressive record of research should enable the Institute to play a leading role in medical and public health research and preventive medicine, and to enrich the field of virus research as in the past.

Some Developments in Carbon & Graphite Research

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UNDER the joint auspices of the University of Newcastle-upon-Tyne, the British Coke Research Association, the Carbon and Graphite Groups of the Society of Chemical Industry (London) and the Institute of Physics and the Physical Society (London), a symposium on 'Carbon and Graphite' was organized during 2-5 July 1968, in the University of Newcastle-upon-Tyne. The symposium was held specially in honour of Lord Wynne-Jones on the occasion of his retirement from the University and from the Directorship of the Northern Coke Research Laboratories in Newcastle. It was attended by about 160 people from research and industry, including 40 from overseas. The papers presented were divided over four broad fields: (1) Structure and properties of coke; (2) Reactivity and utilization; (3) Electronic properties; and (4) Adsorption.

Structure and Properties of Coke

It is generally accepted that the technically important characteristics of coke are determined primarily by the chemical and petrological nature of the coals used, and by the particle size distribution and homogeneity of the coking blend. The influence of these factors on coke properties is exerted largely through their effects on the rheological behaviour and shrinkage phenomena accompanying coke formation. Basic investigations undertaken in the last few decades have thrown much light on the fundamental structural phenomena concerned in carbonization. A general survey of the results of these investigations was presented by H. E. Blayden (British Coke Research Association, Chesterfield). The development of some properties of coke (like molecular weight, presence of free radicals, etc.) having a contributory influence on the strength and mechanical behaviour of coke was also discussed. The occurrence of fissures in coke structure and the experimental difficulty of studying these fissures were specially pointed out.

Recent advances in X-ray data handling and interpretation of the patterns for metallurgical cokes and carbon blacks were discussed by S. Ergun (Bureau of Mines, Pittsburgh), who showed that the layer domains are much larger than indicated by analysis of peak profiles assuming perfect layers. Defects, interstitials and strains modify the peak profiles considerably and the profiles may not yield the proper size of a defective structure. So far no direct correlation has been found between the properties of coke in the pulverized form and its mechanical strength in a block. Apparently it is not the arrangement of carbon atoms or micropores, but the macropores and cracks which determine stability and strength. This led to a study of the

small angle X-ray scattering characteristics of cokes, the results of which were presented by Ergun.

L. S. Singer (Union Carbide Corp., USA) pointed out the importance of the structures of aromatic compounds and their reactions in elucidating the initial and intermediate reactions in carbonization. Free radicals play a vital role here and electron spin resonance techniques are proving to be increasingly useful for such studies.

Reactivity and Utilization

The rapidly growing use of graphite in the electro-thermal, electrochemical, nuclear and refractory industries is focusing increasing attention on the fundamental mechanism of graphite crystal growth. The present state of knowledge in this field was reviewed by H. L. Riley (Wolvercote, Oxford), who discussed (1) the mechanism of graphitization; (2) thermal graphitization and the effects of (i) inorganic impurities, (ii) the character of the carbon, and (iii) the ambient atmosphere; (3) graphite from carbon monoxide; (4) solution precipitation graphitization; and (5) natural and artificial graphites. Attention was specially drawn to the fact that high temperatures in the range 2700-3000°C. generally used in graphitization are not likely in nature and hence natural graphites might have formed at lower temperatures by some dynamic metamorphosis. Present indications are that graphitization is not a purely thermal recrystallization process. The influence of traces of copper oxides and rare earth oxides on graphitization has also been generally recognized in recent years. The maximum observed in the thermal expansion (Δl vs T) curve of carbon monitors is suspected to indicate the temperature at which graphitization starts — the contraction after the maximum must be due to the formation of new covalent bonds leading to graphitization. Here one may recall the earlier ideas of Hedvall that when a solid passes through a transition at high temperature, its reactivity is very much increased; also, foreign atoms or impurities tend to loosen the lattice structure and thus increase reactivity. The general conclusion is that making graphite at temperatures far below 2700°C. is a definite possibility; a good deal of research directed to that goal is already going on in several industrial laboratories.

The importance of carbon in ferrous metallurgy can be seen from the fact that the present total world production of 500 million tons of steel requires about 500,000 tons of carbon. The iron-carbon system was discussed in detail by K. H. Jack (University of Newcastle). Eleven distinct phases have been identified so far in the Fe-C system; two more have been reported, but not confirmed. The properties of iron and steel depend markedly on the distribution of these phases, e.g. nodular

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cast iron containing spherulites of graphite is much less brittle than grey cast iron of the same composition where the graphite is present as flakes. In all iron-carbon interstitial alloys the small non-metal atoms occupy a proportion of the holes between a relatively close-packing of iron atoms. At temperatures below 400°C., the diffusion of metal atoms is so slow that many important phase transformations occur solely by movement of carbon atoms. The metal lattice is perhaps distorted, but its atoms retain their relative positions. Thus, the properties developed by the ageing and tempering of steels are due to the behaviour of carbon, not iron. Very little is known about the interatomic bonding between iron and carbon, but Mössbauer spectroscopy is proving to be a very promising tool for investigating this problem.

A survey of the methods of industrial production of graphite was given by M. Smith (Anglo Great Lakes Corp. Ltd, Newcastle). About 70 per cent of all graphite produced goes as electrodes for use in electric arc steel furnaces. Two other major uses are as anodes in the electrochemical production of caustic soda and chlorine and as nuclear ('isotropic') graphite for power reactors. The rest of the graphite is consumed in a myriad of individually small but specific requirements.

The preparation of carbon fibres from polyacrylonitrile (PAN) fibres was reviewed by W. W. Watt and W. Johnson (Royal Aircraft Establishment, Farnborough). They also described the effect of length changes on the Young's modulus of these films. Tows of PAN fibres are oxidized in air at 220°C. while hanging freely with different loads on them and the length changes measured. The oxidized fibres are then carbonized and heat treated to 2500°C. and their Young's modulus determined. It is found that the moduli increase with increase in length of the oxidized fibres.

The use of graphite as moderator for nuclear reactors was reviewed by Wright, Simmons and Mason (Harwell). This field is dominated by two major problems: irradiation effects on physical properties of graphite and compatibility of graphite with gas coolants. In present-day reactors, each carbon atom may be displaced 20 or 30 times during reactor life, but the conditions are such that permanent lattice damages are small and the stored energy effects are no longer significant. Crystal dimensions do change and affect the behaviour of the polycrystalline aggregate, but the use of isotropic graphites and the relief of internal stress by radiation-induced creep maintain the bulk changes within acceptable limits. Predicting graphite behaviour over a 30-year life under irradiation involves extrapolation of expensive life-dose testing. These tests can now be reduced by using a correlation between bulk dimensional changes and the thermal expansion coefficient. The quality of nuclear graphite is also substantially improved by using petroleum coke, instead of metallurgical coke, as the raw material with its much lower impurity content (particularly rare earth elements). Fundamental studies have also yielded a detailed knowledge of carbon-removal reactions between graphite and gaseous coolants. For instance, under irradiation CO_2 breaks up into many reactive species represented by [O].

$$CO_2 + \text{irradiation} \rightarrow CO + [O]$$
$$C + [O] \rightarrow C(O) \text{ (chemisorbed)}$$
$$C(O) + \text{irradiation} \rightarrow CO \text{ and } CO_2$$
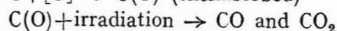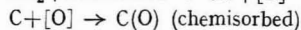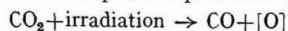
These oxidation reactions could be suppressed to a great extent by adding 0·1 per cent methane to the coolant gas. Evidence for the mechanism of methane inhibition, has been obtained by R. Lind (UK AEA, Culcheth) from the analysis of transients in experiments with ^{14}C-labelled graphites — chemisorption processes and protection by radicals formed by the radiolysis of methane-CO_2 mixtures are indicated. Modifications to coolant composition provide a cheaper, simpler and more effective solution to the problem than changes of graphite properties, though low accessible porosity and the proper pore size distribution are often specified.

Surface investigations of graphite oxidation and of deposition of carbon on metal catalysts were discussed by J. M. Thomas (University College of North Wales, Bangor). For both these problems, topographical studies with gold-decorating technique in electron microscopy is capable of detecting monolayer steps, thus offering a means of arriving at order of magnitude estimates of the number of 'active' sites on the surface. The results of a time-lapse cinematographic study (16 mm. film), carried out in collaboration with P. L. Walker of Pennsylvania State University, were also presented, showing the disproportionation of carbon monoxide, $2CO \rightarrow CO_2 + C$, on a number of catalyst surfaces, including iron, cobalt and nickel. The film shows that the catalytic activity of polycrystalline iron is influenced by the support material, it being less on single crystal cobalt than on single crystal nickel. Other facts revealed by the film are: (i) faceting of the faces of a cobalt crystal occurs during the course of catalysis, (ii) certain types of dislocation cores are active centres for the deposition of carbon, and (iii) two kinds of carbon tend to be deposited on a given surface.

Electronic Properties

The electron transport properties of graphite were reviewed by A. R. Ubbelohde (Imperial College, London). Some electronic properties are much more sensitive than others to structural defects. A scale of perfection of general applicability can be based on the temperature coefficient of resistivity as well as on the absolute resistivity around 300°K. Other electronic properties such as the Hall effect, magneto-resistance and the thermo-electric power are much more structure sensitive. Their dependence on field strength and temperature yields correspondingly more information about the range of charge carriers and about defect structures in near ideal graphites.

Carbon membranes are obtained by the reduction of graphite oxide membranes. The change in electric resistance during the thermal reduction in hydrogen, hydrazine and hydrogen iodide was followed by J. Maire (Le Carbone-Lovaine, Paris). Depending on the pretreatment and the gas used for reduction, graphitization is found to occur at considerably lower temperatures (600-1200°C.). The

electrical resistance of evaporated carbon films on adsorption of oxygen and other gases was discussed by J. C. Orr (University of Dundee). For heat treatment temperatures (HTT) below 100°C., oxygen had no effect on resistance at room temperature, but the oxygen sensitivity increased steadily for HTT above this value. The original resistance could be restored only by evacuating at the temperature to which the films have been previously heat treated. Activation energies for oxygen chemisorption calculated from rates of resistance change between 22° and 203°C. increases from 6 to 14 kcal./mole. Water vapour also increases the film resistance at 22°C., though to a less extent than with oxygen. Helium increases the resistance at −196°C., indicating that physical adsorption does take place.

In reviewing the electron spin resonance characteristics of carbons, Mrozowski (State University of New York, Buffalo) dealt with the directional and the motional averaging, the mixing of the g values of conduction carriers with localized spins as deduced from experimental data, the influence of the position of the Fermi level and of the spreading of graphitic layers by donors and acceptors, etc. Carbon blacks, soft and hard carbons and chars have been studied. The Curie temperature dependence is generally found to be valid; deviations occurring are suspected to be due to the beginning of the conduction electron spins.

The g factor anisotropy of carbons was discussed by A. Marchand (Bordeaux), who studied the variation of g as a function of (i) temperature, (ii) high temperature treatment, and (iii) temperature of deposition of carbon. In most cases, the e.s.r. line of a powdered carbon is centred on a g value which is quite different from the true average g value. Hence, significant measurements can be made only in very special cases as, for instance, rhombohedral graphite, where all crystallites have their c axes nearly parallel, or some carbon blacks.

Free radicals on the surface of carbons and their reactions with oxygen can be followed by e.s.r. studies. R. C. Seymour (University of Bristol) studied e.s.r. and electrical conductivity of carbons formed from pure organic polymers and the effect of oxygen on these properties. The polymers used are polyvinyl chloride (PVC) and acetate, which yield graphitizing carbons, and polyvinylidene chloride (PVDC) which yields non-graphitizing carbons. The effect of oxygen on the e.s.r. properties of PVDC carbons is instantaneous and reversible and may be attributed to physical adsorption. With PVC carbon, physical adsorption of oxygen is time-dependent, the rate being presumably controlled by diffusion into pores. The coefficients of diffusion may be estimated from e.s.r. data. Adsorption at different temperatures also permits approximate calculation of heats of adsorption from e.s.r. data. Long exposure to oxygen at room temperature indicates some chemisorption on PVDC carbon, in addition to the instantaneous physical adsorption. The time processes can be studied separately by e.s.r. Measurements of electrical conductivity show that the carbons are semiconductors and suggest that free radicals formed in the carbon contribute

'impurity' levels. In all these studies, the free radicals cover only about 0·1 per cent of the total surface of the carbons.

J. W. Patrick (British Coke Research Association, Chesterfield) reported the results of a comparative e.s.r. examination of sulphur-carbons prepared by (i) the reaction of 'polymer carbons' with (a) sulphur or (b) with hydrogen sulphide, and (ii) pyrolysis of (a) either mixtures of pure organic materials with elemental sulphur or (b) organic sulphur compounds. Formation of sulphur carbons from (ia) showed some systematic changes in the e.s.r. of carbon. The observed changes can be explained in terms of bonding of sulphur to carbon as surface complexes, possibly forming peripheral heterocyclic structures on the exposed lattices in the carbon surface or sulphur bridges between neighbouring layers. The reaction of carbon with hydrogen sulphide (ib) also results in the formation of sulphur-carbons, but no systematic e.s.r. behaviour is observed. Pyrolytic sulphur-carbons show e.s.r. characteristics and behaviour similar to those of carbons in general. The presence of high concentration of both unpaired electrons and sulphur is considered to be indicative of the sulphur being incorporated into the carbon layers as heterocyclic structures.

Mrozovski has sounded three points of caution for any e.s.r. work on carbon: (1) If there is a line broadening, the absorption intensity cannot be followed except by the best of e.s.r. spectrometers. (2) The absence of an e.s.r. signal does not necessarily mean that there are no free radicals in the carbon sample. (3) Deviations from Curie-Weisz law are deceptive and can often be traced as due to apparatus error or inadequate outgassing of samples. Only when conduction electrons are brought in at very high temperatures can real deviations from the law be observed.

Adsorption

The chemisorption of oxygen on graphitized carbon black surfaces was discussed in detail by P. L. Walker (Pennsylvania State University). Vacuum of the order of 10^{-6} mm. Hg cannot clean carbon surfaces; even 10^{-9} mm. Hg is not sure of cleaning all the surface. Using a mass spectrometer, a differential manometer and an ultrahigh vacuum microbalance, oxygen chemisorption has been monitored at 25°C. over the pressure range 1 millitorr to 1 atm. Elovich plots of the data exhibit distinct breaks, suggesting that there are five different sites for chemisorption. At low pressures, the adsorption rate is so slow that only adsorption on the first site can be followed; at intermediate pressures more sites are covered. Another remarkable observation is that oxygen chemisorption on carbon becomes exceedingly complicated if water is present. The water adsorption on carbon is also very sensitive to the oxygen present. Thus, on O-free carbon surfaces water adsorption is poor and fully reversible. On introducing some oxygen, a monolayer of water can be adsorbed over the chemisorbed oxygen as if the water molecules are sitting over the oxygen atoms. This seems to be the first case where equal amounts of physical adsorption and chemisorption have been measured simultaneously on one and the

same small part of the total surface of an adsorbent. In contrast to this, oxygen has no noticeable effect on carbon dioxide adsorption on carbon. For removing oxygen from the surface, treating the carbon with hydrogen at high temperatures is comparable to ultrahigh vacuum.

S. J. Gregg and J. F. Langford (Brunel University, London) illustrated the errors introduced into the calculation of BET surface areas of microporous carbons from low-temperature adsorption of nitrogen, due to too early filling of the micropores. The nitrogen isotherms on carbon initially and with different amounts of presorbed nonane vapour are parallel in the multilayer region; the vertical separation of the two isotherms, corresponding to the completely empty and completely filled micropores, is equivalent to the micropore volume. This is reminiscent of the practice followed in many industrial laboratories for quick determination of

micropore volume; nonane (or cyclohexane if pores are not too small) is introduced to the evacuated adsorbent or catalyst sample taken on a McBain sorption balance. After attaining equilibrium, nonane is pumped out with an oil pump at room temperature. The amount desorbed is assumed to be from the macropores and that which still remains on the catalyst is in the micropores.

The different types of acidic or basic groups on carbon surfaces and the methods for their identification and estimation were discussed by H. P. Boehm (University of Heidelberg). A detailed review on this topic has earlier been published by him [*Adv. Catalysis*, **16** (1966)].

The symposium was indeed a fitting tribute to Lord Wynne-Jones and an open acknowledgement of his outstanding contributions to the varied aspects of the chemistry and technology of coke, carbon and graphite.

Symposium on Chemicals & Oils from Coal

A Symposium on Chemicals and Oils from Coal will be held at the Central Fuel Research Institute (CFRI), Dhanbad, during 21-23 February 1969. The symposium will broadly cover the following aspects: (1) Development of carbo-chemicals from coal, coal tar distillates and benzole including refining, recovery and use; (2) Direct conversion of coal to oil and chemicals; (3) Chemicals and oil by Fischer-Tropsch synthesis and oxo-synthesis; (4) Catalysis in carbo-chemical synthesis; (5) Production of agricultural chemicals including fertilizers, soil conditioners, pesticides, insecticides, ion exchangers, detergents, etc., from coal; (6) Production of coal chemicals by oxidation, hydrogenation, nitration, halogenation, electrochemical reduction, biodegradation, etc.; (7) New techniques of chemical synthesis, e.g. irradiation, ultrahigh temperature reaction, microwaves; and (8) Analytical techniques for evaluation, characterization and identification of

coal chemicals. Papers will be presented and discussed at the following technical sessions: (I) (i) Recovery, refining and synthesis of carbo-chemicals and their techno-economic consideration vis-à-vis petrochemicals; and (ii) Agricultural, pharmaceutical and other carbonization; (II) Synthesis of oil hydrocarbons and chemicals (hydrogenation and solvent extraction, Fischer-Tropsch synthesis, oxo-synthesis, and catalysis in relation to the above processes); and (III) (i) Chemicals by direct conversion or degradation of coal by oxidation, nitration, electrochemical reduction, etc.; (ii) Fertilizers, soil conditioners and chemicals by biodegradation, biosynthesis, etc.; and (iii) Chemicals by irradiation, ultrahigh temperature reactions in plasma, microwaves, etc.

Further details regarding the symposium may be had from the Organizing Secretary, Symposium on Chemicals and Oils from Coal, Central Fuel Research Institute, P.O. FRI, Dhanbad.

Q-Switching Techniques for Solid State Lasers Operating at Room Temperature

A. N. BHATTACHARYYA, V. V. RAMPAL & N. MANSHARAMANI

Instruments Research & Development Establishment, Dehra Dun

THE idea of release of stored energy in the laser material in a very short duration was first given by Hellwarth[1] in 1961 and later demonstrated by McClung and Hellwarth[2] using electrooptical shutter. During the period of excitation, the loss of excited ions is prevented by keeping an electrooptical shutter in the optical cavity between the total reflecting surface and the laser material, i.e. the cavity quality factor Q is reduced. When sufficient population inversion is attained by excitation energy in the laser material, the shutter is suddenly opened (thus improving the cavity Q) and the stimulated radiation builds up by multiple reflection between cavity reflectors and is released in a giant pulse of high peak power. The phenomenon is known as Q-switching or Q-spoiling. The type of control on cavity Q determines the type of Q-switching technique. The present paper reviews the literature in this field for workers who are interested in developing some particular technique like laser ranging. The phenomenon is of considerable interest in situations where high peak power and short duration are important.

The purpose of Q-switching is not to economize in energy. In fact, with Q-switching the total coherent radiation obtainable with a given flash of excitation is substantially decreased. The main advantage of adopting this technique is in getting a high peak power several orders of magnitude greater than the value obtained from ordinary laser pulse and a well-defined shape and time of the output pulse. Peak powers of the order of 10 billion watts and durations of 0·1 nanosecond are now practically achieved[3].

Switching Speeds

It has been suggested that in order to analyse the time behaviour of the output pulse it is convenient to consider three domains of switching speeds, fast, medium and slow, depending on the relative values of switching time of the output pulse. In the case of fast switching, where the time for switching from a low to high Q value is very small compared to the build-up time of the pulse, the analysis is comparatively simple and has been attempted by various workers[4-7] to estimate the peak power and pulse shape of the output pulse. A typical time behaviour of effective reflectivity, population excess and output beam power for a giant pulse with fast switching is shown in Fig. 1. It may be seen that the value of T_S (the switching time) in relation to T_D (the build-up time) will determine whether the switching is fast, medium or slow. The switching time is a function of the mode of switching, whereas the build-up time depends, among other factors, on the cavity length. However, the main effect of stretching the period of switching is generally to liberate the

energy $\frac{1}{2}\hbar\nu(n_i - n_f)$ over a longer period of time with consequent reduction in peak power.

Methods of Switching

The methods available for Q-switching the laser can be broadly categorized into (i) mechanical systems; (ii) electrooptic and magnetooptic shutters; (iii) ultrasonic cell; and (iv) passive systems.

Each of the above methods has its own merit. Whereas some are preferred for their high switching speeds, others are employed because of their simplicity and low cost.

Mechanical Systems

Q-switching by mechanical means is achieved either by using a rotating chopper wheel[8] between the laser rod and the fully reflecting mirror or by spinning the fully reflecting surface of the laser cavity. This surface may either be a coated mirror or a total reflecting prism. The laser cavity is formed by two reflecting surfaces mounted externally to the laser material, one fully reflecting and the other partially reflecting. The output is obtained from the partially reflecting surface. For Q-switching, after optical pumping has been initiated, laser action has to be prevented till such time when the population inversion reaches a high value. This is done by obstructing the path of light[8] or by keeping the cavity Q low by using a rotating surface[9-17]. When the population inversion reaches a high value, cavity losses are suddenly reduced to a minimum. This is achieved by opening the path of light or by bringing the rotating surface in parallelism. The adjustments
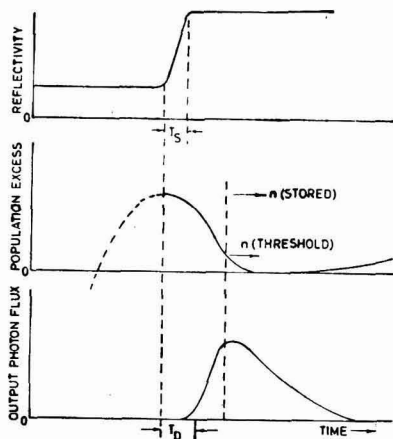
Fig. 1 — Effective reflectivity, population excess and output beam power for a giant pulse with fast switching in a typical time sequence [T_D, build-up time; and T_S, switching time]

of various timings, namely the duration of high loss condition starting from the flashing of optical pump and time taken for switching to low loss condition (the switching time), are related to such factors as the duration of pumping pulse, the speed of rotation of the mechanical system, and the build-up time for the output pulse. For achieving the necessary adjustments of timings in practical conditions (i.e. synchronizing of the firing of flash tube with the rotation of the system) electronic circuitry has to be incorporated using a suitable timing signal pick-up and a delay circuit, so that the firing of flash tube occurs at a predetermined time before the high Q condition is reached. The principal disadvantage of the mechanical switching is its slowness. To achieve a switching time of the order of a few nanoseconds, mechanical rotation problems become very acute. Of the two mechanical systems mentioned above, the rotating prism arrangement is the faster. It is in fact the most favoured mechanical method for the generation of giant pulses.

The effects of the various experimental parameters involved in spinning reflector technique have been investigated and conditions for optimizing the output have been discussed[11,12]. Practical considerations demand proper control of the spinning rate, reflector separation, reflector transmission and energy input if a high power single pulse output of small duration is required. It has been shown that for optimum condition the switching time should be approximately equal to the pulse build-up time. Various methods have been suggested for increasing the spinning rate, using multiple reflections between the spinning reflector and a stationary total reflecting prism, interposing a quartz Lummer-Gehreck plate between the reflector and the laser rod[10] and introducing an afocal system of magnification m between the laser rod and the rotating roof prism[13]. For every high peak power systems, the choice of suitable type of resonant cavity reflectors plays an important part. Dielectric coated optical flats, Porro prisms and glass etalons[18] have been used for the purpose. It is also necessary that even the stationary partially reflecting surface should be mounted external to the laser rod. An important advantage of using a Porro prism as one of the reflecting elements is that alignment problems are reduced[11]. Use of the Porro prism with the edge horizontal and rotating around a vertical axis avoids misalignments due to vibrations of the system[12]. Furthermore the C-axis of the laser rod has to be either parallel or perpendicular to the prism edge, to avoid a threshold increase due to loss of linear polarization in the total reflection process[12].

Electro- and Magnetooptic Shutters

Fast switching can be achieved by using electro-optic shutters placed between the laser rod and one of the reflectors[2,19-22]. A Kerr cell is placed so that its electric field is 45° to the plane of the rod C-axis. When the Kerr cell is on, the polarization of the light that passes through it twice is turned through 90° from the desired plane of polarization so that the feedback is insufficient for oscillations, thus enabling the population inversion to build up to a high value when the flash lamp is fired. The high

Q-switching is done by turning off the Kerr cell. Pockel cell (utilizing the linear electrooptic effect of change of optical property of a piezoelectric crystal with electric field) has also been used as an electro-optic shutter for Q-switching a laser[23,24].

Magnetooptic shutter (employing Faraday effect) has also been used[25]. The advantage of the electro-optic and magnetooptic shutters lies in the availability of fast switching speeds, but additional circuit-like power supplies, etc., make them less desirable in some cases.

Ultrasonic cell — Another method of changing the Q of the laser cavity depends on the deflection of light waves in an ultrasonic field[26-28]. A fluid cell is placed between a reflector and the laser rod. Due to the ultrasonic vibrations communicated to the liquid, the density and hence the refractive index of the liquid is changed, thus deflecting the light beam. The deflection of the light is such that after passing through the cell it falls normal to the already deflected reflector. In the unexcited state of the cell the light falls obliquely on the deflected reflector so that the cavity losses are very high. The high Q condition is thus switched by exciting the ultrasonic cell at the desired instant.

Passive systems — Recently a lot of effort has been directed towards Q-switching the laser by passive[29-49] means. These have the advantages of speed and simplicity. These methods can be classified in two categories, using either photosensitive substances or self Q-switched laser materials.

A photosensitive substance which is highly absorbent initially but becomes transparent (or highly reflecting) on strong illumination is either placed between the laser rod and the reflector or is used as one of the reflectors itself. Coloured glasses[50] and solutions containing organic dyes[33,44,46] have been used for this purpose. Irreversibility of action[51] is a disadvantage in certain cases, but reversible materials are also available[29,30,32,34].

Thin films of semiconductor materials which increase their reflectivity upon strong irradiation have been used as passive Q-switching devices[31,36], but the rapid deterioration of these surfaces is a serious disadvantage.

Self Q-switched laser action has also been obtained using either multiple doped laser material[43] or saturable absorption of short-lived colour centres in singly doped laser materials[40]. In these cases, external means of Q-switching are not needed; composition of the laser material and desired manner of pumping are sufficient requirements for obtaining the characteristic high peak narrow width output of a Q-switched laser.

Practical Considerations

The components to be used in a solid state Q-switched laser have to meet certain specific requirements of quality and precision.

Laser material — Various materials have been used for making the laser rod, the important ones being (i) pink ruby ($Cr^{3+}: Al_2O_3$); (ii) neodymium-doped glasses; (iii) $Nd^{3+}: YAlG$; and (iv) $Nd^{3+}: CaWO_4$. Multiple doping with such ions as Nd^{3+}, Cr^{3+}, UO_2^{2+} Yb^{3+} has also been employed in different hosts. In the case of pink ruby, the concentration of

chromium is normally 0·05 per cent by weight of Cr_2O_3, whereas in the case of neodymium-doped glasses, the doping varies from 1 to 5 per cent by weight of Nd_2O_3. The crystalline material from which the laser rod is made is required to be homogeneous throughout its length and free from seed, bubbles, strains and dislocations. The ends of the rod are to be flat to $\lambda/10$ and parallel to an accuracy of 2 sec. of arc. The rod cylindricity must be maintained to an accuracy of 1 min. of arc. In the case of ruby, the C-axis orientation is also important and should be oriented at 90° with respect to the axis of the rod. In certain cases, the ends of the laser rod are coated with antireflection coatings, but these coatings get damaged for very high peak power levels.

Pumping source — The laser rod is normally pumped by a set of xenon flash tubes capable of giving an output sufficient to pump the laser material beyond threshold. The pulse shape of the pumping light can be modified by the use of a line pulser in the input circuit.

Cavity reflectors — One of the reflectors of the resonant cavity is a partial reflector having a reflectivity governed by the optimum conditions. This partially reflecting surface is either one end of the laser rod coated with dielectric coatings or an optical flat coated with multilayer dielectric coatings. The substrate is of quartz polished to $\lambda/10$ flatness and a wedge of 15 min. of arc or less. The 90° angle of the right angle prism should be accurate to ± 1 sec. of arc. For high peak powers (beyond 10 MW), where optical intensity is too large on a given area, the surface may be made using sapphire as the substrate. For rotating prism arrangements, the prism is normally rotated at 20,000 to 30,000 r.p.m. For specially fast switches, however, rotational speeds up to 90,000 r.p.m. have also been employed. These have been achieved by using air turbines. For high peak powers the coatings on the reflectors deteriorate rapidly with use. For such cases, better and more robust arrangements are continually being sought.

TABLE 1 — Q-SWITCHING USING MECHANICAL ARRANGEMENTS

Laser material	Cavity length cm.	Partial reflector reflectance %	Spinning reflector	Input energy J.	Output peak power MW	Pulse energy J.	Duration nano-sec.	Remarks
Ruby rod[8], 0·5 cm. diam.	—	—	Chopper wheel 1 cm. opening 10000 r.p.m., motor driven	—	—	—	10000	External mirrors used
Ruby rod[9], 0° orient., 7·5 × 0·62 cm.	45	35	TIR prism of grade A Schott glass	1900	2	—	24	Prism surface coated with antireflection coating
	100	30	24000 r.p.m., syn. motor driven	2000	24	—	—	—
Ruby rod[11], 90° orient., 7·5 × 0·62 cm.	60	50	Porro prism, 20000 r.p.m., motor driven	205	2	0·07	30	—
Ruby rod[12], 90° orient., 7·5 × 0·62 cm.	40	70	TIR prism, 90000 r.p.m., air-turbine driven	1000	—	—	20	—
Ruby rod[13], 10·0 × 1·0 cm.	—	50	TIR prism of silica with front surface curvature 9·1 cm.	1000	0·5-0·7	—	2000	Ruby rod one face concave curved with 2·16 cm. curvature external reflectors not used
Ruby rod[14], 60° orient., 17·8 × 0·95 cm.	65	30	Porro prism, 15000 r.p.m., motor driven	1600	5	1·9	50	—
Nd: $CaWO_4$ (ref. 15), 5 × 0·62 cm.	26	99	Porro prism, 24000 r.p.m., motor driven	—	—	—	<100	—
Nd: $CaWO_4$ (ref. 16)	—	80	TIR prism, 24000 r.p.m.	—	—	—	40	—
Ruby rod[16]	—	45	—	—	—	—	30	—
Ruby rod[18], 8·4 × 0·45 cm.	—	17	—	400	—	0·06	50	Sapphire and glass etalon used as reflector
	—	74	—	220	—	0·1	40	
Nd: YAlG (ref. 52), 3·0 × 0·3 cm.	—	99·8	Rotating flat mirror, 6000 r.p.m., motor driven	1000 W.	250×10^{-6}	—	200	Ends of rod coated with antireflection coating; continuously pumped
Ruby rod[54], 11·5 × 1·2 cm.	—	16	TIR prism, 25500 r.p.m.	—	50	—	40-50	Output bandwidth 1·5 cm.⁻¹
Ruby rod[53], 17·8 × 1·6 cm.	178	—	Rotating flat multilayer dielectric mirror, 99% reflecting	13,000	150	5-7	70	—
Nd: YAlG (ref. 17), 3·4 × 0·25 cm.	22	98·4	Multilayer with 50 cm. curvature, 99·9% reflecting, 24000 r.p.m., syn. motor driven	1000 W.	1×10^{-3}	—	200 ± 25	Partial reflector curvature 37·5 cm.

Experimental Data

The results obtained by different techniques are summarized in Tables 1-3. The data are presented broadly under the heads of laser material, type of shutter arrangements, input and output pulse characteristics. The reproducibility of results, however, is very much dependent on the precision of the components used and the perfection of technology employed. The use of a particular technique for a given application is governed by considerations like simplicity of design, ruggedness in operation, economy of space and reliability of components for successive operations.

Applications

The main use of the Q-switched laser is in the field of ranging where the narrow pulse width of the Q-switched laser makes it possible to achieve accuracies of a few metres at distances of a few kilometres. Also high peak powers available with Q-switching enable large distances to be ranged with comparatively simple detection systems. Typically, distances from 10 to 15 km. can be ranged with an accuracy of ±5 m. The pulsed laser range finders have also been used in meteorological research for the study of upper atmosphere and cloud formation.

Conclusion

The technique of Q-switching consists of preventing the normal laser action till sufficiently high population density is reached and then suddenly improving the Q of the cavity so that laser energy is released in a very short pulse of high peak power. This type of output is particularly suitable for ranging applications where narrow pulse width is an advantage towards improvement of accuracy.

To make the system more efficient the importance of proper design of optical coupling, degree of reflector alignment and desired specification of the laser material regarding purity, homogeneity and dimensional tolerances has to be recognized. The variation in efficiency as reflected in the tables can be attributed to the difference in perfection achieved in the above parameters. As the accuracy desired in the reflector alignment is of the order of 1 sec. of arc, even a slight misalignment may cause all the difference in the threshold input and the output obtained. To make the data complete and reproducible it is, therefore, desirable that information on (i) the dimensions and optical quality of the laser material, (ii) the type of optical coupling used, (iii) the degree of alignment achieved, (iv) the type of reflectors and length of cavity, and (v) the threshold energy required may be furnished while reporting the results. Incomplete information as reported in many cases for various reasons is sometimes misleading.

Sufficient scope exists in the field of technology of component development and materials research. Necessity exists for suitable reflectors capable of withstanding high peak powers and efficient pumping sources having desired spectral output. It is desirable that as much of the emission of the flash lamp be utilized for pumping the laser material as possible. For this, effort can be directed in two ways: (i) for a

TABLE 2 — Q-SWITCHING USING ELECTROOPTIC SHUTTERS

Laser material	Cavity length cm.	Reflectance %	Shutter cell	Field applied	Switching time μsec.	Input energy J.	Output peak power MW	Duration nanosec.	Remarks
Ruby rod[2], 2·84×0·9 cm.	—	98, 98	Nitrobenzene Kerr cell with quartz Wollaston prism polarizer	—	0·05 0·11 0·5	—	15 200×10⁻³ 50×10⁻³	30 100 500	For slow switching speed multiple pulses are obtained; peak power is given for the first pulse
Ruby rod[21], 3·0×0·7 cm., 60° orient.	—	75, 75	Kerr cell	45°, quarter wave voltage	0·02	—	300×10⁻³ from each face	120	—
Ruby rod[22], 7·5×0·9 cm.	60	80, 99	Kerr cell with brewster angle polarizer	Half wave voltage	—	1500	10	—	—
Ruby rod[23], 90° orient.	—	—	Two KDP crystal	45° to X and Y axes of crystals, 400 V.	—	—	1	50	—
Ruby rod[9], 90° orient.	50	52, 99	Kerr cell with brewster angle polarizer	45°	—	2400	23	28	—
Ruby rod[25], 7·2×1·0 cm., 90° orient.	—	75, 0	Flint glass cylinder with Nicol prism polarizer	Magnetic field	0·2	424	600×10⁻³	60	—

TABLE 3 — Q-SWITCHING USING PASSIVE DEVICES INCLUDING PHOTOSENSITIVE DYES AND THIN SEMICONDUCTOR SURFACES

Laser material	Cavity reflectors	Passive shutter material	Absorption wavelength A.	Absorption coefficient	Input energy J.	Output peak power MW	Pulse energy mJ.	Duration nanosec.	Remarks
Ruby rod[31]	Polished semiconductor surface	Germanium	—	—	—	—	—	40	Giant pulse is 40 times greater than ordinary laser output
Nd-doped glass[32], 5× 0·62 cm.	—	Polymethine dye 3,3'-diethyl-9,11,15,17-dineo-penthylene-thiapentacarbocyanine iodide	—	0·70	1800	1	—	25	Threshold under ordinary laser action 850 J.
Ruby rod with TIR end[33]	Reflectance 99%	Chloroaluminium or vanadiumphthalocyanines in chloronaphthalene or nitrobenzene, conc. $10^{-6} M$, cell length 3·5 cm.	6943	0·50	—	—	—	20	Chloronaphthalene solution showed tendency to decompose on accidental exposure to intense UV light
Ruby rod[35], 5·0×0·63 cm., 90° orient.	TIR prism and reflectance 50%	(i) Victoria blue B dye (substituted diphenyl-α-naphthyl methane dye) deposited 600 A. layer on glass flat	6940	0·50	—	5-10	—	9-10	—
		(ii) Cryptocyanine (1,1'-diethyle-4,4'-carbocyanine iodide) in methanol conc. 1·8 ×$10^{-6} M$ in. 1×1 cm. cell	7040	0·58	—	5	—	9	—
Ruby rod[36], 6·3×0·63 cm.	Reflectance 65%	Si, Ge, InP, InSb, Ga (As × P₁-X) polished flat	—	0·60	—	—	50-100	30	Materials damaged by giant pulses, but at 50 mJ. the damage was not extensive in first shot; switching threshold 10^6-10^7 W./cm.^{2}
Nd-doped glass[41], 12× 1·2 cm.	Reflectance 98%	Polymethine dye	—	0·60	3000	5	—	35	—
Nd-doped glass[42], 12× 1·0 cm.	Reflectance 90% and 68%	Polymethine dye 1,9-di-(N-ethyl-quinoline-4)-5-acetoxy-non-emethineperchlorate	10300 10900	0·64	—	—	—	—	—
Ruby rod[44]	TIR prism and 40% reflector	Vanadium phthalocyanine	—	—	—	20	—	15	—
Nd-doped glass[45], corning 10×0·95 cm.	—	Polymethine dye	—	—	—	50	500	10	—

given material, choosing a suitable source whose emission matches the absorption band of the material, and (ii) for a given source (e.g. Xe lamp or the Hg arc), improving the absorption characteristics of the laser material so that as much of the source emission is effectively utilized as possible. Multiple doping of the host material is one way of achieving this. Recently, sufficient interest has been created in this field and a number of materials and suitable flash lamps are coming into use.

Another direction in which sufficient improvement could be done is the development of a suitable host material having desirable thermal and mechanical properties. For very high power output good thermal conductivity of the material is a very desirable quality, whereas precise optical working requires sufficient hardness.

Summary

The phenomenon of Q-switching in lasers is of considerable importance, particularly when a high peak power for a short duration is desired. Various types of Q-switching, emphasizing their relative merits and demerits with regard to specific applications, have been discussed. The importance of suitable switching speed in realizing an optimum output has been explained. Further scope of research in this field of technology has been pointed out. Some suggestions are also provided for improving the existing techniques.

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Preparation of High Purity Silicon

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SILICON is the most abundant of all the non-metallic elements on earth. Progress on the chemistry of this element has been rapid in the past few decades. The infusibility of silicon and its compounds and their general resistance to attack by chemical reagents retarded greatly the development of the chemistry of silicon till the discovery of hydrofluoric acid. At present, however, the great theoretical interest and practical importance of silicon can hardly be overestimated.

When elemental silicon was first produced at Niagara Falls as a byproduct in the manufacture of silicon carbide, it found hardly any use. Now silicon is one of the most important elements in the electronics industry. Since its appearance in 1940, there has been rapid progress in that industry resulting in more demand of silicon in much purer state. As a consequence, vigorous research conducted almost all over the world has led to the preparation of a product of high degree of purity.

In the electronics industry silicon is used in the manufacture of rectifiers and transistors. A detailed description of silicon rectifiers is given by Torrey and Whitmer[1]. The increasing use of silicon in transistors is due to its high maximum operating temperature of about 250°C. as compared to 75°C. for germanium. Another factor is the easy availability of silicon, although the rarer germanium is more easily purified. Silicon also finds use in the solar battery[2] which is constructed with wafers of pure silicon to which certain impurities are added.

Silicon is mixed with ceramic materials or carbon and fired to form heat resistant and refractory materials in which some of the silicon remains in elemental form[3]. Several processes for the manufacture of articles like chemical ware, pipes and crucibles, cast mainly of silicon, have been patented[4]. It has been used as a catalyst[5] and as an electrode material in the electrometric titration of acids and bases[6,7]. Silicon mirrors formed by electro-deposition find use in industry and other fields[8]. Large amounts of silicon are being used for deoxidizing metals and in the production of silicides and alloys of silicon. Aluminium alloys containing about 17 per cent silicon possess casting quality superior to that of pure aluminium.

The position of silicon in the Periodic Table is immediately below carbon in Gr. IV. It finds its place in the middle of more positive metallic elements on its left and the more negative non-metallic elements on its right. Since carbon and silicon have similar electronic configurations (C: $1s^2$, $2s^2$, $2p^2$; Si: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^2$, $3d^0$), it may be expected that analogous carbon and silicon compounds would have similar physical and chemical properties. In a broad sense, such is the case. The synthesis of a new compound of silicon is attempted on the basis of experience with carbon. With the increasing knowledge about silicon it will become less necessary to have guidance from carbon chemistry. The valency shell of the silicon atom possesses nearby d orbitals as shown above; the p orbitals of this shell ($n = 3$) do not participate in the π-bond formation. The valency shell of the carbon atom ($n = 2$) does not possess nearby d orbitals, but its ability to form π-bonds is responsible for much of its characteristic chemistry. The variation in their atomic constitution accounts for the differences in the chemistry of carbon and silicon. The study of silicon compounds has shown how they have bridged the gap between organic and inorganic chemistry.

In view of the industrial importance of pure silicon, an attempt has been made to present a critical review of the methods of production of silicon in a reasonably pure form.

Preparation of Silicon

Early methods — Cambi[9] showed that hydrolysis of black vitreous silicon sulphide, SiS, furnished soluble silica and amorphous silicon, having a pale reddish-yellow colour. Deville[10] prepared a new form of silicon which he called graphitoidal silicon and which is related to the ordinary form of silicon much as graphite is related to diamond. Silicon in crystalline form was obtained by Gröppel[11] by heating aluminium silicate, silica and carbon in an electric arc furnace. Von Siemens and Halske[12] found that silicon could be obtained in the form of films or mirrors by placing the surface to be plated in a uniformly heated pipe above the temperature of decomposition of silicon hydride. A large number of references on the preparation of silicon is given by Mellor[13].

Preparation from silica and silicates — The endothermic nature of the reaction of carbon with silica makes it very difficult for this reaction to be carried out except at very high temperatures. Silicon is made on an industrial scale by the reduction of silica with coke in an electric furnace[14-19] at about 3100°F. Silicon carbide is formed as an intermediate product in the reduction of silica with carbon as shown below:

$$SiO_2 + 3C = SiC + 2CO$$
$$2SiC + SiO_2 = 3Si + 2CO$$
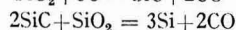
In an effort to increase the yield of silicon by preventing its vaporization and by minimizing the formation of silicon carbide, several silicates have been added in varying ratios to the silica carbon charge[20]. To remove carbon from low grade silicon, it is melted in a crucible which has an alkaline earth carbonate at the bottom. On decomposition of carbonate, carbon dioxide bubbles through silicon and reacts with carbon to form carbon monoxide. Using this method silicon with resistivity about 0·5 ohm has been prepared by Dempster John[21].

During reduction of silica with a metallic reducing agent to silicon in an electric furnace, the upper part of the melt is heated to keep the temperature constant. The slag containing impurities rises to the surface[22]. As early as 1907, the reduction of silicon monoxide with silicon carbide was proposed[23] and a more sophisticated system using hydrogen as a reducing agent was patented[24] in 1961. The distillation of silicon monoxide prior to reduction results in higher purity.

Another approach was to first react silica with aluminium to form silicon and alumina. Free aluminium was removed by leaching with hydrochloric acid and silicon was dissolved in molten tin. Since tin is much less soluble in silicon than aluminium, silicon of higher purity was obtained after its separation from tin[25]. Kolflaath[26] prepared silicon of 99 per cent purity by reducing silica with carbon. However, iron could not be eliminated. If Al_2O_3 is added to quartz in such an amount as to establish an Al : Fe ratio between 1:2 and 1:1 (by wt), then silicon could be treated with hydrochloric acid and Fe, Al and Ca would be removed. Cavigli[27] reviewed the preparation of silicon from silica in an electric furnace. Wagner and Bischoff[28] obtained silicon with a purity of 99·5-99·999 per cent by reducing silica with magnesium.

In several methods silicates are the starting material in place of silica; silicates are readily available and it is easy to reduce them using carbon or aluminium[29,30]. Most of these methods give very impure grade of silicon. A number of leaching systems were used to upgrade it. One of these processes, used to prepare silicon suitable for microwave diodes, consisted in crushing silicon to about 200 mesh, letting it soak in a mixed solution of hydrochloric and nitric acids for several hours, washing with distilled water, sulphuric acid and hydrofluoric acid, boiling, washing and treating with hydrofluoric acid and then giving a final washing[31]. A similar system, adapted to large-scale operation, has been described in a recent US patent[32].

It has been proposed to make semiconductor grade silicon by reducing the silicates in low temperature glasses with molten aluminium and precipitating the silicon from excess aluminium[33]. The silicon thus prepared is saturated with aluminium but presumably the majority of other impurities are separated by leaching processes.

Preparation by decomposition of silane — This process is very simple as it involves only the pyrolytic decomposition of silane. Due to the difficulty in making silane and its instability, the process has not been widely used. Silane explodes and ignites in air and is decomposed by water containing traces of alkali. It reacts explosively with halogens to give silicon halides and in the absence of air, it decomposes to silicon and hydrogen at 400°C.[34,35].

Silane is prepared by the action of metal hydride on some compounds containing silicon bound to F, Cl, Br, I, CN, O, S, N. The most common hydride used is lithium aluminium hydride. The hydride is dissolved in ether and the silicon compound is bubbled through the solution[36]. One specific choice[37] is

$$SiCl_4 + LiAlH_4 = SiH_4 + LiCl + AlCl_3$$
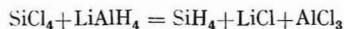
the ether used being tetraethylene glycol dimethyl ether. Another method uses a $SiCl_4$-$NaAlH_4$-$CaAlH_5$ mixture in tetrahydrofuran[38]. Calcium aluminium hydride is added in small amounts only to reduce the boron content appearing after the reduction of silane. Synthetic zeolite beds at −78°C. have been used to remove arsenic and phosphorus compounds, if present, from silane[39].

At about 400°C. silane begins to decompose. The reaction products contain appreciable quantities of higher silanes as well as silicon and hydrogen. At pressures less than 8 torrs, 100 per cent decomposition occurs from 777°C. onwards[37]. The decomposition can occur on the wall of a hot tube, but it is preferable to use a heated silicon seed or filament and deposit silicon directly on it. This prevents contamination from the tube and also eliminates the necessity for leaching away or otherwise separating silicon from the tube. One method of accomplishing this is to heat the tip of the silicon bar inductively and then as deposition occurs, to keep the growing ingot moving, so that the tip remains in r.f. field[40,41]. Another choice[41,42] is to keep the silicon tip molten and lower the seed continuously as the silicon forms and enters the molten pool. To increase the rate of deposition, a number of methods using high frequency radio-waves have been proposed[43-45].

One method[46,47] involves the introduction of a mixture of silane and argon into the electric discharge of cooled electrodes whereby silicon gets condensed on the surface. The decomposition of silane into silicon in static and dynamic systems using nuclear radiation was studied by Held and Goldman[48]. Decomposition in pile irradiations using neutron and γ-radiations at 100-275°C. was examined. Silane was decomposed on an indirectly heated tantalum or molybdenum tube[49]. Mozes and Nicolau[50] prepared silicon (99·999 per cent) by decomposing silane at 900°C. The variables evaluated[51] were the purity of the elemental silicon produced, the efficiency of dissociation and the deposition rate. Kostak[52] decomposed silane on a heated silicon rod between 600°C. and the melting point of silicon. Silane gas was surrounded by another gas, such as hydrogen, at a temperature lower than the decomposition temperature to obtain a coherent deposit[53]. The apparatus for the decomposition of silane gas was improved[54] by arranging an inductively heated graphite sleeve to heat the cold seed first by radiation and restricting the heated zone to prevent evaporation of impurities into silane. The silane jet was kept cold by water. A wiper was also provided to keep the transparent envelope around the decomposition chamber visually clear inside.

Raymond's method[55] involves the building of a continuous, large single crystal of silicon that functions as a seed for further deposition of silicon from silane gas. Sintered high purity flakes of silicon can be produced by passing purified silane into a quartz chamber at a pressure of 5-500 mm.

Hg^{56}. This chamber contains a silicon rod as a resistance heating element which is first heated from outside, then by passing a 60 amp. current through it. Bush[57] prepared silicon of resistivity 3000-6000 ohm-cm. by decomposing SiH_4, purified by addition of 0·1-1 per cent steam before heating to remove B_2H_6. A stream of SiH_4 is passed over a silicon single crystal heated to the decomposition temperature of silane, preferably near the melting point of silicon[58].

Preparation from trichlorosilane — Trichlorosilane is largely used for the preparation of pure silicon. It is generally reduced by hydrogen; the overall reaction may be written as

$$2SiHCl_3+2H_2 = 6HCl+2Si$$
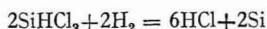
Probably the reaction proceeds as

$$2SiHCl_3+heat \rightarrow SiCl_4+H_2+Si$$
$$SiCl_4+H_2 \rightarrow Si+HCl+polymers$$
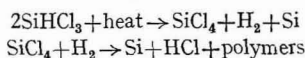
In both hydrogen reduction and thermal decomposition processes, low temperatures favour the production of very small, brownish particles. At 1230°C. silicon begins to have nodular appearance[59]. Hydrogen reduction of $SiCl_4$ or $SiHCl_3$ above 1000°C. produces a distinctly crystalline deposit. In a typical experiment Pauls[60] obtained 1 kg. silicon under the following conditions: (i) temperature of the main deposition zone, 950°C.; (ii) initial hydrogen rate, 100 litres/hr; (iii) final hydrogen rate, 300 litres/hr; (iv) hydrogen bubbled through $SiHCl_3$, at −9°C.; (v) with hydrogen rate of 300 litres/hr, the temperature of $SiHCl_3$ was raised to −5°C.; and (vi) length of run, 100 hr.

Different types of reactors were used, varying from a simple heated quartz tube through silicon particle fluid beds[61] and hot tantalum wires upon which deposition occurs, to deposition on high purity silicon rods (for highest purity silicon). Several methods have been proposed for preventing contamination. One of these consists in depositing a thick layer of carbon on the inside of the tube by the thermal decomposition of methane[62]. A better scheme consists in depositing an additional layer of silica on the tube by the reaction of $SiCl_4$ with high purity water[63] or by burning silicon tetraiodide and hydrogen in pure air[64]. The use of tantalum tube for deposition reduced the costs and contamination, but still the removal of tantalum was necessary. Silicon rod heaters eliminate these drawbacks, but a long high purity silicon rod[65,66] is required as the starting material.

If the molar ratio of trichlorosilane and hydrogen was less than 10, silicon was produced principally by the reaction[67]

$$SiHCl_3 = 1/4Si+3/4SiCl_4+1/2H_2 \qquad ...(1)$$

and when the molar ratio was above 20, silicon production was by the reaction

$$SiHCl_3+H_2 = 3HCl+Si \qquad ...(2)$$
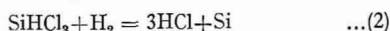
Similar reaction was obtained by Naka *et al.*[68]. The reduction of $SiHCl_3$ is a complex reaction and at high temperature $SiCl_2$ is produced. At zero hydrogen pressure, the thermal decomposition at 800-900°C. proceeds according to Eq. (1) and at hydrogen pressure greater than the pressure of trichlorosilane the reaction at 1000-1100°C. follows Eq. (2)[69].

A purified silicon rod is held between two electrodes in a quartz vessel. Highly purified $SiHCl_3$ and H_2 are passed through the vessel and a heating current at 220-500 V. is passed through the rod. The optimum temperature for ultrapure silicon is 1125°C. Yoshizawa *et al.*[70] reported that the thermal decomposition of trichlorosilane takes place in three ways:

$$4SiHCl_3 \rightarrow 3SiCl_4+Si+2H_2$$
$$2SiHCl_3 \rightarrow SiCl_4+Si+2HCl$$
$$SiHCl_3 \rightarrow SiCl_2+HCl$$
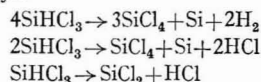
The decomposition is affected by the flow rate. The intermediate product, gaseous $SiCl_2$, explains the etching and dissolving of silicon when hydrogen is in slight excess[71].

Before decomposing or reducing $SiHCl_3$, it is treated with *p*-hydroxyazobenzene or phenylazonaphthol which forms strong complexes with B-halide[72]. Silicon is prepared by thermal decomposition of a 15:1 mole mixture of $SiHCl_3$ with hydrogen injected at a gas velocity of 500 ml./sec. against a silicon filament[73] at 1000°C. The rate of silicon deposition is 30 g./hr at an efficiency of 26 per cent. The silicon filament should have the same purity as the purity of the end product in view. If a single crystal silicon heating wire[74] is used as the filament, the final product is in the form of a single crystal. Niederkorn *et al.*[75] prepared high purity silicon in the form of bars by the reduction of trichlorosilane with hydrogen. They studied the influence of molar ratios of trichlorosilane and hydrogen, the yield and structure of silicon and the efficiency of the process. Special attention was paid towards the construction of the reactor. The highest yield (60·4 per cent) was obtained at 1500°K. at a $H_2/HSiCl_3$ ratio of 49:1. Reduction of $SiHCl_3$ at 1100°C. by hydrogen gave highly pure silicon with 88·5 per cent yield. At low hydrogen concentrations the decomposition according to the reaction $4SiHCl_3 = Si+3SiCl_4+2H_2$ is prominent[76]. At higher concentrations the reduction reaction $SiHCl_3+H_2 = Si+3HCl$ prevails.

The reduction of chlorosilanes by hydrogen above 1100°C. was studied by Sirtl and Reushhel[71] and Bieberschick[77]. In this process, the mixture of hydrogen and trichlorosilane is charged in a quartz reactor pipe containing a filament or rod of extremely pure silicon in a vertical position[78]. The temperature is maintained between 1200° and 1300°C. and the strength of the current is carefully controlled during decomposition by the surface temperature of the filament. In another method[79], the temperature varies between 600° and 1300°C. High purity silicon is produced by a thermal or electrothermal reaction of a silicon halogen compound with high purity hydrogen[80], resulting in the decomposition of silicon from gas phase on a heated carrier body.

Haushahn[81] moved a thin silicon rod with vibration through a quartz tube of 40 mm. inner diameter at the rate of 1-2 cm./hr. The vibration

was caused in the direction of motion with a frequency of 30-50 c/min. The rod was heated by a high frequency coil at 800-1100°C. A mixture of $SiHCl_3$ and H_2 was passed into the tube and the silicon compound was thermally decomposed, depositing silicon on the rod. The reduction of trichlorosilane by hydrogen is illustrated in Fig. 1.

Preparation from silicon tetrachloride — A certain amount of silicon for semiconductors is prepared by the reduction of silicon tetrachloride with active metals, such as magnesium, aluminium, zinc, cadmium, etc., the most suitable reductant being zinc. However, with its much higher melting point zinc poses some problems. These problems can be overcome by melting zinc in one container and then feeding the liquid in a flash evaporator[82]. The temperature of the reaction chamber is kept high enough for the reduction to be reasonably efficient and yet low enough to minimize the side reactions with the container. Following this method Lyon *et al.*[83] used 99·99 per cent pure zinc, cut it into pieces and allowed it to stand in 20 per cent hydrochloric acid for 20-30 min. to remove any loose dirt. Zinc was finally washed and dried.

In another method[84] the following conditions were standardized: (i) diameter of reaction chamber, 8 in.; (ii) length of reaction chamber, 6 ft; (iii) temperature of reaction chamber ≈950°C.; (iv) temperature of incoming $SiCl_4$ and zinc ≈950°C.; (v) length of run, 40 hr; (vi) amount of zinc used, 147 lb.; and (vii) amount of $SiCl_4$ used, 285 lb. The amount of silicon produced was 15·5 lb.

Sometimes finely divided silicon is carried away with the exit gases. To overcome this difficulty, the two reactants are introduced in the reaction chamber in such a manner that there is minimum of turbulence and they initially move towards the hot wall[85]. The reactants are fed into two parallel furnaces such that there is stoichiometric excess of zinc in one and of $SiCl_4$ in the other[86]. Other methods include the passing of $SiCl_4$ over hot silicon[87] and over a pool of molten zinc[88]. In another process[89], $SiCl_4$ is purified by subjecting it to liquid-liquid extraction with 80-100 per cent H_2SO_4. Silicon tetrachloride is then reduced with

Fig. 1 — Preparation of silicon by the reduction of trichlorosilane with hydrogen

pure zinc at a temperature above the boiling point of zinc but below the melting point of silicon.

Extremely pure silicon (99·999 per cent) is prepared by the reduction of $SiCl_4$, $SiBr_4$, $SiHCl_3$ with very pure alkali metal or zinc[90]. The reduction of silicon tetrachloride by zinc vapour was studied by Jernejcic and Skerjane[91]. They used nitrogen, freed from oxygen by passing through a copper tower, as a carrier gas for the vapours of two components. Similar experiments were carried out by Wartenberg[92] and Hartman and Ostapkovich[93].

Recently, Matsumoto and Ishino[94,95] prepared silicon by the reduction of silicon tetrachloride with zinc. They measured the pressure during the reaction of zinc and silicon tetrachloride in a closed system with a Bourdon gauge from room temperature to 1080°C. The samples were prepared in the following mole ratios of zinc and silicon tetrachloride: 1/0·94, 1/0·5, 1/0·39, 1/0·37, 1/0·35 and 1/0·32. About 80 per cent of the reduction was complete below 900°C. Even if the temperature was raised to 1050°C. the maximum yield was 95 per cent. On reacting zinc and silicon tetrachloride taken in stoichiometric proportions, the reaction velocity was found to be proportional to (mole No. of zinc) $\times$ (mole No. of $SiCl_4$)$^{1/2}$; the activation energy of the reaction was 13·4 kcal./mole.

The effect of varying the vapour composition flow rate, zinc pressure and reaction time on the efficiency of reduction was studied. Argon was used as the carrier gas. Keeping $SiCl_4$ and zinc vapour flow rates at 0·88 and 1·52 mole/litre respectively and zinc partial pressure at 0·44 atm., the extent of reaction was almost constant above 900°C.; the rate of silicon deposition was also constant (13 g./hr). Large dendrites silicon crystals ($60 \times 1·0$ mm.) were deposited at high flow rate and thin needles ($30 \times 0·1$ mm.) at low flow rate. While the crystals took part in the disproportionation reaction, they did not materially affect the main reduction. The reduction was a homogeneous gas phase reaction. Silicon tetrachloride flowing in a temperature gradient was reduced by zinc vapour to yield pure silicon[96].

Kamenar and Grdenic[97] described an apparatus in which $SiCl_4$ or $SiBr_4$ vapours were reduced by gaseous sodium in a tantalum-lined vessel. The reduction was carried at 440-460°C. in vacuum. Higher temperatures in hydrogen or argon atmosphere gave less pure product and more violent reaction. Silicon of at least 99·99 per cent purity was produced[98] by the vapour phase reduction of redistilled $SiCl_4$ with purified zinc or cadmium in a horizontally elongated closed chamber. In an experiment, $SiCl_4$ and H_2 were preheated[99] before entering the reaction vessel. Semiconductor purity elemental silicon was obtained by a continuous commercially adaptable method of reducing $SiCl_4$ with hydrogen[61]. Hölbling[100] carried out the reduction in contact with carbon at 1100-1150°C., $SiCl_4$ was purified by refluxing it with copper powder and then treating it with H_2S. The titanium content was reduced from 70 to 518 p.p.m. and the vanadium content from 1·7 to 0·3 p.p.m.[101] respectively. The results showed that the chlorides or oxychlorides of vanadium and titanium were
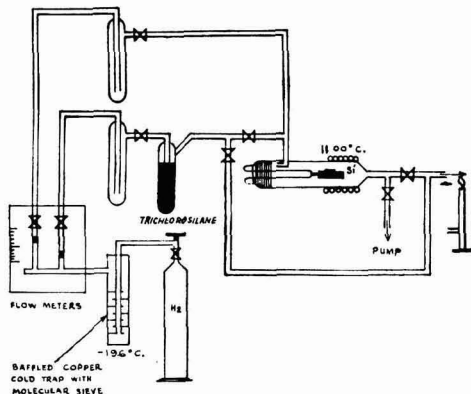
reduced to lower chlorides or others which were less soluble in silicon tetrachloride.

Silicon for semiconductors was prepared from gaseous derivatives by thermal decomposition[102]. The silicon thus produced was deposited on a silicon wire heated by alternating current. Constant temperature was maintained by directing the light emitted by the wire to a photocell, which activated a regulator to adjust the intensity of the heating current. Rummel[103] developed another electromechanical device for controlling the temperature during the deposition of silicon. In this device, an induction coil with a ferrite core regulates the heating current in the silicon wire.

Kurosawa and Minamia[104] and Von Bichowsky[105] reduced $SiCl_4$ with hydrogen between a coaxial tantalum tube and a heated tantalum wire. The yield of silicon increased on increasing the voltage applied between the tantalum parts. The mole ratio of $H_2/SiCl_4$ was 60 and the field strength $1-1·5$ kV. Higher voltage (up to 3 kV.) improved the yield. Silicon deposition took place preferentially on the edge of the ribbon. A tantalum-silicon alloy layer formed and grew with time. Tantalum was removed by treatment with HF for over 65 hr. The yield of silicon depended upon the size and shape of the filament, hydrogen/$SiCl_4$ ratio, drift velocity of hydrogen, temperature, etc.[106]. It was found that the reduction is not a one-step reaction but involves the following three stages:

$$SiCl_4 + H_2 \rightleftharpoons SiCl_2 + 2HCl$$
$$2SiCl_2 \rightleftharpoons SiCl_4 + Si$$
$$SiCl_2 + H_2 \rightleftharpoons Si + 2HCl$$
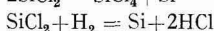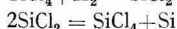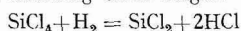
The last reaction proceeded only when $H/SiCl_4$ ratio was large.

In another experiment[107] it was observed that, at temperature above 1100°C., the yield of silicon depends on the mole ratios of hydrogen and silicon tetrachloride but not on the flow rate of the gas mixture. When the $H_2/SiCl_4$ ratio was >300, the yield of silicon was almost constant, i.e. 66 per cent at 1100°C. and 86 per cent at 1200°C. The exit gas from the reaction chamber consisted mainly of trichlorosilane, silicon tetrachloride and HCl.

The reduction of silicon tetrachloride by hydrogen in the gaseous phase on the surface of a heated tungsten or tantalum filament was studied by Nakagawa[108]. He observed that the yield of silicon increases with increasing $H/SiCl_4$ mole ratio almost linearly up to 25-30 per cent with an increase in the reduction temperature. The silicon yield was higher when the filament was positioned perpendicularly to the stream of the participants in the reaction than when the filament was parallel to the gas flow. Nakagawa[109] also studied the effect of varying temperature (1050°, 1100°, 1150° and 1200°C.) mole ratio of H_2 to $SiCl_4$ vapour (40-520) and flow rate (6-153 litres/hr) on the yield of silicon and other products produced during the reduction.

Before reducing the silicon halides they are often purified by direct distillation, but occasionally other methods are used with, or in addition to, distillation. If purities in the range 50-100 ohm-cm. are desired, pyrex or steel columns are adequate; high purity $SiCl_4$ and $SiHCl_3$ are shipped in steel tanks.

However, for higher purity it is advantageous to use quartz columns.

There are considerable difficulties in separating some of the group IIIA and VA halides from those of silicon. The addition of a complexing agent prior to distillation has sometimes been tried. One group of compounds suggested for this purpose is aliphatic and aromatic dinitriles, such as succinonitrile, adiponitrile and acetonitrile[110]. Liquid extraction systems using some of these compounds have also been proposed. Likewise, liquid and gas absorption columns have been used. One of these systems contained activated alumina[111], while in another a column containing an absorbent, e.g. activated charcoal charged with compounds such as CNBr and C_2H_5CN, was used[112]. A process has been reported in which electrodes are immersed in a halide-methyl alcohol mixture; various impurities get deposited at the electrodes[113].

Preparation from silicon tetraiodide — Preparation of silicon by the decomposition of silicon tetraiodide is a straightforward process, and apparently because of the ease of purification, this process was adopted[114-116] earlier to produce silicon of extremely high purity. Low pressure is essential to have a reasonable deposition rate.

One such process[117,118] involved the following operations: (a) reaction of iodine with commercial grade silicon; (b) purification of silicon tetraiodide; (c) distillation of the iodide; (d) decomposition of silicon tetraiodide to form silicon and iodine; and (e) iodine recovery.

A more elaborate process[119] involves an additional purification step — zone refining of silicon tetraiodide before distillation.

Silicon tetraiodide is formed by reacting commercial silicon with iodine at about 600°C. in either a fixed or a fluid bed. Once the required temperature is attained, the reaction does not require further heating, as the combination of iodine with silicon is an exothermic reaction. Another method makes use of the film boiling technique to achieve high efficiency and deposition rate[120]. The heated wire vaporizes the liquid in its vicinity and supplies heat to decompose the iodide. Silicon is deposited on it. An arc was also used in another experiment[121], but the silicon obtained was not of high purity.

Baba and Araki[122-124] produced high purity silicon by decomposing silicon tetraiodide at temperature higher than 1200°C. Silicon tetraiodide was recrystallized with toluene, sublimed under reduced pressure, rectified in an inert atmosphere and purified by zone melting. Iodine from the decomposition of silicon tetraiodide was recycled. Silicon tetraiodide was decomposed[125-127] on the hot surface of pure silicon. The preparation of silicon by the iodide process is illustrated in Fig. 2.

Herrick and Kriebe[118] prepared silicon tetraiodide by reacting commercial silicon and iodine in a fluid bed reactor. Impurities were rejected by solvent crystallization followed by fractional distillation. High purity silicon was prepared by thermal decomposition of silicon tetraiodide having a resistivity over 1000 ohm-cm. Reproducible results were obtained, showing that the quality of the product
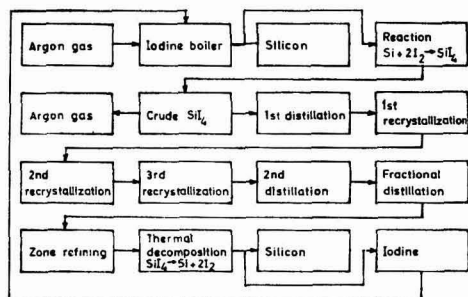
Fig. 2 — Schematic diagram for the preparation of silicon by the iodide process

is controlled by back contamination from the decomposition and crystal growing step. Data from the decomposition of silicon tetraiodide at 1000°C. and low pressure were correlated by the equation

$$\log p = 2{\cdot}18 - \frac{m}{0{\cdot}305}$$

where p is the quantity (lb.) of silicon tetraiodide fed/hr/ft^2 of heated surface and m, the fraction of silicon tetraiodide (g.) converted to silicon (g.). It is postulated that this reaction reaches a stage of equilibrium.

Manning[128] reported the preparation of silicon by iodide process involving the following steps: (i) reduction of silica to silicon; (ii) reaction of silicon with iodine to form silicon tetraiodide; (iii) distillation of SiI_4; (iv) sublimation of SiI_4 in vacuum at 100°C.; (v) dissolution of SiI_4 and its passage through silica gel; (vi) zone refining of SiI_4 by passing it through a series of alternate melting and cooling zones at the rate of $1{\cdot}0$-$2{\cdot}5$ cm./hr; and (vii) reduction of SiI_4 to silicon by passing a mixture of hydrogen gas and tetraiodide vapours on a suspended pure Si body, a portion of which has been heated by induction to 600-850°C. Ultrapure silicon is deposited on the heated portion of the body.

Kurosawa et al.[129-131] studied the reduction of SiI_4 by hydrogen and found that larger the H_2/SiI_4 ratio for a given hydrogen flow rate and temperature, the higher is the yield. At ratios above 60, 90 per cent yield was obtained. It was further observed that the yield of silicon is directly proportional to the temperature.

As pointed out earlier, the purification of silicon tetraiodide prior to decomposition or reduction is necessary. This is generally achieved by recrystallization[132], distillation[114,116], sublimation[133], and zone refining[133-134]. These methods are very useful for the intermediate purification of silicon tetraiodide. McCarty[132] found that silicon of 500 ohm-cm. resistivity can be prepared employing a recrystallization step followed by distillation. Some methods have been discussed in detail by Runyan[135].

Miscellaneous methods — Very pure silicon is made by the reduction of halogen silane[136] at 800-1400°C. The production of pure silicon from methylsilane was investigated by Pinter et al.[137]. Special

consideration was given to the conditions of producing very high purity silicon with low B-level from methylsilanes, as these offer the best possibilities for separating the highest grade silicon from the unwanted accompanying impurities. The technology of producing silicon by thermal decomposition of methylsilanes has the advantage of decomposition temperature (300-400°C.) lower than that of $SiCl_4$ or $SiHCl_3$. The requirements of materials for the design and construction of the device are considerably less, partly because of the allowance for temperature and partly owing to the absence of the corrosive effect of halogen compounds. This method has, however, the disadvantages of the possibility of explosion and of traces of carbon entering the silicon produced as unwanted impurities from the necessarily used organic ethers.

The reaction of hydrogen with trichlorosilicomethane[138] has also been used to prepare pure silicon. Trichlorosilicomethane is treated with hydrogen in a stainless steel reaction chamber at the rate of 145 ml./hr and 192 litres/hr respectively. The temperature of the chamber is maintained at 950°C. and silicon deposits are formed on a silica tube, the yield being 7·3 per cent. When the unreacted trichlorosilicomethane is recycled, the yield increases to 11·5 per cent. In this process, other inert gases like argon or helium may be introduced in place of hydrogen. A pure silicon compound is decomposed at a temperature above the melting point of silicon[139]. Liquid silicon is changed to the form of a rod by collecting it with the help of a continuously lowered drip tube and then cooling the metal.

Various other gas decomposition or reduction processes using silicon tetrabromide[112,140] and silicon dichloride[141] have been tried, but none of them has passed the laboratory stage, probably due to cost considerations. The silicon produced from monosilane was deposited[142] on an electrically heated filament of Ta, W, Mo, C or Si. In the last case, the filament was heated by heating elements or by the heat generated by the passage of an electric current through a temporary coating of, for instance, zinc which raised the silicon filament to a temperature at which it was itself conducting. The vessel containing the silane was water-cooled and gas-tight. The liberated hydrogen was retained in the vessel and/or absorbed by spongy titanium or zirconium within the vessel.

Epitaxial Growth of Silicon

In recent years there has been a growing interest in the use of epitaxial growth of semiconductor films for a variety of new and improved devices. The term epitaxy was introduced by Royer[143] to denote the phenomenon of the oriented growth of one crystal on the other.

One of the important methods for preparing epitaxial layers of silicon in the manufacture of semiconductor components was developed by Mikusek[144]. He studied the mechanism of epitaxial growth of layers and the origin of the crystallographic defects and layer allowing. Silicon was grown epitaxially on a single crystal sapphire[145] and doping by the substrate of silicon films grown

epitaxially on sapphire was also studied[146]. Spectroscopic analysis of the film showed that aluminium was the major impurity. A qualitative description of the changes in crystal structure on heat treatment was also given. Silicon-on-sapphire has been used in the fabrication of metal oxide semiconductor transistors[147]. The silicon used for these studies was grown by the pyrolysis of silane as described in detail by Robinson and Mueller[148]. Substrate doping of silicon, epitaxially grown on silicon, has been studied[149] and attributed to normal diffusion of impurities from the silicon substrate. Polycrystalline films of silicon were studied by Heaps et al.[150]. Some investigators obtained an oriented growth of thin silicon layers on an insulating substrate[151]. Sirtl and Seiter[152] examined the growth and properties of polycrystalline silicon films on oriented silicon layers[153]. The in situ etching of silicon substrate with commercial hydrogen chloride has been used successfully and the resulting[154] silicon films have been found to be generally of good crystal perfection. Chu[155] observed that silicon webs with flat principal faces of [111] orientation were ideal substrates for the epitaxial growth of silicon. This growth was effected by the pyrolysis of silane and the thermal reduction of trichlorosilane in a flow system. Epitaxial layers of good structural perfection were grown on web substrates and accurately oriented [111] substrates at relatively low temperatures (1080°C.) and high growth rates (1·5 μ/min.). Large area solar cells were prepared by the epitaxial growth technique using web substrate[156]. The epitaxial deposition of silicon using hydrogen reduction has been described by Russel[157] and Theurer et al.[158]. Methods for the preparation of epitaxial semiconductor films have been discussed by several authors[159-161]. The factors affecting the growth of epitaxial silicon layers on silicon substrates by reducing silicon tetrachloride with hydrogen using r.f. heating have been studied by Tung. These factors[162] include deposition temperature, concentration of silicon tetrachloride, deposition rate and time. The effect of thickness, resistivity and surface perfection has also been discussed. The epitaxial deposition of silicon layers was investigated by Corrigan, over a wide range of deposition rates and substrate temperatures. The temperature of growth was varied from 930°C. to the melting point of silicon and growth rates of 0·01-5·0 μ/min. were employed.

Purification

Various techniques have been developed for obtaining silicon in its purest form for use in the manufacture of transistors and solar batteries. One method involves passing impure vapour of the metal at 1000-2000°C. through a gas chromatographic column[163] and separating the purified substance. Generally, the impure metal is evaporated with an inert carrier gas. The solid absorbent is preferably silicon carbide, aluminium oxide or silica aerogel.

To avoid contamination by its container, silicon in the form of a 10 mm. rod is suspended downward by a holder into a 25 mm. diameter cylindrical container of pure silica[164]. A coil wound outside the cylinder is used to melt the lower tip of the silicon rod by radio frequency inductive heating. Molten drops of silicon fall from the tip of the rod through a purifying atmosphere of hydrogen and water vapour passing through the cylinder at 2 litres/min. Boron and oxygen impurities in silicon react with hydrogen or water and are thus removed. The silicon rod is lowered into the inductive heating zone at 1-10 cm./hr. The molten drops of silicon fall into a crucible of pure silicon. If the distance of fall of drops is 25 cm., some splashing occurs, but at 50 cm. splashing is negligible. Silicon is also purified by treatment with halogens and/or halogen derivatives in the atmosphere of a gas containing oxygen[165].

Bradshaw and Sargeant[166] obtained pure silicon by melting impure silicon in a graphite crucible, the thinner wall of which was coated with silicon nitride. Silicon cylindrical anode (purity 98·2 per cent) was introduced in the molten mixture of 200 g. of Na_3AlF_6 and 4 g. of SiO_2 in a graphite crucible used as cathode[167]. Electrolysis was carried out at about 4 hr at nearly 1 amp./sq. cm. Silicon deposited on the walls of the crucible was pulverized and treated with a solution (13 per cent) of $AlCl_3$ to dissolve the residual electrolyte. The product was treated with HF and HCl solutions and filtered. The silicon thus obtained was 99·9 per cent pure. An alloy of copper (84 per cent) and purified silicon (16 per cent) was prepared and melted in a crucible containing a mixture of Na_3AlF_6 (200 g.) and SiO_2 (4 g.) as electrolyte. Electrolysis was carried out at 1000°C. with 0·5 amp./sq. cm. current for 4 hr. The molten alloy was made the anode and a graphite rod dipped in the electrolyte the cathode. The deposit on the graphite rod was 99·99 per cent silicon. In another method, the electrolysis apparatus was divided into two compartments[168] by a vertical partition, leaving a passage at the bottom for free circulation of molten alloy between the two compartments.

Silicon of 99·5 per cent purity was produced[169] from crude silicon on a commercial scale by treating its fine powder with hydrochloric acid or sulphuric acid or both as a fine spray or drops with vigorous agitation. The paste obtained was allowed to stand for at least one day before washing and drying. It may also be treated with HF subsequent to the treatment with HCl or H_2SO_4. When allowed to stand for three days and the acid treatment repeated four times, silicon of more than 99·97 per cent purity is obtained.

By heating impure silicon with silicon tetrachloride[170] in a sealed tube having a temperature gradient of 1000/800°C. and 1300/1100°C., it is possible to reduce the metallic impurities to a great extent. Best results are obtained in the 1000-1300°C. range, the yield depending upon the temperature. The metal impurities are also reduced by passing a stream of argon, containing sufficient iodine vapour, through impure silicon. Iodine vapour is added to argon to maintain the pressure of silicon tetraiodide at 50 mm. above the fluidized silicon. Slag formers composed of calcium oxide and silica are added to fused silicon[171]. Oxygen or air is introduced into this melt.

Impurities like aluminium and calcium are oxidized and removed as slag according to the reaction $2Ca + SiO_2 \rightarrow 2CaO + Si$. Silicon platelets are fused under very high vacuum (about 10^{-4} torr) in an electron bombardment furnace instead of being distilled[172]. The volatile impurities and other contaminants introduced into the crucible are eliminated by cooling it with circulating water. Silicon may also be purified by heating it above 1500°C. and allowing it to solidify[173].

Pure silicon is further purified by the zone refining technique. Many elements can be effectively removed from silicon by zone refining. This method cannot, however, remove boron, which is one of the important impurities in silicon. The distribution of boron between solid and liquid silicon during solidification is such that it is necessary to pass a large number of zones through silicon to reduce boron concentration to the desired level.

The zone refining method is not equally effective for the removal of all impurities, because it brings about a physical separation and can be no more effective than a particular impurity permits it to be. If the distribution coefficient K of a particular impurity is known, its behaviour can be predicted. Because of the negative expansion coefficient of silicon in the region of the melting point, it is very difficult to carry out the purification in a vertical container. Therefore, a time-consuming horizontal zone melting process is normally applied. In another method[174], a vertical container is used even for materials with negative expansion coefficients in the melting point region.

The high reactivity of silicon in molten state is a serious difficulty in zone refining, as it reacts with the container. To overcome this difficulty, the 'floating zone technique' was introduced. In this technique, the ends of a vertical rod of silicon are held by clamps and a zone is melted through the entire cross-section. Surface tension holds the zone in the required place, provided the zone is not too long. The floating zone is then moved along the rod by moving the heating coil, thus transporting the impurities.

Conclusion

Considering all the aforementioned facts it appears that the reduction of trichlorosilane by hydrogen offers some advantages like faster deposition rate and ease of removal of impurities like boron or phosphorus from trichlorosilane.

Summary

The importance of silicon, especially of semiconductor grade material, has grown to an enormous extent in recent years. The availability of high purity silicon has brought about a revolution in the electronic industry. The use of micro-miniature circuits based upon silicon has reduced the requirement of the space and improved the reliability. Silicon transistors possess many advantages. They have maximum operating temperature of 250°C. as compared to 75°C. for germanium. Again, silicon occurs much more abundantly in nature than germanium. As a result of these advantages intensive investigations in the improvement of the process
of purification are in progress. The demand for high purity silicon in India is assessed to be 500 kg. per year valued at Rs 50 lakhs.

Large amounts of pure silicon are being used as a raw material for the synthesis of silicones which find applications as lubricants, water-proofing agents, insulating materials, potting compound and low temperature rubber. The demand for silicones has risen steadily. India imports annually about 62 tons of silicones valued at Rs 12 lakhs.

In view of the economic importance of pure silicon, intensive research is in progress to improve the purity of the product and reduce the cost of production. It is observed that the process based upon thermal decomposition of silicon tetraiodide is gradually being replaced by the process involving reduction of trichlorosilane with hydrogen. A critical comparison of various methods of production of high purity silicon has been provided. Some of these methods are under investigation in various laboratories in India, including the Defence Science Laboratory, Delhi.

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Mathematical Models of Polymorphic & Monomorphic Mimicry

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SURVIVAL is one of the most natural instincts of the living species. Therefore, every individual species makes an attempt to reduce its losses arising from attack of predators. Mimicry is one of the ways of doing it. Considering two species — one palatable and the other impalatable to the predator — the palatable species naturally stands greater risk of being exposed to the predator's attack. But if the palatable species develops the same outer appearance by protective colouration as that of the impalatable species, there are chances of its being misunderstood by the predator for the impalatable species, depending on the relative populations of the two species. Thus, mimicry of the impalatable species may be a factor in reducing the losses of the palatable species due to the predator's attack. This is a case of polymorphic or Batesian mimicry[1], wherein the model species is less palatable than the mimic species.

Mimicry may help even if the model species and the mimic species have similar poor palatability, because before associating poor palatability with a particular outer appearance, the predator has to take samples which might be shared by the model and the mimic species. This type of mimicry is called monomorphic or Müllerian mimicry[1]. Both the types of mimicry are amenable to mathematical analysis, which has been attempted in this communication. For ease of analysis, certain complications, such as age-dependent birth and death rates, saturating effects on population of lack of food, overcrowding and cannibalism which lead to density-dependent birth and death rates, immigration and emigration, etc., are not considered, although when they are taken into account the models would become more realistic.

Polymorphic Mimicry

Let at any instant there be p_1 members of the impalatable model species and p_2 members of the palatable mimic species. Then the relative occurrence of palatability is given by $p_2/(p_1+p_2)$. With the assumption that losses in a joint population are proportional to the relative occurrence of palatability in the joint population and shared by the two species in proportion to their individual populations, we get

$$\frac{dp_{1m}}{dt} = K_1 p_{1m} - K_3 \frac{p_{1m} p_{2m}}{(p_{1m}+p_{2m})^2} \quad \ldots(1)$$

and

$$\frac{dp_{2m}}{dt} = K_2 p_{2m} - \frac{K_3 p_{2m}^2}{(p_{1m}+p_{2m})^2} \quad \ldots(2)$$

where suffix m refers to mimicry, K_1, K_2 and K_3 are constants, assumed to be positive. The first terms on the right-hand side in Eqs. (1) and (2) are contributions due to regeneration inclusive of natural death rate and are assumed to be proportional to

395

the instantaneous populations. The last terms on the right-hand side of both the equations are the rates of loss of population because of the predator's attack. Combining Eqs. (1) and (2) we get

$$\frac{dp_{2m}/dt}{p_{2m}} - \frac{dp_{1m}/dt}{p_{1m}} = K_2 - K_1 \qquad ...(3)$$

i.e.

$$\frac{p_{2m}}{p_{1m}} = A \ \exp \ (K_2 - K_1)t \qquad ...(4)$$

where A is a constant to be evaluated from initial conditions

$$p_{2m/t=0} = p_{2m}(0) \qquad ...(5a)$$

$$p_{1m/t=0} = p_{1m}(0) \qquad ...(5b)$$

Therefore, we have

$$\frac{p_{2m}}{p_{1m}} = \frac{p_{2m}(0)}{p_{1m}(0)} \ \exp \ (K_2 - K_1)t \qquad ...(6)$$

Substituting Eq. (6) in Eq. (2) we get

$$\frac{dp_{2m}}{dt} = K_2 p_{2m} - \frac{K_3}{\left\{1 + \dfrac{p_{1m}(0)}{p_{2m}(0)} \ \exp \ (K_1 - K_2)t\right\}^2} \qquad ...(7)$$

Eq. (7) is a linear differential equation and hence can be easily solved to give

$$p_{2m} = p_{2m}(0) \ \exp \ (K_2 t) - K_3 I_p(t) \ \exp \ (K_2 t) \quad ...(8)$$

where

$$I_p(t) = \int_0^t \frac{\exp \ (-K_2 t)dt}{\left\{1 + \dfrac{p_{1m}(0)}{p_{2m}(0)} \exp \ (K_1 - K_2)t\right\}^2} \quad ...(9)$$

The initial conditions of Eq. (5) have been used to evaluate the integration constant while deriving Eq. (8). Using Eq. (6) we get

$$p_{1m} = p_{1m}(0) \ \exp \ (K_1 t) - K_3 \frac{p_{1m}(0)}{p_{2m}(0)} I_p(t) \ \exp \ (K_1 t) \quad ...(10)$$

Equations without mimicry are obtained by putting $p_{2m} = 0$ in Eq. (1) and $p_{1m} = 0$ in Eq. (2) and dropping the suffix m. Solving the resultant equations we get

$$p_1 = p_1(0) \ \exp \ (K_1 t) \qquad ...(11)$$

$$p_2 = \left\{p_2(0) - \frac{K_3}{K_2}\right\} \ \exp \ (K_2 t) + \frac{K_3}{K_2} \qquad ...(12)$$

Having solved the equations of evolution with and without mimicry, it is possible to evaluate the effect of mimicry on evolution. The condition for growing population of mimic species without mimicry is, from Eq. (12)

$$K_2 p_2 > K_3 \qquad ...(13)$$

With mimicry, the condition for growing population is, from Eq. (2)

$$K_2 \left\{\sqrt{p_{2m}} + \frac{p_{1m}}{\sqrt{p_{2m}}}\right\}^2 > K_3 \qquad ...(14)$$

These conditions are shown graphically in Fig. 1. It follows that as a result of mimicry, the condition for p_2 to grow at any given moment can be satisfied

with lower regenerative ability at a given population or for a lower population at a given regenerative ability. Comparison of Eqs. (13) and (14) leads to interesting results. It implies that as a result of mimicry the effective population of the mimic species has changed from p_2 to

$$\left(\sqrt{p_2} + \frac{p_1}{\sqrt{p_2}}\right)^2$$

The condition represented by Eq. (14) can be further written with the help of Eq. (6) as

$$K_2 p_{2m} > \frac{K_3}{\left[1 + \dfrac{p_{1m}(0)}{p_{2m}(0)} \ \exp \ (K_1 - K_2)t\right]^2} \quad ...(15)$$

For p_{2m} to increase monotonously, this condition should be satisfied for all values of time t, i.e. it should be satisfied even for the lowest value of the left-hand side terms in Eqs. (1) and (2) and for the highest value of the right-hand side terms. The latter condition is stricter than the former. The smallest value of the left-hand side term occurs at $t = 0$. The highest value of the right-hand side term occurs at $t = 0$, if $K_1 > K_2$ and at $t = \infty$, if $K_1 < K_2$.

Thus, the conditions for monotonous growth of p_{2m} are

$$K_2 \left[\sqrt{p_{2m}(0)} + \frac{p_{1m}(0)}{\sqrt{p_{2m}(0)}}\right]^2 > K_3; \ K_1 > K_2 \quad ...(16a)$$

$$K_2 p_{2m}(0) > K_3; \ K_2 > K_1 \qquad ...(16b)$$

The first part of the condition represented by Eq. (16a) is both necessary and sufficient, whereas the second part of the condition is sufficient but not necessary. Eq. (16) suggests that the value of K_3 has to be below a certain limit for the monotonous growth of the mimic species. This is clear from Eq. (8) also. It is evident from Eq. (8) that $p_{2m}(t) = 0$ if $p_{2m}(0)/K_3 = I_p(t)$. As $I_p(t)$ is a monotonously growing function of time as shown later, and as $I_p(0) = 0$, it follows that the population of
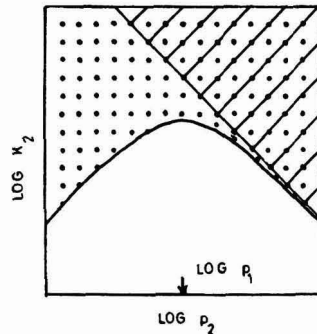

Fig. 1 — Conditions of growing population with and without polymorphic mimicry [The two curves starting from above are for $K_2 p_2 = K_3$ and $K_2 \left(\sqrt{p_{2m}} + \dfrac{p_{1m}}{\sqrt{p_{2m}}}\right)^2 = K_3$. Area with slant lines represents condition without mimicry and that with dots, condition with mimicry]

the mimic species would be exterminated in time if $p_{2m}(0)/K_3 < I_p(\infty)$. Thus, for very high values of K_3, extermination cannot be avoided even by taking recourse to mimicry.

In the absence of mimicry, the condition represented by Eq. (13) should be satisfied even for the lowest value of the left-hand side term. This means that

$$K_2 p_2(0) > K_3 \qquad ...(17)$$

These conditions are depicted in Fig. 2 which brings out the effect of K_1, K_2, K_3, $p_{1m}(0)$ and $p_{2m}(0)$ very clearly. If $K_1 > K_3/4p_{1m}(0)$, the line $K_2 = K_1$ passes from above the maximum of the curve representing

$$K_2 \left[\sqrt{p_{2m}(0)} + \frac{p_{1m}(0)}{\sqrt{p_{2m}(0)}} \right]^2 = K_3 \qquad ...(18)$$

In this case, as $p_{2m}(0)$ falls below $p_{1m}(0)$, the advantage of mimicry becomes more and more marked. As $p_{2m}(0)$ increases above $p_{1m}(0)$, the advantage of mimicry becomes less prominent. Nevertheless, for all values of $p_{2m}(0)/p_{1m}(0)$, howsoever large, mimicry always provides an advantage, even though it may not be very significant. This can be explained physically as follows:

When $p_{1m}(0)/p_{2m}(0)$ is large, the pattern represents a high level of impalatability, and hence mimic species derives an advantage. When $p_{2m}(0)/p_{1m}(0)$ is large, the pattern represents a high level of palatability. Therefore, there is no marked protection, but even then, as some of the beings killed belong to the species being mimicked, losses of the mimic species are lighter to that extent, and hence its population can grow with a little lesser regenerative ability. If $K_1 < K_3/4p_{1m}(0)$, the line $K_2 = K_1$ passes from below the maximum of the curve for Eq. (18). Then mimicry seems to provide advantage in two distinct regions, $p_{2m}(0)/p_{1m}(0) \ll 1$ and $p_{2m}(0)/p_{1m}(0) \gg 1$, but not around $p_{2m}(0)/p_{1m}(0) = 1$. Also when $p_{2m}(0)/p_{1m}(0) < 1$, the population of the mimic species seems to grow monotonously only when

Fig. 2 — Conditions of monotonously growing population with and without polymorphic mimicry [The thick horizontal line represents the conditions $K_1 = K_2$; the dotted horizontal line shows the alternative position of the line $K_1 = K_2$ for lower values of K_1. The other two curves starting from above are for $K_2 p_2(0) = K_3$ and $K_2 \left(\sqrt{p_2(0)} + \frac{p_1(0)}{\sqrt{p_2(0)}} \right)^2 = K_3$. Shading of areas has the same significance as in Fig. 1]

Eq. (16a) is satisfied. This is somewhat strange, because it so appears that as the regenerative ability of the second species is increased beyond a certain limit, it can no longer enjoy monotonously growing population. These conclusions, however, may also arise because of the sufficient but not necessary character of the condition represented by Eq. (16b).

Apart from monotonously growing population it would be interesting to study the conditions for 'relative survival'. Without mimicry, the populations of the two species are in the ratio

$$\frac{p_2}{p_1} = \frac{p_2(0) - K_3/K_2}{p_1(0)} \exp (K_2 - K_1)t + \frac{K_3}{K_2 p_1(0)} \times \exp (-K_1 t) \qquad ...(19)$$

A species interested in survival would always want to keep its relative strength in a joint population growing. Even a transient decrease in the relative abundance in a joint population must be viewed seriously. For the relative abundance to grow monotonously its time derivative must always be positive, i.e. we must have

$$\{p_2(0) - K_3/K_2\}(K_2 - K_1) \exp (K_2 t) > K_1 K_3/K_2 \qquad ...(20)$$

This condition must be satisfied even for the smallest value of the left-hand side term in Eq. (20). This means

$$K_2 - K_1 > K_3/p_2(0) \qquad ...(21)$$

Thus, the second species must exceed the regenerative ability of the first species by a margin for relative survival in the absence of mimicry. The margin is a linear function of the intensity of the predator's attack and an inverse function of the initial population of the species.

On the other hand, if recourse is taken to mimicry, from Eq. (6) it becomes clear that the only condition for relative survival is

$$K_2 - K_1 > 0 \qquad ...(22)$$

This condition should be compared with Eq. (21). The condition depends neither on K_3 nor on $p_2(0)$. The second species has just to exceed the regenerative ability of the first to keep its relative abundance in a joint population improving. To fully appreciate the effect of mimicry, it may be assumed that there were no attacks on either species by predators and both the species were allowed to grow under their natural regenerative rate. This is achieved by setting $K_3 = 0$ in Eqs. (1) and (2). Under this condition also the relative strengths of the two species would follow Eq. (6). Thus, as a result of mimicry, the relative abundance of the two species is held at a level that would prevail if the predator's attacks were altogether absent. This implies that as far as the relative abundance of the two species is concerned, the second species succeeds in fully annulling the effect of the predator's attacks by practising mimicry.

The conditions represented by Eqs. (21) and (22) are shown in Fig. 3 from which it is evident that the mimic species can have a continuously growing relative abundance at lower values of regenerative ability and initial strength as a result of mimicry. Also it is clear that as the initial strength of the

mimic species increases, the advantage provided by mimicry decreases.

Referring again to the equations of evolution, i.e. Eqs. (8)-(12), the integral $I_p(t)$ appearing in Eqs. (8) and (10) and defined by Eq. (9) cannot be evaluated in closed form. It can, however, be evaluated by numerical integration techniques. It has been evaluated for the set of parameter values given in Table 1. Its values are plotted in Fig. 4. Comparing curves I and II, it becomes evident that other parameters remaining the same, change in K_2 brings about an insignificant change in $I_p(t)$. The ratio between the initial populations of the two species seems to have a very strong influence on the integral $I_p(t)$, smaller values of $p_1(0)/p_2(0)$ resulting in larger values for $I_p(t)$.

TABLE 1 — PARAMETER VALUES FOR VARIOUS NUMERICAL CALCULATIONS

Set No.	K_1	K_2	K_3	$p_1(0)$ or $m_1'(0)$	$p_2(0)$ or $m_2(0)$
I	5·0	5·0	2·5	100	100
II	5·0	2·5	2·5	100	100
III	2·5	7·5	2·5	1000	100
IV	7·5	2·5	2·5	100	1000
V	4·5	5·5	100	100	50
VI	5·0	5·0	2·5	1000	50

Under all circumstances the curves $I_p(t)$ are of a saturating type.

The advantage of polymorphic mimicry can be defined as

$$A_{pm}(t) = \left[\frac{p_{2m}(t) - p_2(t)}{p_2(t)} \right] 100\%$$

This is shown in Fig. 5 as a function of time for various sets of parameters listed in Table 1. It is seen that the advantage of mimicry is high for moderately large values of K_3 and large values of $p_1(0)/p_2(0)$ and K_1/K_2. It is also seen that as time advances, the advantage of mimicry becomes steady.

In Fig. 6 the courses that the populations of mimic and model species follow with and without mimicry of either polymorphic or monomorphic type are shown for set 5 of parameter values in Table 1. It is seen that in the case of polymorphic mimicry, the population of mimic species grows faster with mimicry, but that of the model species grows slower with mimicry. Polymorphic mimicry offers advantage to the mimic species at the cost of the model species.

Fig. 3 — Conditions for relative survival with and without polymorphic mimicry [The curve is for $(K_2 - K_1)p_2(0) = K_3$. Shading of areas has the same significance as in Fig. 1]
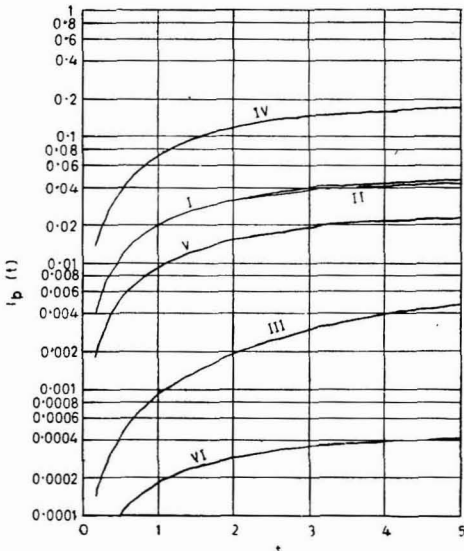
Fig. 4 — Integral $I_p(t)$ appearing in the equations of evolution with polymorphic mimicry as a function of time for sets of parameter values given in Table 1
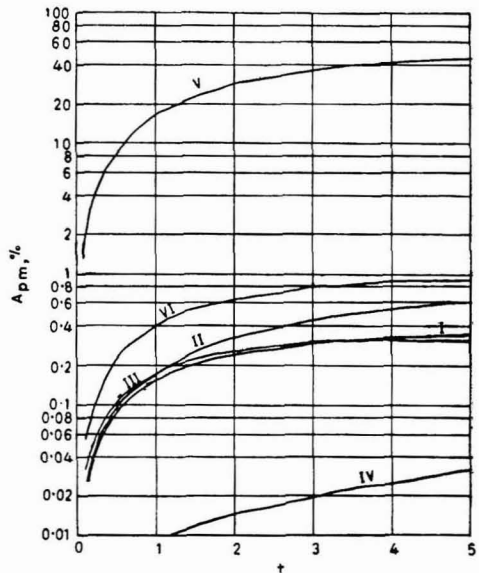
Fig. 5 — Advantage of polymorphic mimicry as a function of time for sets of parameter values given in Table 1
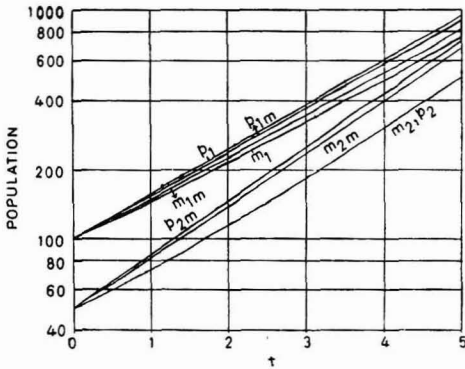
Fig. 6 — Course of population growth of model and mimic species with and without mimicry of either monomorphic or polymorphic type for set 5 of parameter values given in Table 1

Monomorphic Mimicry

Let there be two species of equally poor palatability, the model species having population m_1 and the mimic species having population m_2. As both the species are equally palatable (or otherwise) the total losses due to the predator's attack would be constant. We also assume, as in polymorphic mimicry, that the losses due to the predator's attack are shared by the two species in proportion to their individual populations. With these assumptions we can write

$$\frac{dm_{1m}}{dt} = K_1 m_{1m} - K_3 \frac{m_{1m}}{m_{1m}+m_{2m}} \quad ...(23)$$

$$\frac{dm_{2m}}{dt} = K_2 m_{1m} - K_3 \frac{m_{2m}}{m_{1m}+m_{2m}} \quad ...(24)$$

Here also suffix m stands for mimicry. The various terms have the same significance as the corresponding terms in Eqs. (1) and (2). Combining Eqs. (23) and (24), we get

$$\frac{dm_{2m}/dt}{m_{2m}} - \frac{dm_{1m}/dt}{m_{1m}} = K_2 - K_1 \quad ...(25)$$

But for notations, Eq. (25) is the same as Eq. (3). Hence, the equation corresponding to Eq. (6) would be

$$\frac{m_{2m}}{m_{1m}} = \frac{m_{2m}(0)}{m_{1m}(0)} \exp (K_2 - K_1)t \quad ...(26)$$

Following the same procedure as in the case of polymorphic mimicry, we get

$$m_{2m} = m_{2m}(0) \exp (K_2 t) - K_3 I_m(t) \exp (K_2 t) \quad ...(27)$$

and

$$m_{1m} = m_{1m}(0) \exp (K_1 t) - K_3 \frac{m_{1m}(0)}{m_{2m}(0)} I_m(t) \exp (K_1 t) \quad ...(28)$$

where

$$I_m(t) = \int_0^t \frac{\exp (-K_2 t) dt}{\left[1 + \frac{m_{1m}(0)}{m_{2m}(0)} \exp (K_1 - K_2)t\right]} \quad ...(29)$$

But for the different integral involved, Eqs. (27) and (28) are of the same form as Eqs. (8) and (10).

Equations of evolution without mimicry are obtained by putting $m_{2m} = 0$ in Eq. (23) and $m_{1m} = 0$ in Eq. (24) and dropping suffix m. Solving these equations we get

$$m_1 = \left[m_1(0) - \frac{K_3}{K_1}\right] \exp (K_1 t) + \frac{K_3}{K_1} \quad ...(30)$$

and

$$m_2 = \left[m_2(0) - \frac{K_3}{K_2}\right] \exp (K_2 t) + \frac{K_3}{K_2} \quad ...(31)$$

Having obtained the equations of evolution with and without mimicry it is now possible to study the effect of mimicry on evolution. The condition that the population of the mimic species be growing at a particular instant of time is from Eq. (24)

$$K_2(m_{1m} + m_{2m}) > K_3 \quad ...(32)$$

In the absence of mimicry, this condition becomes

$$K_2 m_2 > K_3 \quad ...(33)$$

These conditions are represented by the curves in Fig. 7. It is seen that for any given value of m_2, the population can grow with lesser regenerative ability if recourse is taken to mimicry. Comparison of Eqs. (32) and (33) gives interesting results. It is seen that the effective population has increased from m_2 to $m_1 + m_2$ as a result of mimicry. As mentioned earlier, the effective population of the mimic species increases as a result of polymorphic mimicry also. The increase in effective population as a result of monomorphic mimicry is of a smaller magnitude than that as a result of polymorphic mimicry. For monotonous growth of population, Eq. (32) should be satisfied for all times. Using Eq. (26), the condition becomes

$$K_2 m_{2m} > \frac{K_3}{1 + \frac{m_{1m}(0)}{m_{2m}(0)} \exp (K_1 - K_2)t} \quad ...(34)$$

This condition should be satisfied even for the largest value of the right-hand side terms and the
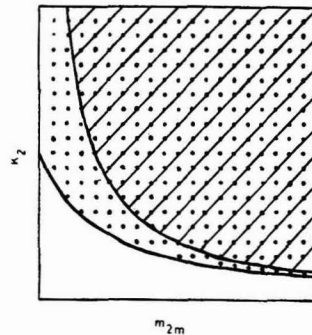

Fig. 7 — Conditions of growing population with and without monomorphic mimicry [The two curves starting from above are for $K_2 m_2 = K_3$ and $K_2(m_1 + m_2) = K_3$. Shading of areas has the same significance as in Fig. 1]

399

smallest values of the left-hand side terms in Eqs.(1) and (2), i.e.

$$K_2[m_{2m}(0)+m_{1m}(0)] > K_3; \; K_1 > K_2 \qquad ...(35a)$$

and

$$K_2 m_{2m}(0) > K_3; \; K_2 > K_1 \qquad ...(35b)$$

The part of the condition represented by Eq. (35a) is both necessary and sufficient, but the part represented by Eq. (35b) is sufficient but not necessary. In the absence of mimicry, the condition becomes

$$K_2 m_2(0) > K_3 \qquad ...(36)$$

These conditions are represented by the curves in Fig. 8 from which the advantage of mimicry is evident. It is seen from Eq. (35) that K_3 has to be below a certain limit for the monotonous growth of the mimic species. This is clear from Eq. (27) also. Eq. (27) shows that $m_{2m}(t) = 0$ if $m_{2m}(0)/K_3 = I_m(t)$. As $I_m(t)$ is a monotonously growing function of time, and as $I_m(0) = 0$, it follows that the population of the mimic species would be exterminated in time if $m_{2m}(0)/K_3 < I_m(\infty)$. Thus, for very high values of K_3, extermination cannot be avoided even by taking recourse to mimicry.

The conditions that the relative abundance of the mimic species be monotonously increasing without mimicry are

$$K_2 m_2(0) > K_3; \; K_1 m_1(0) < K_3 \qquad ...(37a)$$
$$K_2 m_2(0) > K_1 m_1(0) > K_3; \; K_2 > K_1 \qquad ...(37b)$$
$$K_1 m_1(0) < K_2 m_2(0) < K_3; \; K_2 < K_1 \qquad ...(37c)$$

With mimicry, the condition for monotonously increasing relative abundance of the mimic species becomes simply, from Eq. (26)

$$K_2 - K_1 > 0 \qquad ...(38)$$

Thus, as long as this condition is satisfied, mimicry allows the relative abundance of the mimic species to grow monotonously irrespective of the values of K_3, $p_{2m}(0)$ and $p_{1m}(0)$. In the absence of mimicry, the condition

$$\frac{K_2}{K_1} > \frac{m_1(0)}{m_2(0)} \qquad ...(39)$$

must be satisfied in addition to certain other restrictions involving K_3 given by Eq. (37). Under the conditions represented by Eq. (37c), it is evident that the second species can maintain monotonously growing relative abundance in the absence of mimicry, even with a regenerative ability smaller than that of the first species. However, if it takes recourse to mimicry, it can do so only by exceeding the regenerative ability of the first species. Thus, unlike polymorphic mimicry monomorphic mimicry is not advantageous under all conditions.
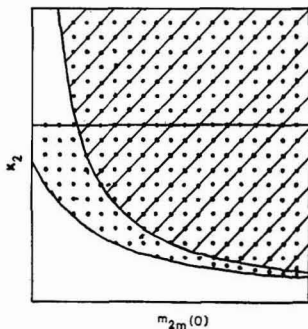
In the absence of mimicry (both polymorphic and monomorphic), conditions of monotonously growing relative abundance of the mimic species involve products of regenerative ability and initial strength, such as $K_2 m_2(0)$, $K_1 m_1(0)$, $K_2 p_2(0)$, $K_1 p_2(0)$, i.e. to certain extent there exists trade-off between initial strength and regenerative ability. As a result of mimicry (both polymorphic and monomorphic) the initial strengths drop out of picture and the conditions of monotonously growing relative abundance of the mimic species depend only on the regenerative abilities of the two species. This is a definite advantage, because a weaker species also can survive if it takes recourse to mimicry.

It is interesting to note that but for notation, Eqs. (6) and (26) are identical. Thus, just as in the case of polymorphic mimicry, as a result of monomorphic mimicry, the relative abundance of the two species is held at a level that would prevail if the predator's attacks were altogether absent. This implies that as in the case of polymorphic mimicry the mimic species succeeds in fully annulling the effect of the predator's attacks, in so far as the relative abundance of the two species is concerned, by practising monomorphic mimicry.

Referring once again to the equations of evolution, i.e. Eqs. (27)-(31), the integral $I_m(t)$ appearing in Eqs. (27) and (28) and defined by Eq. (29) cannot be evaluated in closed form. It can, however, be evaluated by the numerical integration techniques. It has been evaluated for the set of parameter values given in Table 1. The values obtained are plotted in Fig. 9. All the comments about Fig. 4 apply

Fig. 8 — Conditions of monotonously growing population with and without monomorphic mimicry [The horizontal straight line is for $K_1=K_2$; the two curves starting from above are for $K_2 m_2(0)=K_3$ and $K_2\{m_1(0)+m_2(0)\}=K_3$. Shading of areas has the same significance as in Fig. 1]
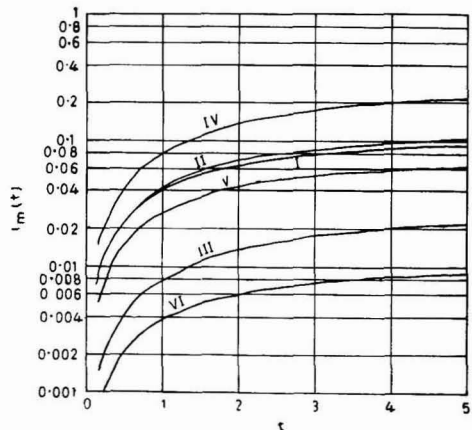
Fig. 9 — Integral $I_m(t)$ appearing in the equations of evolution with monomorphic mimicry as a function of time for sets of parameter values given in Table 1
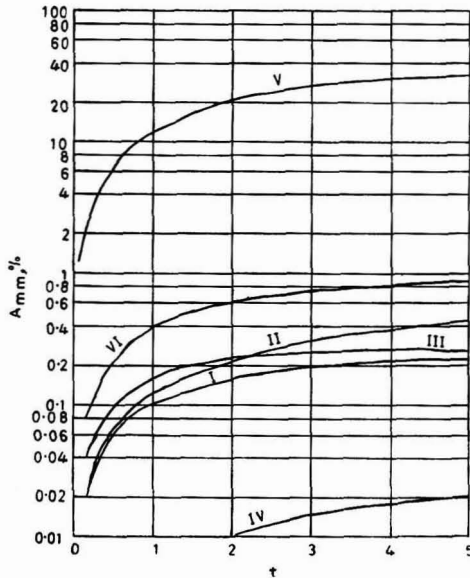
Fig. 10 — Advantage of monomorphic mimicry as a function of time for sets of parameter values given in Table 1

qualitatively in the case of Fig. 9 also. But generally $I_m(t) > I_p(t)$, as can be seen from the definitions of the two integrals.

The advantage of monomorphic mimicry can be defined as

$$A_{mm}(t) = \left[\frac{m_{2m}(t) - m_2(t)}{m_2(t)} \right] 100\% \qquad ...(40)$$

This is represented in Fig. 10 as a function of time for various sets of parameters listed in Table 1. Comparison of Fig. 10 with Fig. 5 reveals that the advantages resulting from polymorphic mimicry are consistently greater than those resulting from monomorphic mimicry for the same set of parameter values. The comments about Fig. 5 apply qualitatively to Fig. 10 as well.

It is seen from Fig. 6 that in the case of monomorphic mimicry, the populations of both the species grow faster with mimicry than without it. Thus, monomorphic mimicry does not offer any advantage to the mimic species at the cost of the model species, but in ' collaboration ' with it. Also, polymorphic mimicry leaves the population level of the mimic species at a higher level than monomorphic mimicry. The same holds good for the model species, although as a result of polymorphic mimicry the population level of the model species comes down and as a result of monomorphic mimicry it goes up. This is possible, because in the absence of polymorphic mimicry the population level of the model species

is much higher than in the absence of monomorphic mimicry. The population level of the mimic species in the absence of either polymorphic or monomorphic mimicry is held at the same level.

Conclusion

Mathematical analyses of polymorphic Batesian mimicry and monomorphic Müllerian mimicry carried out in the present study show that in either case mimicry proves significantly advantageous under heavy attack and when the model species is more predominant, and regenerates at a higher rate. By recourse to either form of mimicry, the relative abundance of the two species is held at a level that would prevail if the predator's attacks were altogether absent. Polymorphic mimicry offers advantages to the mimic species at the cost of the model species, but monomorphic mimicry offers advantage to the mimic species in ' collaboration ' with the model species. Unlike polymorphic mimicry, monomorphic mimicry is not advantageous under all conditions. The advantages accruing from either form of mimicry are a growing function of time, but finally attain a steady value. Thus, natural selection would work in favour of those members which take recourse to mimicry.

With minor modifications, similar analysis can be worked out in the case of military camouflage operations.

Summary

Mathematical models have been set up for Batesian (polymorphic) and Müllerian (monomorphic) mimicry. For simplicity of analysis, factors like age-dependent birth and death rates, immigration and emigration have not been taken into consideration. The analysis reveals that by recourse to either form of mimicry, the relative abundance of the two species is held at a level that would prevail if the predator's attacks were totally absent. In the case of polymorphic mimicry, the mimic species derives advantage at the cost of model species, but in the case of monomorphic mimicry both the species gain, so that the roles of the mimic and model species can be interchanged. With polymorphic mimicry, the advantage gained by the mimic species is unconditional and is available under all circumstances. This does not hold good for monomorphic mimicry. Without mimicry there exists a trade-off between the regenerative ability and initial strength, but with mimicry the relative abundance depends only on the regenerative abilities of the two species and not on their population ratio. This is a definite advantage for less populous mimic species. On the whole, polymorphic mimicry is more advantageous than monomorphic mimicry.

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Ribosomal Proteins of *Escherichia coli* — Their Fractionation, Characterization & Some Properties

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RIBOSOMES from almost all sources are ribonucleoproteins and are composed of two subunits of unequal size. In *Escherichia coli*, these subunits have sedimentation coefficients of 30S and 50S and both of them are made up of 63 per cent RNA and 37 per cent proteins. In solvents containing Mg^{2+} ions at a suitable concentration, one 30S and one 50S subunit combine to form a 70S ribosome, 'the active unit', on which protein synthesis occurs. The 30S and 50S subunits have molecular weights of about $0·9 \times 10^6$ and $1·8 \times 10^6$ respectively; they together constitute the 70S particle of molecular weight $2·7 \times 10^6$. The RNA inside the 30S subunit is a single molecule sedimenting at 16S, but inside the 50S subunit there exist one 23S RNA and one 5S RNA molecule. The exact number of protein components in each subunit is still a matter of conjecture, but until now the best guess has been that about 40 proteins are present in the 50S subunit and about 20 in the 30S subunit. Until recently there was no *a priori* reason as to why the two subunits were needed as such and why either of the two subunits by itself was ineffective in fulfilling all the functions of the ribosome. Recent data from several laboratories[1-3] indicate that only the 30S subunits are capable of codon directed binding of N-formyl-methionine-sRNA (or the peptidyl-sRNA). This site is called the peptidyl-sRNA site. N-formyl-methionine-sRNA can bind to this site; the corresponding sRNA is sometimes called the initiator sRNA. The following general scheme emerges from all these data: (i) The first step is the formation of an obligatory intermediate of 30S-mRNA-N-formyl-methionine-sRNA. The formation of this obligatory intermediate requires GTP, although GTP is reported not to be hydrolysed in this step[4]. (ii) In the next step, 50S subunits are coupled to the obligatory intermediate. Isolated 50S subunits can neither bind mRNA nor support codon directed binding of aminoacyl-sRNA. The joining of 50S subunits to the obligatory intermediate generates an additional binding site for aminoacyl-sRNA. (iii) After the joining of the aminoacyl-sRNA, peptide bond formation takes place. (iv) With the release of the completed polypeptide chain, the 30S and the 50S subunits dissociate and are recycled into the system[5].

GTP is also necessary for the binding of aminoacyl-sRNA to the complex[6] and splitting of GTP is involved in the polypeptide bond formation. Thus, while the 30S subunits have a specific role in initiating protein synthesis, 50S subunits are essential for polypeptide bond formation. These results are in agreement with Monroe's observation[7] that peptidyl transferase, an enzyme which catalyses the formation of the peptide bond, is located on the 50S subunit.

Basically the problem is to ascertain the roles played by the RNA moiety and the protein moiety during the different steps of protein synthesis. Before considering this question, the chemical nature of the rRNA and the r-proteins must be visualized first. In view of the abundant literature on ribosomes, this discussion will be confined to ribosomes from *Esch. coli*. Moreover, our interest here is restricted to the structural and functional aspects of the r-proteins only. Since the ribosomes from *Esch. coli* were first characterized by Tissieres et al.[8] in 1959, sustained research work extending over several years has now brought us to a position where we can say that the r-proteins are a heterogeneous group of protein components, about 30 in number, most of them differing in their primary structure and being basic in nature at neutral pH. The function of the r-proteins at the individual level is not understood, primarily because of their peculiar physico-chemical properties, particularly the solubility properties, which make it difficult to prepare ribosomes lacking one or two well-defined proteins and subsequently to assess their biological activity.

The main methods that have been employed so far to isolate and fractionate the r-proteins are listed in Table 1. Waller and Harris[9] first isolated the r-proteins by treating ribosomes with acetic acid. The procedure used by Frankel-Conrat as early as 1957 to separate the tobacco mosaic virus (TMV) proteins from the virus involves gradual addition of two volumes of acetic acid to a cold suspension of ribosomes (1-3 per cent by wt). The RNA that precipitated was centrifuged after 45 min. The supernatant was then dialysed to remove most of the acetic acid and then freeze-dried for further analysis. The recovery of proteins by this method was about 85 per cent and Waller[10] provided evidence that the remaining 15 per cent proteins were essentially similar to the extracted proteins. Since the majority of the proteins were basic[10], an attempt was made to fractionate them by column chromatography on CM-cellulose. Twelve fractions were obtained by elution with a gradient of $0-0·3M$ acetate buffer of pH 5·6 containing $6M$ urea.

In 1961, Spitnik-Elson[18] made a systematic study of the solubility of r-proteins and she was able to isolate and fractionate the r-proteins of *Esch. coli* by exposing ribosomes to buffers of various salt concentrations and pH. The purpose of her study was to find a mild non-denaturing solvent and to solubilize the proteins at neutral pH. In principle, exposure of ribosomes to high salt concentration activated the latent RNase present inside the ribosomes, thus allowing it to digest the rRNA. The latter, broken into small fragments, could then be dialysed out. The salt concentration, type of salt

TABLE 1 — ISOLATION AND FRACTIONATION OF RIBOSOMAL PROTEINS OF *Esch. coli*

Solvent	Yield %	Method of fractionation	No. of fractions derived	Ref.
Acetic acid (66%)	85	Chromatography on CM-cellulose column; elution with acetate buffer (pH 5·6) 0-0·3M, containing 6M urea	12	9, 10
Acetate buffer (pH 3·9-5·3; μ 0·1-0·5)	30 (pH 5·3; μ 0·4)	—	—	11
Phosphate buffer (pH 5·4-7·9; μ 0·1-0·5)	56 (pH 6·8; μ 0·4)	—	—	11
Sodium chloride (1M)	~100*	—	—	11
Tris (1M; pH 7·4)	100	Ammonium sulphate fractionation	3 (P30, P50 and P70)	11
Lithium chloride (2M) plus urea (4M)	85-90	—	—	12
Acetic acid (66%)	85	Chromatography on CM-cellulose; elution with phosphate buffer (pH8), 0·005-0·3M, containing 8M urea; subsequent fractionation in DEAE-cellulose column with 1M propionic acid	4 including the ribosomal A protein partially characterized	13, 14
Acetic acid (66%)	85	Chromatography on CM-cellulose; elution with acetate buffer (pH 5·6), 0·01-0·4M containing 6M urea; also chromatography on Sephadex G-100 and countercurrent distribution	11 pure proteins from 30S and one from 50S subunit	15, 16
Lithium chloride (3M) plus urea (6M)	100	Chromatography on CM-cellulose; elution with 0·03M lithium chloride, 0·08M urea, 0·1M formate, 0·02M formate and 0·3M barium chloride and formic acid respectively	3 main fractions (F_2, F_3, F_4) representing 90 per cent of the r-proteins and 2 minor fractions (F_1 and F_5)	17

*The yield was 100 per cent only with r-protein concentration ≤0·6 mg./ml.

used, pH of the solution and the temperature of the experiment were the factors that controlled the amount of protein solubilized, e.g. at 37° when dialysis of ribosomes against acetate buffers of different pH (3·9-5·3) and ionic strength (0·1-0·5) was tried, a maximum of 30 per cent of the total r-proteins could be solubilized at pH 5·3 and ionic strength 0·4. Similarly, when phosphate buffers of pH 5·4-7·9 and ionic strength 0·1-0·5 were used, maximum solubility of 56 per cent was achieved at pH 6·8 and ionic strength 0·4; almost complete solubilization of the r-proteins was achieved in 1M NaCl at pH 7 at low protein concentration (0·6 mg./ml.) in the starting material. After examining a variety of solvents, Spitnik-Elson succeeded in solubilizing the total r-proteins by self-digestion of the ribosomes in 1M tris, pH 7·4 at 24° for 12-15 hr. After extraction in this solvent, the r-proteins were fractionated into three parts with ammonium sulphate[11]. These fractions were designated P30, P50 and P70, as they were obtained by 30, 50 and 70 per cent saturation with ammonium sulphate respectively. Together they represented the whole r-protein. They had charge differences varying from excess acidic to excess basic and in isolated condition when P30 was mixed with P70, a

precipitate was formed, indicating the strong tendency of these proteins to aggregate.

Subsequently, Spitnik-Elson[11] reported fractionation of the r-proteins by chromatography on CM-cellulose and demonstrated that about 80 per cent of the proteins constituted a mixture of basic proteins with isoelectric point above pH 9. The remaining 15 per cent proteins precipitated at pH 5·8 and were soluble only at a very low pH.

Leboy et al.[12] in 1964 used 4M lithium chloride and 8M urea and extracted 85-90 per cent of the proteins by adding equal volume of this solvent to a suspension of ribosomes. The precipitated RNA was removed and the supernatant contained the proteins. In contrast to *Esch. coli* ribosomes[19], plant and animal ribosomal proteins can be completely extracted with lithium chloride alone. In the former case, only a part of the protein separates on lithium chloride treatment.

Recently, Moller and Widowson[13] attempted to fractionate the r-proteins and to isolate protein components for chemical analysis. They neutralized the acetic acid extract to pH 7·5 with NaOH, digested with RNase to remove traces of RNA, then dialysed and lyophilized the protein. This protein was dissolved in 0·005M ammonium phosphate

403

buffer containing $8M$ urea at pH 8, adsorbed on a CM-cellulose column and eluted with the same buffer by increasing the salt concentration from 0·005 to 0·3M. At least four well-defined fractions were obtained, of which the first (fraction I), which emerged unretarded, was acidic and hence was further fractionated by a DEAE-cellulose column again with 0·05-0·3M ammonium phosphate and $8M$ urea. Two peaks, a major (70 per cent) and a minor (30 per cent) one were obtained, of which the first, which constituted 5 per cent of the total r-proteins, was named 'ribosomal A protein'. It showed two bands on polyacrylamide gel electrophoresis. The other three fractions were analysed by tryptic digestion, amino acid analysis and polyacrylamide gel electrophoresis. They appeared to be heterogeneous.

Recently, Traut et al.[15] finally succeeded in isolating and partially characterizing 10 pure proteins (homogeneous by polyacrylamide gel electrophoresis), nine from the 30S and one from the 50S subunit. The 30S r-proteins extracted with acetic acid were first adsorbed on CM-cellulose and eluted with acetate buffer of pH 5·6 containing $6M$ urea between 0·01 and 0·4M salt concentration; about 300 fractions of 15 ml. were collected. Further purification of these fractions by chromatography on Sephadex G-100 in $1M$ propionic acid gave 9 protein fractions designated 30_3, 30_4, 30_{4b}, 30_5, 30_7, 30_8, 30_{10A}, 30_{10B} and 30_{11-12}. The purified 50S fraction, called 50_5, was obtained by CM-cellulose chromatography followed by distribution in a two-phase system containing butanol-urea and p-toluene sulphonic acid. Moore et al.[16] later reported the isolation and characterization of 11 proteins from the 30S subunit, on the basis of polyacrylamide gel electrophoresis, amino acid composition determination and sedimentation analysis by the Yphantis method.

The basic disadvantage of the procedure using acetic acid and of methods using lithium chloride and urea is the possibility of irreversible denatura-tion of the r-proteins. Therefore, although such r-proteins could be used for chemical analyses, they were not suitable for the determination of their biological function. The method of extraction either with $1M$ tris or with high salt concentrations suffers from the drawback that it is dependent on the presence of RNase in the system and hence is not applicable to RNase-free strains of Esch. coli. This RNase which is retained along with the extracted proteins may hinder ribosome reconstitution experiments with such r-proteins. SDS or other anionic detergents used in a few cases[20,21] almost always bind irreversibly with protein and present an additional problem of removal of the detergents after the separation of proteins from RNA.

The vast complexity of the r-proteins of Esch. coli was first encountered by Waller[10] during starch gel electrophoresis of the acetic acid-soluble fraction. In acetate buffer of pH 5·6 and $6M$ urea he observed at least 24 bands, of which at least 19 had a net positive charge. Almost simultaneously, Leboy et al.[12] carried out polyacrylamide gel electrophoresis of lithium chloride-urea extracted proteins using β-alanine buffer of pH 4·5 and obtained 28 bands. The results of other investigators summarized in Table 2 indicate that the number of components observed in the 30S and 50S subunits almost always exceeds the total number in the 70S proteins. Several components observed in the 70S ribosome might be different molecules of the same mobility. However, each subunit possesses a set of proteins not represented in the other and also there are a few components commonly present in both 30S and 50S.

Conversion to S-sulpho derivative, reduction and alkylation or carbamylation of the ε-amino groups to block the reaction with cyanate in urea did not produce any significant change in the electrophoretic pattern of the total r-proteins, suggesting the possibility that intermolecular interactions may not have taken place[14].

TABLE 2 — NUMBER OF PROTEIN COMPONENTS IN Esch. coli RIBOSOMES

Extracting agent for r-proteins	Analysis technique	No.* of proteins in			Ref.
		70S	50S	30S	
Acetic acid (66%)	Starch gel electrophoresis in acetate buffer (pH 5·6) with $6M$ urea	24	14	12	10
Lithium chloride (2M) + urea (4M)	Polyacrylamide gel electrophoresis in β-alanine-acetic acid buffer (pH 4·5) with $8M$ urea	28	7	15	12
do	do	25	20	16	22
Acetic acid (66%)	Immunological analysis	—	7	—	23
do	Polyacrylamide gel electrophoresis in formate buffer (pH 3·5) with $8M$ urea	24	—	—	14
do	Polyacrylamide gel electrophoresis at pH 4·5 with $8M$ urea	—	23	14	15

*Unless quoted by the authors in the text, in most cases the figure represents the number of bands that could be counted from the published photographs.

Physico-chemical Characterization

N-terminal amino acid analysis of the acetic acid-soluble proteins made by Waller and Harris[9] showed methionine and alanine to be the two main end groups. Serine, threonine and traces of aspartic and glutamic acids were also found. Both fluorodinitrobenzene and phenylisothiocyanate method gave the same average molecular weight of 25,000. The calculation was made on the basis of the weight of protein/mole of end groups recovered. Amino acid composition and end group analysis of 9 purified proteins from the 30S and one in the 50S subunit have established that most of the r-proteins have distinctive and different primary structures. From the yield of the N-terminal derivative/weight of protein hydrolysed, and amino acid composition, the molecular weight has been calculated to lie in the range 8000-40,000. This analysis was preceded by fingerprinting of the total ^{35}S-labelled r-proteins. About 205 methionine and 45 cysteine residues are present in each 70S ribosome, and these residues are distributed in all but two protein components. A tryptic digestion of performate oxidized ^{35}S-labelled protein in $0 \cdot 1M$ ammonium bicarbonate for 48 hr at 37° with an enzyme-protein ratio of 1:40 and subsequent fingerprinting revealed 120 spots by radioautography. This value is too high for a sample composed of a single protein or repeating units of molecular weight 25,000, which is expected to give only 6-7 spots. The purified 30S proteins, when fingerprinted, also gave distinctly different ninhydrin spots.

Moller and Chrambach[14] carried out sedimentation-diffusion and sedimentation equilibrium analysis and reported an average molecular weight of 25,000 for the r-proteins. The plot of log h_x versus X^2 in the equilibrium study showed curvature indicating heterogeneity. The values of M_w and M_z came to 23,000 and 27,000 respectively. Assuming that equal weight of each class of molecules is present and each species differs in molecular weight by 1000, an interesting calculation of the spread in molecular weight was made by these workers; the molecular weight was found to be in the range 10,000-40,000.

The experiments so far described establish the existence of more than 30 components in the ribosomal proteins, all of which are likely to have different primary structures. Here, a pertinent question is: Do all 70S ribosomes contain the same chemical entity? In other words: Is the composition of each 30S and 50S subunit same? It is difficult to answer this question unequivocally, but ribosomes isolated from the same species at different growth stages are identical in composition. In addition, the generality of their function for the synthesis of thousands of proteins indicates the presence of common structural components. Very recently, Byers[24] has been able to obtain electron micrographs of what are called ' crystalline ribosomes '. When chick eggs and embryos are cooled to 5-15° for periods ranging from several hours to 2 days, crystalline arrays of ribosomes, in the form of sheets, cylinders and even 3-dimensional crystals become visible. Now the problem is to separate the crystals

from cellular material for X-ray crystallography. The tendency to form a well-defined regular structure again indicates that the ribosomes are structurally identical and suggests homogeneity of the individual molecules.

Work on the determination of the secondary structure has not been extensive because of the need for a solvent which could possibly keep the ribosomes in the native form. Sarkar *et al.*[25] found that about 40 per cent of the total r-proteins in acetic acid are soluble in buffers of neutral pH in which ribosomes are stable. Optical rotatory dispersion studies of this soluble portion of the r-proteins gave the value of $[\alpha]_{233}$ mμ as -4000, which is consistent with an α-helix content of 20-25 per cent. Analysis by circular dichroism, a technique complementary to optical rotatory dispersion, gave analogous results[26].

Our knowledge on the function of ribosomal proteins is still very rudimentary. That the proteins may be involved in maintaining the intactness of the 70S particle is suggested by two observations: (i) exhaustive trypsin treatment leads to dissociation of the 70S particles to 50S and 30S subunits, and (ii) treatment of ribosomes with sulphydryl reagents, such as p-chloromercuribenzoate, N-ethyl maleamide, etc., helps dissociation[27].

Kaji *et al.*[28] found that when ribosomes are treated with trypsin, no soluble material is released, but the ribosomes lost some of their functions. However, it is important to note that increasing amounts of trypsin cause a proportional damage to the biological activity of the ribosomes. Thus, as the trypsin concentration increases, the following functions are damaged in a stepwise manner: (i) binding of the ribosomes to mRNA, (ii) binding of sRNA to the mRNA-ribosome complex, and (iii) incorporation of amino acids into protein. Therefore, it is likely that r-proteins have specific functional roles. The presence of secondary structure in the ribosomal proteins might help in establishing their identity and also in settling the question of a definite configurational requirement for the ribosome function.

Attempts to delineate the function of r-proteins have also been made by preparing ribonucleoprotein particles deficient in some of the protein components. In 1966, three reports appeared simultaneously[29-31] on the preparation of such particles. When ribosomes are centrifuged in 60 per cent cesium chloride solution of appropriate Mg^{2+} ion concentration, they band at a density of 1·66 g. cm.$^{-3}$, leaving some of the proteins at the meniscus. Thus, the 50S subunit dissociated into a 40S core particle and some split proteins (SP50) and correspondingly, the 30S subunit gave a 23S particle and SP30.

$$50S \rightarrow 40S + SP50$$
$$30S \rightarrow 23S + SP30$$
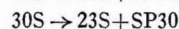
Reconstitution studies of the core particles with the split proteins have been partially successful[22] and this again suggests the specificity of r-proteins in their function.

SP30 and SP50 have now been divided into two fractions each and one of the fractions has been

shown to be unnecessary for sRNA binding. Similar protein-deficient ribosomes have been prepared in the presence of chloramphenicol or $1.5M$ lithium chloride, when several components are released. Kaji and Nakada[32] reported that the 18S particles lack 4-5 proteins and are functionally inactive.

It appears, therefore, that while the necessity of the protein moiety in general in the ribosome function has been well realized, the role of the individual components in the process remains obscure. For this purpose, it would be useful to prepare ribosomes deficient in one or two proteins. An assay of the biological activity of such ribosomes might give some information on the function of these deficient protein components. This problem is complicated due to the occurrence of several enzymes bound to the surface of the ribosomes. *Esch. coli* ribosomes have been reported to contain RNase[33], DNase[34], acid phosphatase[35], leucine amidopeptidase[36], enzymes capable of breaking cysteinyl-glycine[37] and L-prolyl-glycine[38], poly A polymerase[39] and possibly β-galactosidase[36]. It is obvious that many of them are bound electrostatically during the isolation of the ribosomes and are not involved in ribosome function (e.g. RNase), but until this is demonstrated experimentally, the criteria of ribosome purity cannot be established. The other problem which has delayed this kind of study is the solubility of r-proteins. When separated from RNA, the proteins have a strong tendency to aggregate and precipitate in mild non-denaturing aqueous solvents. Sarkar looked for a solvent which could keep all the r-proteins in solution and at the same time does not degrade ribosomes (unpublished results). Such a solvent is of extreme importance for controlled reconstitution studies. Ribosomes were dialysed against buffer-solvent mixtures (50:50, vol./vol.) containing appropriate Mg^{2+} ion concentration and after dialysis the contents of the sac were analysed by ultracentrifuge. Weak proteinic solvents of decreasing dielectric constants were employed to reduce the polarity of the medium, so that the protein-protein interaction does not supercede the protein-solvent interaction. The solvents so far used and their approximate dielectric constants at room temperature are: ethylene glycol, 43; glycerol, 38; methanol, 32.7; ethanol, 24.3; 2-propanol, 18.3; and dioxane, 2.2. Interestingly, except in ethylene glycol and glycerol, in all other solvents (dielectric constant ~ 30 or less), the ribosomes precipitated on dialysis. This precipitation was reversible since on redialysis against tris buffer, the precipitate dissolved and ultracentrifugal analysis displayed the original pattern. Only in the first two solvents, the ribosomes were soluble and stable and did not show any difference in their ultracentrifugal pattern from those obtained in the aqueous media. However, when isolated r-proteins were dialysed against 50 per cent ethylene glycol or 50 per cent glycerol, they were as soluble as in aqueous solvents. These studies indicate that the major factors causing aggregation of r-proteins in the isolated state are not limited to hydrophobic interactions, since reducing the polarity of the solvent does not appreciably increase the solubility. Perhaps electrostatic interactions are equally important and hence the search for a solvent with the potentiality to destroy the protein-protein interaction continues.

Summary

The advantages and disadvantages of the various methods that have been employed so far to isolate and fractionate the ribosomal proteins (r-proteins) of *Esch. coli* are discussed. These methods involve treatment with acetic acid, urea, urea plus lithium chloride, $1M$ tris buffer and, in a few cases, salts or detergents at high concentrations. The presence of at least 25 different protein components in each 70S ribosome particle has been definitely established from electrophoretic analyses on starch gels or on polyacrylamide gels. The distribution of these proteins in the 30S and 50S subunits is indicative of the presence of some common components, although each of these subunits possesses a characteristic set of proteins not represented in the other. Purification of nine components from the 30S subunit and one from the 50S subunit has been achieved by column chromatography on CM-cellulose followed by Sephadex G-100 or by countercurrent distribution. Amino acid composition and fingerprinting of the tryptic digests of these purified proteins reveal the existence of differences in their primary structure. Fingerprinting of the tryptic digests of the ^{35}S-labelled total proteins indicates that the rest of the components are different in their primary structure. Analysis of the N-terminal amino acids, as well as ultracentrifugal analysis by the sedimentation equilibrium method give an average molecular weight of about 25,000 for these proteins. Other results indicate a molecular weight distribution ranging from 8000 to 40,000. Optical rotatory dispersion and circular dichroism studies show the presence of 20-25 per cent α-helix in both 30S and 50S proteins. The significance of the presence of this secondary structure is not yet clear. The present status of our understanding of the structure and properties of r-proteins is inadequate for elucidating their biological function. Ribosomes lacking the ability to bind mRNA, sRNA or to incorporate amino acids into proteins, i.e. partially or completely incapable ribosomes, have been obtained by controlled trypsin digestion or by exposure to a high concentration of cesium chloride. This suggests specific roles for r-proteins in different steps of protein synthesis. The dissociation of 70S ribosomes into 30S and 50S subunits by exhaustive trypsin treatment or by treatment with sulphydryl reagents suggests that r-proteins may also be involved in holding the subunits together. It remains to be established whether all the components are indispensable for the functioning of the 70S particles or how many of these components are superfluous, merely reflecting the adsorption of enzymes or other non-specific proteins on the ribosomal surface during the isolation of the ribosomes. The need for finding a suitable solvent for the r-proteins in which both the ribosomes and the ribosomal RNA are soluble and stable, as a prelude to preparing ribosomes deficient in one or a few well-defined proteins, has been emphasized. Assay of the biological activity of such ribosomes might be useful for delineating the function of r-proteins. The

results of preliminary experiments in this direction have been discussed.

Acknowledgement

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Indian Pharmaceutical Congress

The twentieth session of the Indian Pharmaceutical Congress will be held at the L.M. College of Pharmacy, Ahmedabad, during 24-26 December 1968. Separate scientific session will be devoted to: Industrial pharmacy and industrial microbiology; Pharmaceutical chemistry; Pharmacognosy and phytochemistry; Pharmacology; Educational pharmacy; Professional and forensic pharmacy; Ayurvedic and Unani pharmacy; and Hospital pharmacy. A symposium on ' Progress of pharmaceutical sciences in post-independent India ' will be held on the occasion.

Further details can be had from the Secretary, Indian Pharmaceutical Congress, Third Floor, Government Multistoreyed Building, Ahmedabad 1.

REVIEWS

MULTICHANNEL TIME SERIES ANALYSIS WITH DIGITAL COMPUTER PROGRAMMES by Enders A. Robinson (Holden-Day Inc., New York), 1967. Pp. xxiii+298

This book by Dr Enders A. Robinson is a timely arrival of recognized work by a competent authority in this subject. It has a great topical value because of the current interest in fast Fourier transforms and a general eagerness on the part of computer scientists to make mathematical models lucidly representable, with physical significance, with the aid of fast digital computers.

The present volume has been written in an easy and simple language so that it is equally suitable for a senior student in electrical engineering and physical sciences as for a professional scientist. It is backed up with some seventy original programmes, written by the author himself.

The subject matter has been covered in six different chapters. The computer programmes are in popular Fortran IV with the result that these could be easily tried out as problems for home work by the students and would give a sense of confidence to the student leading him to do more complicated time series analysis, both single channel as well as multichannel.

Chapter I covers basic computer programmes and necessary sub-routines required for polynomial matrix transformations, Z transforms, etc. Chapter II deals with single channel digital filtering and spectral analysis; the treatment is quite exhaustive. The more specialized topic of wave propagation in layered media is dealt with in Chapter III. The author's own bias towards the study of seismic properties and his adaptation for solving geophysical time series analysis with computer programme are amply illustrated in these pages. Chapter IV is primarily concerned with matrix polynomials and necessary sub-routines and would be of considerable value to those who are more concerned with mathematical applications and their solutions with computer programming. Chapter V deals with multichannel digital filtering and spectral analysis which includes multichannel operators, auto-correlation of the inverse multichannel operator, spectral analysis of multichannel time series, stationary Markov processes, and nonlinear filtering theory. Chapter VI deals with multichannel prediction and signal enhancement. This pertains to multichannel Wiener filtering, design of multichannel Wiener digital filters and other areas covering prediction of commodity futures, output energy filters with linear constraints and so on.

The pleasant part of the overall treatment of the subject matter has been the illustrative case studies dealing with geophysical sciences with the result that the student is not lost entirely in theoretical jargon but acquires a physical meaning and significance in dealing with problems involving time series analysis.

On the whole, the subject matter has been well presented and would be found very useful by both the practising engineer as well as the physicist. It would also be of considerable interest to economists and statisticians who would like to deal with similar time series analysis in their own domains.

P. K. PATWARDHAN

ADVANCED QUANTUM MECHANICS by J. J. Sakurai (Addison-Wesley Publishing Co. Inc., London), 1968. Pp. xii+336. Price 140s.

The covariant quantum electrodynamics, though a very attractive mathematical formalism, hides the basic physics, specially for the beginner. This is reflected in books which have started appearing since around 1957. As a result many able researchers in quantum electrodynamics miss the physics behind it.

To remove this defect appears to be one of the important motivations of this book, the coverage of which is essentially electrodynamics and field theory. However, the preface shows that the author possibly would have liked to put in some different materials also. The residue of some such material remains in this book. The book has a orientation not found in recent books on quantum electrodynamics except possibly in a book titled *Introductory quantum electrodynamics* by Powers (Longmans), but the coverage in the present book is much more wider. (We are, of course, not counting Heitler's book amongst ' recent books ' — the excellence of it goes beyond question.)

The book contains four chapters. The first is on classical fields, the second essentially deals with non-covariant formulation of quantum electrodynamics, the third is on Dirac equation and the fourth on covariant perturbation theory. Every chapter has a set of problems at the end.

All through the book, the author has stressed on physics. He has clarified physics behind the mathematical steps as much as possible. The presentation has got its specialities in having certain materials which normally do not appear in recent texts and also in the introduction of certain topics in a novel way. One example of the first contention is the inclusion of the Aharonov-Bohm effect in the first chapter. An example of the second contention is the way in which the modification of the Hamiltonian, in the case of spin, is considered (page 78). The inclusion of Aharonov-Bohm effect is very welcome since it is certainly time that the beginner should know about the important experiments related with this.

The above two examples by no means exhaust the specialities mentioned. The introduction of real parts of the complex fields as K_1, K_2 mesons (page 11); bringing in weak interaction as well as parity non-conservation and two-component neutrino in Chapter 3; the comparison of emission and

absorption of photons in quantum and semi-classical theories; and many others may be added to the list.

However, the author has only the students in mind in writing this book, because there is hardly any reference to original papers. The bibliography lists certain related text only. Despite being very well written, signs of hurrying through printing are not totally absent: Fig. 1-1, though referred to on page 4, does not appear in the book. The appearance of a certain book by P. Roman and published by the same publisher appears to have affected the contents of this book. The mention of Brahma, Visnu and Siva (page 27) does not serve any good purpose.

The book should prove very useful as text and, what is more important, will orient the beginner in a desired way.

G. BANDYOPADHYAY

CARTESIAN TENSORS by Nils O. Myklestad (D. Van Nostrand Co. Inc., Princeton), 1967. Pp. xiii+141. Price $ 3.95

In this short book of 140 pages of text and exercises Prof. Myklestad introduces his readers to the basic concepts of Cartesian tensors and their applications in geometry and mechanics. The pattern of the book is simple. There are twelve chapters, six devoted to plane tensors and six to space tensors. Each set of six chapters are alike, the first is Introduction, followed by Transformation equations; Vector algebra; Bisor algebra; and Applications to geometry and mechanics.

The book is written with mathematical rigour. There is an abundance of sums to be worked out, but the number of worked out sums, essential for a proper appreciation of the theorems and ideas, is small. This makes the book somewhat discouraging to those who wish to study Cartesian tensors on their own. Otherwise, the contents and development are, for the most part, close to what the author claims in the preface.

Editorially, the book perhaps would have been better if, instead of separate treatments for plane and space transformation, vector and bisor algebra, the plane and space parts had received a unified treatment. As it is, one is apt to lose continuity of the one as an outgrowth of the other.

The book is at once elementary and difficult. Perhaps this is unavoidable for a short book trying to cover a considerable extent of a subject. But, it must be said, that the book is nowhere sketchy, although no lines have been wasted in the discussions of such fundamental concepts as multiplication and contraction of tensors; Mohr's circle of bisors or symmetric bisors.

The author assumes a certain level of sophistication from the reader. The reader must have familiarity with calculus, matrix and transformation algebra.

Coming to the application of tensors, the book would have been more useful if there had been a fuller treatment of elasticity and the basic equations of hydrodynamics, the two fields in which tensors may be used with advantage.

On the whole, the book is of undoubted merit and an excellent introduction to Cartesian tensors for mathematically-minded readers.

S. K. NAG

MECHANICAL PROCESSING OF MATERIALS by Serope Kalpakfian (D. Van Nostrand Co. Inc., Princeton), 1968. Pp. xvi+348. Price $ 8.75

Materials processing is an inter-disciplinary subject requiring a sound knowledge of the fundamentals of materials science, applied mechanics, heat transfer and the mechanical behaviour of materials. The industrial aspects of the subject have assumed considerable importance with the spectacular developments in metal-forming technology and with increasing application of sophisticated methods of metal removal like ultrasonic, chemical, and electrochemical milling; electrolytic grinding; and spark erosion machining.

The author has presented the subject of mechanical processing of materials in a lucid manner, giving due emphasis to both theory and application. One significant feature is the stress on the analytical aspects, wherever possible, so as to establish quantitative relationships in topics such as force and power requirements in deformation processes.

In the first three chapters, the student is introduced to mechanical fundamentals, materials science, and material properties. In the fourth chapter, specific processes are introduced. In Chapter 5 is discussed forging, rolling and extrusion. Forming processes are discussed with clarity in Chapter 6. Material removal is presented in Chapter 7. Numerous questions and problems at the end of each chapter stimulate thinking. An extensive bibliography at the end of each chapter will be valuable to both undergraduate and graduate students.

The author deserves congratulations for this excellent book which is commended without reservation to graduate students and practising engineers.

A. RAMACHANDRAN

MEASUREMENT CONVERSION TABLES FOR AROMATICS AND TAR DERIVATIVES AND METHODS OF DETERMINING DENSITY compiled by G. A. Vaughan (The Standardization of Tar Products Tests Committee, Gromersal, UK), 1968. Pp. 155. Price 31s.

This booklet is a very useful compilation. It enables the conversion of a volume or weight of a coal tar product at a known temperature to the volume at a specified temperature, 20°C. Other tables enable the conversion of the density of a material at a known temperature to its density at 20°C. and vice versa. These tables are similar in function to those for petroleum products prepared jointly by the ASTM and the IP. A long-felt need for such a compilation has, therefore, been fulfilled by the author.

For the conversion of densities and volumes, factors are given for pure products such as benzene, toluene, xylenes and styrene and also for commercial products such as motor benzole, pyridine, 2-picoline, 3/4-picoline, aniline and other aromatic materials including light oils, naphthas, phenols,

creosotes, tars and pitches. A number of well-selected examples describe the application of these tables.

The STPTC methods of density determinations have been reproduced in Appendix I which also provides tables for the conversion of densities at 20° or 38°C. to density at various reference temperatures which are in current use. Other tables enable the weight/volume ratio obtained at a particular temperature to be converted to the density at 20°C. in the case of various tar products.

Appendix II gives the mathematical basis of the conversion factors given earlier together with the source of the data used. This would help in the compilation of conversion tables to be used for other pure products not given in the tables.

Appendix III gives tables for the interconversion of Celsius to Fahrenheit degrees and also of standard weights and measures. A particularly useful feature of the tables involving weight given in this section as well as in earlier sections is the interconversion between the British, US and Metric systems.

The factors and tables given for aromatic compounds and coal tar derivatives should prove to be of immense use for tar processing concerns, for buyers of tar products and for laboratories engaged in the testing of such products.

A. N. BASU

SCIENTISTS IN ORGANIZATIONS: PRODUCTIVE CLIMATE FOR RESEARCH AND DEVELOPMENT by D. C. Patz & F. M. Andrews (John Wiley & Sons Inc., New York), 1966. Pp. xii+318. Price $ 10.00

Scientists in India, especially research managers and administrators, would benefit by a study of this book, which presents the results of a major study, undertaken by the Survey Research Centre, Michigan, on the relationship between a scientist's performance and his laboratory environment. The question 'What constitutes a stimulating environment for research personnel?' is crucial and demands critical consideration. Every one appreciates the primacy of the scientist in the research enterprise, but there is hardly enough understanding of the factors that contribute to his productivity and the influence which the environment exerts on his performance.

The authors of the book have attempted to find an answer to this question. Over a period of six years or more, they have collected data from 1311 scientists and engineers working in government, universities and industrial laboratories and analysed them. Some of the data relate to information on scientists and the conditions prevailing in their laboratories; others relate to information and value judgements on the performance of scientists. Among the areas covered by the authors in their survey are: freedom of scientists and desire for self-direction; dedication and involvement in work; satisfaction and opportunities for professional growth; creativity and productivity; age and performance; and coordination in research organizations. The data have been presented in the form of charts and tables, and the implications of the findings for the professional activities of scientists and for R & D organizations have been discussed.

Few studies of the type reported in the book have been undertaken in developing countries. Many of those countries are giving increasing attention to the implantation of science and technology and the belief that investment in science will lead to economic benefits and improvement in the standards of living of the peoples is widespread. There has been a spurt in the demand for men of high ability and advanced training and developing societies everywhere are striving to search out talent and train it for research and development activities. They are establishing institutions and equipping them for research in diverse fields, and the expectation that substantial results would flow from the promotion of research is steadily mounting.

These developments are important. It should be clearly understood, however, that research organizations provide more than facilities for research; they provide the environment, the setting, the social milieu in which the scientist has his functioning. The setting may stimulate his creative faculties and help achievement; it may suppress his enthusiasm and initiative and smother excellence. Much depends on research management and administration. If it cherishes high standards and the leadership is vigorous, competent and dynamic, there will be an inexorable striving for excellence and upsurge of achievement; if the leadership is incompetent, slovenliness descends on the organization and it is not easy for any member, however talented, to remain uninfluenced in his behaviour. To use the words of Ralph Barton Perry, the leadership must maintain 'an express insistence upon quality and distinction'; if it does not, the consequences are too clear — deterioration in standards, shoddy performance, trivial results and utter mediocrity.

It would appear necessary, as a part of the efforts that are being made everywhere to promote science and technology, to have a close and deep look into the managerial and administrative aspects of research organizations with a view to ascertain how far they have been able to inspire scientists to great heights of achievement. So often do we hear of such expressions as creativity, breakthroughs, and outstanding achievements, used in connection with scientific developments, but it is not always clear whether they are used with a clear appreciation of their meanings and implications or parroted with a view to evoke applause from the public which is not always critical or well informed about science.

An objective assessment of the results of research from various institutions vis-à-vis research administration and research expenditure is clearly needed. The book under review sets out various criteria for measuring the performance of scientists and it has been pointed that it is possible to modify crucial laboratory factors to enhance the productivity of scientists. The data presented in the book pertain to American laboratories, but there is no gainsaying that motivational and environmental factors which enhance intellectual functioning are similar everywhere. The book is warmly recommended to research administrators.

B. N. SASTRI

Solar energy and neutrinos

As the energy of the sun is attributed to thermonuclear reactions, it is also presumed a small percentage of the energy escapes in the form of neutrinos. Measurement of the properties of the neutrino flux would, therefore, help in distinguishing between the various models of solar energy production. The snag lies in the detection of neutrinos which is extremely difficult. An experiment being carried out at the Brookhaven National Laboratory, however, has made some headway in this direction [*Phys. Rev. Lett.*, **20** (1968), 1205]. The preliminary results of this experiment have clearly indicated that the carbon-nitrogen cycle cannot be an important source of solar energy.

In the Brookhaven experiment, an attempt has been made to detect neutrinos by means of the nuclear reaction in which a neutrino converts a nucleus of Cl-37 to Ar-37, which is itself radioactive. The detector consists of a tank containing 390,000 litres of tetrachloroethylene; the interaction of neutrinos with the nuclei of Cl-37 can be recognized by the amount of Ar-37 produced. To eliminate the chances of Ar-37 production by protons from cosmic ray muons, the whole detection system was placed 4850 ft below the ground.

This detection system is best suited for the comparatively energetic neutrinos produced by the radioactive decay of B-8 nuclei in the sun. In fact, the experiment has been planned on the belief that the detection of neutrinos from the decay of B-8 would be roughly a thousand times more efficient than the detection of neutrinos from the proton/proton reaction which dominates the production of solar energy. The flux of neutrinos from B-8 on the sun is calculated to be just over ten million/cm.^{2}/sec. at the surface of the earth, or about 1/10 of the flux of the less energetic neutrinos from the proton/proton reaction. This implies that, depending on the accuracy of the above results, neutrinos from B-8 should be responsible for the formation of 2-7 atoms of Ar-37 in a day.

The above, however, is only a preliminary result and more time is required for this experiment to be fully productive. Nevertheless, it is important that experimental measurements are already sufficiently precise to provide an experimental proof that the sun can only derive a small part of its radiated energy from the carbon-nitrogen cycle.

Proton radiography

Radiographs similar to X-ray pictures have been produced by energetic protons from an accelerator [*Science, N.Y.*, **160** (1968), 303]. The radiographs have shown very good contrast but poor spatial resolution. A proton radiograph of a stack of aluminium absorbers with an inserted aluminium foil, constituting only 0·2 per cent of the total thickness of aluminium, clearly showed the outlines of the foil, although the edges were a little hazy.

Protons from the external beam of the Harvard cyclotron were passed through a lead scatterer that reduced their energy from 160 to 137 meV. and spread the beam from a diameter of 0·2 cm., where it struck the scatterers, to 10 cm. at a point 3 m. downstream where radiographs were made.

The device would be useful in medical radiography and in detecting flaws in technical materials.

Laser-induced Raman spectroscopy

Complete vibrational analysis of a molecule under pressure has been made possible by the application of laser-induced Raman spectroscopy of solids under high pressure in conjunction with infrared data. The high pressure Raman technique can also be used for observing weak infrared absorption [*Chem. Engng News*, **46** (No. 21) (1968), 52].

When a laser beam replaces the conventional monochromatic light source in Raman spectroscopy, the spectral lines are intensified. Employing a Cary No. 81 laser, Raman spectrophotometer and a Spex 1400 double spectro-meter in tandem with a helium-neon laser (90 mW.), chemists at Argonne National Laboratory, USA, have obtained the Raman spectra of several solids at pressures up to 35,000 atm. in a diamond cell.

In a typical experiment, the frequencies of absorption of iodic acid in the 700-800 cm.$^{-1}$ region shifted to lower frequencies by as much as 25 cm.$^{-1}$ under pressure. This has been attributed to iodine-oxygen stretching vibrations. Raman band at 111 cm.$^{-1}$ of red tetragonal mercuric iodide shifted to 119 cm.$^{-1}$ under pressure with a new peak at 143 cm.$^{-1}$. When the pressure was raised to 13,000 atm. only the 143 cm.$^{-1}$ band could be seen with a shoulder at 138 cm.$^{-1}$. This is due to the conversion of the red form to the yellow rhombic form.

Computerized high-resolution mass spectrometer

An on-line, real-time, computerized system for obtaining high-resolution mass spectral photoplate results has been developed at the American Cyanamid Research Laboratory, Stamford, USA. The system combines an automatic comparator-densitometer to read transmission values every 0·5 micron and a digital computer connected by 500 ft of direct cable.

The comparator reads the photoplate at up to 125 mm./min. This corresponds to 400 data conversions per sec. being sent to the computer for readings taken every 0·5 micron. Every time the encoder output changes (each 0·5 micron), the position and transmission values are sent to the computer's central processing unit as a single word.

Computer logic and programmes compare each piece of data with the background, which is continuously updated in the computer during scanning. This is one of the significant advantages of this system. The programme for following the background can compensate for scratches and dark spots. Only data above the

411

background by a preset amount are stored on a random access disk. These data correspond to the peaks in the mass spectrum.

Before the photoplate is scanned, input parameters are sent to the computer with a teletypewriter located near the comparator. Previously written questions are asked by the machine language acquisition programme; the comparator operator answers each question with a number. This stepwise procedure continues until the input parameters are fulfilled, and the computer instructs the operator to begin measurement. A typed message informs the operator when the run is completed.

By the end of the plate scan, the computer has stored on a magnetic disk the transmission-distance profiles of all spectral peaks. Each peak's data are conveniently compartmentalized and easily recognized by succeeding programmes. This on-line system overcomes the difficulty experienced by people who record on gapped magnetic tape. With direct recording into tape, data may be lost during the gapping process. A complete spectrum on a photoplate can be scanned in about 3 minutes.

As the comparator slews back to begin reading another exposure, the computer transfers the acquired data on to an SDS Magpak. This way a number of high-resolution mass spectrometry photoplates can be scanned and stored data can be processed at a time convenient to the computer personnel.

After all peak centres and areas have been calculated by the computer, programmes convert these data to exact masses and elemental compositions, which are listed in tabular form or put in the form of an element map.

In the element maps obtained by the Cyanamid scientists with their system, usually 70 per cent of the differences between the determined masses and the theoretical masses are within 1 millimass unit.

The Cyanamid system has proved useful in studying the structures of complex organic molecules of dyes, pharmaceuticals and agricultural chemicals. The advantage of this system over other computerized ones is in the availability of computer logic for making decisions while the photoplate is being scanned. The computer can adjust for background changes during the scanning process [*Chem. Engng News*, **45** (No. 43) (1967), 31].

A new method for ionization measurement

A new method has been developed for determining the yield of free ions formed by irradiation of a liquid with high energy X-rays [*Science, N.Y.*, **160** (1968), 301]. The method involves the application of a clearing field after the termination of irradiation. This field should be strong enough to pull all the ions to the electrodes so fast that negligible volume recombination occurs.

The method has been successfully used to determine ion yields in a number of liquids at 23°C. The charge collected (after a 0·5 msec. pulse of 1·6 MeV. X-rays) for neopentane, *p*-dioxane and *n*-hexane was found to bear a linear relationship with the radiation dose in millirads. The cell used had a collecting electrode 1·5 cm. in diameter and a plate separation of 0·42 cm. At the doses used, the initial half-life of the ions varied from about 3 to 30 sec. The collection time was of the order of only 0·1 sec. at a field of 3 kV./cm., so that ion recombination during the radiation pulse and ion collection was negligible.

The intercepts of the straight-line plots mentioned above depend on the background conductivity, $\varkappa$; it is negligible for hydrocarbons but appreciable for 1,4-dioxane. The yield sought is proportional to the slope of the straight lines. The charge collected is independent of strength and time of application of the clearing field above 2 kV./cm. and 0·5 sec.

The precision of the method is better than ± 10 per cent. The value of G (ions of either sign formed per 100 eV. input) for *n*-hexane is in fairly good agreement with the previous best value of $0·10 \pm 0·01$. The low value for 1,4-dioxane confirms determinations thought to be less accurate. The remarkably high values for branched-chain hydrocarbons are in qualitative agreement with previous values.

A novel synthesis of *o*-esters of thiocarboxylic acids

The synthesis, reported from the Sagami Chemical Research Centre, Kanagawa, Japan, involves reaction of orthoesters with hydrogen sulphide in the presence of catalysts, viz. $ZnCl_2$, $FeCl_3$, etc. The superiority of this method over the conventional ones lies in the stability and easy availability of the reactants, orthoesters; freedom from side reactions; and recovery of the unreacted reactants by fractional distillation.

o-Ethyl thiobenzoate has been obtained in 80 per yield by bubbling dry hydrogen sulphide into a flask containing 20 g. of triethyl orthobenzoate and 100 mg. of zinc chloride followed by direct fractional distillation of the contents. *p*-Toluenesulphonic acid is less effective as a catalyst (yield 12 per cent) than zinc chloride (yield 80 per cent) [*Tetrahedron Lett.*, (No. 17) (1968), 2083].

Simultaneous determination of pyrithiamine and thiamine in biological materials

A precise and sensitive method for the separate determination of pyrithiamine (PyT) and thiamine in biological materials has been reported [*J. Vitamin.*, **14** (1968), 67-76]. The method, based on different oxidation behaviours of these two compounds with cyanogen bromide or potassium ferricyanide, and on the different characteristics of the fluorescence spectra of the oxidation products, can detect as low as 0·3 and 0·03 mμ moles of PyT and thiamine respectively per assay. In the new method, the interference of PyT in the determination of thiamine in the presence of PyT has been overcome by using cyanogen bromide instead of ferricyanide as the oxidizing agent. Interfering substances in biological materials can be successfully removed by adsorbing PyT and thiamine on permutit followed by elution with hot KCl-HCl solution.

Thiamine and PyT in biological materials are extracted by homogenizing and heating in an acidic medium, followed by deproteinization with metaphosphoric acid, adsorption on permutit and elution with hot KCl-HCl. For the

determination of PyT, an aliquot of the eluate is oxidized with alkaline ferricyanide (1 per cent in 10 per cent NaOH) and the oxidation product, after extraction into iso-butanol, is determined fluorometrically using a spectrophotometer with an excitation at 430 mμ and emission at 460 mμ. In thiamine determination, the same eluate is oxidized with cyanogen bromide and the isobutanol extracted thiochrome is determined at 375 mμ exciting and 420 mμ emitting wavelengths.

Indian Institute of Petroleum, Dehra Dun

The annual report of the Institute for 1966-67 records the progress in respect of various projects in hand — a majority of them sponsored by the refineries and marketing divisions of the Indian Oil Corporation, defence establishments, railways, the Ministry of Petroleum and Chemicals, and the petroleum processing industry. At the conclusion of the first phase of collaboration with the Institut du Petrole, France, the collaboration was extended in specific areas for 3 years, the major project undertaken under the extension being that on the production of protein concentrates from petroleum fractions. The Institute received aid from the United Nations Development Programme for the development of a Petrochemistry Division.

Under the programme of evaluating crudes and products, the Institute undertook the evaluation (including TBP distillation) of crudes from Lakwa, Nahorkatiya and Kathana, Lakwa crude Lube oil distillate and a 2:1 blend of Nahorkatiya and Lakwa crudes.

The production of food grade hexane from Ankleswar naphtha was attempted. Optimum condition for dearomatizing the 65-70° cut containing about 5·1 per cent aromatics using sulphuric acid or oleum have been established. The yield obtained is 94 per cent on the basis of the cut or 1·78 per cent on the basis of the crude.

Studies on alkylation of LPG with sulphuric acid of different concentrations as catalyst have shown that, as the dilution of the acid increases, the extent of alky-

lation diminishes, but the dimerization of isobutylene to C_8 olefins increases. Know-how has been developed for producing iso-octane from tertiary butyl alcohol and equipment required for producing 450 litres of pure iso-octane per annum has been fabricated. The possibility of producing naphthenic acid from the wash solutions from the Barauni Refinery has been established. Copper and cobalt naphthenates of industrial specifications have been prepared from the naphthenic acid isolated from the wash solutions.

Hydrogenation studies have been carried out on inferior kerosene, coker kerosene and aromatic extracts. In a programme of study on the polymerization of olefins, the polymerization of the olefin-rich gas obtained by the catalytic steam cracking of naphtha and Burshane mixed with hydrogen was studied under varying conditions of feed flow rates using 80 and 98 per cent sulphuric acid as catalyst.

Indigenous thermistors have been tried successfully as detectors to improve the sensitivity of the gas chromatograph developed at the Institute. A simple mechanical reflux splitter has been designed and fabricated. The splitter consists of a cylindrical collector on whose wall vertical weirs are cut uniformly. The collector is fixed inside a chamber provided with two outlets, into which the weirs open. By isolating the weirs that discharge into the product outlet and allowing the rest to flow back into the distillation column, the reflux ratio can be easily adjusted. A bi-fuel control mechanism has been developed for boosting the power output of CI engines under high altitude conditions. The loss of power due to breathing difficulty at high altitudes has been minimized by a device designed and fabricated to automatically vary the carburettor jet size with altitude up to 5400 m. Several modifications have been effected in the existing designs of domestic appliances such as chimneyless lamps, hurricane lanterns, pressure stoves and wick stoves.

Detection of very low concentration of CO and CO_2 has been achieved by hydrogenating the gases to methane followed by

passing the gas mixture through a flame ionization detector. The difficulty experienced in the separation of xylene isomers in their estimation by gas chromatography has been overcome by using a suitable combination of columns and careful selection of operating conditions. A new rapid colorimetric method for determining barium in petroleum products has been evolved. Reforming of aromatic extracts, oxidation of paraffin wax, disposal of acid sludge, combustion of Iomex and naphtha, and reclamation of used oils are some of the other main projects in hand.

Some of the important techno-economic and other surveys carried out concern: (i) LDO utilization pattern; (ii) petroleum jelly demand; (iii) feasibility of manufacture of detergent alkylate at Koyali; (iv) scope of expansion of Barauni Refinery using Assam crudes; and (v) feasibility and economics of production of various grades of aviation gasoline.

Physical Research Laboratory, Ahmedabad

The annual report (1966-67) of the laboratory covers the details of research carried out in the fields of cosmic rays, astrophysics, radio and X-ray astronomy, solar-terrestrial relationship, aeronomy and geomagnetism, and theoretical physics.

Recording of cosmic rays at ground level has been continued at Ahmedabad, Kodaikanal and Gulmarg while the same at Trivandrum has been discontinued. Analysis of the data from the recordings of the high resolution mu meson counting at Chacaltaya, Bolivia, has been continued and initial results have been published. The purpose of recording the data is to find variations in cosmic ray intensity having short periods. Power spectrum and digital filtering methods have been used. The range of frequencies investigated (1-30 c/hr) has not been investigated previously.

A super neutron monitor has been fabricated. A new circuitry has been developed for studying azimuthal variation of cosmic rays. An experiment has been planned for measuring mu meson spectrum and the ratio of positive to

negative particles in the energy range 0-1000 MeV. Profile and fine structure of daily variations, their solar and terrestrial relations, and the characteristics of long- and short-term changes in cosmic ray intensities have also been studied.

Cosmic and X-ray studies have been carried out with balloon-borne detectors. A fission counter for neutrons has been developed by the electro-deposition of salts of thorium or uranium on the cathode of a cylindrical counter. Nuclear emulsions exposed at various balloon heights have been scanned for neutron-induced evaporation stars and recoil protons. A plastic scintillator detector (area, $2 \cdot 25$ m.^{2}), viewed by two photomultipliers in coincidence, has been set up 700 ft below the ground to detect muons of energy 100 GeV. The efficiency of the detector for single particles is 85 per cent.

Ionospheric studies including hourly soundings of the ionosphere over Ahmedabad and Thumba, measurement of drift and absorption on $2 \cdot 6$ Mc/s., recording of Faraday rotations of ionospheric beacon satellite signals, etc., have been carried out. A Langmuir probe payload along with a magnetometer payload has been developed and flown. The probe functioned efficiently and recorded some special features.

Effective nuclear interactions and the structure of nickel isotopes have been studied. A satisfactory description of the low-lying spectra of nickel isotopes has been found by parameterizing the short-distance part of the interaction between neutrons in the upper half of the f-p shell of the nickel isotopes $(A = 58\text{-}65)$ in terms of four s-state radial integrals. The structure of low-lying states of the cadmium nuclei has been studied. Another study has provided a satisfactory explanation for the occurrence of rotational spectra in the s-d shell and its absence in the f-p shell in terms of the formation of intrinsic states with large quadrupole moments in the beginning of the $2s$-ld shell but not in the lf-$2p$.

The instruments fabricated and put to regular use during the year are: (i) crystal controlled electronic clock; (ii) single channel pulse height analyser; (iii) frequency and period counter; (iv) counting rate meter; and (v) sub-carrier discriminator.

Spectroscopy Letters

This new monthly journal started by Marcel Dekker Inc., New York, aims at the rapid communication of valuable observations in spectroscopy. Annual subscription is $ 3.00.

Journal of Biomechanics

This quarterly journal, started by Pergamon Press, London, is sponsored by the Highway Safety Research Institute, UK. It publishes original research papers on all aspects of biomechanics, both human and non-human, and includes papers from the medical, dental and basic sciences as well as from the field of engineering.

Chromatographia

This new bimonthly journal aims at providing rapid communication in chromatography and related techniques. In addition to original papers and research notes on the latest advances in separation, identification and combination techniques and automation, particular emphasis is placed on fundamental theory common to all chromatography and methods of accurate quantitative analysis. The journal is started jointly by Pergamon Press and Friedr. Vieweg & Sohn, Braunschweig.

Tissue & Cell

This quarterly journal has been started by Oliver & Boyd Ltd, Edinburgh. It is devoted to the study of structure and function not only at the cellular and sub-cellular level but also at the level of cell groupings into the tissues and organs of the animal body. Annual subscription is £ 10.

Announcement

A Symposium on Science as a Profession will be held at Kanpur on 19 and 20 January 1969 under the joint auspices of the Science and Technology Society, Kanpur, and the Scientific Workers' Association. There will be four sessions devoted to (1) National planning and scientific know-how; (2) Staff selection, career planning and facilities for higher education; (3) Working conditions, creativity and efficiency; and (4) Summing up and highlighting views of industry. Further details can be had from the Convener, Symposium on Science as a Profession, Post Box No. 320, Kanpur.

FORTHCOMING INTERNATIONAL SCIENTIFIC CONFERENCES, 1969

Date	Name	Place
28-31 Jan.	International Symposium on Information Theory	Ellenvile, NY
19-21 Feb.	International Solid State Circuits Conference	Philadelphia
Spring 1969	International Conference on Sheet-Metal Working	USA
24-27 March	International Convention of the Institute of Electrical and Electronic Engineers	New York
25-28 March	International Symposium on Autoclaved Building Products	Hanover
27-28 March	International Congress for Heating, Ventilating and Air-Conditioning	Frankfurt-am-Main
31 March-4 April	International Symposium on Concrete Bridge Design	Chicago
13-18 April	International Conference on Fracture	Brighton, UK
16-18 April	International Conference on Magnetics	Amsterdam
21-25 April	International Conference on Structure, Solid Mechanics and Engineering Design in Civil Engineering Materials	Southampton, UK
22-25 April	International Symposium on Cotton Textile Research	Paris
22-26 April	International Pulp and Paper Instrumentation Symposium	Vancouver
April (4th week)	International Symposium on the Chemistry of Natural Products, in Particular Steroids and Terpenes	Mexico

New Publications

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Supplement to the Wealth of India — Raw Materials: Vol. IV

This well-illustrated supplement provides information in an easy-to-grasp form on: (i) zoological names of 376 fishes of economic value, found in Indian water, along with their English names; (ii) description and distribution of the fishes; (iii) coastal, deep sea and fresh water fisheries; (iv) ingenious devices for catching and preserving fish; (v) fisheries in various States; (vi) manufacture of fish oil and manure; (vii) analytical values of fish-foods and their byproducts; and (viii) marketing practices and data concerning fish trade. An annotated bibliography of 220 references and an exhaustive index are provided.

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by
DR G. KRISHNAN
Director, Zoological Research Laboratory, Madras University

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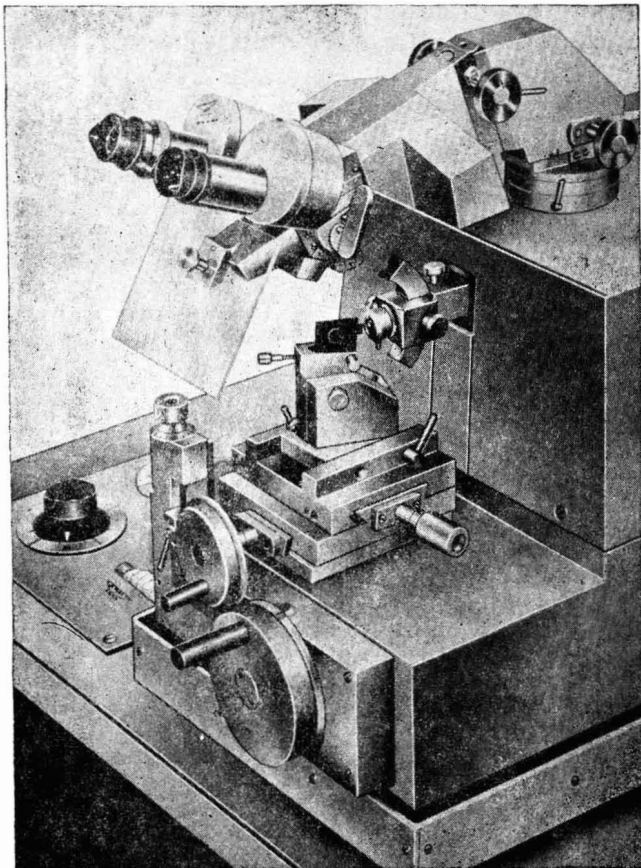**PRICE Rs 12.00, Sh 24 or $ 3.50**

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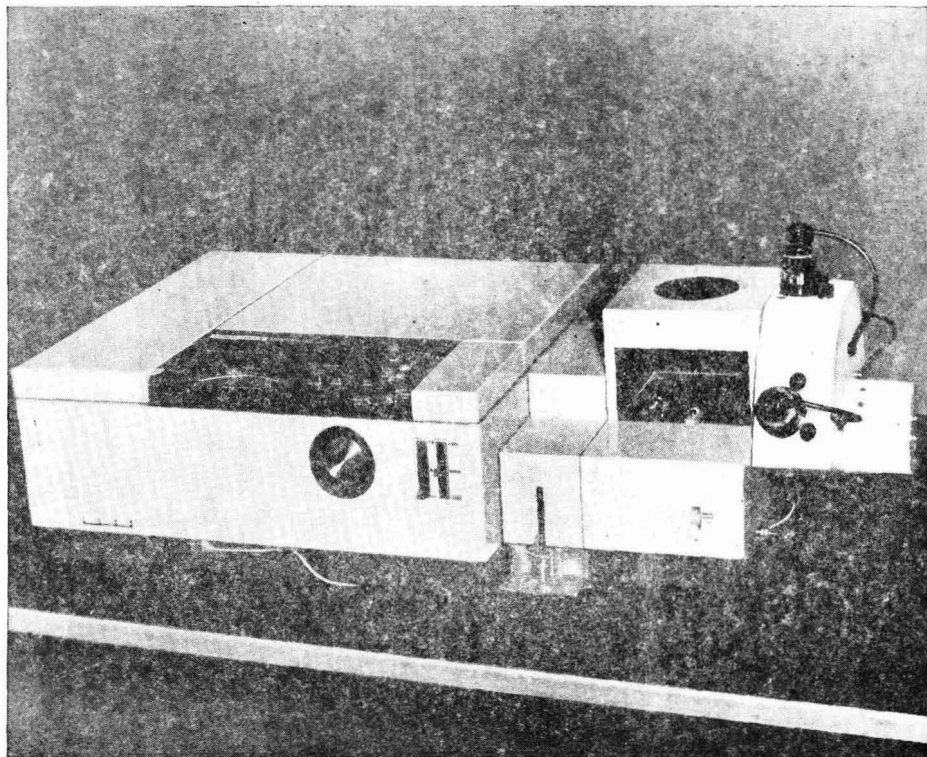## BOOKS & MONOGRAPHS

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