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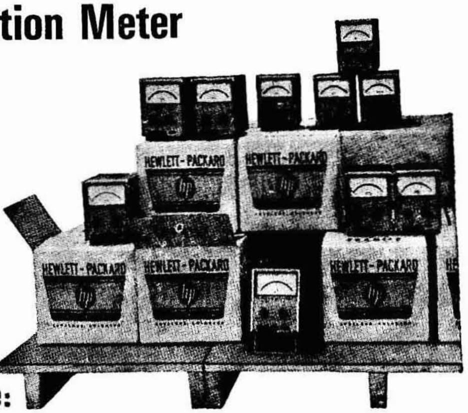

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THIN LAYER CHROMATOGRAPHY: A LABORATORY HANDBOOK edited by Egon Stahl (Springer-Verlag, Berlin & Academic Press Inc., New York), 1965. Pp. xvi+553. Price DM 68

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VOLUME 25 NUMBER 9 SEPTEMBER 1966

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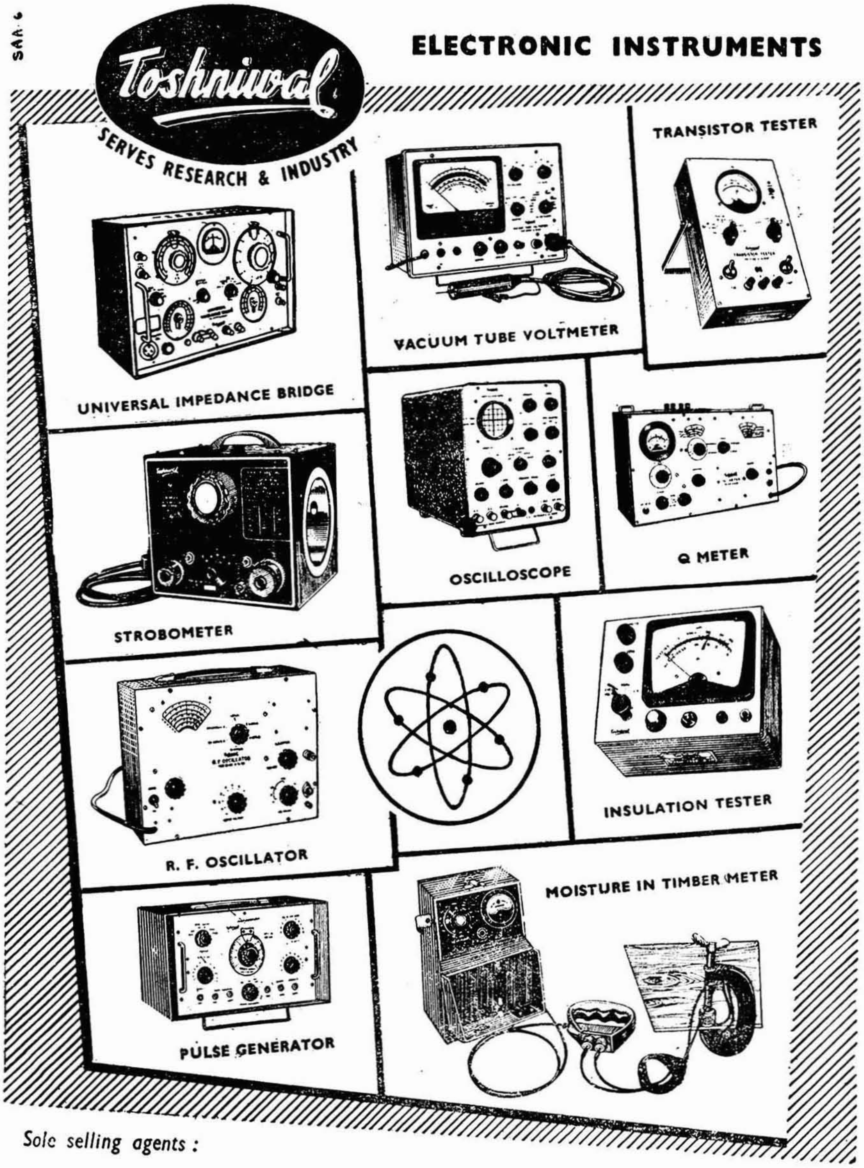

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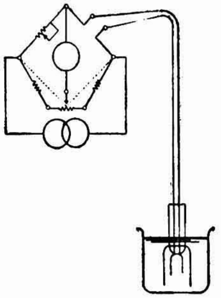

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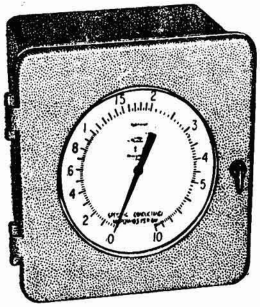

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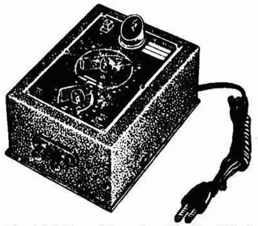

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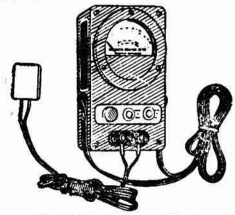

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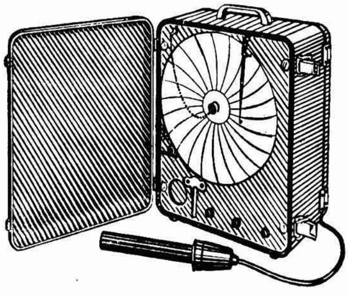

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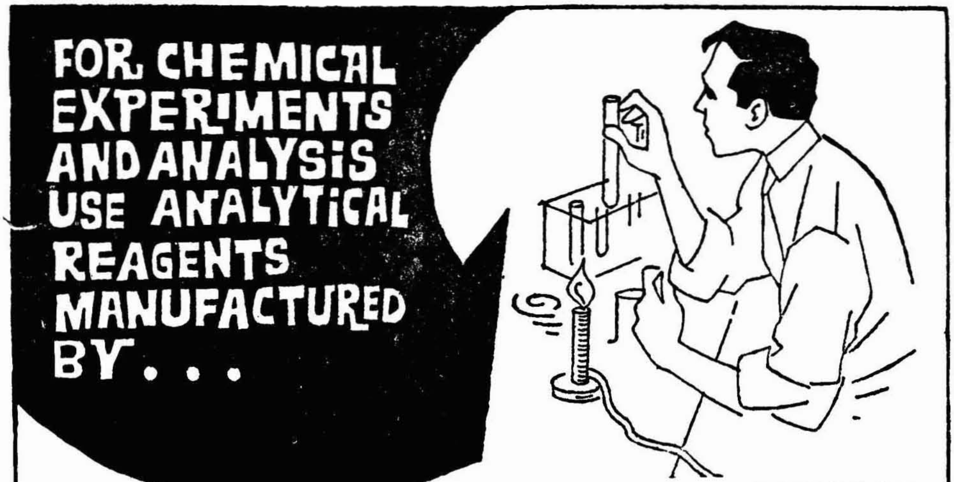

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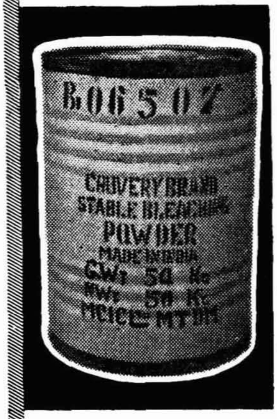

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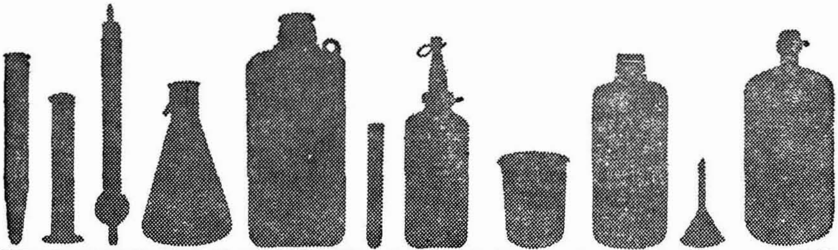

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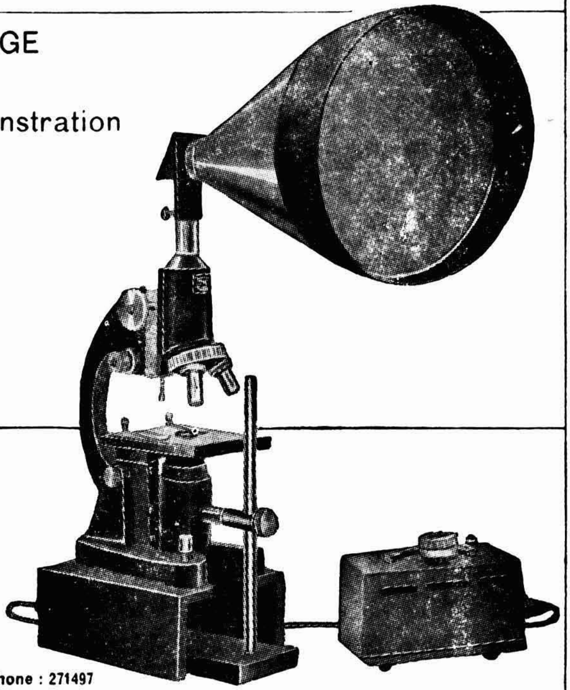

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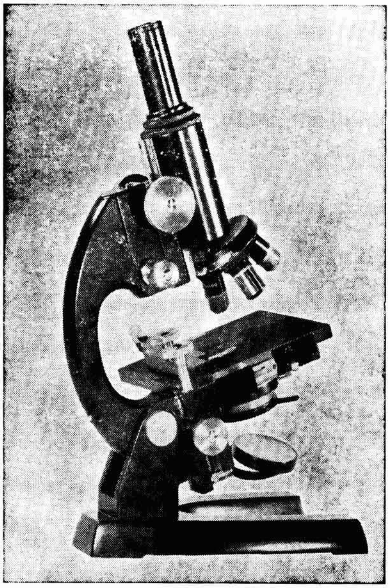

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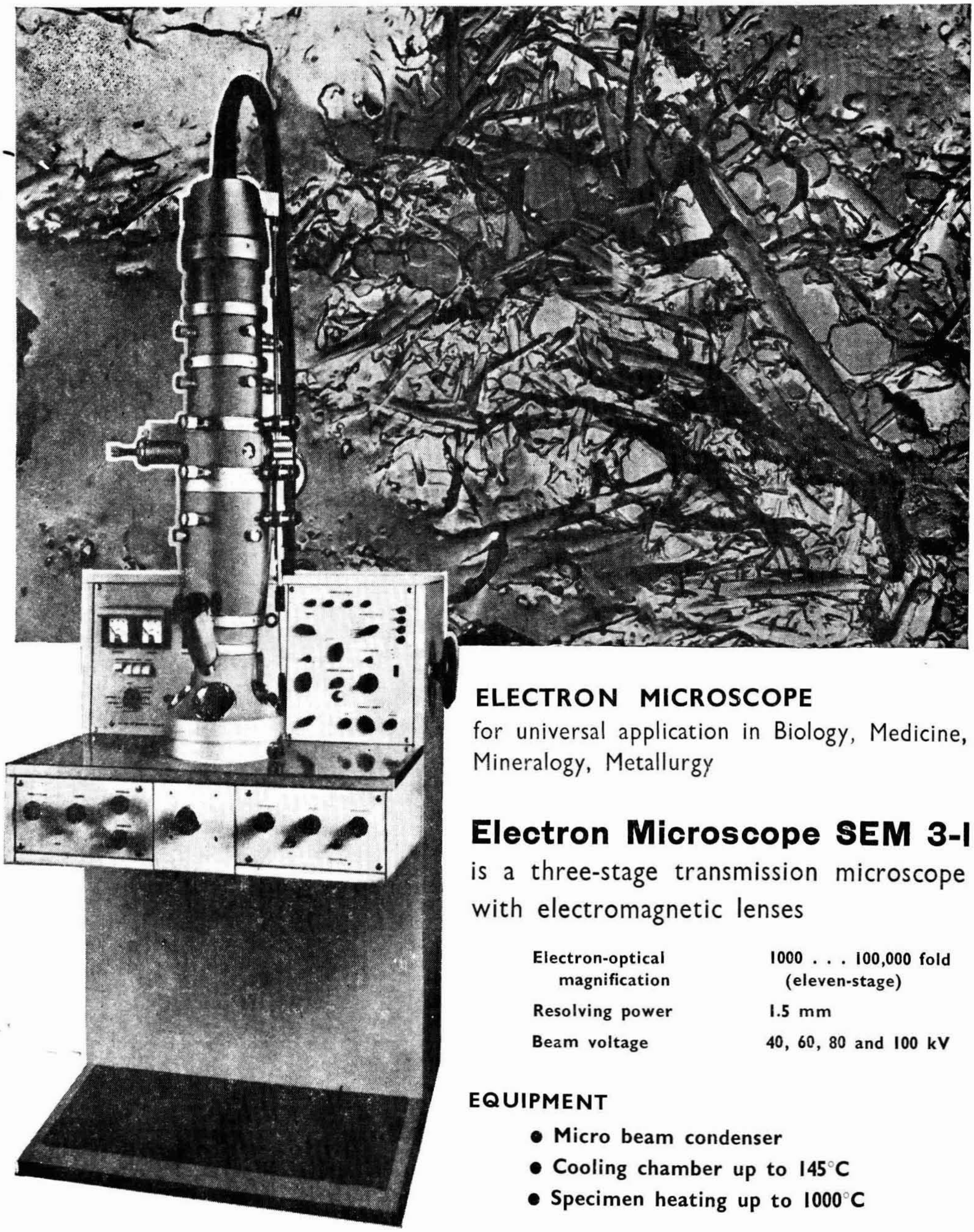

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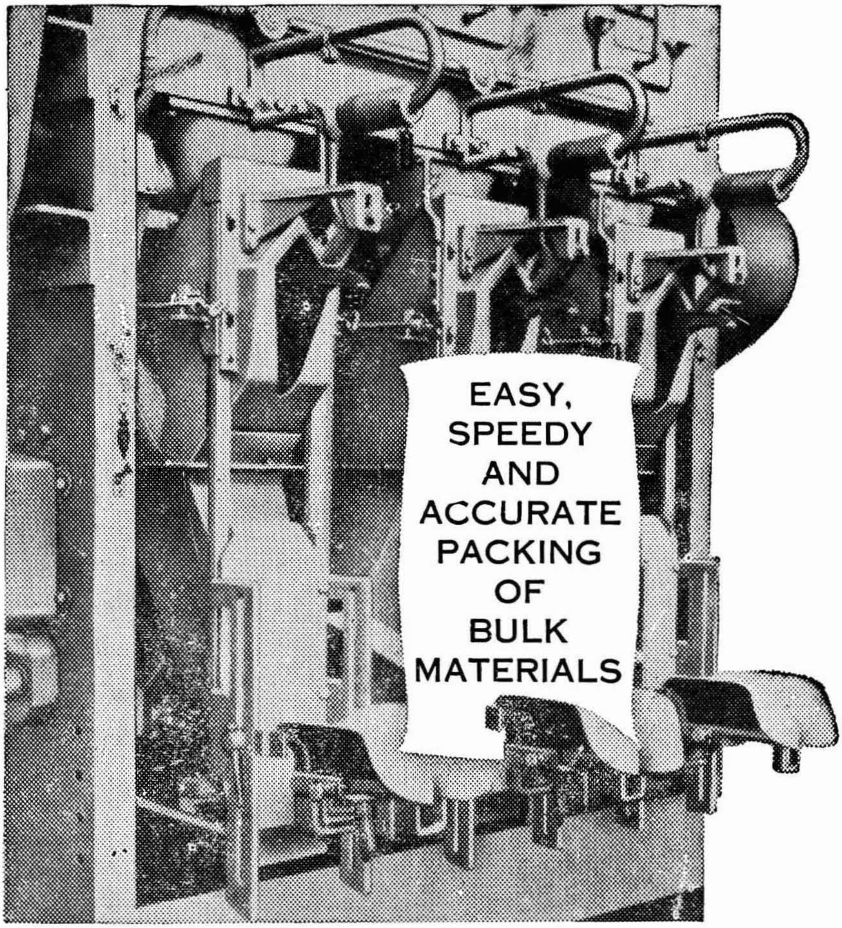

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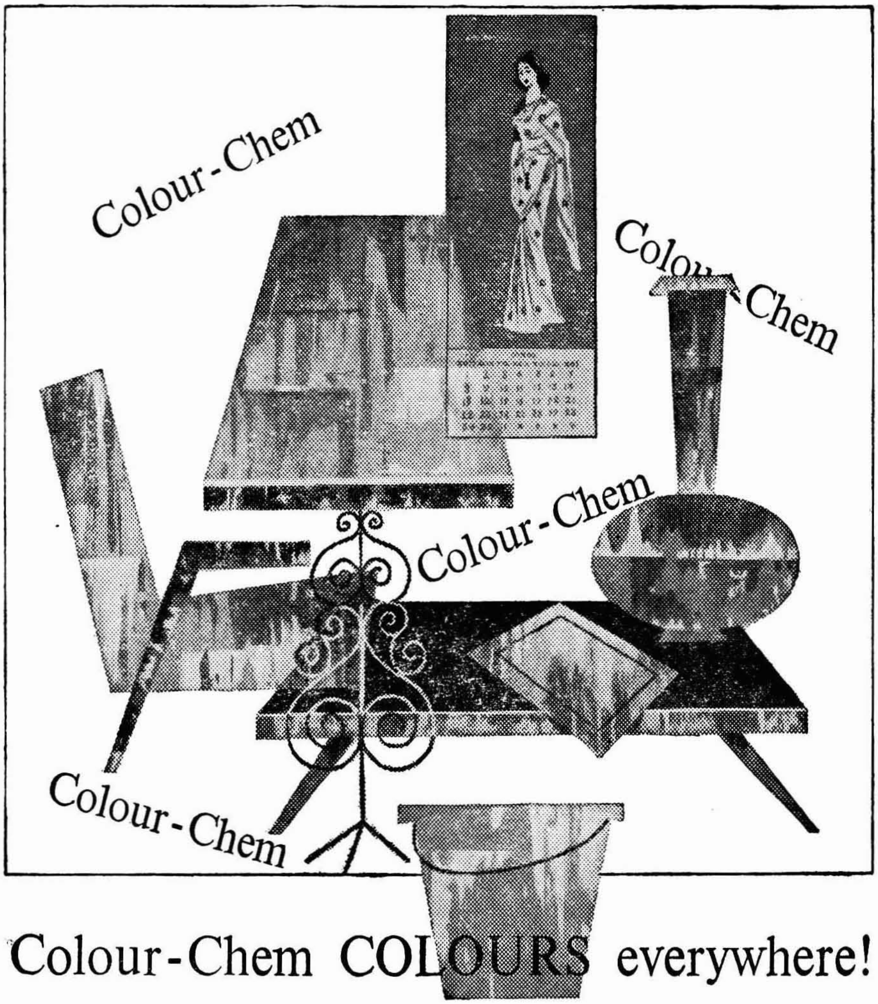

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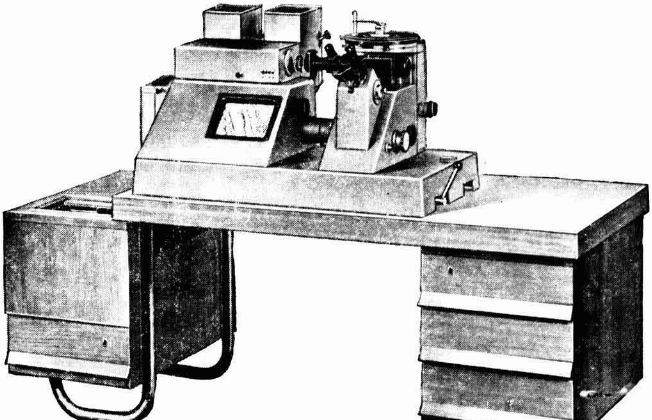

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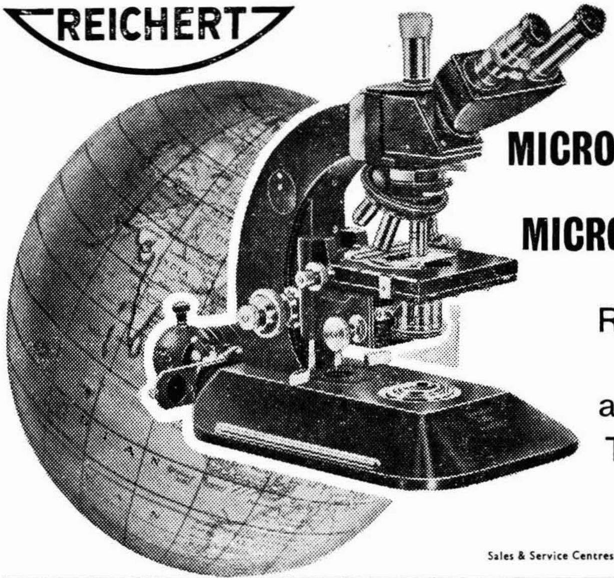

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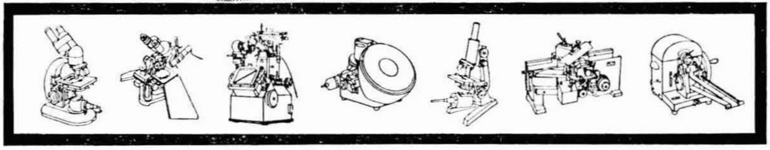

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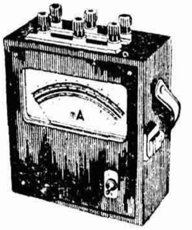

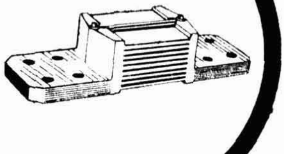

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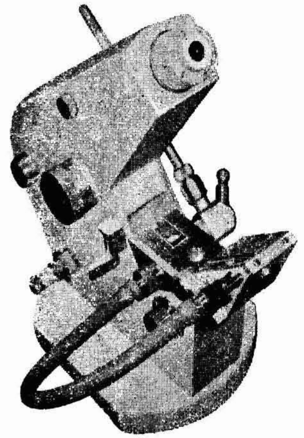

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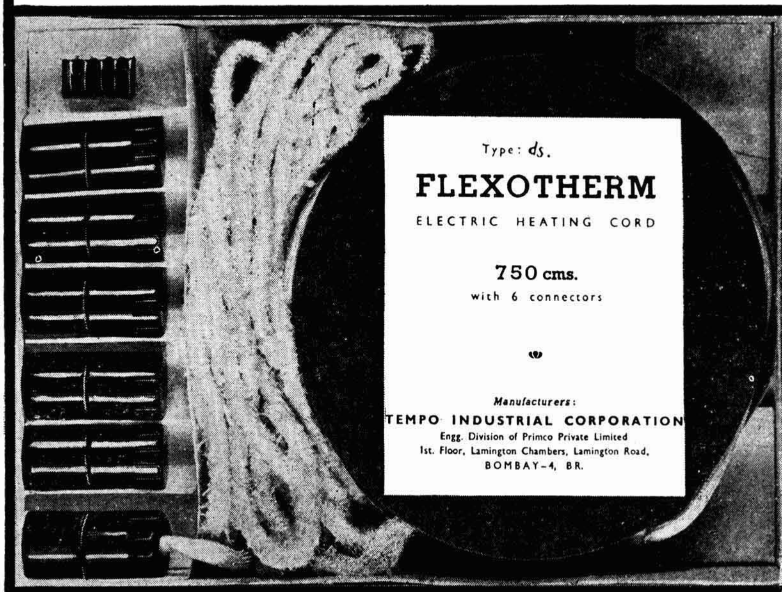

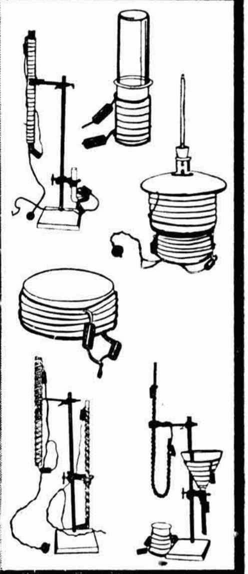

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Current Topics

Science Education & Research: Recommendations of the Education Commission

THE Education Commission appointed by the Government of India in July 1964 " to advise Government on the national pattern of education and on the general principles and policies for the development of education at all stages and in all aspects " submitted its report on 29 July 1966. Part II of the report devotes two chapters to higher education relevant to science education and research which are dealt with in a separate chapter. The Commission is of the opinion that if education is to develop adequately in the next 20 years, expenditure on education should rise from Rs 1444 million in 1950-51 to Rs 6000 million in 1965-66 and Rs 40,364 million in 1985-86, and after 1985 there should be greater emphasis on higher education and research. The Commission has also called for a drastic reconstruction of our education making it science based, as this step alone can provide the foundation as also the instrument for the nation's progress.

Considerable emphasis is laid on the quality of higher education and research in universities. It is recommended that at least 6 major universities be developed where first class post-graduate work and research of international standard is made possible. These universities, selected from the existing ones, should include an Indian Institute of Technology and an Agricultural University.

To bring about a real improvement in the present state of science education and research, the Commission feels the need for a rigorously selective approach in respect of post-graduate studies and research. It is suggested that students best suited for post-graduate work should be carefully selected and a small number of centres of excellence built up. The programme of the University Grants Commission (UGC) for setting up advanced centres of study should be strengthened and 50 such ' clusters ' covering agriculture, engineering and medicine established in some of the most promising universities in the next 5-10 years.

Eighty per cent of the post-graduate and research work is to be organized in the universities and at the university ' centres ', and institutions doing basic research outside the university are to be brought within the university or linked with universities. The Commission has recommended that selected post-graduate students should spend a term or two of their training in another university or research institution specializing in the subject of their interest. Whenever practicable, research workers in the Council of Scientific & Industrial Research (CSIR), the Atomic Energy Establishment, and other research institutions outside the university system should be invited and induced to become teachers, full-time or part-time, for long or short periods.

Facilities for increased enrolment in professional courses are to be provided, especially in agriculture, engineering and medicine, and in science at the post-graduate level. The proportion of enrolment at the post-graduate stage to the undergraduate stage is to be raised from the present 11 to 30 per cent by 1986. Post-graduate courses in engineering are to include at least one year's experience in industry and research to be directed towards problems in industry. It is recommended that a regular doctorate degree for developmental work within industry in addition to a doctorate degree by thesis be created.

On the question of scientific manpower utilization the Commission feels that we should strive for high efficiency — higher even than that in industrially advanced countries. Priorities and programmes in education and research are to be determined on the basis of hard ' indigenous ' thinking and national needs. Apart from taking steps to improve the quality of post-graduates and research workers, the Commission has suggested that the output of post-graduates in science and mathematics be increased several fold in the coming decades.

Means for efficient use of existing equipment have to be found and it is recommended that UGC and CSIR encourage and support some of the universities and national laboratories to organize instrument calibration and repair service. It is suggested that applied work such as developing new techniques, designing and fabrication of instruments and apparatus should receive proper recognition.

An important measure recommended by the Commission which has a bearing on higher education and research is the constitution of an Advisory Body on National Science Policy. It is recommended that the Scientific Advisory Committee to the Cabinet be reorganized and provided with an effective secretariat and professional component adequate to its tasks. The Chairman of the Advisory Body should be a professional scientist, engineer or science administrator of high standing. Deliberate support and encouragement of advanced study and research in our universities should become a fundamental goal of our national science policy. Within the UGC organization, an important place should be given to production of objective information, by the most advanced methods available, on university research in India and its impact on Indian society.

The implementation of these and other important recommendations of the Commission will largely depend on the resources available and how wisely and effectively they are utilized.

Metallurgy of Substitute Ferrous & Non-ferrous Alloys—A Symposium

P. K. GUPTA
National Metallurgical Laboratory, Jamshedpur

IN the wake of depleting mineral reserves and their shortages and the almost total absence of some, research and applied technological effort are continuously directed towards mineral conservation on the one hand and making the most optimum use of available resources on the other. In doing so, unconventional uses have to be made of different metals and their alloys through the judicious development of 'substitute' ferrous and non-ferrous families of alloy compositions. The subject of substitute alloys has always tended to be somewhat controversial, when considered on the basis of indigenous availability of the primary metals, not only in relation to metallurgical acceptability of the substitute alloys but also vis-à-vis their production economics, consumer acceptance and serviceability. During World War II, considerable strides were made in different countries to develop substitute alloys such as the low tungsten high speed steels, substitute En series of alloy steels with much lower alloy contents, etc. Some of these substitute alloys have come to stay while others are being upgraded in relation to requirements of stringent properties for rigid service characteristics. In the field of alloy, tool, special and stainless steels, the growth of substitute alloy steels has been outstanding, while search and research are being ceaselessly made to formulate still better and superior substitute alloy compositions. An international symposium on 'Metallurgy of Substitute Ferrous & Non-ferrous Alloys' was organized by the National Metallurgical Laboratory (NML) from 27 to 30 April 1966 to catalogue and focus attention on known families of substitute alloys in relation to others offering potential scope for research and development. The symposium was attended by many distinguished scientists and metallurgists from overseas as also by about 200 delegates from India.

The symposium was inaugurated by Shri T. N. Singh, Union Minister for Iron and Steel; Sir Jehangir Ghandy, Chairman, Executive Council, National Metallurgical Laboratory, presided over the function.

Dr B. R. Nijhawan, Director, NML, welcoming the delegates stressed the importance of the short-term and long-range research and development work on substitution and development of substitute alloys because of chronic foreign exchange shortage in the country. The present emergency has also highlighted the importance of research and development work in this direction, on which the NML had started active work even when there had been no emergency. He surveyed some of the major basic and applied research projects of NML on substitute ferrous and non-ferrous alloys including stainless steels, alloy tool steels, etc., for producing diverse end products to exacting specifications and practical needs. He observed that such pioneering work carried out at NML is rewarding and presents interesting industrial potentialities.

Shri T. N. Singh, Union Minister for Iron and Steel, inaugurating the symposium, observed that the subject of the symposium cannot be overemphasized in the context of the present foreign exchange shortage and meagre deposits of some strategic metals. He advocated the use of substitute materials, particularly the substitution of galvanizing by aluminizing, and attached highest importance to aluminizing process developed by NML. He expressed his intention to have a whole section of aluminizing plant in one of the public sector steel plants. Shri Singh highly commended the valuable assistance which the steel industry in India has received from NML and paid a warm tribute to Dr B. R. Nijhawan and his colleagues for their devoted work and dedication to research in many spheres of mineral and metal industry.

Sir Jehangir Ghandy, Chairman, Executive Council, NML, observed that NML had been actively engaged on the development of substitute alloys such as nickel-free austenitic stainless steels, nickel- and cobalt-free electrical resistance alloys, nickel- and copper-free coinage alloys, manganese bearing brasses, tool and die steels, iron-aluminium alloys, aluminium bearing alloys and substitute processing techniques such as aluminizing of steel. On behalf of the Executive Council of the NML, Sir Jehangir conveyed his appreciations to Dr B. R. Nijhawan and his colleagues for their commendable progress in different research fields. Sir Jehangir also announced the award of a gold medal and conferring of Honorary Membership by Japan Iron & Steel Institute on Dr B. R. Nijhawan, who is the first Indian to receive this internationally distinguished honour. The coveted Bhatnagar Memorial Award to Dr Nijhawan by the Council of Scientific & Industrial Research, New Delhi, for his outstanding contributions in engineering sciences was also referred to.

Shri N. N. Wanchoo, Secretary, Ministry of Iron and Steel, stressed that even if complete substitution of strategic metals is not possible, partial substitution will also help a great deal. He praised NML for its work in the field of substitute alloys and organizing symposia on metallurgical subjects of topical interest. He also greatly appreciated the valuable assistance rendered by NML to the Indian iron and steel complexes in solving their problems of both short-term and long-range importance.

Technical Sessions

Thirty-six papers covering various facets of substitute alloys were presented and discussed in seven technical sessions.

Research and Development Work on Substitute Alloys at NML

At the first session, five papers were presented. The leading paper by B. R. Nijhawan (NML) discussed the scope of research and development work on substitute alloys at NML. Dr Nijhawan dealt with in detail the various research projects undertaken at NML such as (1) development of substitute alloy, tool and stainless steels including high temperature creep resistant alloys, (2) transformation and ageing characteristics of substitute alloys and stainless steels, (3) development of iron-aluminium alloys and iron-manganese-aluminium composition for high temperature oxidation resistance application, (4) substitute magnetic materials, (5) nickel- and copper-free coinage alloys based on aluminium-magnesium and manganese composition, (6) substitute nickel- and cobalt-free electrical resistance heating elements, (7) manganese bearing substitute brasses, (8) hot-dip aluminizing of steel to replace galvanizing of steel, (9) substitute surface treatments like PVC-coated steel and chromated steel sheets, (10) substitute aluminium electrical grade conductors, (11) aluminium based substitute alloys including antifriction aluminium bearing alloys, (12) improved mild steel for structural purposes and development of indigenous low alloy high strength steels, (13) thermo-mechanical and processing treatments for ultrahigh strength steels, (14) physical metallurgy of substitution of alloys, (15) substitution on refractory products, (16) survey of the scope and economics of substitution, and (17) industrial scale application and economics of substitution of metals. The results of these pioneering investigations offer interesting industrial potentialities and commercial scale production of a number of projects has been taken up, e.g. coinage alloys, nickel- and cobalt-free electrical resistance alloys, hot-dip aluminizing, substitute magnetic materials, etc.

Metal Matrix Composite Materials

H. M. Burte, F. R. Bonanno, L. D. Blackburn, J. A. Herzog and W. F. Stuhrke (Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, USA) gave the underlying principles of fibre reinforcement and discussed the potential of metal matrix composites and their advantages over other types of composite materials under severe environment of temperature, vacuum and stress. The employment of composite technology may permit the large-scale substitution by aluminium for the more scarce metal copper in high voltage electrical transmission. The improved strength and strength retention at high temperature of axially reinforced aluminium composites will permit significant increase in the power carrying capability of the aluminium. Apart from the potentiality of metal matrix composites, the authors furnished 'micro-mechanics' of filament characteristics and filament-matrix interactions to elucidate the modulus of elasticity, tensile strength, strength of filament, and macro- and microstructure of different types of composites.

Copper Consumption in Industrial Countries

L. R. Vaidyanathan and M. J. Smith (Indian Copper Information Centre, Calcutta, and International Copper Development Council, London), while suggesting considerable saving in copper consumption by design improvement, proper selection of copper alloy, metal spraying and electroplating, expressed the view of retaining the use of copper and its alloys where international competition has to be met in the export market and in all items of equipment for home use where long-range efficiency cannot be obtained by substitute products. Worldwide consumption of copper for various end products was also furnished.

Substitution of Imported Materials in Railways

K. C. Choudhuri (Research Development & Standards Organization, Ministry of Railways, Chittaranjan) presented the work done by Indian Railways for substitution of the imported materials and gave details of non-ferrous and ferrous imported materials which can be substituted with indigenous materials. The field thus relates to (i) use of spheroidal graphite cast iron bearing shells in place of bronze bearing shells of carriage and wagon bearings, (ii) substitute for leaded bronze solid axle boxes of the steam locomotives, (iii) development of aluminium base bearing alloys to replace bronze and antifriction metals, (iv) development of electrical contacts based on indigenous materials used for signal relays, (v) development of contact springs based on indigenously available material for use in signal equipment, (vi) use of insulated aluminium cables in place of copper cables for train lighting and signalling, (vii) substitution of galvanizing by aluminizing, etc.

Economic Utilization, Recovery and Substitution of Strategic Non-ferrous Metals

M. Subramanian, R. N. Misra, P. P. Bhatnagar and B. R. Nijhawan (NML) dicussed the scope of substitution and conservation of Cu, Zn, Pb, Sn and Ni in relation to their multifarious end uses. Various means suggested to reduce consumption trends of non-ferrous metals are (i) lowered metallic loss and higher recovery and yield figures during extraction of metals and subsequent processing, (ii) improved technological production methods, (iii) refining of non-ferrous wastes and metallurgical byproducts, and (iv) secondary refining.

Aluminium Alloys

In the second technical session, Rajendra Kumar and Manjit Singh (NML) presented the results of research work on electrical conductivity of substitute aluminium alloys. Effects of binary solute additions of silicon, iron, manganese and magnesium, each up to 1·0 per cent on the electrical conductivity and tensile properties of electrical grade (99·7-99·8 per cent purity), aluminium were studied. It was found that the conductivity of commercial aluminium can be improved by removing the soluble impurities by heat treatment, suitable alloy additions or both through precipitation of their intermetallic compounds. Based on research results, an alloy has been made from commercial pure aluminium in the form of wire which conforms to all the specified tests of the Indian Standards Institution. H. K. Lloyd (University College of South Wales) and C. H. Oxlee (Royal Armament Research & Development Establishment, UK) examined the effects of aluminium and iron as separate additions on the mechanical properties and corrosion resistance of copper-manganese-zinc alloys. Both aluminium and iron improve the strength of the basic alloy, but iron is more effective. Aluminium additions confer a marked improvement on the corrosion resistance of the basic alloy whereas iron addition is generally detrimental. α-Alloys containing up to 4·18 per cent aluminium have been recommended as the most attractive alloys for commercial use as substitute for nickel-silver.

Ved Prakash (NML) discussed the development of substitute magnetic materials based on iron-aluminium alloys, barium-ferrite and intermetallic compounds of manganese. Iron-aluminium alloys develop high permeabilities in the range of 15-16 per cent aluminium when the alloy is in disordered state and has least values of crystal anisotropy and magnetostriction. These alloys can replace nickel alloys for many applications. Tetragonal and hexagonal metallic and non-metallic crystals like Mn-Al and barium-ferrite can replace Alnico alloys in several applications.

Development of substitute electrical resistance alloys for heating elements dispensing with nickel and cobalt was discussed by R. Choubey, S. Choudhuri, B. N. Das and B. R. Nijhawan (NML) in a paper based on the work carried out at NML. The substitute alloys are based on Fe-Cr-Al system having 10-20 per cent Cr and 3-8 per cent Al with small but significant addition of Zr and misch metal. The production technology of these substitute alloys from melting to the finished wire has been standardized for implementation on industrial scale. The physical properties such as electrical resistivity, grain growth, high temperature scaling resistance, accelerated life tests, etc., compare favourably with conventional alloys.

Tin-Lead Alloys

F. N. Rhines and W. A. Anderson (University of Florida, USA) described a number of alloys which have been proposed as soft solders and as substitutes for the standard tin-lead compositions. It was pointed out by the authors that no alloy can be expected to serve all the purposes of tin base alloys. The alloys containing reduced amounts of tin rather than tin-free solders will be most acceptable for soldering copper. Tin-lead-cadmium composition is found to be promising in this application. Among the tin-free solders, lead-cadmium and lead-silver series are most attractive.

Copper-Manganese Alloys

A. K. Lahiri, K. P. Mukherjee and T. Banerjee (NML) dealt with the properties of some copper-manganese alloys to determine their suitability for use in place of copper-zinc alloys for some specific applications. Three groups of alloys, e.g. Cu-Mn, Cu-Mn-Zn and Cu-Mn-Ni, were investigated with copper, manganese, zinc and nickel varying from 95 to 65, 5 to 40, 5 to 25 and 2 to 8 per cent. The single phase alloys showed high strength combined with good ductility and deep drawing properties in consideration of which these can be substituted for conventional brasses, such as bolts and tie-rods, shafting, rivets, valves, automobile lamp bodies, lamp bases, domestic and industrial plumbing, etc. The possibilities of using 65 per cent Cu-25 per cent Zn-10 per cent Mn for cartridge cases need examination, but this alloy can be substituted for manganese-bronze when corrosive conditions are not very severe.

Low Carbon High Chromium Alloys

In the third session, five papers were presented. J. Banerjee and G. P. Chatterjee (Durgapur Steel Plant, HSL) dealt with development of a low carbon high chromium master alloy for production of different types of chromium steel. This alloy can substitute the conventional imported low carbon ferrochrome utilized for the above purpose. Laboratory scale experiments to produce the low carbon high chromium master alloy have been carried out at Research & Control Laboratory of the Durgapur Steel Plant and very encouraging results have been obtained.

Nickel-free Austenitic Stainless Steels

Sustained work at NML on the substitution of nickel in austenitic stainless steels has resulted in the development of nickel-free austenitic stainless steel which formed the subject of a paper presented by B. R. Nijhawan, P. K. Gupte, S. S. Bhatnagar, B. K. Guha and S. S. Dhanjal (NML). The Cr-Mn-N austenitic stainless steel developed possessed higher tensile strength than 18/8 chromium-nickel stainless steel in solution treated condition. Impact toughness of this steel showed the characteristics of the conventional stainless steel. Results of swift cupping test indicated higher drawing pressure for this steel than 18/8 stainless steel. X-ray diffraction study revealed the stability of austenitic steel even after cold reduction up to 30 per cent. Results of corrosion tests showed similar resistance of this steel to 18/8 type stainless steel. Reference to production technique for incorporating high nitrogen contents in the melt and subsequent processing cycles has been made.

J. K. Mukherjee and B. R. Nijhawan (NML) presented the results of the basic study made on nature and structures of precipitated phases in substitute chromium-manganese-nitrogen austenitic stainless steel containing 18-22 per cent Cr, 12-14 per cent Mn, 0·4-0·8 per cent nitrogen and 0·05-0·3 per cent carbon, using X-ray diffraction and spectrographic analysis techniques. The authors stated that the austenitic phase in the chromium-manganese-nitrogen steels remained stable up to 30-40 per cent of cold reduction. With further cold work a b.c.c. phase, having a lattice parameter of 2·868 A., was observed; Cr_2N and Cr_3C_6 types of precipitates were observed during ageing treatments depending on the carbon or nitrogen content of the steel. The activation energy of formation of Cr_2N type of precipitate during ageing was found to vary from 33·85 to 38·71 kcal./g.mole. The matrix remained austenitic after prolonged subcritical ageing and no ferrite was detected.

Electrolytic Manganese as Ferro-alloy Substitute

B. C. Kar and T. Banerjee (NML) discussed the applications of electrolytic manganese as a substitute ferro-alloy in relation to abundant manganese ore resources in India and the work done at NML on the production of electrolytic manganese. The authors illustrated the scope of such substitution with practical service applications with electrolytic manganese for diverse end uses, particularly in foreign countries, and how these can be implemented on an industrial scale in India.

Applications of Aluminium and Its Alloys

Five papers were presented at the fourth session. P. Jacomet (Aluminium Français, France) reviewed the recent developments of aluminium conductors for public and industrial consumption in France and described the technical improvements to be achieved in order to permit the introduction of aluminium in a field occupied traditionally by copper. Very high voltage transmission systems, overhead distribution systems, signal and telecommunication cables, underground cables, busbars, etc., are some of the latest applications of aluminium, while research is in progress in France to introduce aluminium strips into windings for transformers and electrical machines in general.

The use of aluminium foil in electrical windings was also taken up by B. N. Bose (Indian Foils Ltd, Calcutta). The author presented the techniques developed for insulating, winding and joining aluminium foils and strips and discussed their typical uses such as in transformers, lift magnets, automotive horn and generator coils.

Dharmendra Kumar and V. S. Surana (Hindustan Aluminium Corp. Ltd, Renukoot, Mirzapur) gave an account of the specific mechanical and physical properties and design consideration which favour use of aluminium and its alloys in various applications and discussed the factors for redesigning in aluminium in place of structural steel. In another paper from the same organization, Dharmendra Kumar, G. C. Jain and V. K. Agarwal discussed the various technical and economical factors about the new ACAR conductors which offer a remarkable range of flexibility to meet specific design requirements. In addition to being suitable substitutes for scarce EC grade aluminium metal, the new conductors offer many benefits for a wide range of applications. The authors stated that there is a very wide area of usage where the new conductor can be utilized with advantage and also as a substitute for the conventional ACSR conductors. The technical and economic advantages envisage promising future for this type of conductor.

Substitute Alloys as Bearing Materials

D. Scott (National Engineering Laboratory, UK) in a paper on ' Substitute alloys as bearing materials ' discussed the metallurgy of plain and rolling bearings, their properties, uses and comparison of substitute materials. As substitute bearing material, aluminium alloys offer the best combination of strength, wear and corrosion resistance. Successful techniques of bonding to steel have rapidly increased the potential of aluminium in automotive bearing applications. To improve the fatigue life and reduce the incidence of premature failure of rolling bearings, the materials should be as free as possible from deleterious, brittle type non-metallic inclusions. The substitution of vacuum treated steels for air melted steels improves performance. For specific applications substitute high speed tool steels of lower alloy content are satisfactory but it is essential to control the heat treatment carefully to ensure optimum hardness, satisfactory carbide distribution and minimum retained austenite content. Lubricating surface films formed *in situ* on treated surfaces by special environments may be a way of enabling simple materials to be used as substitutes for complex highly alloyed materials.

Substitute Special Steels

The papers which were presented and discussed in the fifth session covered mainly the subject of substitute special steels. U. P. Mullick (Institute of Consulting Engineers, Calcutta) reviewed the critical raw materials and substitutes in the light of India's self-sufficiency and stressed the need for intensive prospecting and critical investigation on alloying properties in alloy, tool and special steels. R. Chattopadhyay, B. K. Guha, S. S. Bhatnagar and B. R. Nijhawan (NML) presented their work on improved mild steel for structural purposes. The authors stated that by making use of strengthening mechanism in mild steel containing residual alloying additions, it would be possible to use a cheaper steel in structure needing a more highly alloyed steel, and a significant reduction in cost can be achieved. Also, by replacing mild steel with this improved variety, thinner sections can be used in structures. The investigation covered low alloy 0·5 per cent molybdenum-boron bainitic steels, low carbon Nb-V-N and Nb-Ti steels. It was found that 0·5 per cent Mo-B-Nb bainitic steels would be useful for applications needing higher strength but its poor welding characteristics would not make it suitable for use in structures where welding is necessary. The Nb-V-N steels showed both high yield strength and low impact transition temperature, and its carbon content is maintained below 0·1 per cent for giving good welding properties. Further work is, however, needed to optimize the composition and working condition. The Nb-Ti steel has higher yield strength than Nb-V-N steels and where higher strengths are needed at the expense of some toughness, this steel can be used in place of Nb-V-N steels.

D. P. Chatterjee, G. Mukherjee and M. K. Datta (Alloy Steel Project, HSL, Durgapur) gave a study of some carburizing and hardenable steel with and without nickel and molybdenum for automotive industries. A few grades of steels can be popularized in India and it has been found that with suitable heat treatment, steels with manganese, chromium and vanadium can be used for wide varieties of parts in the automobile industry.

High Strength Steels

J. K. Mukherjee (NML) outlined the ausforming process and effects of composition and processing variables on the mechanical properties of high strength steel in relation to their potential applications. Based on electron microscopic, X-ray diffraction and other related studies on mechanical and physical properties of ausformed and conventionally treated steels, the author suggested that the following mechanisms are responsible for the properties of the steels: (i) increased strain hardening of the martensite inherited from austenite, (ii) increase in the dislocation density, (iii) precipitation of carbides in the metastable austenite, and (iv) improved dispersion of carbides subsequent to tempering.

As there is acute shortage of tungsten resources in India, development of substitute low tungsten tool steel was investigated by R. K. Dubey, A. K. Das, P. K. Gupte and B. R. Nijhawan (NML) in relation to optimum heat treatment cycles and resultant physical properties vis-à-vis conventional 18/4/1 high speed tool steels. After studying the various factors, e.g. effect of austenitizing on the hardness, effect of quenching media, effect of single and double tempering treatments, microstructure, etc., the authors observed that substitute tool steels containing 0 7-0·8 per cent carbon, 6 per cent tungsten, 4-5 per cent chromium, 1-1·4 per cent vanadium, 0·6 per cent aluminium and 0·3 per cent titanium developed adequate tool hardness in the quenched and double tempered conditions, comparable to 18/4/1 high speed steel. Low tungsten steel containing boron, zirconium and aluminium-titanium in combination showed adequate hardness in the as-cast condition and these steels are being rolled and forged for further study.

R. Choubey, B. R. Nijhawan, P. K. Gupte, B. N. Das, S. S. Bhatnagar and K. Prasad (NML), in their paper on the development of substitute high temperature creep resistant alloys, discussed the possibilities of using Cr-Mn-N austenitic stainless steel as a high temperature creep resistant material in place of conventional alloys containing nickel, cobalt, tungsten, etc. The creep properties of Cr-Mn-N steel (C, 0·47; Cr, 18·0; Mn, 14·0; and N, 0·32 per cent) have been found to be strongly dependent on solution temperature. Preferred range of solution treatment temperature is 1050-1100°C. Optimum creep properties are obtained at C/N ratio of about 1 : 1. The Cr-Mn-N steel appears to be suitable for application as engine valve operating at temperatures around 650°C.

Conservation of Non-ferrous Metals

Six papers were presented at the sixth technical session. A paper from Defence Research Development Organization, Kanpur, reviewed the various methods of conservation of non-ferrous metals by protective treatments and substitution by aluminium. Conservation of non-ferrous metals can be achieved by prolonging their life by passivation treatments. Tin can be passivated by a 30 sec. dip at 80°C. in a solution containing sodium dichromate (3 g.), sodium hydroxide (10 g.) and wetting agent (2 g.) in one litre of water. Lithoform treatment followed by painting with red oxide, zinc chromate and two coats of Al.G.S increased the life of galvanized sheets in marine atmosphere by many fold. Aluminium can be passivated by MBV treatment. Brass cartridge cases susceptible to dezincification have shown considerable resistance after passivation treatment. Bright anodized aluminium can be substituted for nickel- and chromium-plated materials. The conservation of copper, lead and zinc powder/pigments in paint formulation is possible by aluminium pigments, both leafing and non-leafing type, which are manufactured in the country. B. R. Nijhawan and C. Sharma (NML) examined the substitution of copper and other scarce non-ferrous metals and pointed out the need of popularizing aluminium and its alloys as substitutes. The authors stressed the need for long-range research on the subject. They suggested that the cost of aluminium should be brought down in line with the world prices and the specifications for application of aluminium and its alloys in place of brass, copper, etc., should be revised.

Aluminizing of Steel

Substitution of galvanizing by aluminizing of steel was dealt with by S. M. Arora, A. N. Kapoor, P. K. Gupte and B. R. Nijhawan (NML). Based on the pilot plant trials carried out at NML, the techniques of aluminizing developed at NML were found to be extremely suitable for substituting galvanized products. Field trials carried out on aluminized and galvanized wire have established the superiority of aluminizing over galvanizing. Telegraph and telephone wire, ACSR core wire, high tension transmission tower members and other hardwares have been successfully aluminized at the pilot plant of NML and optimum conditions to achieve desired results have been worked out. Based on the work carried out at NML, aluminizing has been accepted by Government of India as a substitute for galvanizing.

Use of Clad and Composite Metal

In a paper entitled ' Economic uses and substitution of non-ferrous metals and alloys ', B. N. Das (NML) advocated the use of clad and composite metal in place of the individual metal. Cladding is done by bonding two or more metals to impart to the composite most useful property of each metal. The technique of cladding stainless steel to mild steel has been developed at NML and it can be used in chemical industries where heavy vessels made entirely of stainless steel are utilized. Similarly, the author suggested use of steel rollers cladded with copper for textile printing purpose where the printing rollers are made entirely of copper. Spring material made of copper and suitable grade of steel can substitute phosphor-bronze or copper-beryllium spring. The author also drew the attention of the work carried out in the USSR where bearings made of pressed wood are in use for a large number of applications in place of metal bearings and described the metal economy that can be effected in domestic application by using plastic and ceramic wares.

Aluminium Base Bearing Alloys

The scope of aluminium base bearing alloys was discussed by B. N. Das and S. K. Banerjee (NML). The results obtained so far indicated that use of antimony and lead in small percentages in substitute aluminium base alloys offer potential scope as plain bearing alloys. The question of substitute bearing alloys was also examined by N. J. Wadia and A. S. Prasad (Tata Iron & Steel Co. Ltd, Jamshedpur). The results of a study on substitute bearing alloys of Alzen type (containing Al-Zn-Cu) and some zinc and aluminium base alloys were presented. Hardness, tensile strength, impact strength and age-hardening characteristics of these alloys have been compared with those of conventional alloys.

Selenium and Tellurium in Ferrous Materials

In the last technical session four papers were presented. R. H. Aborn (American Smelting & Refining Co., USA) discussed the beneficial effects obtained by introducing selenium and tellurium to ferrous materials. Addition of selenium and tellurium to cast iron results in getting a hard, wear resistant surface and maintains a tough underlying body to meet severe operating conditions.

Revised Indian Standards

H. P. Ghose and B. S. Krishnamachar (Indian Standards Institution) explained the efforts made by their Institution in bringing about variety reduction and in issuing emergency standards and amendments. The IS Specification No. 1570-1961 has brought down the variety of steels from approximately 1000 types to 140 types for general engineering purposes. More rationalization of alloy and special steels is under way and it is expected that it will be possible to further reduce the variety of steels to about 50 only. The various Technical Committees of ISI are also reviewing the standards relating to substitution of non-ferrous and scarce metals and alloys wherever possible.

Physical Metallurgy of Substitute Alloys

The physical metallurgy of substitute alloys was discussed by Rajendra Kumar and Ved Prakash (NML). The study relates to (i) phase transformation including reaction kinetics, (ii) structural features such as their distribution and influence of vacancies and stacking faults, (iii) volume change, (iv) nature of carbides and carbide transformations in alloy steels, (v) precipitation hardening including coherency of precipitates and (vi) plastic deformation.

Theoretical Basis of Metal Substitution

The last paper dealt with theoretical considerations in the substitutions of some common elements in alloy steels. P. Tewari, S. S. Bhatnagar and B. R. Nijhawan (NML) reviewed the theoretical basis of metal substitution in relation to limitations in practice on applied desiderata of potential substitute alloys. The need for carrying out scientific studies on the subject prior to large-scale studies was emphasized.

Conclusion

Many of the overseas scientists and delegates expressed the view that the symposium was extremely useful and the subjects discussed were of great interest. Mr Jacomet, Chief Engineer, Aluminium Français, observed that exchange of technical information with France should be intensified and that such an exchange would be of mutual benefit to India and France. He complimented Dr B. R. Nijhawan and his colleagues for the good work done in the various branches of metallurgy and particularly in the field of substitute alloys. Mr M. J. Smith, Director, International Copper Development Council, said that he was greatly impressed with the research and development work under way at NML. The development work on substitute alloys, particularly the work done on aluminium alloy bearings, Mr Smith said, should not only be of importance to India but also to other countries where a constant search is being made for developing new alloys. Lt W. F. Stuhrke, Air Force Materials Laboratory, Ohio, USA, shared the sentiments expressed by the delegates from UK and France, and observed that substitution problems in USA are engaging the attention of the materials engineers. Referring to the problems investigated by NML, Lt Stuhrke said that the results achieved by the laboratory are praiseworthy, and in particular he considered the development work done on nickel-free stainless steel as one of international importance.

Emerging Emulsions*

R. E. STAUFFER & E. A. MACWILLIAM

Emulsion Research Division, Kodak Research Laboratories, Rochester, New York

FROM its beginning, photography has been recognized as a powerful tool of the scientist and technologist. The photographic industry has moved at an ever-accelerating pace to apply the results of research to a bewildering array of products.

Although numerous photographic systems are known, the most versatile is based on the photosensitivity of silver salts, particularly the salts of chlorine, bromine and iodine. These sensitive salts are suspended in a colloidal matrix, and the mixture, called an ' emulsion ', today is supplied in sheets or rolls on film or paper, on glass, as a liquid, or as unsupported thick layers known as ' pellicles '.

Photographic materials record information received as bits or packets of electromagnetic radiation or as high energy particles. The emulsion can integrate successive packets of energy, which may arrive in increments below the threshold sensitivity of the material. This integration may require long exposures, e.g. in astrophotography.

Trends in New Materials

Information may be recorded by the eumulsion as the traditional picture produced by a simple camera or as the result of combination with some other optical device such as a telescope or microscope. Or the image may be a shadowgram produced by a human being, metal casting, or other object interposed in a beam of penetrating X-rays. Information may be stored on films or papers by coding it as alphanumeric, digital, or other characters. After the film or paper has been processed, the images may be in black-and-white or in two or three colours.

Four trends in new materials are evident : (i) a steady increase in the sensitivity or speed of films and plates; (ii) an increase in the number of materials available for photography in colour; (iii) the rapid trend toward simplifying production of the finished photograph by the user; and (iv) introduction of many new photographic processes based on the chemistry and physics of new photosensitive systems, especially for document copying and graphic arts.

Advances in Sensitivity

Black-and-white films have increased in speed, on the average, about twofold every 10 years from 1850 to the present. At the same time, advances in sensitivity have been used to produce films with low speed but extremely fine grain, good sharpness, and resolving power beyond the capabilities of present optics.

On the other end of the scale, new developments have made possible ultrasensitive films capable of recording, with a fractional second exposure, scenes lighted with only four foot-candles of illumination. By combining high speed films with an image-intensifier tube, motion pictures of moonlit scenes have been produced which show recognizable details invisible to the unaided eye.

In astronomical photography, where exposures extend from minutes to many hours, an increase in sensitivity may either reduce the time required to make a picture or increase the information content of the picture. Two new Kodak special plates, types 080-01 and 087-01, accomplish these goals. The first, useful on any telescope, approximately halves the time required to get a picture compared to that with previously available plates. The second, when used on instruments with apertures of *f*/6 or faster, e.g. high aperture Schmidt telescopes, more than doubles the number of detectable stellar objects.

Another trend has been the extension of the sensitivity of silver halide emulsions by dye sensitizing throughout the visible spectrum and beyond into the infrared. The limit of sensitivity is now a little over 1300 mμ.

Radiation Effects

Beyond the violet end of the visible spectrum, silver halides are inherently sensitive to ultraviolet and shorter wavelength X-rays and γ-rays. In fact, ultraviolet radiation was discovered in 1801 by Ritter and almost simultaneously by Wollaston through the effect of such radiation on silver chloride. In 1895 Roentgen showed that the invisible radiation produced in a Crookes tube, which caused fluorescence in some substances, also affected the photographic plate.

With the rapid development of nuclear physics, special plates were introduced which featured relatively fine and uniform grains, high concentrations of silver halide, and increased total thickness of emulsion. Because of the high track visibility achieved, precision measurements of mass-energy relationships from track data are possible (Fig. 1). The plates also have the ability to record extremely high energy particles, such as cosmic rays from outside the earth's atmosphere and particles accelerated in cyclotrons and bevatrons.

Pellicle Emulsions

Besides these special plates for nuclear studies, unsupported layers of emulsions called pellicles have been devised for recording nuclear events caused by cosmic rays. Pellicles range in thickness from 50 to 1200 μ and are often used in blocks many centimetres thick. After exposure to cosmic rays or other types of radiation, the pellicles making up the block are stripped apart, processed, then examined under the microscope, and the tracks of the cosmic particles followed from one pellicle to another. There is an increasing tendency to use bubble chambers in place of pellicle blocks to trace the

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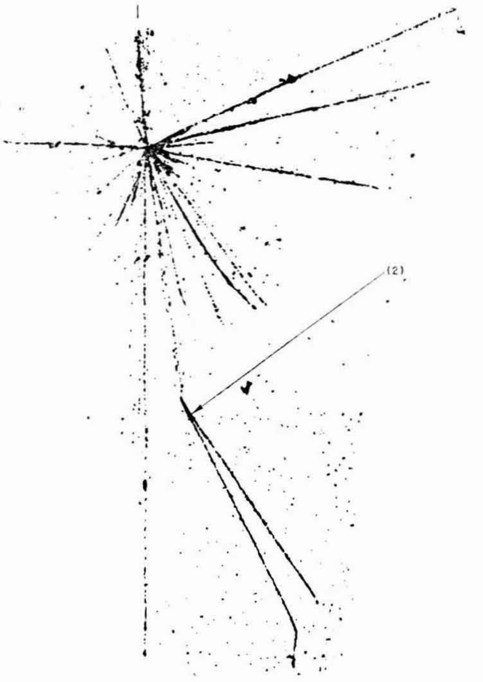


Fig. 1 — Nuclear collision observed in Kodak NTB-3 emulsion, exposed at 93,000 ft altitude and 30° geomagnetic latitude [Calcium nucleus with 100 BeV. energy collides with a silver or bromine nucleus of the photographic emulsion. Explosion emits 42 charged particles, one of which creates a second explosion]

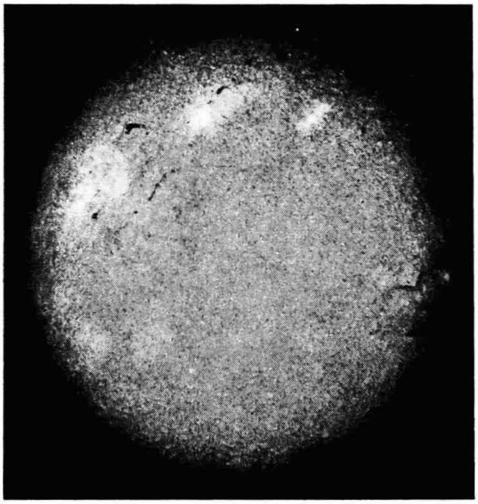


Fig. 2 — Photograph of sunspots taken at Sacramento Peak Observatory, New Mexico, USA, on Kodak's new special solar recording film, type SO 375 [Less than 1/10,000th of the sun's visible light reached the film, as a filter excluded all but a 1/2-angstrom-wide band in the red spectrum. The photo was taken in February 1966, during relatively minimal sunspot activity]

paths of the particles involved in nuclear events. Light reflected from these bubble tracks is recorded on suitable photographic films for subsequent analysis.

One region of short wavelength radiation is very strongly absorbed both by air and by the gelatin used in photographic emulsions. This region, called the ' vacuum ultraviolet ', could not be recorded on photographic films until Schumann showed in 1893 that if silver halide emulsions were prepared free of gelatin, they could be used to record rays of this wavelength. Special films and plates such as Kodak SWR Plate, Kodak-Pathé SC-7 Film (ultraviolet sensitive), and special solar recording film type SO 375, are being employed in research on solar radiation and the composition of the outer atmosphere (Fig. 2).

Emulsions with high sensitivity to the emissions from radioactive tracer elements are used in studies of vital processes. Thin tissue sections or other microscopic samples are overcoated with photographic emulsion either by stripping a precoated layer of emulsion over the sample or by flowing on liquid emulsion. After appropriate exposure and processing the distibution of the radioactive tracer elements can be specified within a few microns and photographed against the background of the actual tissue.

Photographic films are used to record images transmitted by radio and displayed on a cathode ray tube (CRT). In this way, spectacular ' photographs ' of the Moon and Mars were made at close range. In the latter case, a memory device in the United States' Mariner-4 probe recorded the pictures and relayed them to earth twice during the succeeding 19 days over the 140,000,000 miles intervening between the planets. One of these spectacular photographs is reproduced (Fig. 3).

Similar reconstructed photographs obtained from earth-circling satellites of the Nimbus and Tiros series have provided meteorological and geophysical data of great value. These pictures are obtained with both visible and infrared light.

These CRT images are produced by photographing the light emitted by a phosphor which is excited by the electron beam in the tube. A substantial improvement in the quality of such reconstructed pictures can be achieved by producing the photographic image inside the CRT by direct impact of the electron beam on the film. Experimental direct electron-recording films which must meet many requirements not normally imposed on a photographic film are under development by the Eastman Kodak Company.

Image intensifiers which convert an X-ray image to an electrically amplified picture on a CRT are becoming more widely used in medicine. They allow immediate monitoring of internal processes, without the delay inherent in photographic processes. Once again, photography is used to record the CRT image for later study.

An important trend in modern films has been the introduction of emulsions on polyester type supports,

Fig. 3 — Photograph of the surface of the planet Mars taken by Mariner-4 in July 1965 [The photograph was taken at a distance of 7800 miles and shows an area 170 miles by 150 miles. The light area between the two dark areas — Mare Sirenum and Mare Cimmerium — is known as Atlantis. A 75-mile wide crater enclosing smaller craters is seen dimly. At the time the picture was taken, Mariner-4 had been in flight for 228 days and was 130,000,000 miles from the earth. The Mariner-4 picture was radioed back to earth in the form of digital data, which was recorded initially on magnetic tape. Then, from the tape, the picture was projected on a cathode ray tube, and the image was photographed on Recordak Special Dacomatic Film. This is a Kodak film designed especially for the recording of computer data that are projected on cathode ray tubes for rapid read-out. When the above photograph is viewed with the data block at the left, North is at the top]

such as Cronar and Estar, which hold their size through humidity variations much better than conventional cellulose acetate-supported films. These films, although introduced for use in the graphic arts, are finding acceptance in many other areas as well.

Use of Paper Support

Not all the innovations have been in film. Many new products have been introduced with paper supports, some of which are especially designed for recording data from oscillographs and CRT's. The chief features of these new products are increased sensitivity and simplified processing. This is exemplified by high speed recording papers of the ' direct print ' types which provide visible records from high speed multichannel oscillographs.

The writing speeds reached by these papers are as high as 100,000 in./sec., and the record is brought to full legibility by a subsequent dry photo-development step accomplished in a few seconds by passing the exposed record under a bank of photo-developing lamps at a level of about 1000 foot-candles of illumination, or more slowly by post-exposure at lower levels of illumination.

Minimum Processing

Another approach to films or papers that yield images with minimum processing has been to utilize the chemical development step, but to incorporate some or all of the process components in the sensitive materials.

An extreme example is a special Kodak paper which contains all the components for development and is processed after exposure by passing the paper through a hot chamber or over a hot platen at a temperature of 240-300°F.

Again the record is not permanent, but can be made permanent, if desired, by a suitable series of fixing-washing-drying steps after the records have received their first examination. A paper of this type was used in connection with the telemetry of the Mariner-2 Venus probe.

Besides dry photographic papers of the types described, a number of so-called self-developing papers and films have been introduced in recent years. These materials are developed and stabilized by simplified wet processes. Many are designed to work with simplified processing equipment. Examples include Kodak Gravure Resist Contact Film, a silver-salt-sensitized film for preparing the ' stencils ' used to control the etching of gravure printing cylinders, and a new paper for rapid preparation of prints from microfilm negatives using Documat, Duostat, Fotorite, and Polymicro equipment.

Simplified Mechanism

Another approach to simplifying the photographic process depends on the solvent-transfer or diffusion-transfer mechanism in which a single processing solution is applied to the exposed negative material, which is then brought into face-to-face contact with a receiving sheet.

During development of the negative image, the remaining positive silver halide image is dissolved by complexing agents for silver ion, such as thiosulphate ion, present in the processing solution, and then is transported by diffusion to the receiver, where it is reduced *in situ* to a positive silver image. The process, thus, is a developer-stabilizer system yielding a direct positive.

Among the variety of Polaroid Corporation materials utilizing this principle are high and medium speed sheet and roll films for continous-tone photography, materials for preparing projection transparencies, for lantern slides, and similar uses. A newer film has been introduced which provides a positive print and a negative on film which can be handled and utilized as a normal film negative. A high speed, high contrast film, called Polaroid Pola-Scope, type 410 Land Film, is designed to record low-light-level sources, such as short duration cathode ray oscilloscope traces.

A modification of this procedure has a special receiving material, Kodak Bimat Transfer Film, type 21A, which, while not obviously wet, contains a solution of all the chemicals necessary to develop and fix the negative. Using this Kodak Bimat Film, a camera film can be processed to a reasonably stable negative with a minimum of apparatus and inconvenience by simply rolling the Bimat Film in tight contact with the film. This is especially useful in aerial photography where immediate access to photographs is necessary but where liquids are inconvenient and there is no room for bulky apparatus. With certain films a usable positive transparency may also be recovered in the Bimat receiver.

Transfer Advantages

The diffusion-transfer process is employed to produce photocopies on simple office equipment. In this process, the negative is immersed in a single solution and the negative sheet and receiver then are squeezed into intimate contact and held there for about a minute before the damp positive copy is stripped away.

The advantages of transfer processes of producing images from silver-halide-sensitized papers and films have been utilized widely in the rapidly growing documentation field. In one system, exemplified by the Verifax copy process, development hardens the gelatin of the negative image and the remaining untanned positive gelatin image is transferred to a receiver where it forms a black image.

Electrostatic Charging

Electrostatic systems depend on light-sensitive semiconductors such as selenium or zinc oxide which are sensitized by electrostatic charging. On exposure to light, the semiconductor forms a latent image in the form of an electrostatic charge pattern on the sensitized surface. The image is developed by dusting a powdered pigment over the surface.

In the case of the selenium surface, the pigmented image is transferred from the semiconductor to a sheet of paper to produce the copy. The selenium surface then can be cleaned, resensitized by charging, and reused. This system has been developed and utilized by the Xerox Corporation in a series of document-reproducing devices.

Electroconductography also depends on light-sensitive semiconductors, but electrolytic conduction is used to produce an image by depositing a metal, such as silver from ionic solution, in the conduction image areas. This process is available for preparing prints from microfilm negatives under the name 3M Photocon.

The magnetic recording of visual images on tape, although not strictly a photographic process, is becoming increasingly important in television work as well as in medical radiography. Its advantage is, of course, its immediate accessibility and the fact that no wet processing is required. The image is viewed when necessary by presenting it on a CRT from which it may be recorded on photographic film as described previously.

Images by Heat

Thermography, as the name implies, is the process of producing images by heat. In this case, the document is placed in close contact with a sensitized sheet containing chemical reactants which are kept apart until the temperature exceeds a critical value. At this point the chemical components react to produce a dye or pigment and hence a duplicate of the original image. This simple process offers several advantages.

Thermography has the advantage, like silver-halide-sensitized, direct print materials, of being a truly dry, simple process. Unlike silver halide, it is virtually insensitive to the visible spectrum, and is inherently of very low photosensitivity even in the infrared region.

Photochemical reactions in organic substances, which make them less soluble in a solvent, allow the photographic preparation of masks resistant to metal-etching solutions. As a result, chemical agents are being used to an increasing degree to dissolve unwanted material from metal parts in place of grinding, machining, or other mechanical processes to shape material. Because of the high resolution of photographic emulsions, thin metal coatings may be etched to provide lines (' wires ') only 1/10,000th of an inch wide between proportionately small transistors, resistors, and other elements of microelectronic circuits.

Colour Photography

Modern colour photography dates from the introduction of Kodachrome film in 1935. Prior to that time, colour photography required complex apparatus and cumbersome techniques to produce pictures, and the processes were not suited to widespread application.

Today, numerous colour photographic materials are produced on film and paper supports. Colour films and prints are being used in photomicrography, medicine, surgery, biology, and every branch of science. Even the science of astronomy, which has relied most heavily on monochrome photography, has turned to the use of colour photographic materials.

In keeping with the trend to simplify monochrome photography for the user, manufacturers have improved colour photographic materials to permit the customer to manipulate the processing where desired, and at the same time have markedly improved speed, colour quality, and image permanence. The Polaroid Corporation, for example, with its PolaColour Film, provides the amateur with a means of obtaining a colour print within two minutes of the time of exposure.

Aerial photographs in natural colours or in false colours, in which infrared light is recorded as a red image on a displaced colour scale, are increasing in use. Besides the normal use of such photographs for mapping, for road planning, and for taxation surveys, plant pathologists are able to distinguish from aerial views the type of trees or crops and even to distinguish whether they are diseased or healthy (Fig. 4). Geologists can more accurately identify geophysical features and archaeologists can distinguish man-modified areas from the natural background.

Special materials for applications outside the field of natural-colour recording have begun to appear. One of these is a two-colour photographic material called Kodak Linagraph 705 Paper. The paper was developed to fulfil special needs in seismographic exploration.

Other Advances

Although this article deals primarily with light-sensitive emulsions, advances in photographic technology have not been limited to emulsions. Recent years have seen rapid evolution of more convenient processes for developing and stabilizing the image, and development of sophisticated equipment to utilize the processes.

Because of the extreme spatial resolutions that can be recorded on photographic plates, which is at least 10^9 yes-or-no signals per square inch, the plates will certainly find widespread use in the data-recording and information-sorting systems of the future. The combination of the intense coherent light of lasers with these high resolution plates may make possible holograms which can be used in

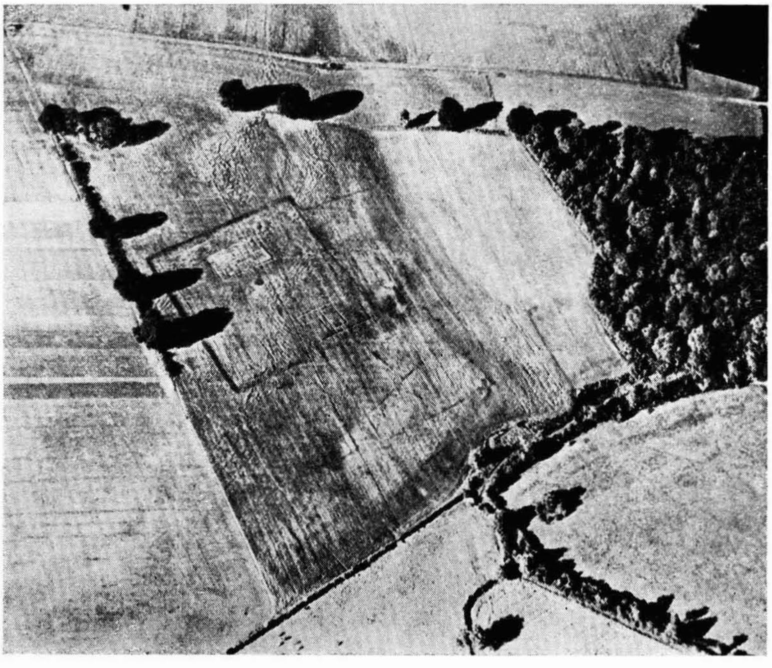


Fig. 4 — An application of aerial photography in archaeology [Crop markings, showing ancient British and Roman sites]

character-recognition systems approaching the effectiveness of the human brain.

More and more sensitive materials, faster and simpler processing, and new ways of recording electronic radiation — these appear to be the directions in which photography is moving.

It is not possible in this brief article to discuss the myriad applications of the materials and systems dealt with, but applications are expanding at such a rate that the newest innovations in photographic technology become part of the researchers' equipment almost before they are out of the developmental stage.

Recent Developments in the Kinetics of Exchange Reactions

S. V. ANANTAKRISHNAN

Department of Chemistry, Madras Christian College, Tambaram, Madras 59

THERE have been a number of excellent reviews on isotope effects[1-5] which have sections on the subject under survey. The present review is confined to only the work in the last few years.

General and Theoretical

Theoretical aspects of isotope exchange have not received as much attention as one might expect, but there are a few that call for attention. Even though it is not directly linked up with isotope exchange, Eyring's treatment[6] of departures from equilibrium kinetics is a suggestive contribution. Condensation, association and atom recombination are processes involved in the study which are quite relevant. The macroscopically simple reaction $H_2 \rightarrow H+H$ is found to be suitable for treatment by multiple barrier kinetics. The rate equation is represented by

$$dC_n/dt = \sum_{i=0}^{N} k_{n_i}C_i - \sum_{j=0}^{N+1} k_{j_n}C_n + d\rho_n/dt$$

The second term takes into account an adsorbing barrier while the remaining terms deal with transport and may be put down in the form

$$dC_n/dt = -\sum_{i=0}^{N} A_{n_i}C_i + d\rho_n/dt$$

where

$$A_{n_i} = -k_{n_i} + \left(\sum_{j=0}^{N+1} k_{ji}\right)\delta n_i \text{ and } k_{ii} = 0$$

The equation is solved assuming that transition probabilities k are independent of time and concentration and the matrix has positive eigenvalues and also contain only the nearest neighbour transition probabilities. The solution of the transport equation treats $C_k(t)$ and $\rho_k(t)$ as linear combinations of eigenvectors of the matrix A and applies an orthogonality relation to these vectors. A rate of passage over the highest barrier is got as a function of the rate constant for equilibrium kinetics. The results obtained compare very well with the earlier work of Eyring and his collaborators.

An aspect of the transition state is the possibility of metastable transitions and this is particularly noticeable in mass spectral studies of isotope effects. Applying quasi-equilibrium theory, Vestal[7] obtains for the rate of unimolecular reactions

$$k(E) = 1/h[W^*(E-e_0)/\rho(E)]$$

where E is the internal energy of the decomposing molecule ion; $\rho(E)$, the density of states for normal configuration; and e_0, the activation energy of the reaction. $W^*(E-e_0)$ = number of states of activated complex configuration with non-fixed energy less than or equal to $(E-e_0)$. This leads to a $k_{\text{min.}} = 1/h\rho(e_0)$. Metastable transitions are possible only if quantity is less than the maximum rate of production of the metastable state. Vestal makes the interesting observation that the minimum rate for CHD_3^+ is twice that for CD_4^+.

An isotopic exchange can be generally represented in the form

$$aA_1 + bB_2 = aA_2 + bB_1$$

Rees *et al.*[8] obtained the equilibrium constant of such a system in terms of partition functions, assuming only harmonic vibrations of molecules. They found that the constant can be put in the form[9]

$$K_{eq} = (Q_{A_2}/Q_{A_1})^a/(Q_{B_2}/Q_{B_1})^b$$

where

$$Q_2/Q_1 = \prod_i^{3n-5} (u_{2i}/u_{1i})\left(\frac{\exp - u_{2i}/2}{\exp - u_{1i}/2}\right)\left(\frac{1-\exp - u_{1i}}{1-\exp - u_{2i}}\right)$$

This may be compared with Bigeleisen's equation[9]

$$\ln Q_2/Q_1 = \sum_i^{3n-6} \ln\frac{u_{2i}}{u_{1i}} \sum_i^{3n-6} \delta_i \coth x_i$$

as well as the simpler Urey expression[10]

$$\alpha^k = \frac{n/(1-n)}{N(1-N)}$$

where α is the separation factor and n and N represent the number of molecules of the heavier isotope in solution and in the gas phase. An application of the equation to ^{13}C isotope enrichment using the reaction

$$CO_2+H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2+H_2O$$

showed that this slow reaction catalysed by carbonic anhydrase involves three equilibria

$$^{13}CO_{2(gas)} \rightleftharpoons {}^{12}CO_{2(aq)}$$
$$^{13}CO_{2(gas)} \rightleftharpoons H^{12}CO^{-}_{3(aq)}$$
$$^{13}CO_{2(gas)} \rightleftharpoons {}^{12}CO^{2}_{3(aq)}$$

Added metal ions, *p*H and temperature, all play important roles in the process.

Reference may be made here to Kreevoy's interesting observation on deuterium isotope effects[11] that deuterons tend to accumulate in those positions where they are mostly confined by energy barrier.

In the study of isotopic separation, it is useful to evaluate the Morse potential. In a discussion on the chromatographic separation of isotopic and nuclear spin species, White[12] using the partition functions with the states $l = 0, 1, 2$ and $m = l, l-1$ indicates how by an iterative procedure the constants of the Morse potential could be determined.

Examining the problem of potential energy surfaces, Johnston and coworkrs[13] found that a proper picture of a well with symmetrical saddle points in hydrogen-deuterium isotope effects can be given only by a potential energy function using tunnel correction.

On the other hand, Melander[14] ignores the tunnelling effect and derives the functions for potential and kinetic energy with the curve of reaction coordinate postulated for the exchange reaction. Melander's study includes a bold treatment considering each hydrogen as an independent three-dimensional oscillator. A remarkably close agreement between theory and experiment is noticed. A novel approach by Klots and Benson[15] on the use of the cell theory of liquids which is justified in aqueous solutions leads to an understanding of the isotope effects in the solution of oxygen and nitrogen in water, the heavier species being more soluble in both cases.

Exchange Reactions Involving Hydrogen

The isotopes of hydrogen continue to hold considerable interest in exchange reaction studies. In the hydrogen ion-molecule reaction involving the isotopic species, intramolecular isotope effect with a complex X^+ intermediate appears plausible[16]. The following reactions are envisaged to account for the kinetics:

$$H_2^+ + H_2 \longrightarrow H_3^+ + H$$
$$D_2^+ + D_2 \longrightarrow D_3^+ + D$$
$$HD^+ + HD \longrightarrow H_2D^+ + D \text{ or } HD_2^+ + H$$
$$H_2^+ = D_2 \longrightarrow HD_2^+ + H$$
$$HD^+ + H_2 \longrightarrow H_2D^+ + H$$
$$HD^+ + D_2 \longrightarrow D_2H^+ + D$$

An important aspect of isotope fractionation that continues to interest workers is the exchange between water and hydrogen ions or hydroxyl ions. The use of various physical properties and the overall equilibrium

$$2D_3O^+ + 3H_2O \rightleftharpoons 2H_3O^+ + 3D_2O$$

as well as Bigeleisen's rule of geometric mean[17] enabled Heinzinger and Weston[18] to evaluate the equilibrium constant K_L in the reaction

$$H_2O + ODH_2^+ \rightleftharpoons HDO + OH_3^+$$

These authors[19] also found that for the purpose of isotopic fractionation water molecules are weakly bonded to OH. An aspect of this exchange reaction of some interest is the one on adsorption columns. A surface study of the OH groups of aluminium hydroxide using infrared showed three different types[20]. The high frequency band at 3785 cm.$^{-1}$ showed 30 per cent exchange in 10 min., while the other bands at 3740 and 3710 cm.$^{-1}$ showed less than 9 per cent exchange in the same period. It has also been noticed that the logarithmic rate law was similar to chemisorption and the inclusion of even 0·6 per cent Pt considerably increased exchange rate. Exchange catalysis by carbon has led to differing views[21,22]. Presumably, the real catalyst is an adsorbed metal cation where there is catalysis of exchange.

Exchange reactions in protophilic solvents other than hydrogen have received considerable attention especially in the USSR[23]. The high proton affinity of NH_2^- has been used not only in measuring the relative acidity of hydrogen atoms in hydrocarbons but also in studying the exchange rate in liquid ammonia. The Russian workers observe that compared to exchange reactions in ethanol, the reactions in liquid ammonia were very much faster (10^4 to 10^6 times). Potassium amide is an effective catalyst for the exchange reaction in liquid ammonia and similarly the alkoxide ion is found to have a similar effect on exchange reaction in ethanol. The remarkable difference in the rates reported in ethanol requires verification. The importance of the dielectric constant of the solvent is shown in a comparison with several amines as the exchange medium. Another aspect which requires confirmation is the reported salt effect on exchange rates which seem to parallel ammonolysis rates.

Exchange reactions in liquid ammonia appear to be a function of NH_2^- concentration and a recent study[24] indicates that the overall rate constant is given thus

$$k = k_1 \; NH_2^- + k_2 \; NH_2^- \; K^+$$

The reaction appears to involve the following steps:

(i) Formation of a complex:

$$NH_2^- + HD \rightleftharpoons [NH_2^-, \; HD]$$

(ii) Dissociation of the complex:

$$[NH_2^-, \; HD] - \begin{cases} \rightarrow NH_2D + H^- \\ \rightarrow NH_3 + D^- \end{cases}$$

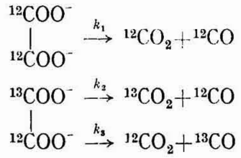
(iii) Rapid regeneration of amide

The rate constants are found to conform respectively to the equations $\log k_1 = 4{\cdot}910 - 2000/T$ and

$\log k_2 = 6{\cdot}616-2000/T$ and the activation energy is about 9·0 kcal.

Exchange Reactions Involving Carbon, Nitrogen, Oxygen and Bromine

There has been a spate of work on the exchange reactions of carbon, nitrogen, oxygen and the halogens. Decarboxylation reactions find a segregation of isotopes. Zielinski[25] has found Bigeleisen's approach unsatisfactory with quinaldic acid and obtains a ratio $k_{^{12}C}/k_{^{13}C}$ lower than those of dicarboxylic acids. Yankwich and Zavitsanos[26] reported isotope effects in the pyrolytic decomposition of zinc oxalate. It is noticed that the intramolecular isotope effect falls off from 0·79 to 0·36 per cent between 282° and 500°C. Using the Wilson-Johnston method[27] in calculation they examined the reactions below:



$$\begin{array}{l} {}^{12}COO^- \\ \quad | \qquad \xrightarrow{k_1} {}^{12}CO_2+{}^{12}CO \\ {}^{12}COO^- \end{array}$$

$$\begin{array}{l} {}^{13}COO^- \xrightarrow{k_2} {}^{13}CO_2+{}^{12}CO \\ \quad | \\ {}^{12}COO^- \xrightarrow{k_3} {}^{12}CO_2+{}^{13}CO \end{array}$$

and found

$$\frac{k_2}{k_3}=\frac{(X_d)_t}{(X_m)_t};\ \frac{k_1}{2k_2}=\frac{\alpha_0}{(X_d)_0};\ \frac{k_1}{2k_3}=\frac{\alpha_0}{(X_m)_0}$$

There appears to be an initial acceleration followed by a decay period in the reaction.

The use of strongly basic Dowex-2 resin as ion exchanger leads to ^{14}C enrichment in the ternary system CH_3OO^--HCOOH-HCl, and with multiple column operation an enrichment factor of 2 could be reached[28]. In the reaction

$$H^{12}COOH+H^{14}COO^- \rightleftharpoons H^{14}COOH+H^{12}COO^-$$

the enthalpy change is reported to be −4·3 cal. mole while the entropy change is $-6{\cdot}3\times10^{-3}$ cal. mole^{-1} deg.$^{-1}$ at 25°C.

Chemical reactions figure prominently in the nitrogen-oxygen isotope exchange[29-31]. Scrambling among the oxides of nitrogen is so rapid that no distinction is possible between $O^{14}N^{14}NO_2$, $O^{15}N^{14}NO_2$ and $O^{15}N^{15}NO_2$ and similar situation is noticed with isotopic oxygen too. However, the equilibrium constant is greater for nitrogen exchange than for oxygen exchange. Using a mass spectrometer, and nitrogen monoxide with nitrogen dioxide as catalyst the exchange rate is given by

$$\frac{N^*O\ NO^*}{N^*O+NO^*}\cdot\frac{1}{t}\ln f$$

with the rate being proportional to NO_2 concentration though the rate constant remains nearly at $2{\cdot}16\times10^{-7}$. The temperature coefficient of the reaction gives values for the Arrhenius activation energy of 10·0 kcal. and $\log A = 10{\cdot}6$ sec.$^{-1}$ which compares with the dissociation of dinitrogen tetroxide. Taylor's observations[29] though more extensive are inadequate for suggesting any mechanism for the reaction. Both nitric acid (10M) and liquid dinitrogen trioxide exchange with nitric oxide, the liquid phase concentrating the heavier nitrogen isotope. The reaction in N_2O_3 is also faster. Oxygen exchange is more noticeable with more dilute nitric acid where the reaction may be represented by

$$N^{16}O+H_2{}^{18}O_{(liq.)} \xrightleftharpoons{6M\ HNO_3} N^{18}O+H_2{}^{16}O_{(liq.)}$$

though the mechanism is quite complicated. The heavier oxygen isotope is concentrated better using carbon dioxide in the presence of a variety of catalysts, with half times for exchange ranging from 1·25 to 13·5 sec.

TABLE 1 — CATALYTIC ISOTOPE EXCHANGE

Catalyst	E kcal.	A litre mole^{-1} sec.$^{-1}$
Ru(III) chloride in 4M HCl	$23{\cdot}8\pm0{\cdot}5$	5×10^{14}
Co(II) cyanide in 0·5M KCN	$7{\cdot}0\pm1{\cdot}0$	1×10^{2}
NaOH in water	$24{\cdot}0\pm2{\cdot}0$	8×10^{11}
KNH_2 in NH_3	10	$\sim6\times10^{11}$
Pt on charcoal in water	5·8	—

An important development in isotope exchange between hydrogen and water is the use of homogeneous catalysis[32]. Table 1 gives some interesting features.

The last one is clearly an exchange with chemisorbed hydrogen while the first two involve the complexes of the transition elements. The observations with Ru(III) are similar to the ones reported by Halpern[33] with Fe(III). A factor still to be explained is the increase in exchange rate with added salt. In the base catalysed exchange reaction there are indications of an intermediate complex $(HDOH)^-$ in the exchange process. The kinetics of the bromine-hydrogen reaction with isotopic hydrogen[34] follows the well-known path with exchange rate governed by the reactions

$$Br+H_2 \xrightarrow{k_2} HBr+H$$

$$Br+HD \xrightarrow{k_{5a}} HBr+D$$

$$Br+HD \xrightarrow{k_{5b}} DBr+H$$

and the rate given by

$$\frac{k_2}{k_{5a}+k_{5b}}=\frac{\ln[H_2]\ [H_2]_0}{\ln[HD/HD]_0}=\frac{\log\ (1-f)}{\log\ (\rho/\rho_0)(1-f)}$$

The reactions with chlorine and iodine show little difference in the exchange rates. Theoretical calculations have been made using both Bigeleisen's theory and others, but agreement with experiment was little better than 40-80 per cent.

Exchange Reactions Involving Complex Metal Ions

Exchange reactions involving complex species are on the increase. Using ^{135}Sb as tracer, the hydrogen chloride catalysed exchange between Sb(III) and Sb(V) in carbon tetrachloride gives a complex rate law[35]. Oxygen exchange in the bis-oxalato platinate(II) ion and the free oxalate show a rate dependence on hydrogen ions[36] of the type

$$R = 4k_1[H^+][H_2C_2O_4] + k_2[H^+][HC_2O_4^-]$$

and

$$R = 8[k_a(H^+) + k_b(OH^-)][Pt(C_2O_4)_3^{-2}]$$

Above *p*H 5·5, the acid catalysed path is dominant.

The use of labelled oxygen atoms brings up the question of steric problems in the hydration of ions. While Ni^{2+}_{aq} and Fe^{3+}_{aq} exchange in less than 0·05 sec., Al^{3+} has an exchange half-life greater than 0·05 sec. By the use of flow techniques, Taube[37] has been able to show that in all these fractionation takes place in the first coordination sphere of the cations.

It is interesting to find[38] that oxygen in CrO_4^{2-} is labile and oxygen exchange is first order with respect to CrO_4^{2-} in alkaline solutions but becomes second order with respect to Cr(VI) below *p*H 7·2. Oxygen exchange in PuO_2^{2+}, however, appears to be quite complex[39]. In the absence of chlorine or other scavengers, the reaction is autocatalytic. The results of Rabidean and Masters[39] also show an extraordinary extrapolation of a linear plot to obtain the time for half reaction, while the data given go to less than 10 per cent exchange in a study of the effect of added Pu(III). PuO_2^+ catalyses the change while Pu(IV) shows no exchange in 30 hr. Fluoride ion catalysis is pronounced. Further work is necessary before the actual mechanism of the process can be understood.

Unlike CrO_4^{2-}, the permanganate ion shows an inverse deuterium isotope effect in alkaline solution[40]. The suggested mechanism is

$$MnO_4^- + OH^- \rightarrow MnO_4^{2-} + .OH$$
$$OH^- + .OH \rightarrow .O^- + H_2O$$

but the information available cannot be considered adequate for establishing the course of the reaction. Exchange reactions involving the transition metals are largely those of either ligand exchange or central atom exchange. In spite of the large amount of work, the position cannot be said to be very clear. With silver, isotopic exchange is said to be rapid and a single step reaction[41]. Similarly, the rates of zinc tracer exchange with zinc compounds is too rapid to measure[42]. A number of other transition element compounds with organic radicals, however, have measurable exchange rates and in quite a few cases mechanisms can be proposed[43].

An instance of isotope exchange under non-aqueous conditions is provided by the study of Fe(II)-Fe(III) system in dimethyl sulphoxide[44]. A first order dependence on the total iron in each valence state, $\Delta H = 9{\cdot}0 \pm 0{\cdot}6$ kcal./mole and ΔS, -20 ± 2 e.u. are the features of the exchange reaction. An interesting feature of the reaction is that while the rate constant is independent of perchloric acid concentrations above $7 \times 10^{-6} M$, in its absence the exchange rate is immeasurably fast even at the extremely low concentration of $5 \times 10^{-6} M$.

In dealing with isotopic fractionation in electron transfer process one has often to consider non-bridging ligands. The electron transfer reaction Cr(II)-Co(III) using various ammine complexes of the latter showed little rearrangement or difference in isotope fractionation[45].

The labile nature of the carbonyl group, at least for exchange purposes, has been shown by nickel tetracarbonyl[46] for both carbon and oxygen exchange with the former having a larger temperature coefficient (Table 2).

$$Ni(^{12}CO)_4 + {}^{13}CO \overset{k_1}{\rightleftharpoons} Ni(^{12}CO)_3(^{13}CO) + {}^{12}CO$$

$$Ni(C^{16}O)_4 + C^{18}O \overset{k_2}{\rightleftharpoons} Ni(C^{16}O)_3(C^{18}O) + C^{16}O$$

TABLE 2 — EXCHANGE REACTIONS OF NICKEL TETRACARBONYL

	Temperature, °C.		
	−10	10	18
		C-Isotope exchange	
k_1	<0·015	0·17	0·27
$t_{1/2}$(min.)	>3·7	0·52	0·28
		O-Isotope exchange	
k_2	<0·003	0·019	0·026

Tetravalent tin is of interest as an octahedral coordinating species which is readily solvolysed. It is observed that the acid dissociation of the aquometal ions shows definite isotope effects[47], the proton transfer being a function of log $(OH_3)^+$ or log $(OD_3)^+$.

Isotopic Exchange in Substitutions and Rearrangements

Catalytic exchange is often resorted to in synthetic organic chemistry and Garnett's report[48] is of interest in this aspect. The observations lead to a concept of an associative and dissociative π complex substitution mechanism in aromatic systems (Chart 1).

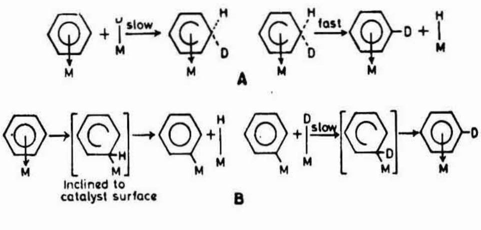


Chart 1 — Associative (A) and dissociative (B) complex substitution mechanisms in aromatic systems

The results of exchange rule out randomization and the rate determining step appears to be the reaction between chemisorbed benzene and chemisorbed hydrogen.

Amide catalysed exchange in liquid ammonia appears to be quite a fruitful field. Hall *et al.*[49] as well as Shatenshtein[50] report similar results where comparison is possible. The Russian work is quite extensive and partial rate factors vary over very wide limits from 10^6 to 0·4.

Exchange of hydrogen atoms in the aliphatic system appears to be much more complex. Of the platinum group, platinum-rich alloys are most active, but even with methane and deuterium there is no rational order of appearance of substituted methanes[51]. The rate studies of Kandel[52] with tritium also shows the complex kinetics.

Bunton *et al.*[53] have studied the hydrolysis of esters using tracers and observe extensive exchange of oxygen with the solvent water and notice also mechanistic variations with *p*H and concentration.

The π complex mechanism useful in substitution finds an application also in the isomerization and isotope exchange in the stilbenes[54]. The out-of-plane bending vibrations of C-H and C-D bonds provide a convenient means of following the course of the exchange reaction. In the interpretation a comparison between the Horiuti[55] and the Farkas[56] mechanisms is used in favour of the former.

Deuteroxide catalysis in the exchange reactions of methylene cyclopropane mono- and dicarboxylic acids with D_2O at constant ionic strength suggests a carbanion intermediate in which the trianion has lower energy barrier[57].

Both bromides and iodides exchange with halogen in halogen substituted compounds by a second order reaction[58,59]. The iodide exchange reaction is found to conform to Eyring's theory in the dielectric constant region 12·57-34·69 in carbon tetrachloride-nitrobenzene mixtures but deviates at lower dielectric constant values of the medium.

Radiation Induced Exchange

Increasing interest is evinced in radiation induced isotope exchange. Gaseous nitrogen has been observed to undergo radiolytic exchange both with X-rays and γ-rays and a pronounced wall effect is noticed. The following mechanism suggested[60] is quite plausible:

$N_2 \rightsquigarrow N_2^+ + e^- \longrightarrow N_2^*$ or $N_2 \rightsquigarrow N_2^*$

$N_2^* + N_2 \longrightarrow 2N_2^\times$ or $^{15}N^{15}N + ^{14}N^{14}N \longrightarrow 2\,^{15}N^{14}N$

$N_2^* + N_2 \longrightarrow N_2 + 2N$ (^4S state, atoms in ground state do not exchange)

$N + N + (M) \longrightarrow N_2^\times + (M)$

$N_2^* + (M) \longrightarrow N_2$

An alternative picture of the exchange has been suggested by the work of Dawes and Back[61]. These authors using mass spectrometry and ion drift measurements suggest a random combination of atoms by neutralization of N_2^+ or N_4^+ or by dissociative excitation. Taking the effect of added oxygen as well as nitric oxide they suggest an alternative mechanism

$N_2 \rightsquigarrow N_2^+ + e$

$N_2 \rightsquigarrow 2N$

$N_2^+ + N_2 \longrightarrow N_4^+$ (internal exchange by uncertain mechanism)

$N_4^+ + NO + e^- \longrightarrow 2N_2$

$N + NO \longrightarrow N_2 + O$

Another radiation induced exchange is with water vapour and β-rays[62]. The rate remains constant over a considerable range of water vapour pressure and is found to be a second order function of tritium concentration

$$d(\mathrm{HTO})/dt = 3{\cdot}6 \times 10^{-5}(\mathrm{T_s})^2$$

A chain mechanism has been suggested.

Photochemical separation of the isotopes of mercury[63] is a novel application of radiation which involves the excited mercury atom in the reaction with an alkyl halide.

Exchange Reactions in Organic Synthesis

The use of borohydride in labelling organic compound is found to be a useful means of introducing deuterium and tritium[64]. An even more useful technique is the development of an electrodeposition method[65] for following moderately fast reactions of the type

$$CH_3I + NaI^* \rightleftharpoons CH_3I^* + NaI$$

Enzyme Reactions

A very fruitful field in exchange kinetics is in the study of enzyme reactions. The report of the steric course of enzyme reactions at *meso* carbon atoms by the use of hydrogen isotopes[66] opens up a wide field. The significant observation is made that in succinic acid and in citric acid the CH_2COOH groups are different. Another feature noticeable is the observation that the isotope effect in the enzyme action on deuterosuccinate is absent when the fully substituted enzyme is used[67]. Both compounds react at the same rate. A complication one has to guard in enzyme studies as observed by Bigeleisen[68] is the need for studies under varying *p*H since ΔpK for protic and deuteroacids and bases may differ by 0·3-0·6 *pK* units.

Summary

The recent work on the kinetics of exchange reactions with special reference to reactions involving hydrogen, carbon, oxygen, bromine, nitrogen and complex metal ions has been critically reviewed. Isotopic exchange in substitution reactions and rearrangements in synthetic organic chemistry, radiation (X-, γ- and β-rays) induced exchange, exchange reactions in organic syntheses and enzyme reactions are some of the other important topics discussed.

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Chemistry & Technology of Myrobalan Tanning

GEETA KANJILAL & Y. NAYUDAMMA

Central Leather Research Institute, Madras

MYROBALANS, the fruits of *Terminalia chebula*, are available in abundance almost throughout India[1]. The tree grows under a variety of climatic conditions[2]. About 40,000 tons of myrobalan nuts are exported annually and about 20,000 tons find use in the indigenous tanning industry[3]. Myrobalan fruit analyses to : moisture, 10·0; tannin, 24·6-32·5; non-tannins, 13·9-16·4; and insolubles, 41·1-50·1 per cent; the *p*H of the infusion is 3·4-3·5. Though other parts of the tree also contain considerable amounts of tannin, myrobalan tannin implies the tannin of the fruit alone[4]. Usually mature fruits are collected by shaking the tree and dried in thin layers[5], preferably in shade[6]. The tannin is extracted under a variety of conditions[7-10].

Myrobalan is one of the most important vegetable tanning agents of hydrolysable type. One of the principal advantages of myrobalans, from the tanners' point of view, lies in their acid forming properties, for they contain a much higher percentage of sugars (3-5 per cent) than most tannins. This helps fermentation of the tan liquor and consequent plumping of the leather. It is one of the chief bloom yielding tans due to the high content of ellagi-tannic acid and is especially useful in the production of sole leather. It is widely used in

EI tanning to get weight and to fix good colour resistant to light and ageing; it is also used in making book-binding leathers. Myrobalan tannin is generally blended with other more astringent and quickly penetrating tans. It is used alone for tanning sole leather in an indigenous method known as 'Lhori' or 'bag' tannage[11] in India. Myrobalan extract has also been successfully tried for pretanning cow and buffalo hides[12].

Besides its use in tanning, myrobalan is used in ink manufacture, textile industry, oil drilling and for softening boiler feed water. The use of myrobalan pulp from tanning industry wastes for preparing activated carbon[13] and chemicals like ellagic acid and furfural has also been suggested (Banerjee, S., unpublished work).

Defects in Myrobalan Tannin

Myrobalan tannin has certain drawbacks when used alone. These are : (i) slow rate of penetration of tannin, (ii) poor yield of leather, and (iii) production of spongy leather with high water absorption, poor abrasion resistance, low shrinkage temperature, dark colour, cracky and bronzy appearance. Due to these defects myrobalan tannin is not being fully utilized, in spite of India's monopoly in the field. On the contrary, India has to import wattle bark and extract to meet the demands of the tanners. Therefore, the modification of myrobalan tannin so that it can be utilized as a self-tanning agent is a problem of considerable economic value. A prerequisite to the modification of myrobalan tannin is the need to understand its complex nature — its composition and characteristics of the various constituents.

Chemical Composition of Myrobalan

Although chemical investigation of myrobalan started as early as 1876[14], its chemistry could be successfully studied only recently. Systematic and exhaustive studies[4,15-37] have shown that myrobalan nuts contain the following compounds : (i) chebulinic acid, (ii) chebulic acid, (iii) chebulagic acid, (iv) corilagin, (v) terchebin, (vi) 1,3,6-trigalloylglucose, (vii) 1,2,3,4,6-pentagalloylglucose, (viii) ellagic acid, (ix) gallic acid, (x) glucogallin and many sugars such as glucose, sorbitol, fructose, sucrose, gentibiose and traces of arabinose, maltose, rhamnose and xylose. Some typical plant amino acids are also present besides small quantities of phosphoric, succinic, quinic, shikimic, dihydro and dehydroshikimic acids.

It is rather difficult to categorize the different constituents according to their tanning potency. Studies on the fixation of polyphenolic constituents by collagen[38] have shown that the fixing ability of a specific component is greatly influenced by its origin. From tanning studies carried out with individual components like chebulinic acid[39] and fractionated[40] myrobalans the tanning potencies of these fractions have been determined.

Physico-chemical Characteristics of Myrobalan Tannins

Myrobalan tannins are fairly complex in nature and exist in varying degrees of agglomeration[19]. They also differ considerably in their susceptibility to hydrolytic breakdown.

Myrobalan tan liquor reverses the birefringence of collagen fibres; gallic acid (nontan) present in the liquor is responsible for this[41].

Biosynthesis

From exhaustive studies on the isolation and identification of myrobalan tannin constituents, Schmidt and Hathway[42] suggested a mechanism for the biosynthesis of myrobalan tannin. 5-Dehydroshikimic acid (dehydroshikimic acid has been isolated in myrobalan tan liquor) can be oxidized to gallic acid by aeration in alkaline solution. Growth experiments on glucose media showed 5-dehydroshikimic acid to be a direct precursor of gallic acid with shikimic acid and 5-dehydroquinic acid as near but not immediate precursors[43]. Hexahydroxydiphenic acid has been found to be a chemical precursor of ellagic acid. It has been suggested by the same authors that oxidative coupling of two galloyl residues, either free or in the bonded state, yields a diester type of derivative of hexahydroxydiphenic acid from which derivatives of chebulic acid might arise by processes involving oxidation, benzilic acid rearrangement and either hydrolytic cleavage or decarboxylation. Possibly the formation of chebulinic acid and the related tannins of *Terminalia chebula* takes place by way of a stepwise combination of several phosphorylated cyclohexane carboxylic acid units of shikimic acid type with a glucose molecule. Detailed enzymic studies are necessary before the mechanism of biosynthesis of myrobalan tannin can be fully understood. From the leaves which are the seats of active metabolic activity, shimikic, dehydroshikimic and quinic acids have been isolated[4]. These compounds have been identified in the nuts also, but not in the other parts of myrobalan plant. More amino acids have been found in the nuts than in the leaves. Drying increases the number of amino acids in the nuts. A study of tannin extracts from fresh myrobalan nuts of three different degrees of maturity revealed that the total tannin and nontan content is the same in each case, only salts being absent in the final stage.

Sludge Formation

One of the drawbacks in the use of myrobalan tan liquors is their sludge forming tendency on standing. This is attributed to one or more of the following reasons[44]: (i) crystallization of chebulinic acid from the liquor; (ii) separation of ellagic acid held in colloidal suspension by the tannins present; (iii) decomposition of tannins by enzymes into their simpler constituents, one of which is ellagic acid; (iv) oxidation of the tan liquor; and (v) hydrolysis of tannins; the first and the last are the main causes of the formation of insolubles.

It has been found that (i) myrobalan tan liquors free from enzymes but containing ellagitannins do not deposit ellagic acid, and (ii) enzymes are not responsible for the deposition of chebulinic acid.

The exact mechanism of sludge formation is not known, but the most probable explanation is the disturbance in the balance of the mutual solubility of the different constituents in the tan liquor by some external or internal influence. Slight disturbance in the balance sets in the precipitation of certain constituents resulting in 'bloom' or sludge formation. The disturbance may be due to external causes such as aerial oxidation or hydrolysis by mould growth or internal causes such as enzymatic hydrolysis (enzymes being present in the nut itself). Withdrawal of certain tannin constituents during the process of tanning itself results in the precipitation of insolubles (the cause being again imbalance in the tan liquor).

Addition of chemicals to prevent fermentation and mould growth has been tried with promising results[45,46]. Heat treatment and chlorination of the myrobalan tannin prevent sludge formation to some extent, but the tanning property of the liquor does not improve[10] (Sastry, K. N. S., unpublished work). Ultraviolet irradiation[10] of myrobalan tan liquor for different lengths of time helps in checking fermentation and consequently sludge formation to some extent, but the finish obtained is not of superior quality. Addition of sulphonic acid derivatives prevents sludge formation to a considerable extent. The use of sodium hexmetaphosphate, however, does not give positive results (Rao, V. S. S., unpublished results).

Modification of Myrobalan Tannin

Several approaches have been tried for modifying myrobalan tannin so that it can be utilized more efficiently.

Solvent extraction — The extract of myrobalan nuts with solvents like chloroform, acetone, etc., was found to give better finish to leather than myrobalan liquor as such[4]. It has higher tan/nontan ratio and buffer index[7] and causes less mould growth than aqueous infusion.

Heat treatment — For destroying the enzymes present in the nuts prior to leaching, myrobalan nuts (whole and crushed) were subjected to sudden heating ($\approx$ 120°C.) in an air oven for different lengths of time. This treatment reduced sludge formation to a great extent, but the tan liquor darkened and insolubles increased slightly. Heating of myrobalan extract powder was carried out in vacuum as well as in an air oven for different periods which reduced the sludge formation to a considerable extent (Sastry, K. N. S., unpublished results).

Oxidative and degradative studies on myrobalan involving heating myrobalan tan liquor at 105°C. in sealed tubes for different periods showed gradual degradation of tannins.

Treatment with ultraviolet light — Ultraviolet irradiation of myrobalan extract powder[47] for several hours increases the T_s of the leather tanned with it and also eliminates the moisture absorbing property of myrobalan extract. Decrease in tan content and increase in insolubles have been observed on exposing myrobalan liquor to ultraviolet light[47].

Chlorination — Passage of chlorine gas through myrobalan tan liquor has been reported to prevent sludge formation almost completely, but the finish imparted to the leather is not satisfactory[48] (Sastry, K. N. S., unpublished results).

Treatment with salts — In analogy with sweetening of chestnut extract[49,50], an attempt was made to improve myrobalan liquor by reducing its acidity. Addition of NaOH, Na_2CO_3, Na_2PO_4, $NaHCO_3$, Na_2SO_3, NH_4OH, $Na_2B_2O_7$ and sodium citrate at different concentration levels and under different conditions, either singly or in combination, has been tried. Myrobalan liquor with borax added at 3 per cent level has been found to yield better quality leather. Still further improvement was possible when a combination of borax and sodium bisulphite (both 3 per cent on solid weight) was used instead of borax alone. These chemicals prevent sludge formation to a considerable extent.

Partial deacidification of the tan liquor by the addition of salts like NaCl, Na_2SO_4, Na_2PO_4 and borax increases the rate of penetration, but reduces the fixation of tannin (Banerjee, S., unpublished results). Use of myrobalan liquor after neutralizing its acidity with precipitated chalk yields a very soft and yellow-coloured leather.

In another attempt, addition of certain salts like sodium fluoride, oxalic acid, sodium thiosulphate, formaldehyde, sodium sulphite and sodium tartrate has also been reported to improve the tanning character of the myrobalan tannins (Olivannan, M. S., Selvarangan, R. & Nayudamma, Y., unpublished results). The resulting liquor gives higher fixation of tannin and has less water solubles.

Addition of salts like sodium acetate, sodium formate, calcium acetate and calcium formate in small amounts has been found to bring about considerable improvement in the leather forming property of tan liquor (Kanjilal, G., unpublished results). Preparation of myrobalan tan liquor in acetate buffer produces good leather yielding liquor besides preventing mould growth and sludge formation. Among the various salts tried, sodium acetate and calcium formate have been found to be the best and most economical.

Miscellaneous treatments — Studies on the co-sulphonation and condensation of myrobalan tannins with raw oils, and sulphited oils, using formaldehyde and hexamine as condensing agents have shown that sulphitation decreases the tan content by almost one-half (Rao, V. S. S., unpublished results). Myrobalan when treated with phenol-sulphonic acid (1/3 myrobalan) and formaldehyde does not produce sludge and the tan content increases. Pelts tanned with myrab-hexamine mixture containing sodium bisulphite in different proportions yield leather with high T_s value, but the sludge formation increases. To eliminate some of the nontans from tan liquor, dialysis[10,51] of the liquor has been tried, using naturin, sausage casing and cellophane paper membranes. The first two have been found to be better than cellophane paper which permeates all the constituents. But the dialysed solution does not possess better leather making property.

Combinations of Myrobalan with Other Tanstuffs

Myrobalan and other vegetable tannin combinations — Myrobalan is commonly used in combination with other vegetable tanning materials like wattle, avaram and konnam in EI tanning, and with babul, wattle and goran in sole leather tanning.

Myrobalan-mineral tanning agent combinations — Myrobalan strips Cr and Al if it is used as a retanning agent and hence it is not used for retanning leather. However, it is used as a pretanning agent followed by Al, Cr treatment[52]. There is a considerable rise in T_s value. This treatment is most useful in the preparation of heat resistant leathers and for finishing of EI tanned kips. Myrab-Al combination has been successfully used in single bath tannage for the manufacture of soft leather[53].

Myrobalan-syntan combination — Treatment of myrobalan tannin with cresol-sulphonic acid condensation products and in some cases with formaldehyde, sodium sulphite and urea along with the condensation product, checks sludge formation to some extent. Pelt tanned with myrab tan liquor deacidified with ω-sulphonated cresol and treated with urea produces satisfactory leather in respect of colour, strength and other properties, but the yield of leather is poor (Banerjee, S., unpublished results). Myrobalan in combination with Basyntan FC and Basyntan extra-1-solid and some other BASF syntans has been reported to produce satisfactory finished leathers[54] (Banerjee, S., unpublished results).

Addition of β-naphthol syntan and also a condensate of sulphonic acid and naphthalene after neutralization prevents sludge formation to a considerable extent (Mukherjee, D., unpublished results).

Summary

The recent advances in understanding the chemistry of myrobalan, the fruit of *Terminalia chebula*, and the mode of biosynthesis of myrobalan tannin are reviewed. The inherent defects which stand in the way of full utilization of myrobalan have been discussed and various treatments for modifying the material so that it may be efficiently utilized have been reviewed. Among the different approaches towards modification, *p*H control of the tan liquor seems to be the most promising treatment. By controlling *p*H, not only mould growth and sludge formation can be prevented, but also superior quality leathers can be obtained. The use of acetate buffers and salts like sodium acetate and calcium formate gives satisfactory results.

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Methods in Nucleoside Syntheses*

H. G. GARG
Twyford Laboratories, London NW 10

THE term 'nucleoside' was first introduced by Levene and Jacobs[1] for the carbohydrate derivatives of purines and pyrimidines isolated by the hydrolysis of nucleic acids, but now is applied to natural and synthetic glycosyl derivatives of purines, pyrimidines and many other heterocycles.

Interest in chemically prepared nucleosides has remained high, in spite of the difficulties encountered in their synthesis, due to the fact that unusual purine and pyrimidine nucleosides have been obtained from natural sources, e.g. angustmycin[2], nucleocidin[3], cordycepin[4-8], nebularin[9,10], psicofuranine[11], crotonoside[12], puromycin[13], the aminonucleoside[14] from puromycin, homocitrullylaminoadenosine[15], helminthosporium sp. No. 215[16], gougerotin[17,18], amicetin[19,20], bamicetin[19], etc., and several of them have antitumour properties at non-toxic dose levels; for some of them, no data have been published[21].

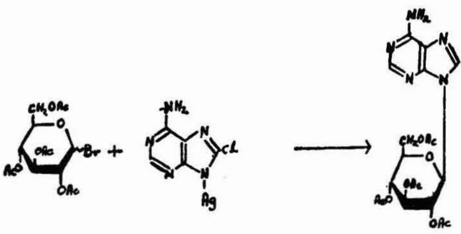
Several reviews[22-31] have appeared that are concerned with the subject of nucleosides. The purpose of this article is to summarize briefly these reviews and to relate them to recent developments. The literature coverage in this review is essentially complete through 1965.

SYNTHESES OF NUCLEOSIDES

The following methods are used for the preparation of nucleosides: (a) Metal salt method; (b) Hilbert-Johnson method; (c) Trimethylsilyl method; (d) Direct condensation of the purines with various sugars; and (e) Nucleoside interconversions.

Metal Salt Method

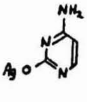
Fischer and Helferich[32] first condensed silver 2,8-dichloroadenine and theophylline with 2,3,4,6-tetra-O-acetylglucopyranosyl bromide (I) and obtained 2,8-dichloro-9-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl) adenine (II) and 7-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl) theophylline respectively.



I II

Davoll and Lowy[33] observed that chloromercuri derivatives of purines, rather than silver purines, gave better results. Since then, the synthesis of nucleosides of purines, pyrimidines and other heterocyclics using mercury salts has become a practical method.

The silver and mercury salts of pyrimidines yield different products with the same glycosyl halide. Ulbricht[34] suggested that chloromercuripyrimidines, dipyrimidinylmercury and pyrimidine silver salts are oxygen derivatives (e.g. III and IV), and these derivatives react with glycosyl halides to give, initially, O-glycosides, many of which, under the conditions of the reaction, rearrange to N-glycosides. Recently, the rearrangement of O-glucoside (V) with mercuric bromide to N-glucoside (VI) has been reported[35]. In a preliminary report[36], mechanism A for the rearrangement was suggested. An alternative mechanism B has been proposed by Wagner and Pischel[37].



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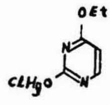

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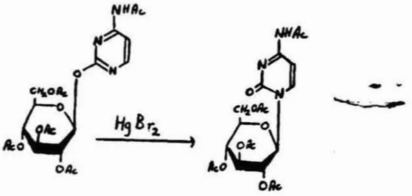

V VI

Winstein *et al.*[38] demonstrated that the salt effects on the rate of ionization of organic substrates can become enormous in poorly ionizing solvents. Of a number of salts investigated[38], lithium perchlorate proved effective in promoting ionization, by preventing ion-pair return ('covalent return'). However, it was found to be ineffective in O → N-glycoside rearrangement. Mechanism A is, therefore, the one which is more likely.

In most of the early reports, the isolated products have been the N^9-nucleosides with *trans* configuration for the base and the protected hydroxyl group on C-2. The explanation of the anomeric configuration obtained with these different sugars can be found in Tipson's *trans* rule[39] as extended by Baker[40]. Baker and coworkers[41,42] have also found exceptions to the C-1 — C-2 *trans* rule. Recently, Wolfrom

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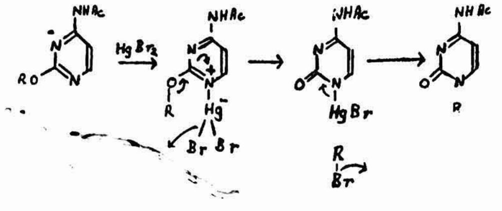
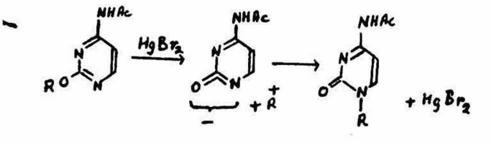
*Abbreviations used: Ac, acetyl; Bz, benzoyl; Tr, trityl; Ts, *p*-toluenesulphonyl; Mes, methanesulphonyl; ph, phthaloyl; PN, *p*-nitro; T, *p*-toluyl; Cbz, carbobenzyloxy; Bzl, benzyl; Et, ethyl; Me, methyl; and IP, isopropyl.



Mechanism A



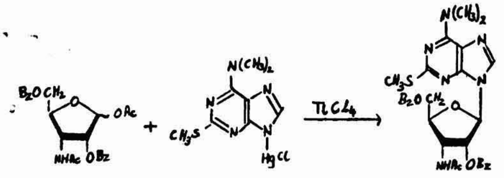
Mechanism B

= 2,3,4,6 – Tetra – O – acetylglucopyranosyl

et al.[43] synthesized both anomeric nucleosides of 2-amino-2-deoxy-D-glucose.

Table 1 lists the mercury salts of various purines, pyrimidines, etc., which have been successfully condensed with halo sugars to obtain the nucleosides.

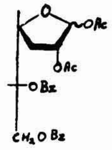
A method of preparing aminodeoxyglycosylpurines is to treat a mixture containing the chloromercuri salt of a purine and an acylated aminosugar with $TiCl_4$ in an inert hydrocarbon or halogenated hydrocarbon[44] solvent at 50-90°. Thus, 2-methylthio-6-(dimethylamino)-purine chloromercuri salt (VIII) was condensed with 1-(O-acetyl)-2,5-di-O-benzoyl-3-acetamido-3-deoxy-D-ribofuranoside (VII) in ethylene chloride in the presence of $TiCl_4$ to give (IX).



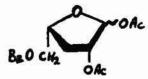
VII VIII IX

The following were prepared by similar techniques: 2-methylthio-6-dimethylamino-9-(2′-acetamido-2′-deoxy-3′,4′,6′-tri-O-acetyl-β-D-glucopyranosyl)-purine; 6-dimethylamino-9-(2′-acetamido-2′-deoxy-3′,4′,6′-tri-O-acetyl-β-D-glucopyranosyl)-purine; 2-methylthio-6-dimethylamino-9-(2′,5′-di-O-benzoyl-3′-acetamido-3′-deoxy-α-D-arabinofuranosyl)-purine; 6-dimethylamino-9-(2′,5′-di-O-benzoyl-3′-acetamido-3′-deoxy-α-D-arabinofuranosyl)-purine; 6-dimethylamino-9-(2′,5′-di-O-acetyl-3′-acetamido-3′-deoxy-α-D-ribofuranosyl)-purine; 6-chloro-9-(2′,5′-di-O-benzoyl-3′-phthalimido-3′-deoxy-β-D-ribofuranosyl)-purine; 6-chloro-9-(2′,5′-di-O-benzoyl-3′-acetamido-3′-deoxy-D-ribofuranosyl)-purine; 2,6-dichloro-9-(2′,5′-di-O-benzoyl-3′-phthalimido-3′-deoxy-D-ribofuranosyl)-purine; 6-mercapto-9-(2′,5′-di-O-benzoyl-3′-phthalimido-3′-deoxy-β-D-ribofuranosyl)-purine; 6-methylthio-9-(2′,5′-di-O-benzoyl-3′-phthalimido-3′-deoxy-β-D-ribofuranosyl)-purine; 9-(2′,5′-di-O-benzoyl-3′-phthalimido-3′-deoxy-β-D-ribofuranosyl)-purine; 6-chloro-9-(2′,3′-di-O-benzoyl-5′-phthalimido-5′-deoxy-β-D-ribofuranosyl)-purine; 9-(2′,3′-di-O-benzoyl-5′-phthalimido-5′-deoxy-β-D-ribofuranosyl)-purine; 6-dimethylamino-9-(2′,3′-di-O-benzoyl-5′-phthalimido-5′-deoxy-β-D-ribofuranosyl)-purine; 2-methylthio-6-dimethylamino-9-(2′-acetamido-2′-deoxy-4′,6′-O-benzylidene-β-D-glucopyranosyl)-purine; 2-methylthio-6-dimethylamino-9-[2′-acetamido-2′-deoxy-3′-mesyl-4′,6′-(O-benzylidene)-β-D-glucopyranosyl]-purine; 2-methylthio-6-dimethylamino-9-[2′-acetamido-2′-deoxy-4′,6′-(O-benzylidene)-β-D-allopyranosyl]-purine; 2-methylthio-6-dimethylamino-9-[2′-acetamido-2′-deoxy-3′-O-acetyl-7′,6′-(O-benzylidene)-β-D-allopyranosyl]-purine; 2-methylthio-6-dimethylamino-9-(2′-acetamido-2′-deoxy-3′,4′,6′-tri-O-acetyl-β-D-allopyranosyl)-purine.

Recently, 1,2-di-O-acetyl-5,6-di-O-benzoyl-3-deoxy-D-galactofuranose (X) and 1,2-di-O-acetyl-5-O-benzoyl-3-deoxy-L-arabinofuranose (XI) have been condensed with chloromercuri-6-benzamidopurine in the presence of titanium tetrachloride[45].

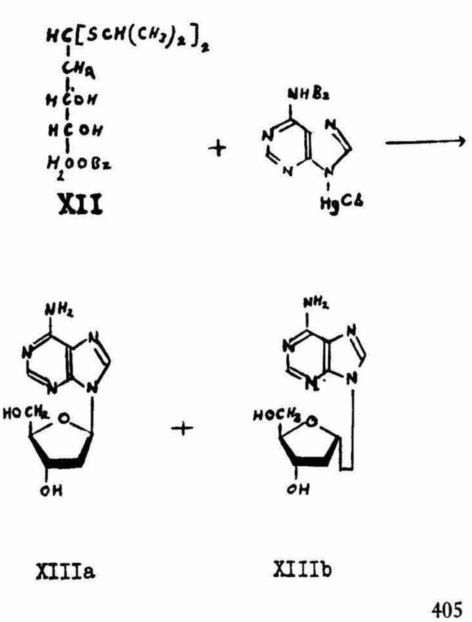


X



XI

Condensation of 5-O-benzoyl-2-deoxy-D-ribose diisopropyl dithioacetal (XII) with chloromercuri-6-benzamidopurine, followed by removal of the acyl groups, gave 2′-deoxyadenosine and its anomer[46] (XIIIa and XIIIb).



XII

XIIIa XIIIb

TABLE 1 — VARIOUS PURINES AND PYRIMIDINES WHICH HAVE BEEN CONDENSED WITH VARIOUS HALO SUGARS TO GET NUCLEOSIDES

Halo sugars	Ref.
N^6-ACETYLPURINE DERIVATIVES	
2,3,5-Tri-O-acetyl-D-ribofuranosyl chloride	124
D-Psicosyl chloride tetraacetate	125
Hepta-O-acetyl-α-lactosyl bromide	126
Hepta-O-acetyl-α-cellobiosyl bromide	127
Penta-O-acetyl-1-bromo-1-deoxy-1-O-methyl-aldehydo-D-galactose aldehydrol	128
2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl bromide	128
2,3,4,6-Tetra-O-acetyl-D-glucopyranosyl bromide	33
3,4,5,6-Tetra-O-acetyl-1-bromo-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose aldehydrol	129
3,4,5,6-Tetra-O-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-O-ethyl-D-glucose aldehydrol	130
3,4,5,6-Tetra-O-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-O-methyl-D-glucose aldehydrol	130
3,4,6-Tri-O-acetyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranosyl bromide	43
Penta-O-acetyl-1-O-benzyl-1-chloro-1-deoxy-D-galactose aldehydrol	131
Methyl 2,3,4-tri-O-acetyl-α-D-glucopyranosyl-uronate 1-bromide	132
N^6-BENZAMIDOPURINE	
Tetra-O-acetyl glucosyl bromide	33
5-O-Benzoyl-D-ribofuranosyl bromide 2,3-cyclic carbonate	133
2-Deoxy-3,5-di-O-*p*-nitrobenzoyl-D-ribosyl chloride	134
2-O-Acetyl-5-O-methoxy carbonyl-3-O-(*p*-toluenesulphonyl)-D-xylofuranosyl chloride and bromide	135
2,3,5-Tri-O-benzoyl-6-deoxy-D-allofuranosyl chloride	136
2,3,5-Tri-O-benzoyl-6-deoxy-L-talofuranosyl chloride	137
2,3-Di-O-acetyl-5-deoxy-D-ribofuranosyl chloride	42
3,4,6-Tri-O-acetyl-2-benzylsulphonamido-2-deoxy-α-D-glucopyranosyl chloride	125, 138
Penta-O-acetyl-1-O-benzyl-1-bromo-1-deoxy-D-galactose aldehydrol	131
2-Chloro-3,5-diacetyl-2-deoxy-D-arabinofuranosyl chloride	139
2-Deoxy-3,4,6-tri-O-*p*-nitrobenzoyl-α-D-ribo-hexopyranosyl bromide	140
2,5-Di-O-benzoyl-3-β-deoxy-D-ribofuranosyl bromide	114, 141
2,3,5,6-Tetra-O-acetyl-β-D-galacto-furanosyl chloride	143
N^6,N^6-DIMETHYLAMINOPURINE DERIVATIVES	
2,3-Di-O-acetyl-5-deoxy-D-ribofuranosyl chloride	42
2,3,5-Tri-O-acetyl-D-ribofuranosyl chloride	144
2,3,5-Tri-O-benzoyl-D-ribofuranosyl bromide	144
2,5-Di-O-acetyl-3-phthalimido-3-deoxy-β-D-ribofuranosyl chloride	145
2,6-DIACETAMIDOPURINE DERIVATIVES	
2,3,5-Tri-O-acetyl-D-ribofuranosyl chloride	33, 124
2,3,5-Tri-O-benzoyl-6-deoxy-L-talofuranosyl chloride	146
2,3,5-Tri-O-benzoyl-6-deoxy-D-allofuranosyl chloride	136
Hepta-O-acetyl-α-lactosyl bromide	126
2,3,4,6-Tetra-O-acetyl-glucosyl bromide	33
Hepta-O-acetyl-α-cellobiosyl bromide	127
2,5-Di-O-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl chloride	148
2,3,5,6-Tetra-O-acetyl-β-D-galactofuranosyl chloride	143
6-CHLOROPURINE	
2,5-Di-O-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl chloride	149
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	106
2,3-Di-O-acetyl-5-deoxy-5-fluoro-D-ribofuranosyl chloride	111
2,5-Di-O-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl chloride	150
2,5-Di-O-benzoyl-3-deoxy-β-D-ribofuranosyl bromide	142
2,5-Di-O-benzoyl-3-phthalmido-3-deoxy-β-D-ribofuranosyl chloride	150
2,5-Di-O-benzoyl-3-acetamido-3-deoxy-β-D-ribofuranosyl chloride	150
2,3,5,6-Tetra-O-acetyl-β-D-galactofuranosyl chloride	132
2-O-Acetyl-3-O-benzoyl-5-deoxy-D-xylofuranosyl chloride	151
2-METHYLMERCAPTO-6-DIMETHYLAMINO PURINE DERIVATIVES	
2,3,5-Tri-O-acetyl-β-D-ribofuranosyl chloride	144
2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl chloride	144
2,3,5-Tri-O-benzoyl-D-xylofuranosyl chloride	152
2,5-Di-O-benzoyl-3-N-acetyl-3-deoxy-D-arabinofuranosyl chloride	153
2,6-DICHLOROPURINE DERIVATIVES	
2,3,5-O-Acetyl-D-ribofuranosyl chloride	108
2,3,5-O-Benzoyl-D-ribofuranosyl chloride	108
2,5-Di-O-benzoyl-3-phthalimido-3-deoxy-β-D-ribofuranosyl chloride	150
6-MERCAPTOPURINE DERIVATIVE	
2,5-Di-O-benzoyl-3-phthalimido-3-deoxy-β-D-ribofuranosyl chloride	150
6-METHYLTHIOPURINE DERIVATIVE	
2,5-Di-O-benzoyl-3-phthalimido-3-deoxy β-D-ribofuranosyl chloride	150
2-ACETAMIDO-6-CHLOROPURINE DERIVATIVE	
2-Deoxy-3,5-di-O-*p*-toluyl-D-ribofuranosyl chloride	142, 154
2,6-DIBENZAMIDOPURINE DERIVATIVE	
2,5-Di-O-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl chloride	113
2,5-Di-O-benzoyl-3-deoxy-D-ribofuranosyl bromide	142
5-NITROBENZIMIDAZOLE DERIVATIVE	
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	155
6-NITROBENZIMIDAZOLE DERIVATIVE	
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	155
3-BENZYLHYPOXANTHINE DERIVATIVES	
2,3,5-Tri-O-acetyl-D-ribofuranosyl chloride	156
2,3,5-Tri-O-benzoyl-α-D-arabinofuranosyl bromide	[illegible]

TABLE 1 — VARIOUS PURINES AND PYRIMIDINES WHICH HAVE BEEN CONDENSED WITH VARIOUS HALO SUGARS TO GET NUCLEOSIDES — *contd*

Halo sugars	Ref.
2-ACETAMIDOHYPOXANTHINE DERIVATIVE	
2,5-Di-O-benzoyl-3-deoxy-D-ribofuranosyl bromide	157
6-BENZAMIDO-3-BENZYLPURINE DERIVATIVES	
Tri-O-acetyl-D-ribofuranosyl chloride	158
5-O-Benzoyl-D-ribofuranosyl bromide 2,3-cyclic carbonate	158
6-(N-METHYLBENZAMIDO)-PURINE DERIVATIVE	
2,5-Di-O-benzoyl-3-deoxy-D-ribofuranosyl bromide	114
THYMINE DERIVATIVES	
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride or bromide	147
2,3,5-Tri-O-benzoyl-D-xylofuranosyl bromide or chloride	147, 159
2,3-Di-O-benzoyl-5-deoxy-5-phthalimido-D-ribosyl chloride	160
Tri-O-benzoyl-α-L-rhamnopyranosyl bromide	161
Penta-O-acetyl-1-O-methyl-1-chloro-1-deoxy-D-galactose aldehydrol	131
2,3,5-Tri-O-benzoyl-α-D-arabinofuranosyl bromide	58
N-ACETYL CYTOSINE DERIVATIVE	
Tri-O-benzoyl-D-ribofuranosyl chloride	160
2,5-Di-O-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl chloride	160
2,3-Di-O-benzoyl-5-deoxy-5-phthalimido-D-ribosyl chloride	160
2,3-Di-O-acetyl-5-deoxy-5-fluoro-D-ribosyl chloride	111
Tri-O-benzoyl-α-L-rhamnopyranosyl bromide	161
3,4,6-Tri-O-acetyl-2-deoxy-2-acetamido-D-glucopyranosyl chloride	104
3,4,6-Tri-O-acetyl-2-deoxy-2-carbobenzyloxy-amino-D-glucopyranosyl chloride	104
3,4,6-Tri-O-acetyl-2-deoxy-2-carbomethoxy-amino-D-glucopyranosyl chloride	104
Hepta-O-acetyl-α-lactosyl bromide	105
Hepta-O-acetyl-α-cellobiosyl bromide	105
2,3,5-Tri-O-benzyl-D-arabinofuranosyl chloride	162
4-ETHOXY-2-(1H)-PYRIMIDINONE DERIVATIVES	
2,5-Di-O-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl chloride	160
2,3-Di-O-acetyl-5-deoxy-5-fluoro-D-ribofuranosyl chloride	111
2,3,5-Tri-O-benzoyl-α-D-arabinofuranosyl bromide	58
2,3,5-Tri-O-acetyl-D-lyxofuranosyl chloride	58
2-THIOURACIL DERIVATIVE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	163
5-(ETHOXYCARBONYL) CYTOSINE DERIVATIVE	
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	164, 165
5-FLUOROURACIL DERIVATIVES	
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	166
2-Deoxy-3,4,6-tri-O-acetyl-D-glucopyranosyl bromide	167

Halo sugars	Ref.
AZATHYMINE DERIVATIVE	
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	168
4-DIPHENYLMETHYL-6-TRIFLUOROMETHYL-as-TRIAZINE-3,5-(2H,4H)-DIONE DERIVATIVE	
2-Deoxy-3,5-di-O-toluyl-D-ribofuranosyl chloride	173
5-BROMOURACIL DERIVATIVE	
2-Deoxy-3,4,6-tri-O-acetyl-D-glucopyranosyl bromide	167
5-IODOURACIL DERIVATIVES	
2-Deoxy-3,4,6-tri-O-acetyl-D-glucopyranosyl bromide	167
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	51
5-ALLYLURACIL DERIVATIVE	
3,5-Di-O-*p*-chlorobenzoyl-2-deoxy-D-ribofuranosyl chloride	169
5-NITROURACIL DERIVATIVE	
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	170
1-DEAZAPURINE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	171
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	171
2,3,4,6-Tetra-O-acetyl-D-galactopyranosyl bromide	171
2,3,5-Tri-O-acetyl-D-xylopyranosyl bromide	171
6-CHLOROIMIDAZO-(*b*)-PYRIDINE	
2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl chloride	172
6-BROMOIMIDAZO-(*b*)-PYRIDINE	
2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl chloride	172
IMIDAZO-(*c*)-PYRIDINE	
2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl chloride	172
7-NITROIMIDAZO-(*c*)-PYRIDINE	
2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl chloride	172
TRIAZOLO-(4,5-*b*)-PYRIDINE	
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	174
TRIAZOLO-(4,5-*c*)-PYRIDINE	
2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl chloride	174
2,8-DICHLOROADENINE	
2-O-Acetyl-3-O-tosyl-5-O-methoxycarbonyl-D-xylofuranosyl chloride	114
6-AZA-3-(DIPHENYLMETHYL)-URACIL	
2,3,5-Tri-O-benzoyl-D-xylofuranosyl chloride	175

TABLE 2 — VARIOUS NUCLEOSIDES SYNTHESIZED BY HILBERT-JOHNSON METHOD

Halo sugars	Ref.
2,4-DIETHOXYPYRIMIDINE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide or chloride	47, 48, 177
2,3,4,6-Tetra-O-acetyl-D-galactose bromide or chloride	176, 177
Tri-O-acetyl-D-xylopyranosyl bromide or chloride	176, 177
Tri-O-acetyl-D-arabinopyranosyl bromide or chloride	176, 177
Tri-O-acetyl-L-arabinopyranosyl bromide or chloride	176, 177
2,3,5-Tri-O-acetyl-D-ribofuranosyl bromide	49
3,4,6-Tri-O-acetyl-D-glucopyranosyl chloride	178
3,4,6-Tri-O-acetyl-2-deoxy-2-acetamido-D-glucopyranosyl chloride	104
3,4,6-Tri-O-acetyl-2-deoxy-2-carbobenzyloxy-amino-α-D-glucopyranosyl chloride	104
3,4,6-Tri-O-acetyl-2-deoxy-2-carbomethoxy-amino-D-glucopyranosyl chloride	104
Hepta-O-acetyl-α-D-lactosyl chloride	105
Hepta-O-acetyl-α-cellobiosyl chloride	105
2,3,4-Tri-O-acetyl-6-O-trichloroacetyl-α-D-glucopyranosyl bromide	105
2,3,4-Tetra-O-acetyl-6-(2-deoxy-2-benzamido-3,4,6-tri-O-acetyl-β-D-glucopyranosyl)-D-glucopyranosyl chloride	105
2-Deoxy-3,4,6-tri-O-*p*-nitrobenzoyl-α-D-arabino-hexosyl bromide	179
2-Deoxy-3,4,6-tri-O-*p*-nitrobenzoyl-α-D-ribo-hexosyl bromide	179
2,4-DIMETHOXYPYRIMIDINE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	180
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	52, 181, 182
3,5-D-O-*p*-chlorobenzoyl-2-deoxy-D-ribofuranosyl chloride	182
3,5-Di-O-*p*-nitrobenzoyl-2-deoxy-D-ribofuranosyl chloride	182
2,3,5-Tri-O-benzyl-D-arabinofuranosyl chloride	162
Hepta-O-acetyl-α-D-lactosyl chloride	104
5-METHYL-2,4-DIMETHOXYPYRIMIDINE	
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	52
3,5-Di-O-chlorobenzoyl-2-deoxy-D-ribofuranosyl chloride	181
3,5-Di-*p*-nitrobenzoyl-2-deoxy-D-ribofuranosyl chloride	181
5-IODO-2,4-DIMETHOXYPYRIMIDINE	
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	51
5-CHLORO-2,4-DIMETHOXYPYRIMIDINE	
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	182
5-BROMO-2,4-DIMETHOXYPYRIMIDINE	
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	182
5-FLUORO-2,4-DIMETHOXYPYRIMIDINE	
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	170
5-NITRO-2,4-DIMETHOXYPYRIMIDINE	
3,5-Di-O-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride	170
2,4-DIMETHOXY-5-TRIFLUOROMETHYLPYRIMIDINE	
2,3,5-Tri-O-benzyl-D-arabinofuranosyl chloride	162
2,4-DIETHOXY-5-FLUOROPYRIMIDINE	
3,4,6-Tri-O-*p*-nitrobenzoyl-2-deoxy-α-D-arabino-hexopyranosyl bromide	183
2,4-DIETHOXY-5-METHYLPYRIMIDINE	
3,4,6-Tri-O-*p*-nitrobenzoyl-2-deoxy-α-D-ribo-hexopyranosyl bromide	140
2,3,5-Tri-O-acetyl-D-ribofuranosyl bromide	184, 186, 187
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	185, 186
2,3,4,6-Tetra-O-acetyl-D-galactopyranosyl bromide	186
2,3,5-Tri-O-acetyl-D-arabinofuranosyl bromide or chloride	173, 186
2,3,5-Tri-O-acetyl-L-arabinofuranosyl bromide or chloride	177, 186
Tri-O-acetyl-D-xylofuranosyl chloride	177

Hilbert-Johnson Method

A method for the synthesis of pyrimidine nucleosides was described by Hilbert and Johnson[47] who prepared β-D-glucopyranosyl uracil (XV) by the reaction of 2,4-diethoxypyrimidine with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide (I) followed by hydrolysis.

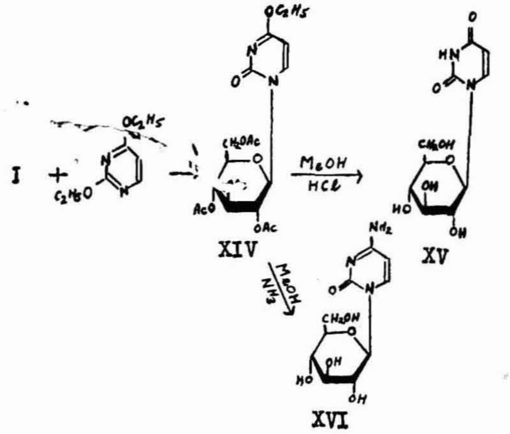
Treatment of the protected nucleoside intermediate with methanolic ammonia gave β-D-glucopyranosyl cytosine[48] (XVI).

Todd and coworkers[49] in 1947 were the first to synthesize cytidine (Chart 1), a natural nucleoside, by this method. In some cases both anomers are obtained[50-52]. Since then a number of nucleosides have been synthesized by this method. They are listed in Table 2.

Trimethylsilyl Method

A new method for the synthesis of pyrimidine and purine nucleosides, based on Birkofer's original discovery[53,54] of the activation of heterocyclic ring-nitrogens by silylation, was described by Nishimura and coworkers[55-61]. Trimethylsilyl ethers of uracil (XVII), on fusion at 180-190° with 2,3,5-O-tribenzoylribofuranosyl chloride (XVIII), produced 1-(2′,3′,5′-tri-O-benzoylribofuranosyl)-trimethylsilyl uracil (XIX), which on treatment with aq. ethanol gave 1-2′,3′,5′-tri-O-benzoyl-β-D-ribofuranosyl uracil (XX). Similarly, prepared nucleosides are listed in Table 3.

It was shown earlier[56] that all the nucleosides possessed β-configurations in glycosidic centres. However, Nishimura and Shimizo, recently, were



XIV XV XVI

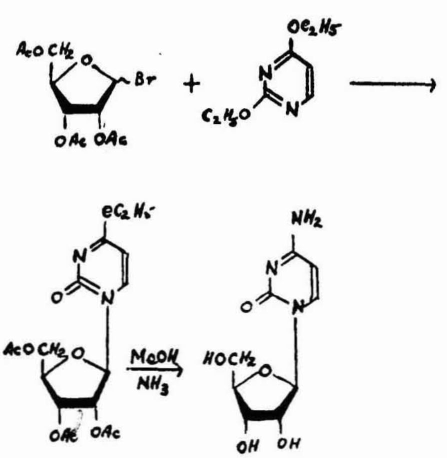
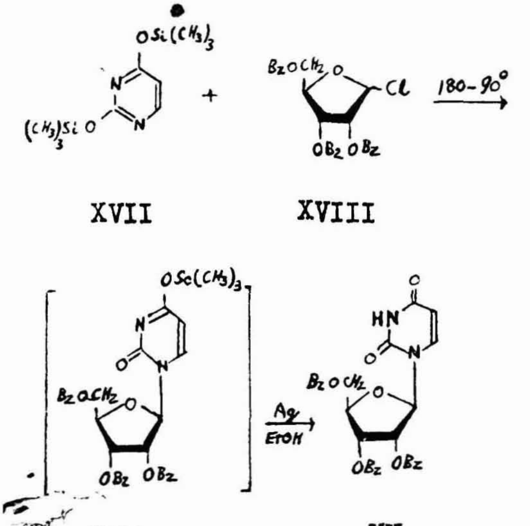


Chart 1 — Synthesis of cytidine



XVII XVIII XIX XX

TABLE 3 — NUCLEOSIDES PREPARED BY TRIMETHYLSILYL METHOD

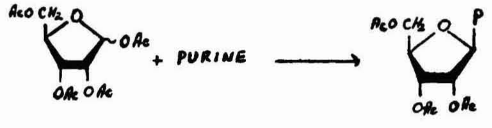
Acylhalogeno sugar	Ref.
BIS-(TRIMETHYLSILYL)-URACIL	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	55, 56, 188
2,3,5-Tri-O-benzoyl-α-D-arabinofuranosyl bromide	58
2,3,5-Tri-O-acetyl-D-lyxofuranosyl chloride	58
2,3,4,6-Tetra-O-acetyl-D-galactopyranosyl bromide	188
2,3,5-Tri-O-acetyl-L-arabinopyranosyl bromide	188
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	188
3,5-Di-O-(*p*-toluyl)-2-deoxy-D-ribofuranosyl chloride	188
BIS-(TRIMETHYLSILYL)-THYMINE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	55, 56, 188
2,3,5-Tri-O-benzoyl-α-D-arabinofuranosyl bromide	58
2,3,5-Tri-O-acetyl-D-lyxofuranosyl chloride	58
2,3,4,6-Tetra-O-acetyl-D-galactopyranosyl bromide	188
2,3,5-Tri-O-acetyl-L-arabinopyranosyl bromide	188
2,3,5-Tri-O-benzoyl-D-ribofuranosyl chloride	188
3,5-Di-O-(*p*-toluyl)-2-deoxy-D-ribofuranosyl chloride	188
BIS-(TRIMETHYLSILYL)-N-ACETYLCYTOSINE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	55, 56
2,3,4,6-Tetra-O-acetyl-D-galactopyranosyl bromide	188
2,3,5-Tri-O-acetyl-L-arabinopyranosyl bromide	188
BIS-(TRIMETHYLSILYL)-N-BENZOYLADENINE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	56, 57
2,3,5-Tri-O-acetyl-D-ribofuranosyl chloride	55
BIS-(TRIMETHYLSILYL)-HYPOXANTHINE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	56, 57
2,3,5-Tri-O-acetyl-D-ribofuranosyl chloride	55, 56
TETRABIS-(TRIMETHYLSILYL)-URIC ACID	
2,3,5-Tri-O-benzoylribofuranosyl bromide	54
BIS-(TRIMETHYLSILYL)-5-HYROXYMETHYLCYTOSINE	
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide	188
BIS-(TRIMETHYLSILYL)-4-ETHOXY-5-METHYLPYRIMIDINONE (2)	
2,3,4,6-Tetra-O-acetyl-D-galactopyranosyl bromide	188
6-TRIFLUOROMETHYL-3,5-BIS-TRIMETHYLSILYLOXY-AS-TRIAZANE	
2-Deoxy-3,5-di-O-*p*-nitrobenzoyl-D-ribofuranosyl chloride	188
6-BROMO-3,5-BIS-(TRIMETHYLSILYLOXYL)-AS-TRIAZINE	
2-Deoxy-3,5-di-O-*p*-nitrobenzoyl-D-ribofuranosyl chloride	189

able to isolate 9-α- and 9-β-nucleosides in case of adenine[57], thymine[58] and uracil[58].

Direct Condensation of Purines with Various (Protected) Sugars

The methods used in the synthesis of purine nucleosides by direct condensation of a base with a sugar derivative can be classified into two types: (i) heating fully O-acetylated D-pentoses and hexoses with various purines in the presence of a catalyst; and (ii) condensation of the purines with acylglycosyl halides in a solvent with or without hydrogen halide acceptors.

Shimadate and coworkers[59] developed a method of nucleoside synthesis, which involves heating 1,2,3,5-tetra-O-acetyl-D-ribofuranose (XXI) with various purines and a catalyst (e.g. *p*-toluenesulphonic acid) to yield β-nucleosides (XXII).



XXI XXII

Zinc chloride, conc. sulphuric acid[62], sulphamic acid[63], chloroacetic acid[64], bis-(*p*-nitrophenyl) hydrogen phosphate and its methyl derivative[65] have also been used as effective catalysts for the fusion method.

Goodman and coworkers[66] obtained after deacylation both α- and β-nucleosides by the fusion of 6-nonanamidopurine (Q = CH) or 6-nonanamido-8-azapurine (Q = N) with 1,2,3,5-tetra-O-acetyl-D-xylose (Chart 2).

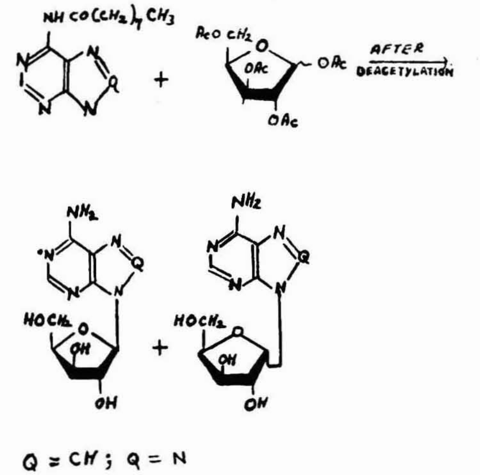


Chart 2 — Preparation of α- and β-nucleosides by the fusion method

Non-catalytic fusion[67] of 1,2,3,5-tetra-O-acetyl-β-D-ribofuranose with 6-chloro-, 6-iodo-, 6-cyano-, 2-chloro-6-iodo-, 6-chloro-2-iodo- and 2,6,8-trichloropurines gave the corresponding ribonucleosides in 10-67 per cent yields.

Schramm *et al.*[68] observed that the condensation of adenine with D-ribose in the presence of polyphosphate ester gave adenosine. The synthesis of 2′-deoxyadenosine using polyphosphate ester has been shown to give a mixture of at least six products[69].

Direct Condensation of Purines with Acylglycosyl Halides

When adenine was reacted with 2,3,5-tri-O-benzoyl-D-ribofuranosyl bromide (R=Bz; X=Br) in acetonitrile, the 3- and 9-isomers of (2′,3′,5′-tri-O-benzoyl-β-D-ribofuranosyl)-adenine (R = Bz) was obtained in 25 and 18 per cent yields respectively[70] (Chart 3).

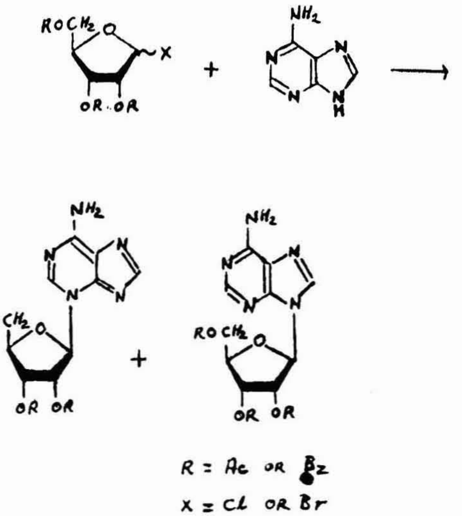
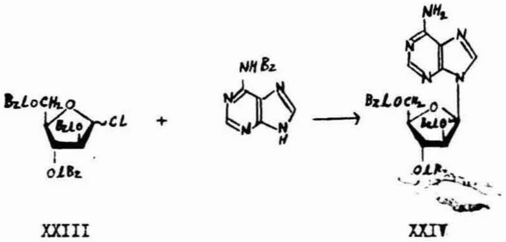


Chart 3 — Synthesis of 3- and 9-isomers of (2′,3′,5′-tri-O-benzoyl-β-D-ribofuranosyl)-adenine

Condensation of 2,3,5-tri-O-benzyl-D-arabinofuranosyl chloride (XXIII) with N-benzoyladenine in the presence of molecular sieve (Fisher Scientific Co., USA, type 4A, $\frac{1}{16}$ in. pellets) in dichloromethane gave after debenzoylation 9-(2′,3′,5′-O-benzyl-β-D-arabinofuranosyl)-adenine[71] (XXIV).



XXIII XXIV

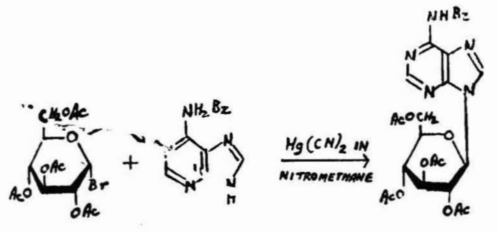
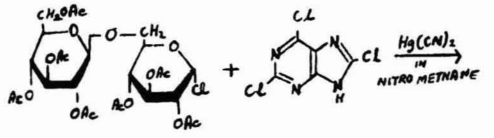


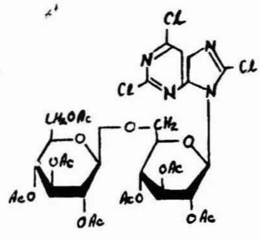
Chart 4 — Synthesis of a 9-nucleoside by the method of Yamaoka *et al.*[72]

Yamaoka *et al.*[72] developed a method, which involved the direct condensation of certain purines, such as free N-acyladenine, chloropurines, theophylline, N^6-benzoylcytosine, and benzimidazole with acylglycosyl halides in nitromethane containing hydrogen halide acceptors [Ag_2O, $Hg(CN)_2$, $Zn(CN)_2$, AgCN or KCN] to give the corresponding crystalline 9-nucleosides in yields 20-40 per cent higher than the conventional processes. This method also eliminates the step for formation of the metal salts (Chart 4).

A nucleoside, gentibiose (XXVI), containing a disaccharide, has also been prepared by adopting this procedure.



XXV



XXVI

Nucleoside Interconversions

By oxidation — An interesting path to the nucleosides of 3-amino-3-deoxyaldoses has been found by Fox and coworkers[73-76]. Periodate cleavage of uridine produced a dialdehyde without breaking the glycosidic linkage. Addition of nitromethane led to renewed cyclization. After reduction of the nitro group, 1-(3′-amino-3′-deoxy-β-D-glucopyranosyl)-uracil was obtained (Chart 5).

Treatment of adenosine with metaperiodate followed by condensation with nitromethane yielded a mixture of 3′-deoxy-3′-nitrohexopyranosyl adenines which were converted to 3′-amino-3′-deoxyhexopyranosyl nucleosides (Chart 6).

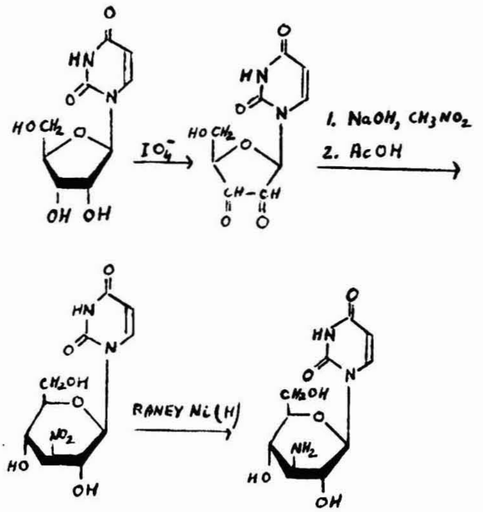


Chart 5 — Preparation of a nucleoside of 3-amino-3-deoxyaldose by the method of Fox and coworkers[73-76]

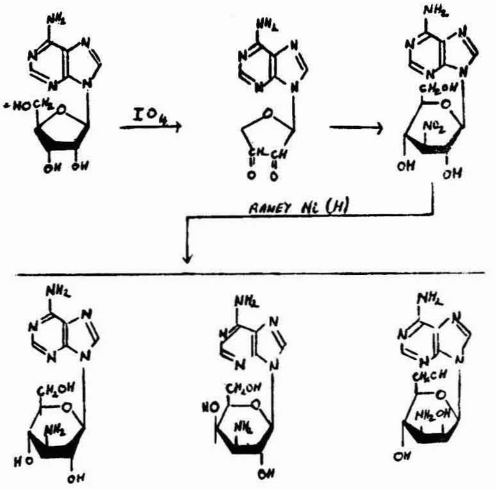
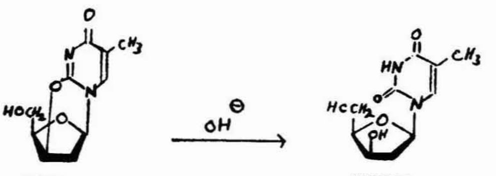


Chart 6 — Synthesis of 3′-amino-3′-deoxyhexopyranosyl nucleosides

By anhydronucleosides — The use of anhydronucleosides as a route for preparing other pyrimidine nucleoside analogues have been used by Michelson and Todd[77] for the conversion of $O^2,3^1$-cyclothymidine (XXVII) to 1-(2′-deoxy-β-D-*threo*-pentofuranosyl)-thymine (XXVIII).



XXVII XXVIII

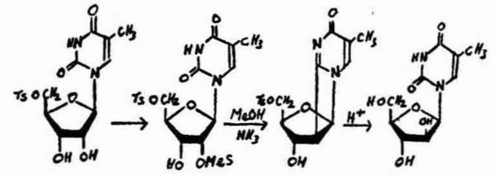
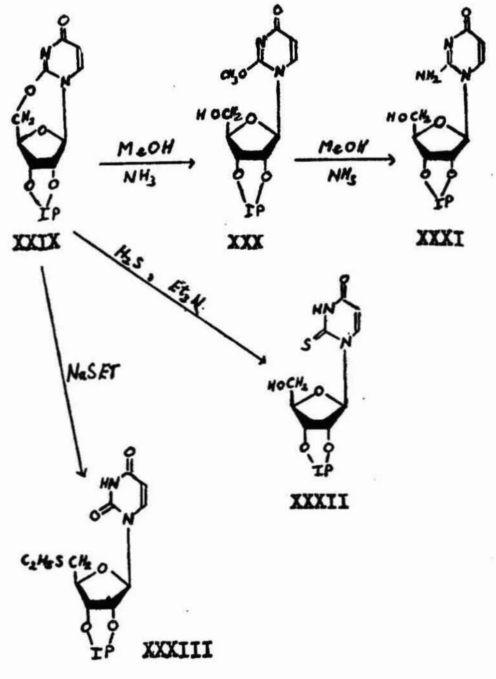


Chart 7 — Synthesis of spongothymidine

This method has been extended[78] to the synthesis of spongouridine.

Fox *et al.*[79,80] synthesized ' spongothymidine ' by virtue of the epimerization sequence (Chart 7).

The anhydronucleoside process has also been used for replacing the oxygen atom at C-2 of the aglycone residue with other substituents. Thus, 2',3'-O-isopropylidene-O^2,5'-cyclouridine (XXIX) is readily hydrolysed to 2',3'-O-isopropylideneuridine.



Treatment of the cyclouridine (XXIX) with methanolic ammonia at room temperature afforded (XXX) which on prolonged treatment with methanolic ammonia gave (XXXI); compound (XXIX) with hydrogen sulphide plus triethylamine in DMF or with sodium thioethoxide gave (XXXII) and (XXXIII) respectively[81]. Similarly, O^2,2^1-cyclouridine gave the 3'-deoxyuridine[81] (Chart 8).

The 2'-O-tosyluridine derivative (XXXIV), when reacted with sodium iodide, is converted into the 2'-iodonucleoside (XXXV), which upon reduction under alkaline conditions, yields 2'-deoxyuridine (XXXVI)[82,83].

The synthesis of 5'-amino-5'-deoxyuridine from uridine has been achieved[84] (Chart 9). Conversion

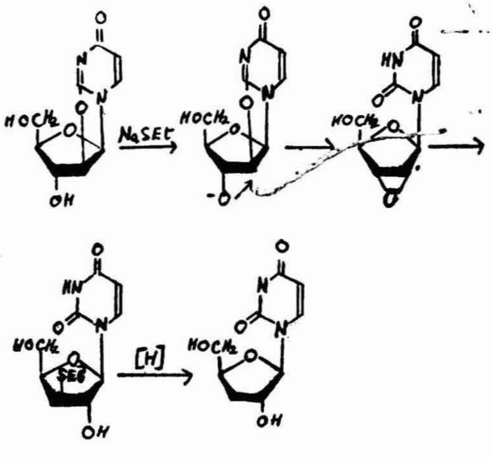


Chart 8 — Synthesis of 3'-deoxyuridine

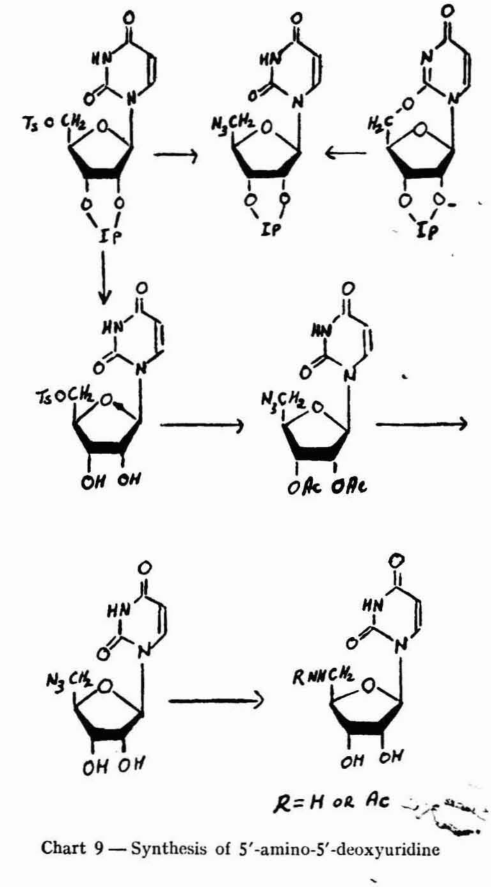
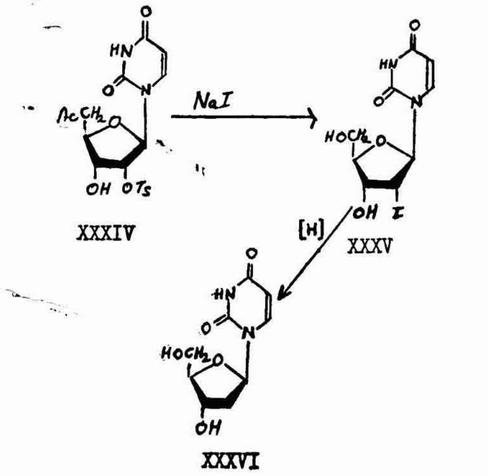


Chart 9 — Synthesis of 5'-amino-5'-deoxyuridine



XXXIV

XXXV

XXXVI

of thymidine to 5′-amino-5′-deoxythymidine by a similar sequence has also been effected.

Mesylation of 3′-O-acetylthymidine affords 3′-O-acetyl-5′-O-mesylthymidine which on deacetylation with methanolic ammonia gives 5′-O-mesylthymidine[85] (Chart 10). Similarly, mesylation of 5′-O-tritylthymidine gives 3′-O-mesylthymidine. Treatment of 5′-O-mesyl-O^2,3′-cyclothymidine with aq. alkali effects 'aryl-oxygen' fission of the anhydro bond with the formation of 1-(2′-deoxy-3′,5′-epoxy-β-D-*threo*-pentofuranosyl)-thymine. Cleavage of the epoxide ring with dil. sulphuric acid yields 1-(2-deoxy-β-D-*threo*-pentofuranosyl)-thymine[86] (Chart 11).

Treatment of 5′-O-trityluridine with thio-carbonyldiimidazole gives 2-(2′-anhydro-1-(5′-O-trityl-β-D-arabinofuranosyl)-uracil, which on de-tritylation and treatment with dil. alkali yields 1-β-D-arabinofuranosyluracil[87] (Chart 12). 3′-Amino-3′-deoxythymidine has been synthesized by the reduction of the corresponding 3′-azido derivative over platinum oxide[88] (Chart 13). The synthesis of 2′,5′-dideoxycytidine and other derivatives of 2′-deoxycytidine has been reported recently starting from 2′-deoxy-5′-O-tritylcytidine[89] (Chart 14).

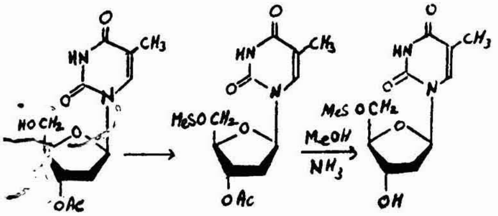


Chart 10 — Synthesis of O-mesylthymidine

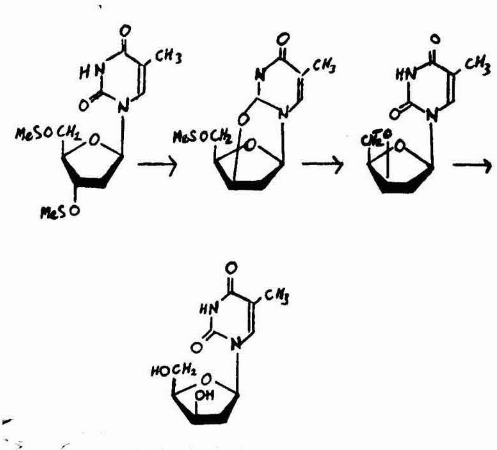


Chart 11 —Synthesis of 1-(2-deoxy-β-D-*threo*-pentofuranosyl)-thymine

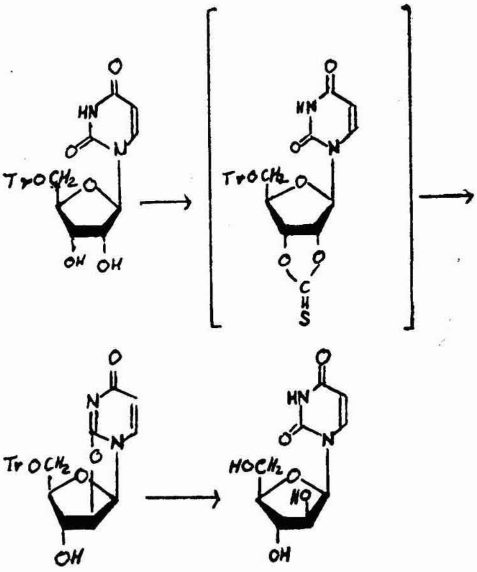


Chart 12 — Synthesis of 1-β-D-arabinofuranosyluracil

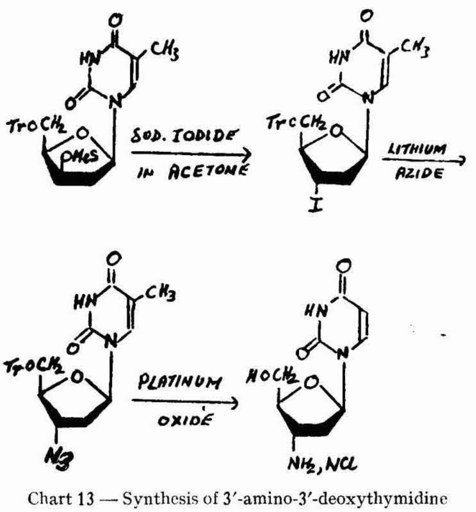


Chart 13 — Synthesis of 3′-amino-3′-deoxythymidine

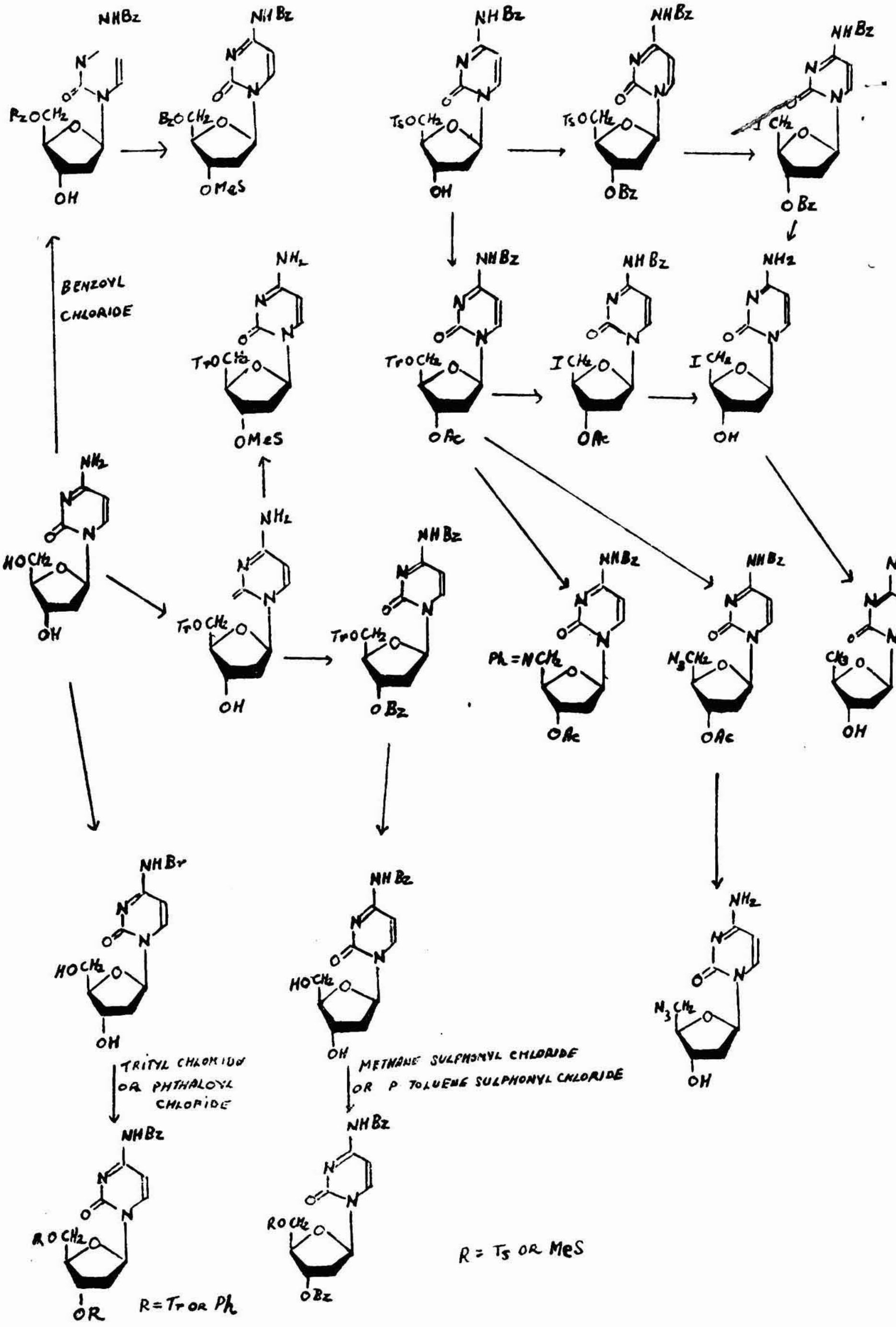
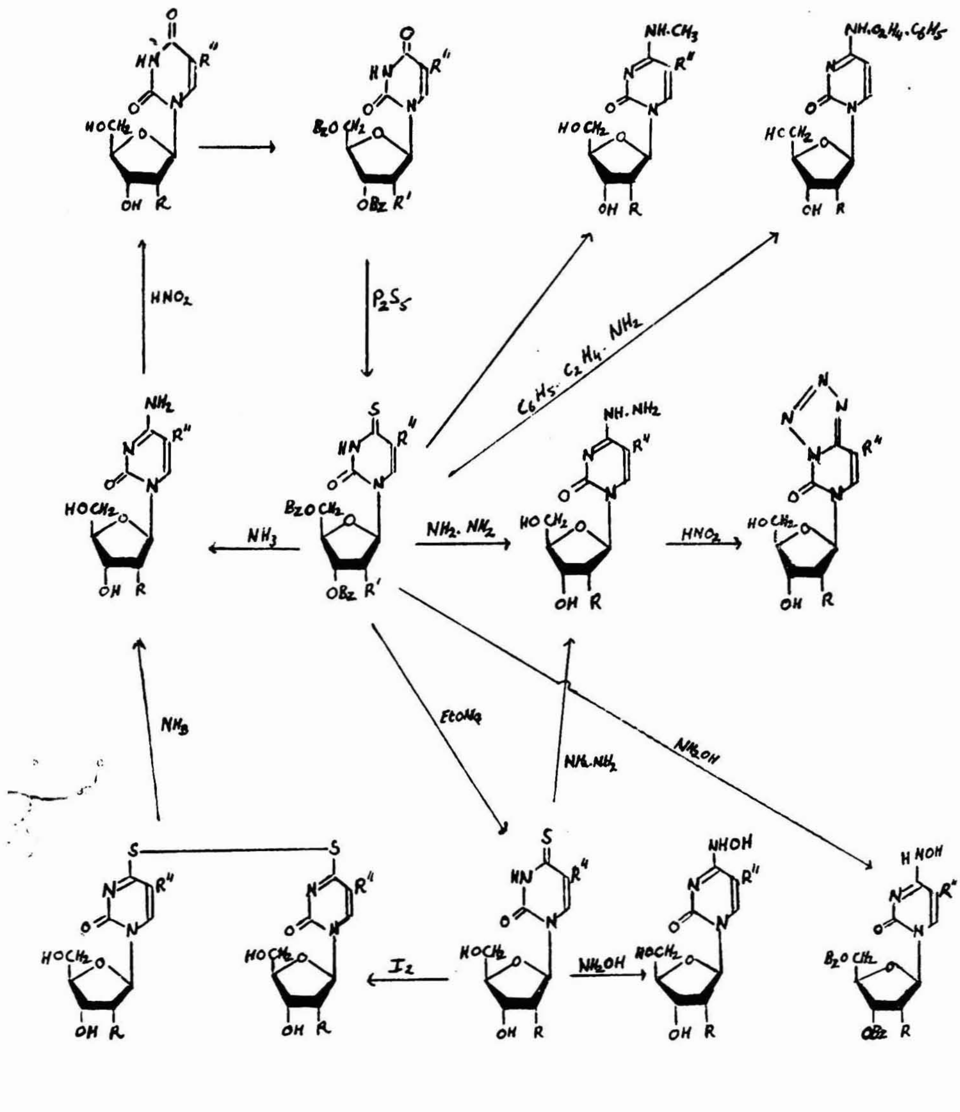


Chart 14 — Synthesis of 2′,5′-dideoxycytidines and other related 2′-deoxycytidine

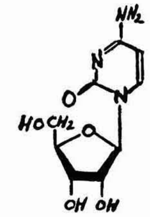


a series, R,R' = H, R" = CH_3

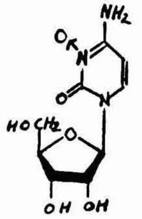
b series, R = OH,R' = OBz, R" = H

c series, R = OH, R' = OBz, R" = CH_3

Chart 15 — Synthesis of pyrimidine nucleosides by thiation procedure



XXXVII



XXXVIII

Cytidine (XXXVII) has been oxidized to cytidine 3-N-oxide (XXXVIII) with *m*-chloroperbenzoic acid[90].

By thiation of pyrimidine nucleosides — A number of pyrimidine nucleosides have been synthesized by Fox *et al.*[91] (Chart 15) by use of the thiation procedure. Other thiation reactions have recently been reported[92] (Chart 16).

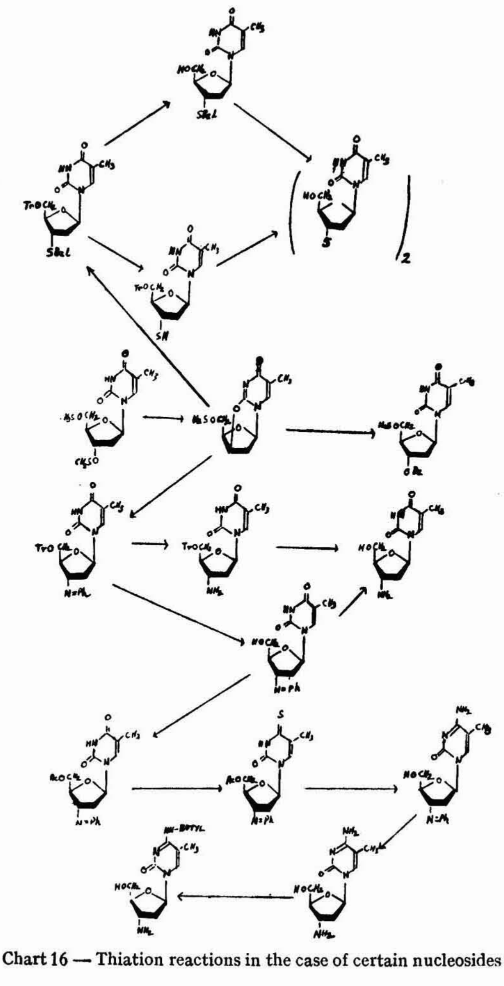
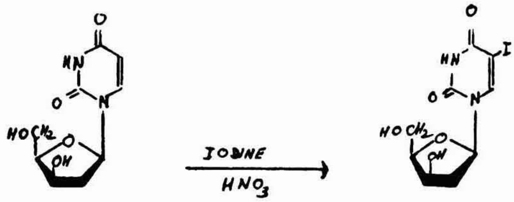


Chart 16 — Thiation reactions in the case of certain nucleosides

Conversion of Pyrimidine or Purine Moiety: Halogenation of Nucleosides

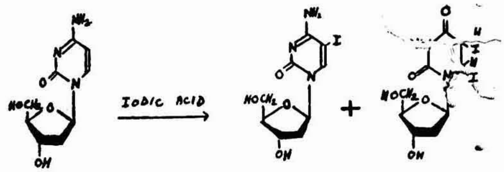
Conversion of pyrimidine nucleosides to 5-substituted analogues was reported originally by Levene and LaForge[93] who prepared 5-bromouridine by treating uridine with bromine water, which on treatment with liquid ammonia gave 5-aminouridine[94]. 5-Chloro-[95], 5-iodouridine-[96] and 5-hydroxy-[94] analogues were also prepared.

Recently, 1-(2′-deoxy-β-D-lyxofuranosyl)-5-iodouracil (XL) has been synthesized from 1-(2′-deoxy-β-D-lyoxofuranosyl)-uracil (XXXIX) and iodine in the presence of *N*-nitric acid[97].



XXXIX XL

Halogenation of 1-arabinofuranosyl- or a poly-O-acylated 1-arabinobinofuranosyl uracil gave 5-halouracil derivative[98]. Iodination of 2′-deoxycytidine (XLI) in the presence of iodic acid gives 5-iodo-2′-deoxycytidine (XLII) and 5,6-dihydro-5,6-diiododeoxyuridine (XLIII)[99].

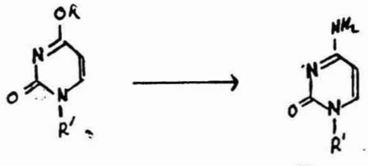


XLI XLII XLIII

Bromination of acetyl derivatives of adenosine, deoxyadenosine, guanosine and inosine yield, after deacetylation with ethanolic ammonia, the corresponding 8-bromopurine nucleosides[100]. N-Iodosuccinimide in the presence of catalytic amount of *n*-butyl disulphide acts as an iodination agent. Thus, guanosine and xanthosine were converted into the corresponding 8-iodo derivatives[101].

Hydroxyl groups in the heterocyclic ring can be replaced by chlorine using N,N′-dialkylchloromethylene ammonium chloride as chlorinating agent, e.g. 6-chloro-9-(β-D-ribofuranosyl)-purine was obtained, starting from the 2′,3′,5′-tri-O-acetyl derivative of inosine[102].

Hydroxyl groups in the sugar can be replaced by iodine using triphenyl phosphate methiodide and triphenyl phosphite diiodide as iodination agents[103]. The following compounds have been prepared by



XLIV **XLV**

R = Alkyl; R' = Sugar

this method: 5'-deoxy-5'-iodo-2',3'-O-isopropylideneuridine, 5'-deoxy-5'-iodouridine, 5'-O-acetyl-3'-deoxy-3'-iodothymidine, 3'-deoxy-3'-iodothymidine, 3'-deoxy-3'-iodo-5'-O-*p*-nitrobenzoylthymidine, 3',5'-dideoxy-3',5'-diiodothymidine, and 2',3',5'-trideoxy-3',5'-diiodouridine.

4-Alkoxy-2(1H)-pyrimidone derivatives (XLIV) are converted to the corresponding cytosine (XLV) with ethanolic ammonia[104,105].

Fischer and Helferich[32] were able to prepare the D-glucosyl analogues of adenine and guanosine by the appropriate transformations of 2,6-dichloro-9-β-D-glucopyranosyladenine.

The chlorine atoms in the 2- and 6-positions of the nucleoside are much more reactive than the chlorine atoms of 2- and 6-chloropurine. Furthermore, the 2-chlorine in the dichloro-nucleoside is, in certain reactions, less reactive than the 6-chlorine atom. Hence, nucleophilic substitution of chloropurine nucleosides has permitted the preparation of a large variety of purine nucleosides (Chart 17)[42,106-115].

The synthesis of 9-β-D-ribofuranosyl uric acid has been accomplished in several steps from guanosine (Chart 18)[116]. 2-Amino-9-β-D-ribofuranosyl-6,8-purinedione was also synthesized.

Refluxing aq. hydrazine and 8-bromoguanosine yields 8-aminoguanosine, the first reported 8-aminopurine nucleoside. 8-Aminoadenosine was also prepared from 8-bromoadenosine via 8-azidoadenosine which was converted to (I) by catalytic reduction (Chart 19)[116].

The synthesis and cleavage of the cycloadenosine derivative has been investigated (Chart 20)[115].

An alternative synthesis of 2',3'-dideoxyadenosine has recently been reported (Chart 21)[117].

3'-Amino-3'-deoxyadenosine (XLVI) has been oxidized to 3'-amino-3'-deoxyadenosine-1-N-oxide (XLVII)[118].

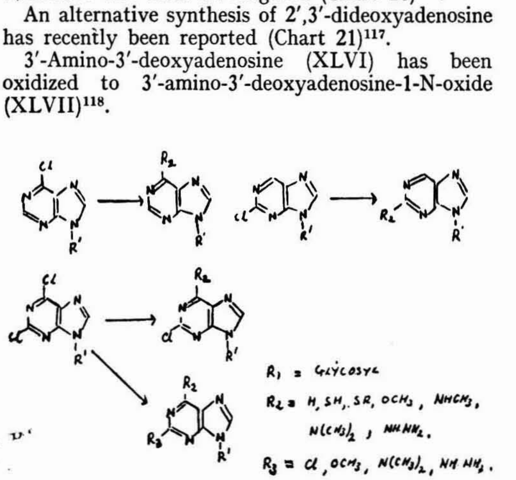


Chart 17 — Synthesis of some purine nucleosides

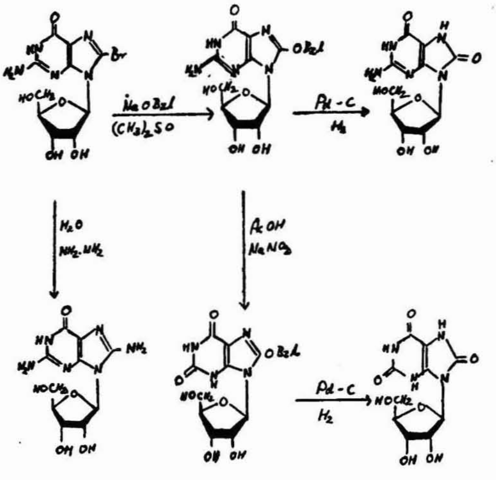


Chart 18 — Synthesis of 9-β-D-ribofuranosyl uric acid

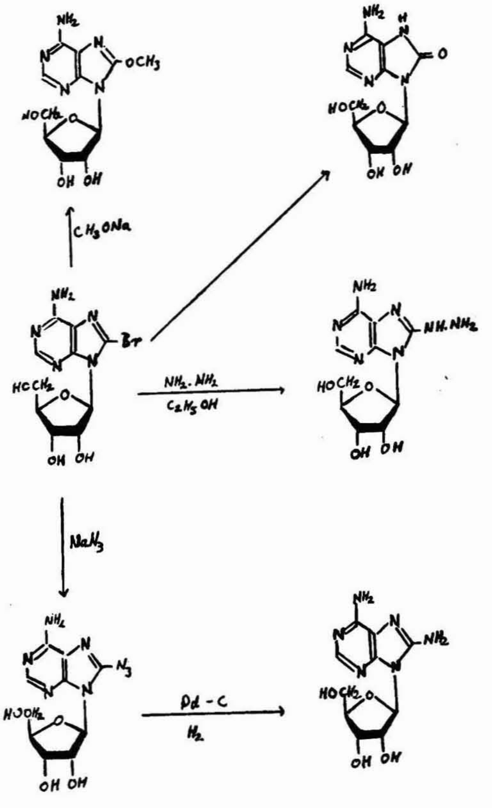
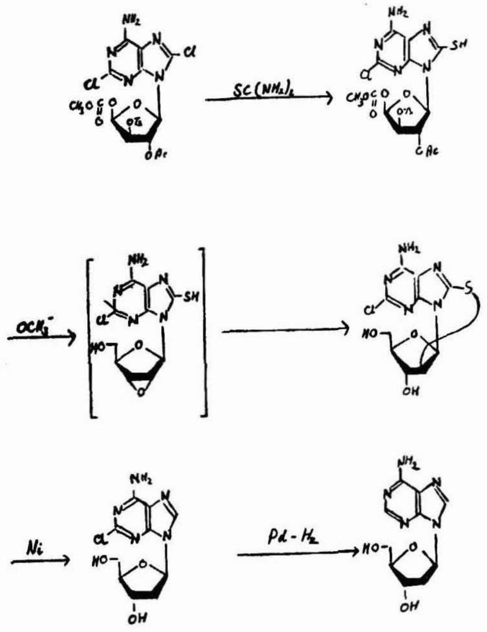


Chart 19 — Synthetic routes for obtaining 8-aminoadenosine



[Chart 20 — Synthesis and cleavage of the cycloadenosine derivative of 8-aminoadenosine

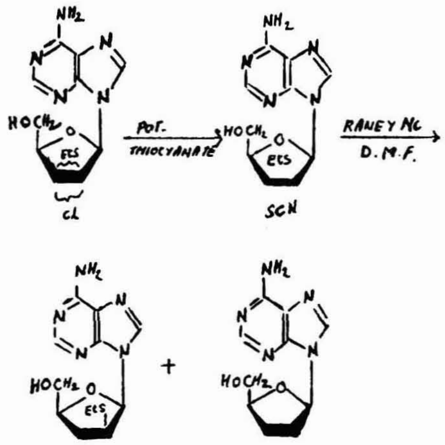
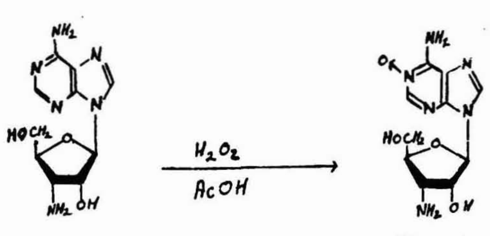


Chart 21 — Synthesis of 2′,3′-dideoxyadenosine

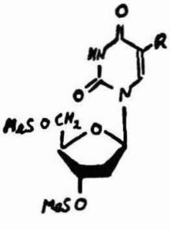


XLVI

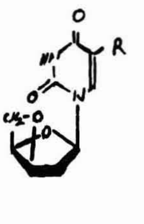
XLVII

2′,3′-Unsaturated Nucleosides

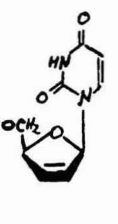
The action of aq. sodium hydroxide on 2′-deoxy-3′,5′-di-O-(methylsulphonyl)-uridine (XLVIII, R=H) gave (XLIX, R=H). Treatment of (XLIX, R=Me) with potassium *tert*-butoxide (2 equiv.) in DMF yielded the 2′,3′-unsaturated nucleoside (L)[119].



XLVIII

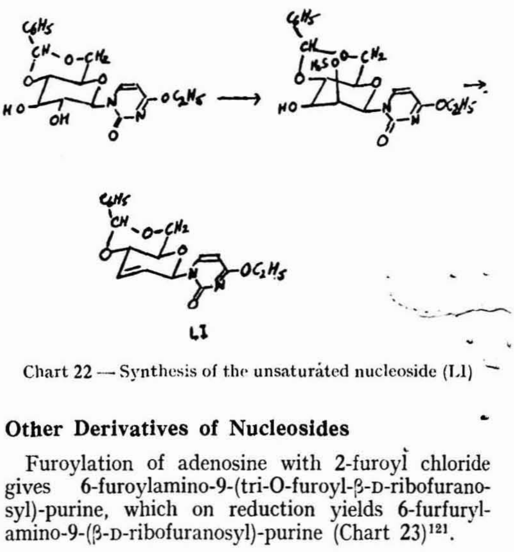


XLIX



L

Stevens *et al.*[120] obtained the unsaturated nucleoside (LI) by the following sequence (Chart 22):



LI

Chart 22 — Synthesis of the unsaturated nucleoside (LI)

Other Derivatives of Nucleosides

Furoylation of adenosine with 2-furoyl chloride gives 6-furoylamino-9-(tri-O-furoyl-β-D-ribofuranosyl)-purine, which on reduction yields 6-furfurylamino-9-(β-D-ribofuranosyl)-purine (Chart 23)[121].

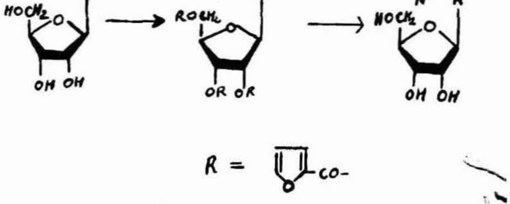
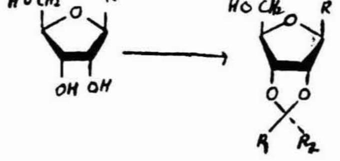
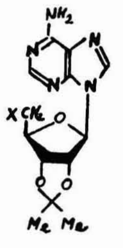


Chart 23 — Synthesis of 6-furfurylamino-9-(β-D-ribofuranosyl)-purine

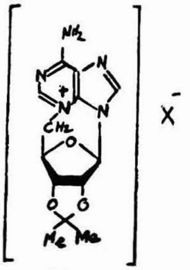
Condensation of guanosine, uridine or cytidine with benzaldehyde in the presence of zinc chloride at low temperature (0-5°) gave the protected nucleosides as shown below[122]:



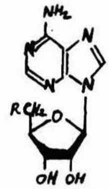
R = Guanyl, Uracilyl or Cytosilyl
R′ = Ph and R_2 = H



LII



LIII



LIV

$X = p\text{-}MeC_6H_4SO_3$

The isomerization of 5′-O-p-tolysulphonyl-2′,3′-O-isopropylidene adenosine (LII) to a cyclonucleoside salt (LIII, X = p—$MeC_6H_4SO_3$), occurring in nucleophilic substitution reactions, can be avoided by N-acylation, which allows various exchange reactions[123].

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REVIEWS

AN INTRODUCTION TO ELECTRONIC COMPUTERS by Gordon B. Davis (McGraw-Hill Book Co. Inc., New York), 1965. Pp. 541. Price $ 9.75

Electronic digital computers are increasingly playing a vital role in the day-to-day life in industrially advanced countries. In India, the computer industry is bound to gather momentum in the near future. It is, therefore, very important that the scientists and the professional engineers should receive proper training in computer sciences at graduate and post-graduate levels in the universities and institutes of technology. This book, therefore, is a very welcome arrival from the point of view of the teaching profession.

The book is an excellent introduction to both the hardware as well as software aspects of digital computers. The text avoids both the shallowness of the brief introduction approach and also the narrowness of the approach which ties the student to a single computer. The division between hardware and the software is almost half to half, which is desirable to avoid tendency to emphasize only one aspect. The first four chapters deal primarily with machine organization. The next few chapters deal primarily with machine-oriented instructions and provide excellent text for understanding these aspects. Chapters 11 through 15 cover problem-oriented languages, namely Fortran and Cobol in a very lucid manner, providing numerous problems for home study and self-instructions. The entire treatment of the text is non-mathematical, simple and direct in its approach with plenty of illustrations to bring home the specific point in a simple manner, and for easy understanding of the text. The other special features of the book are a chapter on ' evaluating computers ', which is rather interesting and chapter 17 which presents future trends in computer hardware and software. Another interesting feature of the book is the information contained in the 4 appendices which ranges from a list of computer manufacturers to ' data processing management association certificate programmes '.

All in all this book has substantially contributed in filling up the pressing need for a good text at the undergraduate level for self-study and regular instructions. The book is highly recommended both for the students and for the teacher.

P. K. PATWARDHAN

PLASMAS — LABORATORY AND COSMIC by Forrest I. Boley (D. Van Nostrand Co. Inc., New York), 1966. Pp. 154. Price $ 1.75

This book is one of the publications in the ' Momentum Series ' published for the Commission on College Physics. It gives an excellent presentation of the fundamental characteristics of laboratory and cosmic plasmas of current interest. The physical concepts are developed systematically and mathematics is kept to a minimum. Besides dealing with the general properties of plasmas, the book deals with instabilities, plasma waves, high temperature laboratory plasma and controlled thermonuclear fusion experiments. The naturally occurring plasmas discussed are the sun, solar wind, ionosphere and plasma beyond the solar system. This book is one of the best which have appeared on the subject and can be recommended even to a reader who is not a specialist in this branch of physics.

F. C. AULUCK

PROCEEDINGS OF THE SUMMER SEMINAR IN MAGNETOHYDRODYNAMICS edited by P. L. Bhatnagar (Indian Institute of Science, Bangalore), 1965. Pp. ix+376. Rs 12.50

The proceedings embody the review talks and original papers presented at the Summer Seminar in Magnetohydrodynamics held in May 1963 at the Department of Applied Mathematics, Indian Institute of Science, Bangalore, under the direction of Prof. P. L. Bhatnagar. There are eighteen good reviews on some of the outstanding problems like wave propagation, stability pinch effect, motion of charged particles, plasma oscillations and sunspot magnetic field. Attempts have been made to discuss these topics both from the fluid and the kinetic approach. Nine original papers dealing with various problems of magnetohydrodynamics are also reported.

The book gives an excellent review of the subject from the theoretical point of view and can be recommended to a beginner on the subject of magnetohydrodynamics.

F. C. AULUCK

INTERACTION OF METALS AND GASES: Vol. 1—THERMODYNAMICS AND PHASE RELATIONS by J. D. Fast (Philips Technical Library, Eindhoven; Distributors for India, Burma and Pakistan: B.I. Publications, 359, D. Naoroji Road, Bombay 1), 1965. Pp. x+302. Price Rs 40.00

The book under review by J. D. Fast, the Chief Metallurgist of the Philips Research Laboratories which deals mainly with thermodynamics and phase relations with reference to the interaction of metals and gases, covers cogently and briefly the available extensive material in the literature on the broad important subject of metal-gas problems. The aim as the author opines is to bring out a text-book for the student of metallurgy and a guideline to the practising industrial metallurgist and chemist.

The subject in the first volume has been conveniently divided into 9 chapters, the first being mainly a simple introduction to thermodynamics, which is very well presented. The concept of chemical equilibrium, based on chemical affinity and potential in chemical reactions is explained next, which is followed by a detailed explanation of procedure for the calculation of equilibrium with very useful practical examples. Typical cases of attack of metals by gases resulting in the formation of new phases, selective and internal oxidation and porosity are discussed at length. Also serious deleterious effects like the loss of ductility, brittle failure and peculiar difficulties caused by the presence of the gases in the metallurgy of steel, copper, tungsten, titanium, zirconium, molybdenum, vanadium, hafnium, niobium and tantalum are explained and discussed. The utilitarian aspect of the interaction of metals and gases for such useful metallurgical processes like case hardening of certain types of steels, production of grain oriented magnetic steel, and 'getters' in high vacuum application is also dealt with lucidly.

Well presented, this book is a must for the serious researcher in the metal-gas reactions as well as to the practising metallurgist and chemist.

A. A. KRISHNAN

MOLECULAR SYMMETRY: AN INTRODUCTION TO GROUP THEORY AND ITS USES IN CHEMISTRY by D. S. Schonland (D. Van Nostrand Co. Inc., New York), 1965. Pp. xii+298. Price 70*s*.

Although the value of group theoretical methods for the study of molecular properties is now well recognized, among chemists the actual number of users of this powerful tool has remained limited. This has been apparent because most of the books on group theory are addressed to mathematicians and physicists and they assume too much by way of mathematical background. The need for a book that appeals to the chemist has been only partly satisfied by the publication of Cotton's *Chemical applications of group theory*. The effort that Dr Schonland has made to address students of chemistry on this abstract subject is, therefore, most welcome. The mathematical background he assumes is that of a graduate student who has had a first course in quantum mechanics. The book is intended to help those 'who, without calling themselves theoreticians', would like to make practical use of the theory and it may be said at the very outset that the author has largely achieved his aim.

After an introduction to the scope of the book, the basic principles are set forth in six chapters (second to seventh) covering 138 pages. The development follows the natural sequence. The reader is first introduced to symmetry operations and molecular point groups. The mathematical framework necessary for the discussion of symmetry properties is developed next. The other stages in the sequence are matrix representation of symmetry operations, reducible and irreducible representations and their properties, and, finally, the use of representation theory in quantum mechanics. Once the theoretical section is properly digested, the reader should experience no difficulty in following the applications discussed in the last three chapters entitled 'Molecular vibrations', 'Molecular orbitals' and 'Electronic spectra'. The examples chosen for discussion in the last two chapters are mainly those of benzene and transition-metal complexes.

The author has presented the material in a good pedagogic style and not as a set of definitions and theorems. There has been no loss of rigour however. The policy of discussing 'a few things in fair detail' has produced a book that does not neglect depth of understanding for the sake of variety. The problems given at appropriate places and the mathematical appendices attached, including a long list of character tables, serve a useful purpose. The book is recommended highly to all chemists interested in the applications of group theory.

P. MADHAVAN NAIR

THERMAL NEUTRON SCATTERING by P. A. Egelstaff (Academic Press Inc., New York), 1965. Pp. xv +523. Price 115*s*.

The book deals with many interesting aspects of thermal neutron scattering by solids and liquids leading to a study of the dynamical motion of atoms in the condensed state of matter. The book combines both experimental and theoretical aspects of the problem suitable for post-graduate students and researchers in this field. The first chapter summarizes the theoretical aspects of neutron scattering, both elastic and inelastic, from condensed matter. The next three chapters deal extensively with instrumentation, while the rest of the book gives a comprehensive summary of the results achieved so far in various fields of application. Among the applications are the study of thermal vibrations of crystal lattice, spin waves in ordered magnetic substances, dynamics of molecular motion and the dynamics of atomic motion in liquids. The various chapters have been contributed by people who have specialized in those particular fields and the book has been edited in a very useful fashion. It will prove to be creative reading to solid state physicists in general.

P. K. IYENGAR

MECHANICAL WORKING OF STEEL II: Vol. 26, edited by T. G. Bradbury (Gordon & Breach Science Publishers, New York), 1965. Pp. ix+542. Price $ 27.50 (cloth); $ 14.50 (paper)

The present volume, which is a continuation of the series started two years back, contains papers presented at the conference held at Chicago during 30-31 January 1964. The papers deal with bar and semi-finished products of the free machining qualities, flat rolled products and pipe and tubular products. While the articles on role of oxygen in free cutting steels and factors affecting the machinability of free machining steels are of considerable practical interest both to practising metallurgists as well as to mechanical engineers concerned with machine shop practice, the subjects tend to be of specialized interest to some restricted aspects of the problem of machining of steel. The paper on measurement of machining performance in steels is an exhaustive study of different test procedures.

The chapter on flat rolled products dealing with the metallurgical aspects of cold rolled products such as 'recrystallization behaviour effect of the rolling load' throws new light on the present knowledge in this field. The two articles on ageing of flat rolled steel products as investigated by electron microscopy and the strain ageing, quench ageing and magnetic ageing in low carbon steel are reports on a detailed study of the problem which is engaging the attention of steel sheet and strip producers all over the world. The third part of the book deals with current matters of interest to all pipe and tube manufacturers. The article on continuous casting process and the suitability of continuous cast blooms for pipe making will support some of the claims made for the continuous casting process.

The volume will be a very useful addition to a technical library as it makes a useful contribution on the current knowledge on the mechanical working of steel.

K. N. P. RAO

ALLOYING BEHAVIOUR AND EFFECTS IN CONCENTRATED SOLID SOLUTIONS: Vol. 29, edited by T. B. Massalski (Gordon & Breach Science Publishers, New York), 1965. Pp. ix+445. Price $ 22.50 (cloth); $ 9.50 (paper)

This is a collection of eight articles of widely varying lengths, but representing a fairly consistent body of material. The time elapsed between the symposium and the publication is over two years. This, although surprising, does not mean that the articles are that much out of date. Most of them contain references to papers published in 1964.

The first three of these (by Cohen, Rayne and Blandin respectively) deal with electronic properties. Cohen's article (The electron theory of simple metals and alloys) will be hard and somewhat abstruse reading for most metallurgists and experimentalists if only because it is too terse. To these the other two articles will be more useful since they compare experimental results with theoretical deductions at every stage.

King's article on atomic volume and size correlations effectively demonstrates that the mean volume per atom in a solid solution is independent of the coordination number. Haasen's article on structural defects in solid solutions is extremely readable and, among other things, nicely summarizes the known interactions between dislocations and solute atoms. Duwez's article presents some new ideas on metastable solid solutions. Those who deal with solid solutions every day will find much useful information in all these articles.

But the highlights of the collection are the exhaustive articles by Christian and Swann (Stacking faults in metals and alloys, 165 pp.) and Sato and Toth (Long period superlattices in alloys, 125 pp.). The former is a masterly review of the present knowledge of that elusive if not obscure property: stacking fault energy. It also beautifully illustrates the close relationship between mechanical properties and conduction electrons. Sato and Toth's article is a fresh attempt to discuss the relative stabilities of the basic and long period superstructures in terms of the electron energy and the antiphase boundary energy.

Thirty years ago Mott and Jones said, in their now famous book, that the work of Taylor (1934, introducing dislocations as agents of plastic deformation) "inspires the hope that soon it may be possible to apply the methods of atomic physics to the property of metals which is of the greatest technical importance, namely that of strength". The book under review is witness to the continual fulfilment of that hope. If there is one single thing that the book may be said to emphasize, either directly or by implication, it is that, as said in the editor's preface, the electronic theories of imperfect structures must also include dislocations and stacking faults. And this is a very welcome emphasis.

A. S. PARASNIS

THEORY OF OPTIMUM AERODYNAMIC SHAPES edited by Angelo Miele (Academic Press Inc., New York), 1965. Pp. xix+454. Price $ 16.50

Subtitled 'External problems in the aerodynamics of supersonic, hypersonic and free-molecule flows', this publication is timely, indeed overdue, being the first attempt at presenting a coherent and well-organized picture of the considerable advances achieved in this field over the past twenty years or less. The problem of the design of optimum two- and three-dimensional shapes for minimum drag at supersonic speeds has become increasingly important to the aerospace vehicle designers, and the remarkable success of mathematical techniques in this application has made it one of the relatively few areas in aerodynamics where theoretical results have been of such direct interest to the practical engineer.

The first part of the book provides an engineering introduction to the calculus of variations as the basic mathematical key to the later parts. The application of the mathematical tool and some basic results in the domains of linearized and non-linearized supersonic flows for minimum drag design of two- and three-dimensional wings and bodies of revolution are given in the next two parts, which also include an interesting exercise in the design of maximum-thrust rocket nozzles. This is followed by the consideration of slender and non-slender shapes at hypersonic speeds and in free-molecule flows in the final three sections.

The book is essentially a compilation of original contributions, but careful editing by Prof. Miele, who has himself contributed significantly in this field, has enabled a degree of uniformity to be achieved in the overall presentation. The book is unhesitatingly recommended as a reference to workers in the field, and to a lesser degree, as a classroom text in view of the advanced level of the treatment.

D. M. RAO

HIGH SPEED PULSE TECHNOLOGY: Vol. I — CAPACITOR DISCHARGES–MAGNETOHYDRODYNAMICS–X-RAYS–ULTRASONICS by Frank Früngel (Academic Press Inc., New York), 1965, Pp. xiii+620. Price $ 24.00

Very rarely one comes across a scientific work which is so expertly written and encompasses such variety of diverse applications in a single volume as the treatise produced by Dr Frank Früngel which presents the entire field of capacitors and their associated circuitry in relation to high voltage and high current pulses. The original text is in German and has been expanded almost 60 per cent in the English version. The translation of the original German work into English has been done exceedingly well.

The text is rich in its scientific content and covers detailed deliberations on diverse subject matter such as MHD, plasma guns, high temperature phenomena, exploding wires, high magnetic fields, shock waves, metal forming techniques, etc. These things have been treated in a phenomenological way by the author with excellent illustrations and direct approach in the method of treatment of the entire subject. The subject matter is lucid and should be very useful to both the students and the professional as a text as well as a reference work.

Vol. I is divided into 10 chapters covering 500 and odd pages with three chapters in the second volume. The author has touched upon basic considerations in respect of capacitors in various simple circuits and then gone on to switching techniques, line conductors, conversion of capacitor energy to voltage pulses and interesting applications, such as X-ray flashes, neutron generators, high temperature plasma, creation of very intensive magnetic fields and metal forming.

The second volume deals with fast nanosecond techniques at high power levels and general high speed cinematographic and communication techniques, including laser applications.

Another very important feature of the book is its excellent scientific bibliography covering over 1000 references to original works. The subject index is very detailed and runs into some 15 pages. Indeed the author deserves congratulations and thanks for not only bringing out such a classic but for completing it, as Prof. Edgerton points out in his foreword.

P. K. PATWARDHAN

THE BIOCHEMISTRY OF ANIMAL DEVELOPMENT: Vol. I — DESCRIPTIVE BIOCHEMISTRY OF ANIMAL DEVELOPMENT edited by Rudolf Weber (Academic Press Inc., New York), 1965. Pp. xiii+648. Price $ 23.00

The two-volume treatise proposes to provide an introduction to a biochemical interpretation of developmental mechanisms.

Vol. I which covers descriptive biochemistry of animal development is divided into three parts: (1) Biochemistry of ovum and fertilization, (2) The role of biochemical patterns in embryogenesis, and (3) Informational molecules and embryonic development. J. Brachet presents a clear picture of the history of chemical embryology. J. Williams reviews the chemical constituents and physiology of the eggs. Although much is known of the physiology of eggs, the submolecular constitution of the eggs or of the control mechanisms regulating cytodifferentiation of the mosaic eggs is not well known. Alberto Monroy gives an excellent review of the biochemical aspects of fertilization, with particular reference to changes in metabolism. The general suggestion is made that maturation of the egg inhibits the metabolic activities residing in the cytoplasm and the nucleus; fertilization may remove the repressor(s) resulting in an expression of the nuclear genetic system.

One of the most complex aspects of embryogenesis is the progressive differentiation of many types of cells from a single fertilized egg. The differentiation of structures dependent on the development of enzymes, activation of genes and DNA-dependent RNA and protein synthesis as a result of response to intrinsic and extrinsic factors acting on the chromosomal apparatus, have been ably discussed at length by Tryggve Gustafson, J. R. Collier, E. M. Deuchar, Florence Moog, J. B. Solomon, Matthys Staehelin and Philip Grant. The repressor control circuits suggested by Jacob and Monod and the relationship of allosteric inhibition of enzymes serves as an important working hypothesis for the analysis of development. This, however, may not be the only mechanism accounting for sequential changes seen during development. This volume marks a landmark in our understanding of the biochemistry of the intricate processes of early development and differentiation. There is no doubt that this book will be most valuable to all interested in the subject.

M. R. N. PRASAD

PHYSICO-CHEMICAL TECHNIQUES OF ANALYSIS: Vol. I, by P. B. Janardhan (Asia Publishing House, Bombay), 1965. Pp. viii+356. Price Rs 32.00

This text-book is primarily intended for the student who has a genuine interest in instrumental methods of analysis. There are not many books written by Indian authors on the level of this text. The contention of the author that every topic in this book has been developed right from its elementary stage may, however, be questioned. During the past decade few branches of research in chemistry have experienced the rapid advances comparable to those associated with the technique of analysis. The compact treatment in this book of the modern methods of instrumental analysis provides a theoretical background as well as some useful practical details.

The topics dealt with in consecutive chapters are: absorptiometry, conductometric and high frequency analysis, chromatography, spectrography, Raman spectroscopy, mass spectrometer, X-ray methods of analysis, and magnetography. Index and numerous references in the text are adequate for advanced reading.

It is difficult to assess the quality of a text-book without giving it a fair trial in a regular course of teaching at the advanced level. Out of the topics incorporated in this book there are some which are quite comprehensive, while the presentation of others could probably be improved. A typical example is the thorough treatment of chromatography and optical methods of analysis. The chapters on high frequency titrations, magnetochemical analysis and coulometry deserve further elucidation. Many of the diagrams also leave much to be desired. An elementary treatment of electronic circuits would have been a welcome addition. This is not, however, a serious deficiency and the book should find wide acceptance among teachers and students of analytical chemistry. Dr Janardhan has managed an excellent organization of material and the book deserves a place in all libraries which claim to provide analytical literature.

G. S. DESHMUKH

STARCH: CHEMISTRY AND TECHNOLOGY: Vol. I — FUNDAMENTAL ASPECTS edited by R. L. Whistler and E. F. Paschall (Academic Press Inc., New York), 1965. Pp. xviii+579. Price $ 22.00

This book is the first of a set of two volumes of a competent review on various fundamental aspects of the chemistry and technology of starch and comprises 21 chapters written by authors who are recognized for their experience and knowledge of the subject.

While information about analytical and experimental procedures and specialized methods required for work on starch and its various fractions has already been covered by another recent publication of the Academic Press, forming Volume IV of the series in 'Methods in Carbohydrate Chemistry', the present volume is mainly concerned with the fundamental aspects of starch chemistry in which information on analytical and experimental laboratory procedures is restricted.

The first three chapters of the book deal with the historical and economic aspects of the starch industry and discuss its future. This is followed by four chapters on the occurrence and development of starch in plants and genetic control of its development, minor constituents of starch and fundamental concepts on the enzymic synthesis of starch in plants and pathways of enzymic conversion of starch into D-glucose.

The oligo- and megalosaccharides of starch, their structural analyses and uses are described in the next chapter which is followed by a chapter describing an interesting group of substances known as cyclomyloses, cyclodextrins or Schardinger dextrins. These are macrocylic non-reducing D-glucosyl polymers containing six or more residues bonded by α-(1→4) linkages. The method of separation of members of this group differing in degree of polymerization is based on the interesting method of their selective precipitation exploiting the variation in the diameter of the cavity of the ring. Fully acylated members of this group have been used recently as the stationary phase of gas liquid chromatography and need for further research in this field has been stressed.

The next two chapters deal with the evidence on the structure of starch which includes the application of X-ray methods. This is followed by chapters on gelatinization of starch, its organic complexes, fractionation of starch, physical properties of amylose and amylopectin in solution and mechanical properties of starch paste.

Development of low-cost radiation sources has made it possible these days to utilize radiation for sterilization of food materials. This has made it imperative to study the effect of radiation on starch, which is fully covered by the next chapter, which includes also the effect of radiation on cellulose and other polysaccharides.

The last four chapters describe the various degradative and non-degradative reactions of starch. The non-degradative reactions involve mainly the esterification and oxidation at C 2, C 3 and C 6 positions leading to interesting and useful products. The degradative reactions described are pyrolysis of starch for the production of various types of pyrodextrins, acid hydrolysis for the production of D-glucose, other lytic reactions, such as acetolysis, hydrogenolysis, hydrozinolysis and methanolysis and alkaline degradation of starch. This volume helps one in having a close look at the rapid advances which have been taking place in recent years in the chemistry of starch. It will be a valuable reference book for carbohydrate chemists and for those who are concerned with fundamental and applied aspects of starch chemistry.

The printing and get-up of the book are excellent.

J. L. BOSE

PUBLICATIONS RECEIVED

COMPUTERS IN BIOMEDICAL RESEARCH: Vol. 2, edited by R. W. Stacy & B. Waxman (Academic Press Inc., New York), 1965. Pp. xix+363. Price 112*s*.

APPLIED INFRARED SPECTROSCOPY edited by D. N. Kendall (Reinhold Publishing Corp., New York), 1966. Pp. xv+560. Price $ 23.00

FLUIDIZATION AND RELATED PROCESS — A SYMPOSIUM (Council of Scientific & Industrial Research, New Delhi), 1966. Pp. xi+271. Price Rs 24.00; 48*s*.; $ 8.00

THERMOANALYTICAL METHODS OF INVESTIGATION by Paul D. Garn (Academic Press Inc., New York), 1965. Pp. xvi+606. Price $ 19.50

APPLICATIONS OF MASS SPECTROMETRY TO ORGANIC CHEMISTRY by R. I. Reed (Academic Press Inc., New York), 1966. Pp. ix+256. Price 63*s*.

MASS SPECTROMETRY edited by R. I. Reed (Academic Press Inc., New York), 1965. Pp. x+463. Price 105*s*.

RADIATION DAMAGE IN GRAPHITE, International Series of Monographs in Nuclear Energy, Vol. 102, by J. H. W. Simmons (Pergamon Press Ltd, Oxford), 1965. Pp. xii+242. Price 80*s*.

FUNDAMENTALS OF CHEMISTRY: A MODERN INTRODUCTION by F. Brescia, J. Arents, H. Meislich & A. Turk (Academic Press Inc., New York), 1966. Pp. xv+816. Price $ 8.95

PROBLEMS IN PARTICLE PHYSICS by A. N. Kamal (McGraw-Hill Book Co. Inc., New York), 1966. Pp. vii+126. Price 38*s*.

VIBRATIONS, WAVES AND DIFFRACTION by H. J. J. Braddick (McGraw-Hill Book Co. Inc., New York), 1966. Pp. x+217. Price 36*s*.

CLASSICAL MECHANICS by T. W. B. Kibble (McGraw-Hill Book Co. Inc., New York), 1966. Pp. xv+296. Price 42*s*.

RECENT PUBLICATIONS

RADIATION BIOLOGY: Part 1, edited by A. Zuppinger (Springer-Verlag, Berlin), 1966. Pp. 680 approx. Price $ 60.00

RADIATION BIOLOGY: Part 2, edited by A. Zuppinger (Springer-Verlag, Berlin), 1966. Pp. 640 approx. Price $ 57.50

INTEGRATED CIRCUIT ENGINEERING — BASIC TECHNOLOGY by G. R. Madland, R. L. Pritchard, H. K. Dicken, D. B. Kret, R.D. Richardson, F.H. Bower and others of the staff of Integrated Circuit Engineering Corporation, Phoenix, Arizona (Boston Technical Publishers Inc., Massachusetts), 1966. Pp. 408. Price $ 22.50

NOTES & NEWS

A new massive nuclear particle

The discovery of the most massive nuclear particle known so far has been reported [*Phys. Rev. Lett.*, **16** (18 April 1966), 16]. The new particle, a nucleon resonance (observed only in particle accelerators) known as N*3245, is three and a half times as heavy as a proton. The lifetime of the new particle (longer than 10^{-22} sec.) is fairly long by nucleon resonance standards. The long lifetime is believed to be due to the particle having a greater spin than other nucleon resonances. Though the place of the new particle in the general scheme of the nucleus has not been decided, it is said to belong to the proton family.

The N*3245 was discovered in the complex reaction of particle production and decay that followed a 180 degree elastic scattering of pi mesons and protons. The pi mesons, produced by beaming protons at 13·5 GeV. of energy using a zero gradient synchrotron into a copper target, were scattered into protons in liquid hydrogen and the resulting particle reactions were recorded on a scintillation counter.

Use of solid state detector for X-ray spectroscopy

A new system of detectors for use in X-ray emission spectroscopy studies, viz. the use of semiconductor diodes as detectors, has been developed at the University of California's Lawrence Radiation Laboratory, Berkeley, USA. In the system used in the laboratory, gamma rays from radioisotopes are used as the primary radiation and the semiconductor diode detector converts secondary X-rays emitted by the sample to an electrical signal at high efficiency. A complete spectrum of the samples' characteristic emissions, with energy peak resolution of about 1 keV., is obtained and displayed in a few seconds of operation. This arrangement eliminates the high voltage X-ray tube used as the primary radiation source in conventional X-ray spectrography. The only electrical input required is a 120 V. line current which could be had from a portable battery powdered unit.

In conventional X-ray spectrography, since the X-rays from the sample are scattered by a crystal surface, the angle of diffraction varies with the wavelength and hence to plot a spectrum accurately small differences in angle of reflection must be determined with the use of a precision goniometer. The new system by contrast measures radiation intensities at all wavelengths simultaneously. The sample is exposed to gamma radiation from a radioisotope (americium-241 or cobalt-57) and secondary X-rays emitted by the sample pass through a thin beryllium window into the detector chamber, which operates under high vacuum. A semiconductor diode, either silicon or germanium depending on the range of elements being analysed, turns the radiation into an electrical input. The amplified signal produces a spectrum almost immediately as a pulse height analyser display with the proper combination of radioisotope and diode material. Overall efficiency of energy detection is 100 to 1 million times greater than that of a conventional X-ray spectrograph. Further, it is possible with this new system to produce clear spectra of *K* radiation peaks of characteristic X-rays of even heavy elements which cannot be excited by X-ray tubes using voltages usually available with conventional instruments.

The use of semiconductor detectors may open the way to a rugged, compact X-ray emission spectrograph adapted to field use as, for example, for a rapid analysis in a mine or an oil well. Further, in industry it can be used for fast, non-destructive, quantitative analyses of elements present in milligram or smaller quantities in a sample. One defect of the system is that the noise level may set a lower limit on the energy spectra available and spectra of elements below scandium in the periodic table are not resolved at present by the system. However, it is hoped that the noise level can be reduced sufficiently by equipment refinement [*Chem. Engng News*, **44** (No. 1) (1966), 42].

Two new X-ray galaxies

Two new X-ray galaxies with powers 100 times greater than their combined radio and optical ' brightness ' have been identified by Dr H. Friedman and his colleagues at the US Naval Research Laboratory. The new galaxies, Cygnus A and N-87, are among the strongest radio sources in the sky, and their X-ray strength is 10^{10} times that of the sun.

The discovery was made by a simple instrument during a five-minute flight above the atmosphere in an *Aerobee* rocket. Another important discovery made by this flight was that X-ray sources can fluctuate in power like the variable stars; Cygnus X_r-1, another galactic X-ray source first observed in 1964, recorded only a quarter of its original X-ray brightness.

The energy output of the two new galaxies cannot be explained by known physical processes. Friedman feels that either they are an entirely new class of celestial objects or the current theories of stellar energy processes needs revision [*Sci. J.*, **2** (No. 6) (1966), 11].

Complete star catalogue

The first comprehensive catalogue of stars that can be used for finding the positions of nearly 250,000 heavenly light sources, prepared by the Smithsonian Astrophysical Observatory, Cambridge, Massachusetts, is now available from the Superintendent of Documents, US Government Printing Office, Washington DC 20402.

The new catalogue has been produced with the help of an electronic computer by combining in one, uniform, four-volume, 2700-page compilation, all the available information on star locations hitherto scattered in various separate star atlases. Before this compilation was available, astronomers sometimes had to consult as many as 50 different sources to check the position of a star they were scanning. The precise information was assembled by a team of astronomers, mathematicians and computer programmers and reduced to a common reference system. A special 'electronic printing' procedure, involving computer programmed tapes and photographing, on to printing plates, the signal images on a TV-like tube produced by the tapes, saved the costly and tedious job of type setting and proof reading this formidable amount of closely packed numerical data.

The catalogue gives the position, proper motion photographic and visual magnitude, spectral type and other essential data for each star, thus providing an instant reference to the entire sky. The catalogue identifies and locates every known star in the heavens down to those of the ninth magnitude as well as many much more faint. Under the best conditions, stars of sixth magnitude can be seen by the naked eye; a good binoculars will show stars of ninth magnitude.

One of the first uses of the catalogue is in the preparation, now in progress, of the most accurate maps of the heavens ever produced. The catalogue, in a hardbound edition, is priced $ 20 [*Sci. News*, **89** (No. 17) (1966), 297].

Equilibrium constants of incompletely ionized electrolytes

Equilibrium constants for the ionization and dissociation of incompletely ionized electrolytes in liquid ammonia have been determined for the first time. Dr J. J. Lagowski of the University of Texas, Austin, has developed a spectrophotometric technique to study the equilibria between a weakly acidic electrolyte and its ion (Eq. 1) and an ion pair and its dissociated ions (Eq. 2)

$$HX+NH_3 \overset{K_i}{\rightleftharpoons} (NH_4^+,X^-) \quad ...(1)$$

$$(NH_4^+,X^-) \overset{K_d}{\rightleftharpoons} NH_4^+ + X^- \quad ...(2)$$

o- and *p*-nitroacetanilides were among the first compounds to be studied. The ionization constant for the *ortho* isomer is 2×10^{-2} at -55°C. and the dissociation constant 2×10^{-4}. For the *para* isomer the constants are 9×10^{-2} and 10^{-4}. The spectra of both the anilides in ammonia, and in acidic and basic media suggest that they behave like partially ionized acids. They are characterized by two bands, a low wavelength band corresponding to the unionized molecule and a high wavelength band corresponding to the anions and the ion pairs. The addition of electrolytes like potassium iodide do not change the shape or position of the bands indicating that an ion aggregate containing an anion cannot be distinguished spectrally from the free anion; however, the intensity of the low wavelength bands changes markedly indicating that the position of equilibrium changes with change in the activity of the species in solution.

The degree of ionization can be calculated from the spectral data. For both anilides at -55°C. and 10^{-4} molal, it is about 25 per cent.

Another compound that has been studied is *o*-nitrophenol. In liquid ammonia it has an equilibrium constant of $3{\cdot}90\times10^{-4}$ at -33°C. But the spectral data indicate complete ionization. Therefore the reported equilibrium constant corresponds to the dissociation constant, K_d.

Dr Lagowski plans to use this new method to establish a scale of acidities in liquid ammonia solutions [*Chem. Engng News*, **44** (No. 3) (1966), 51].

Gel technique for growing crystals

A gel technique for growing crystals developed at the Pennsylvania State University is particularly suitable for certain materials which defy conventional growth processes like those that resist all plausible solvents or those which cannot withstand heat. The method depends on the diffusion and reaction of chemicals within a silica gel, and when properly done it yields crystals of high optical perfection and large size, hitherto unattainable. The gel used is effectively a three-dimensional network of quartz. Because of its physical nature, the gel yields to the growing crystals, permitting them to expand without external restraint. In contrast to growth process in solution, in the new method, the crystal grows in a non-turbulent environment. Mercuric iodide, lead iodide, thallium iodide, lead sulphide, calcite, silver oxalate and various citrates and tartrates are among the compounds crystallized so far by the new technique, either in the pure state or with controlled additives to modify the crystal properties. Some of the crystals exhibit light sensitive electrical properties which may be of practical interest [*Sci. J.*, **2** (No. 1) (1966), 7].

Valence isomerization of a *cis*-dienone to an α-pyran

The valence isomerization of *cis*-dienones to α-pyrans has been earlier invoked to explain certain otherwise enigmatic results without isolating the species. The first example of such a valence isomerization has now been provided.

A sample of 1-oxa-2,5,5,9-tetramethyl - 1,5,6,7,8,10 - hexahydronaphthalene has been isolated by irradiation of trans-β ionone. The NMR spectrum of the product is in complete accord with α-pyran structure for the product except for a series of weak bands which had two striking features: (i) they were not removed by further purification of the pyran; and (ii) formed a part of a series of bands expected for unknown *cis*-β-ionone. It was further noted that the spectrum of *cis*-β-ionone showed an increase in intensity with increasing temperature and consequent decrease in the intensity due to α-pyran. The total spectrum reverts to its original form when the temperature is returned to normal.

The rate of valence isomerization has been determined by perturbing the equilibrium and measuring the rate of reversion. The rate is followed by measuring the decrease in the peak height of the larger peak in the doublet at δ 6·03. In view of the high rate of dienone to pyran isomerization the failure to isolate both valence isomers earlier seems reasonable [*J. Amer. chem. Soc.*, **88** (1966), 619].

A new calcium silicosulphate

While studying the high temperature phase equilibria in the system $CaO\text{-}SiO_2\text{-}SO_3$, a new compound of molar composition $(2CaO.SiO_2).CaSO_4$ has been located. The compound has been prepared from calcium carbonate (99·9 per cent pure), crushed quartz (99·95 per cent pure) and AnalaR $CaSO_4\,2H_2O$ by ignition for 150 hr at 1150°C. in platinum boats in a platinum-rhodium resistance furnace. For successful preparation the mixture has to be finely ground (300 mesh sieve) in between periods of heating. X-ray diffraction pattern gave the indication of compound formation after about 2 hr heating. On continued heating, the X-ray diffraction patterns of the reactant and dicalcium silicate became progressively weaker until, after 150 hr, they reached intensity levels representative of trace quantities.

The X-ray diffraction pattern of the new compound resembles that of a compound detected earlier by Sundins and Peterson [*Radex Rundschau*, (1960), 100] as a green mineral which colours the sulphate rings accumulating in cement rotary kilns. The optical properties of the two compounds are also similar and both compounds are coloured green in ordinary. The slight differences in X-ray pattern may be due to the impure compound from the rotary kilns [*Nature, Lond.*, **210** (1966), 408].

New method for studying mammalian melanocytes *in vivo*

A new method developed by Snell *et al.* of Yale University School of Medicine for studying mammalian melanocytes enables the observer to study the activity of a single melanocyte or a group of melanocytes in their natural undisturbed environment for a considerable length of time.

The method consists in anaesthetizing black C_{57} mice (3-4 weeks old) with 'nembutal' (80 mg./kg. body weight) given intraperitoneally. The hairs of the pinna of the ear are removed by a depilating agent (Neet). Glycerine is gently massaged into the epidermis to improve the optical properties of the epidermis so that the melanocytes become more clearly visible.

The dorsal surface of the pinna is placed downwards on to a glass slide and the edges are glued in position with rubber cement. The microscope objectives are then lowered on to the pinna and glycerine added to immerse the lens. A particular field can be observed continuously for a number of hours. It has been observed that ether plus 'nembutal' is a satisfactory combination, if the melanocytes are to be observed for a long time.

The method is simple as compared to the earlier methods for observing melanocytes either by a split skin preparation or by tissue culture and is particularly suited to time-lapse photography. It is being used to study the influence of hormones and other agents on the morphology of mammalian melanocytes, and the circulatory and follicular changes accompanying the hair cycle [*Nature, Lond.*, **210** (1966), 219].

Progress Reports

Paint, colour and allied research in Britain

The thirty-eighth annual report of the Research Association of British Paint, Colour and Varnish Manufacturers for the year ending 30 June 1964 reviews the major research activities of the Association. The main areas of work have been: (1) pigment media; (2) pigment-medium relationship and paint making; (3) paint application and properties of paint films.

Water-based coatings received priority of attention. Studies have been carried out on glossy emulsion type coatings, particularly on the factors limiting the gloss, the aim being to obtain a better understanding of film-formation. The various reactions in water-soluble alkyd-amino resin systems on storage have been studied, particularly the behaviour of the alkyd or polyester component, ageing conditions being so chosen that essentially only hydrolytic stability was considered. Studies on curing of water-soluble alkyds with hexamethoxy methylmelamine have indicated that stoved films of alkyd/hexamethoxy methylmelamine are considerably more flexible than corresponding films prepared using a partially methoxylated melamine as cross-linking agent. This has been attributed to the greater tendency of the polymethylated melamine to react with the alkyd rather than with itself. Among other problems under active research are yellowing of drying oils; curing of films from two-pack systems based on organic polyisocyanate adducts and hydroxyl terminated polyesters; constitution of fish oils in relation to their performance; evaluation of heavily fluorinated compounds as resin components; and evaluation of adhesion and dispersion promoting capacities of different organo-metallic compounds.

Priority has been given to studies aimed at increasing the efficiency of paint milling and improving the ease of dispersion and dispersion stability of paints. Infrared spectroscopic studies have been conducted on pigment-medium interface to determine the nature of adsorbed layers on pigment surfaces. The flocculation behaviour of phthalocyanine pigments in alkyd media has been investigated, with particular reference to the effects of particle size and the extent of flocculation. Detailed studies on the electrophoretic behaviour and stability of dispersions of pure rutile titanium dioxide in solutions of Aerosol OT in xylene have shown that a striking correlation exists between surface potential and flocculation, although not in direct relation to the adsorption of the agent. Data obtained using alumina, carbon black and copper phthalocyanine green point to the importance of the nature of the solid surface in stability behaviour of dispersions in non-aqueous media.

Studies on the effect of surface contaminants on the adhesion of paint films have shown that addition of trace amounts of various fatty and other organic acids to the surface affects adhesion in several ways. Reduction of the low molecular polar component and blocking of hydroxyl groups improves the adhesion of alkyd paints. Small additions of hydrocarbon oils and waxes to a paint have been found to give a hydrocarbon-rich surface layer.

In connection with studies on the mobility of ions in paint films, the effect of level of pigmentation or the application of a potential difference on the release of ions from, and the movement of ions through, chromate pigmented epoxide/polyamide films has been investigated. Considerable differences have been observed in the effect of pigmentation on the rate of release of ions from films containing zinc potassium chromate compared with strontium chromate pigmented films.

An accelerated dirt pick-up test using an electrostatic precipitator indicated a close connection between tackiness and dirt pick-up of gloss paints. A number of factors affecting dirt pick-up have been studied and it has been found that the presence of crystalline bloom can increase dirt pick-up especially at high humidities.

New Periodical

Indian Geohydrology

The first volume (October 1965) of this new journal, the organ of the Indian Association of Geohydrologists, contains in addition to the speeches made during the inaugural meeting of the Association held on 23 December 1964, a number of research reports which will be of interest not merely to geohydrologists but also to geologists, irrigation engineers and even soil physicists. The volume is priced at Rs 6. Further information may be had from the Indian Association of Geohydrologist, Geological Survey of India, Lucknow.

Dr B. D. Tilak

Dr B. D. Tilak has been appointed Director, National Chemical Laboratory, Poona.

Dr Tilak (*b.* 26 September 1918) had a brilliant academic career at Bombay University taking his B.Sc. (Chem.) and B.Sc. (Tech.) degrees in 1937 and 1939 respectively. Immediately after, he took to teaching and research in the same university and was awarded Ph.D. degree in 1943. He proceeded to Oxford in 1944 and received his D.Phil. degree from Oxford University in 1946. He has been holding teaching and research posts in the Department of Chemical Technology, Bombay University, since 1940. He became Professor of Dyestuff Technology in 1950 in the same Department.

Organic chemistry and chemical technology have been the major fields of research carried out by him and he has made valuable contributions in these fields. He has been the Investigator-in-Charge for a number of industrial and fundamental research schemes of CSIR and other bodies, and his work in dyestuff technology has earned him a name in industry. He has published over hundred original research papers in Indian as well as foreign scientific journals on pure and applied organic chemistry. He was awarded the Basudev Banerjee Medal and Prize for the year 1959-60 by the Indian Chemical Society for his contribution in organic chemistry and K. G. Naik Gold Medal by the Baroda University in 1959 for the best contribution made by an Indian chemist in the field of industrial research during the last 5 years. He is consultant to Indian Dyestuff Industries, Kalyan, and Messrs Aniline Dyestuffs & Pharmaceuticals Private Ltd, and his guidance is being utilized by many other firms.

In 1951 he attended, as a Government of India delegate, the Diamond Jubilee Celebrations of the American Chemical Society. He visited dyestuff factories in USA and Western Europe in 1952. During 1960-61, he proceeded to Harvard University and worked under Prof. R. B. Woodward. In 1961, he was awarded D.Sc. degree in organic chemistry by the Oxford University. He visited Poland, East and West Berlin, Czechoslovakia and Yugoslavia in 1962 as consultant to Aniline Dyestuffs & Pharmaceuticals Pvt Ltd, and participated in the Second International Colour Symposium held at Schloss Elman, West Germany, in April 1964.

Dr Tilak has been associated with CSIR as a member of its Pharmaceutical & Drugs Research Committee during 1959-62. At present, he is a member of the Board of Scientific & Industrial Research and its Sub-Committee and Working Group of CSIR on its plans for Fourth Five Year Plan. Dr Tilak is a Fellow of the National Institute of Sciences (India), and the Academic Council and Technology Faculty, University of Bombay. He is a member on several scientific research and cultural organizations including ISI Committee on standardization of dyes for food, and coal tar intermediates.

Announcement

▪ *Kalinga Prize Award for* 1966 — Dr Eugene Rabinowitch, editor and one of the founders of the *Bulletin of the Atomic Scientists*, has been selected as the fourteenth winner of the Kalinga Prize for popularization of science. Dr Rabinowitch has had a long and distinguished career both as a scientist and as a leading figure in international cooperation in science. After studying chemistry in Germany, he worked with Niels Bohr in Copenhagen in 1933. He went to the United States in 1938 where he took part in the Manhattan Project. He became the editor of the *Bulletin of the Atomic Scientists* in 1945. He has been taking an active part in the ' Pugwash ' movement. As early as 1945, he coauthored a report warning against the political consequences of nuclear weapons.

Since 1947, Dr Rabinowitch is a member of the faculty of the University of Illinois. Apart from numerous scientific articles written in the past 40 years, Dr Rabinowitch has to his credit books on uranium chemistry, photosynthesis and the implications of modern science for the world of the present and the future.

FIRST GET-TOGETHER OF RESEARCH AND INDUSTRY PUBLICATIONS

The Council of Scientific & Industrial Research (CSIR) organized a two-day First Get-Together of Research and Industry in New Delhi during 20-21 December 1965.

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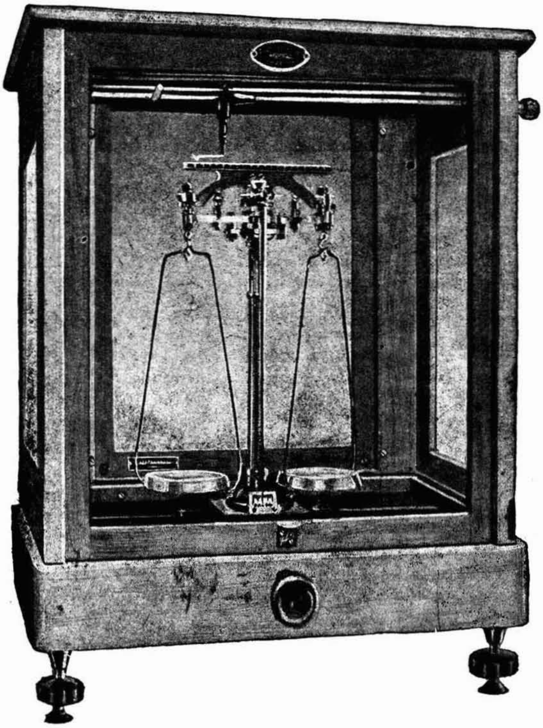

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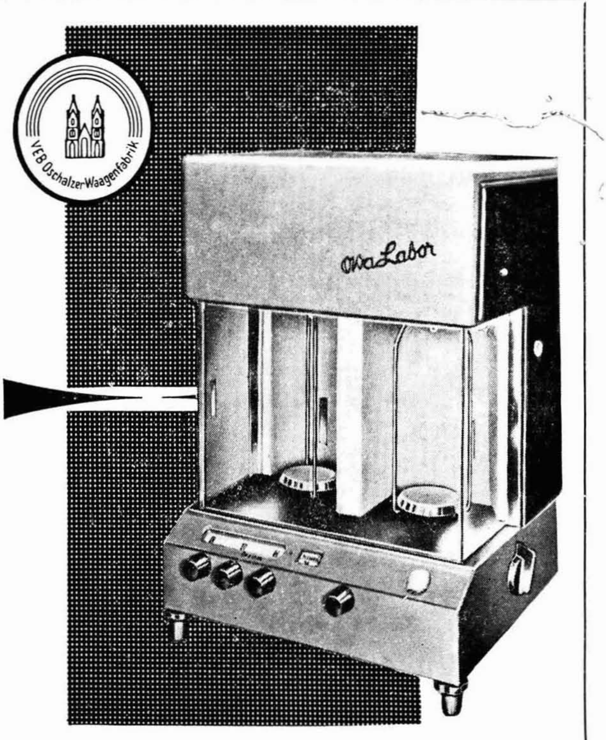

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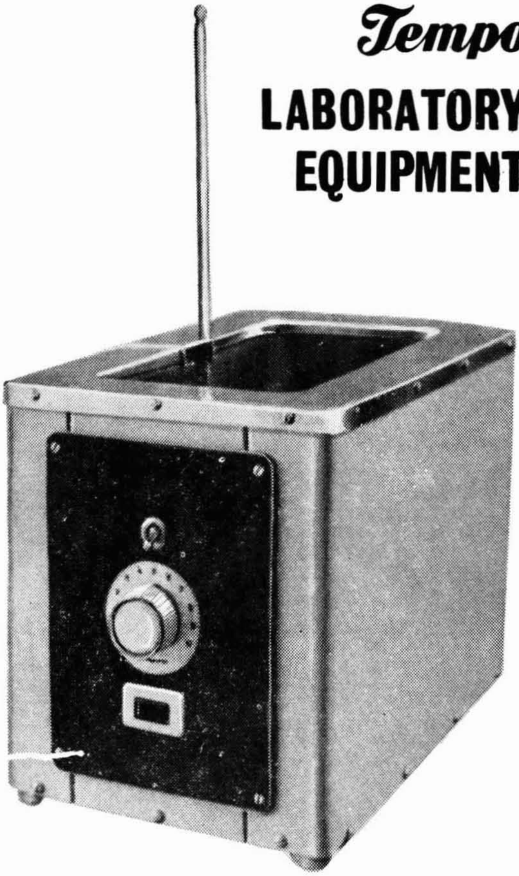

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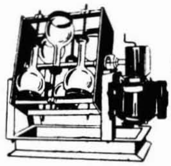

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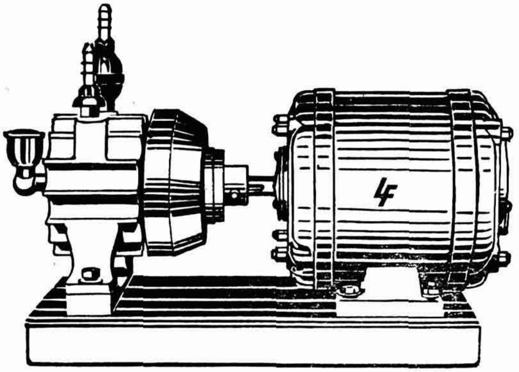

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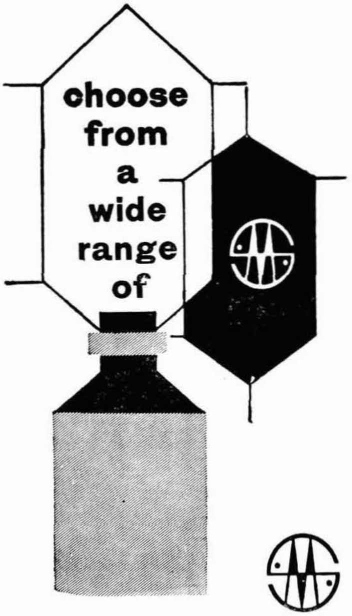

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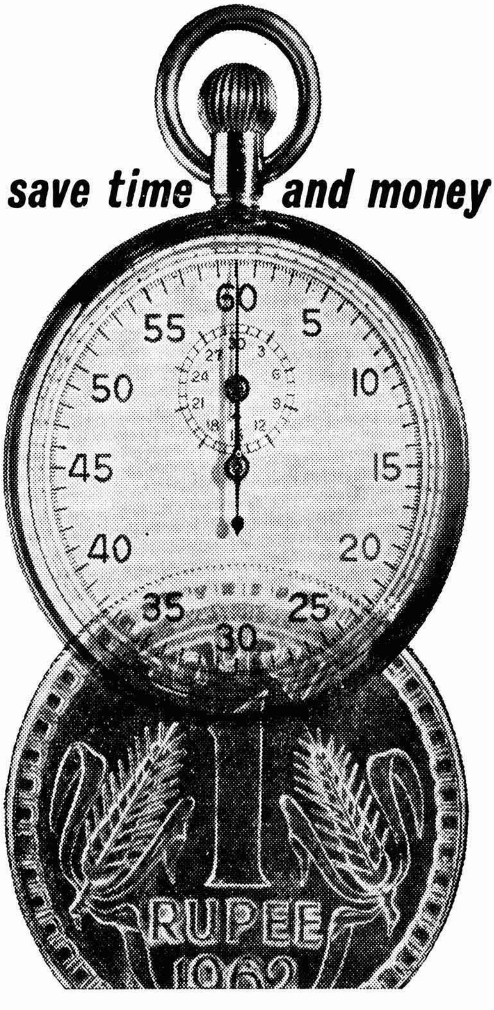

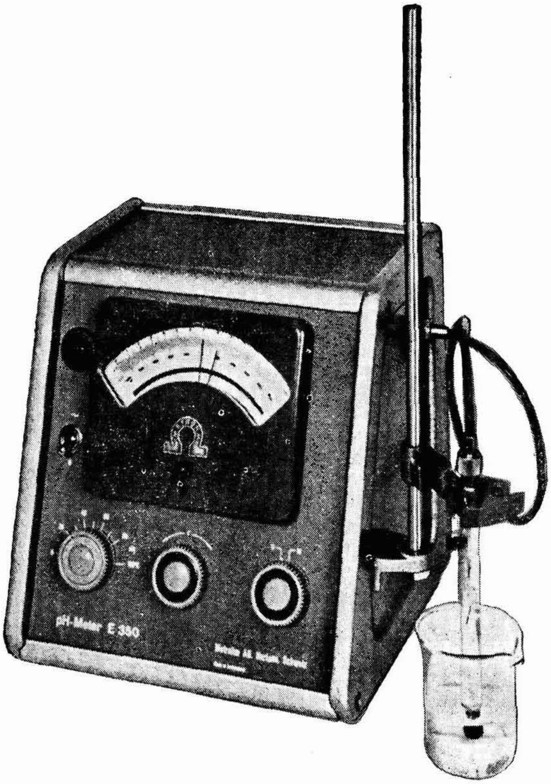

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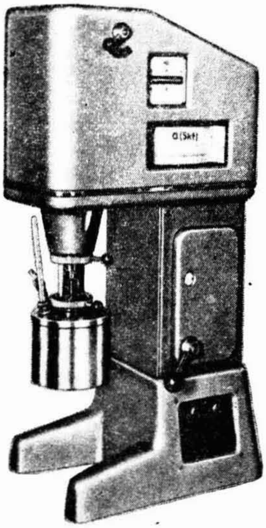

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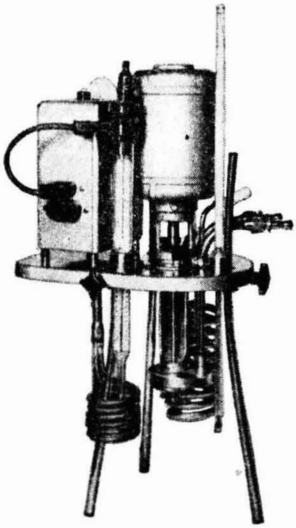

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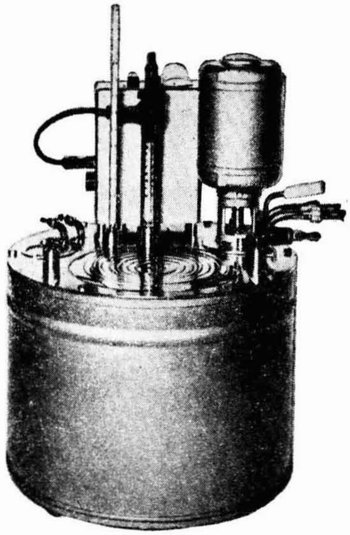

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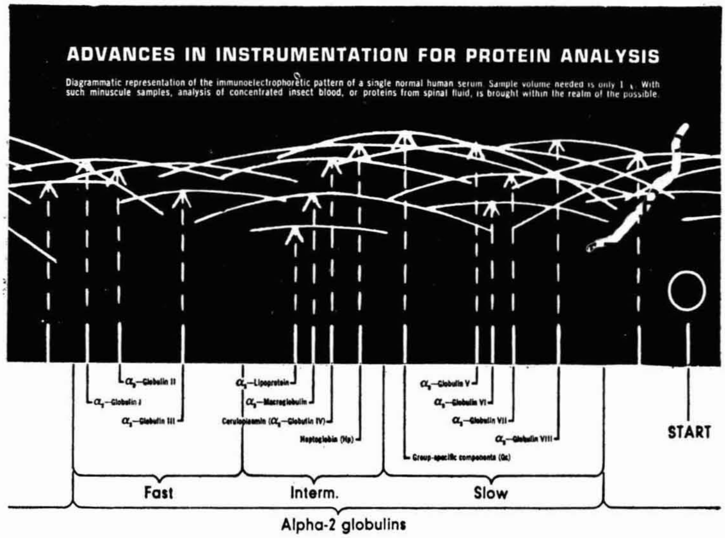

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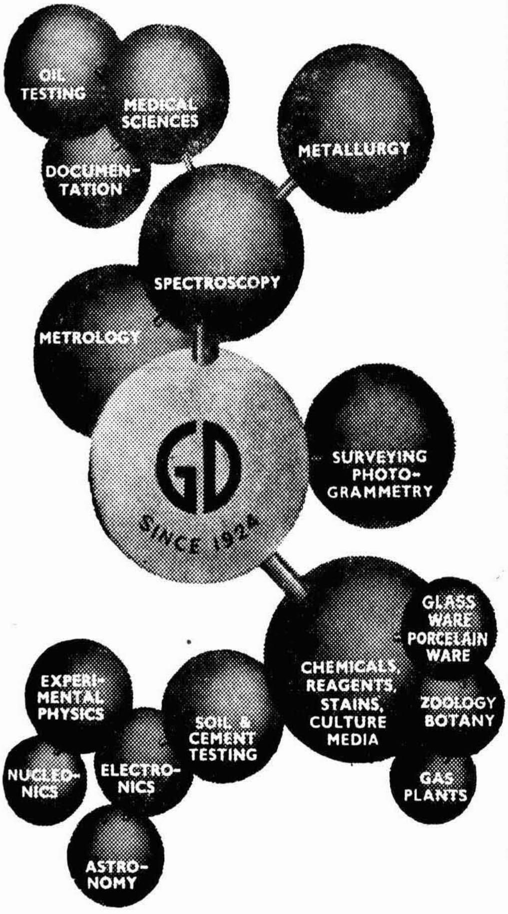

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