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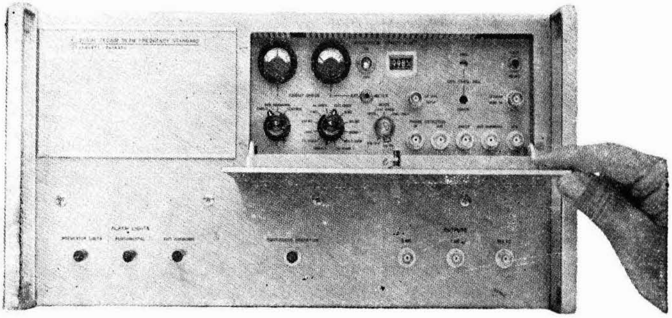

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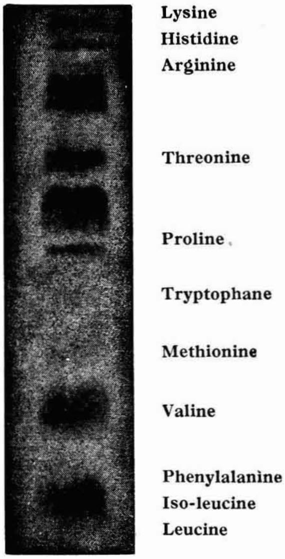

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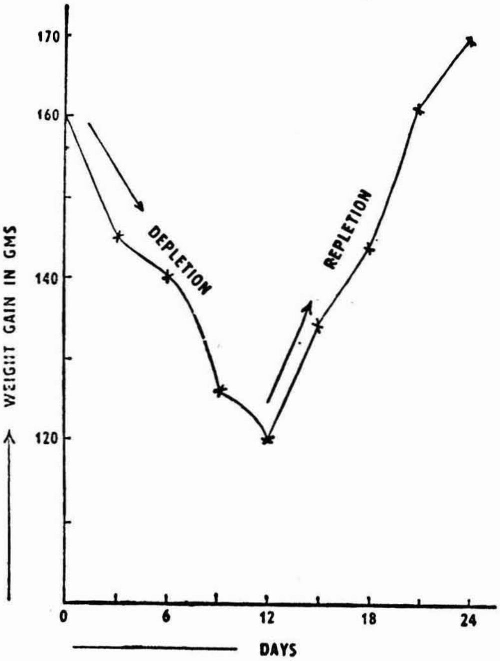

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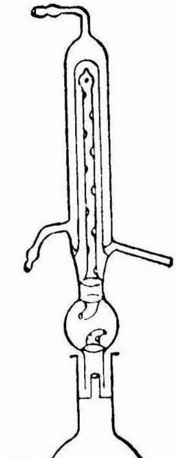

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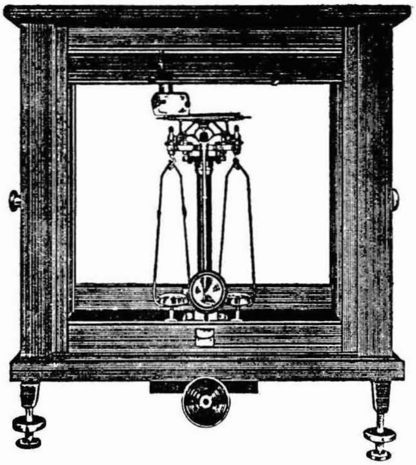

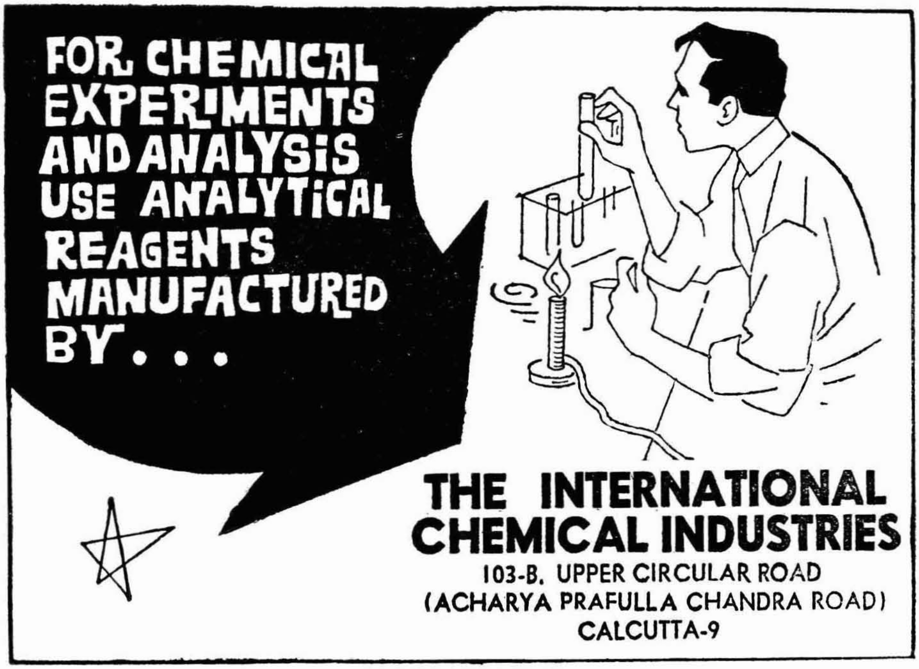

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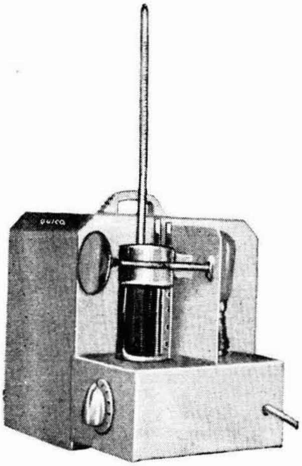

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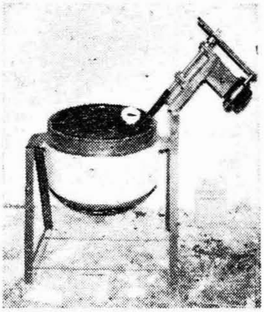

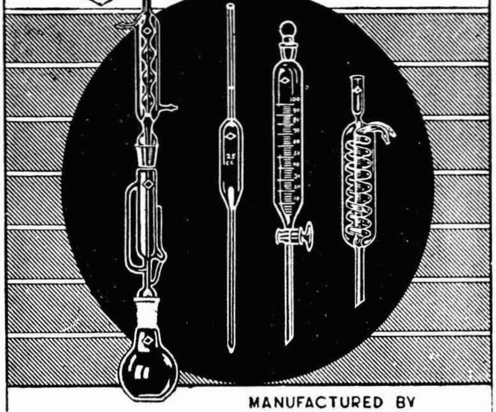

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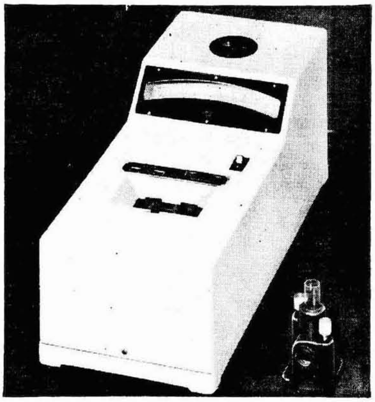

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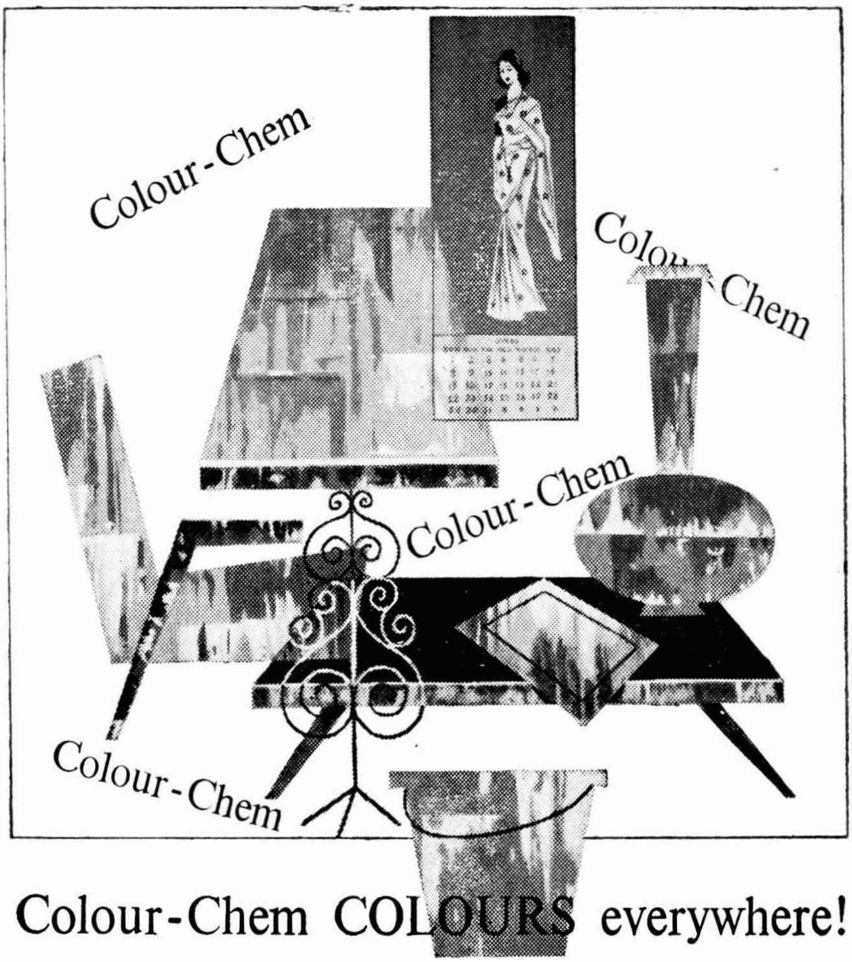
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Current Topics

Investment in Scientific & Technological Research during the Fourth Five Year Plan

INVESTMENT in scientific and technological research, with special reference to developing countries, has been a much debated subject. It is accepted that expenditure on research is a major national investment, and that the rate of growth of science and technology in developing countries should be faster to yield tangible results. However, it has often been difficult to make an objective assessment of such investment, which is an important prerequisite for any planned economic development programme. A working paper* recently prepared by Dr S. Husain Zaheer *et al.* is perhaps the first attempt to arrive at such an estimate. During the first three five-year plans, allotments for research were considered as part of the allocations made to various ministries and no separate allocations were earmarked for research. Specifically, the working paper deals with the question: What should be the quantum of investment in science and technology during the Fourth Plan period ?

Expenditure on scientific research during 1961-62 has been estimated at Rs 469 millions or 0·32 per cent of the national income. This is considered to be rather meagre and the working paper suggests that investment in research should be increased so that there is a substantial rise in the rate of growth of science and technology. In working out the total investment in research during the Fourth Plan period, the conclusions arrived at on the basis of earlier surveys†‡ have been taken into consideration, viz. (i) there is imbalance in support to research in different areas by the Central and State Governments, and (ii) the expenditure in a laboratory, irrespective of the research programme, follows a pattern depending upon the stage and level of its development and of its being capital intensive or otherwise. To remedy the situation indicated by these two surveys, the working paper has suggested a higher rate of growth for areas which have been neglected so far but are vital for national development. Also, taking into account the trend of research expenditure in the national laboratories, the working paper has worked out the quantum of investment on scientific and technological research by the Central and State Governments in various universities and research establishments, and by the organized industry.

It has been projected that the total investment on scientific and technological research during the Fourth Plan period, based on the rate of expenditure during the period 1957-58 to 1962-63, should be Rs 8897·2 millions or 0·79 per cent of the national income. This figure has been arrived at assuming a minimum of 5 per cent and a maximum of 25 per cent increase per annum in the growth rate of expenditure at the beginning and end of the plan period respectively. Capacity to absorb increased research allocations, level of development of the sector, relevance to national problems, availability of trained personnel, technological level and requirements of the sector, and other factors have been taken into consideration in suggesting this quantum of investment.

For the Central Government sector, 10 per cent of the total expenditure for the sector in 1965-66 has been taken as research expenditure on new projects for 1966-67, assuming that new projects will grow at the rate of 25 per cent per annum during the plan period. The data thus obtained reveal that the total projected expenditure in all sectors by the Central Government during the Fourth Plan period would be Rs 4446 millions. Of this, 21·8 per cent of recurring and 34·9 per cent of capital expenditure will go for the Atomic Energy Establishment, and 20·0 per cent of recurring and 37·7 per cent of capital expenditure will be incurred by the Council of Scientific & Industrial Research. Defence research will account for 10·5 per cent of recurring and 15·6 per cent of capital expenditure.

In respect of State Governments, it has been observed that the investment pattern of the States has ignored the role of science and technology in development programmes, and attention is largely concentrated on education and social programmes. It is pointed out that what is required is a greater quantum of investment by the States on scientific and technological research to promote the application of science and technology for industrial development. Therefore, a total outlay of Rs 740·8 millions is projected for research in various sectors by the States, of which the outlay for scientific and industrial research alone is Rs 150·5 millions.

Financing of research in universities and higher technological institutes has so far been restricted to ad hoc research schemes and fellowships. It is suggested in the working paper that university laboratories should be developed to take up research on advanced fundamental problems and establish advance centres or schools for research. In the absence of necessary data for arriving at a criterion

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**Investment in scientific and technological research during the Fourth Five Year Plan period*, S. Husain Zaheer, A. Rahman & N. Sen, Survey & Planning of Scientific Research Unit, Council of Scientific & Industrial Research, New Delhi.

†*Government expenditure on scientific research*, A. Rahman, A. Ghosal, N. Sen, N. R. Rajagopal, (Mrs) S. Das Gupta, S. H. M. Hussaini & A. K. Roy, *J. sci. industr. Res.*, **22** (1963), 479.

‡*A study of expenditure in national laboratories*, A. Rahman, A. Ghosal, N. Sen, N. R. Rajagopal, (Mrs) S. Das Gupta, S. H. M. Hussaini & A. K. Roy, Survey & Planning of Scientific Research Unit, Council of Scientific & Industrial Research, New Delhi.

for suggesting allocations for research in this sector, it is suggested that a provision of Rs 10,000 per teacher be made for research at the beginning of the Fourth Plan period and which may be increased to Rs 14,600 by the end of the plan period. It is estimated that there will be about 4000 teachers engaged in research at the beginning of the plan period and the number at the end of the plan period would be 8000. On this basis, the projected research expenditure in this sector has been estimated at Rs 388 millions.

Expenditure on research by the organized industry is meagre and the Central Government is by and large providing substantial support for research both in the spheres in which industry is much interested and in those in which it is not. It has been suggested in the working paper that a beginning should be made with an average outlay of 1 per cent of the value added by industry, i.e. one-fourth to one-fifth of the value of production in organized sectors of industry during the Fourth Plan period, and maintained at this level till the industry itself realizes the need for investing more. This 1 per cent investment, it is suggested, should be made available by an industrial unit to a research association on the basis of its installed capacity. On these premises, the projected expenditure by the organized industry has been put at Rs 193·44 millions in 1966-67 and Rs 343·11 millions in 1970-71, the total for the plan period being Rs 1317·14 millions or 14·8 per cent of the total investment on research.

As observed by the authors of this working paper, the document should serve as a basis for useful discussion and for initiating serious study of this important problem. This working paper should help not only in arriving at a broad-based decision as to the quantum of research investment to be made but also initiate intensive studies on the deployment of such investment for obtaining best results.

Fresh Water Resources & Desalination

IN the wake of rapid industrial and economic growth in different countries of the world, the problem of balancing the resources and requirements of fresh water has assumed great importance. In spite of the apparent abundance of water everywhere, a sizeable portion of water resources in most of the countries is brackish in nature, and, therefore, not directly available for any of its major uses — human, agricultural and industrial. The problem is of particular significance to some of the developing countries (notably those in the tropical regions), where large tracts of land with brackish water resources constitute an impediment to industrial and agricultural development programmes. The first organized attempt to tackle the problem at international level has been the recent survey of the water desalination problems in developing countries, conducted under the auspices of the United Nations, with the support of the Ford Foundation and the Office of the Saline Water of the United States Department of Interior. The survey covering 74 countries was aimed at (1) determining which water-short areas with economic growth potential in developing countries appear to have possibilities for the economic use of desalinated water; (2) collecting economic and technical data on plants, processes, etc., for operation in the countries and territories examined; and (3) making available information on costs, prices and utilization pattern of water from conventional sources. The report* of the survey (covering the period up to the end of 1962), while providing information on water conditions in water-short areas in 42 developing countries, discusses the recent advances in desalination technology, the principal desalination processes, their economics and related problems.

During the past few years intensive research activity has been going on in several countries in the field of desalination of brackish waters and a fair measure of success has been achieved in the development of economical desalination techniques suited to different conditions. The most promising lines of development have been the use of solar energy in regions where sunlight is available in abundance and the use of water distillation plants in conjunction with nuclear power reactors. According to a recent report from USA, a 1000-1500 MW capacity nuclear power generator can be expected to supply 500-800 million gallons of water per day at 20-25 cents per thousand gallons. In India, the main work in the field has been on solar water distillation and the development of ion-exchange resins and membranes at the Central Arid Zone Research Institute, Jodhpur; National Physical Laboratory, New Delhi; National Chemical Laboratory, Poona; and the Central Public Health Engineering Research Institute, Nagpur. While India can profitably take advantage of the technological advances elsewhere, her programmes of research and development in the field have necessarily to be oriented taking cognizance of her own regional and geographical conditions, and availability of fuel and other materials. Thus, while Rajasthan offers promise in respect of the exploitation of solar energy, the most economical fuels for the distillation plants in Gujarat area would be from petroleum crudes. Similarly, the projected nuclear power station in Madras State may provide the best means of solving the fresh water problem of the region if a distillation plant is planned on the basis of utilization of waste heat from the reactor. Ion-exchange resins based on indigenously available low-cost materials like cashewnut shell offer another fruitful line of development.

A prerequisite to the formulation of a policy and programme at the national level is the availability of accurate statistics on the existing fresh and brackish water resources as well as the pattern of water utilization on a countrywide basis. Also, a host of technological problems, both fundamental and applied, have to be solved. The problem of augmenting fresh water resources by desalination involves a diversity of factors — economic, geographical, climatic, etc., and it is necessary to work out a broad-based national policy and programme for the purpose. The task is best entrusted to a high power Desalination Board, more or less on the lines of the Office of the Saline Water of the US Department of Interior.

Water desalination in developing countries (United Nations, New York), 1964. Pp. 325. Price $ 4.00.

First Matscience Summer School, 1964

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THE First Matscience Summer School on Theoretical Physics was held in Bangalore from 24 August to 13 September 1964. When the idea of a summer school was proposed, the Council of Scientific & Industrial Research (CSIR) not only welcomed it but also extended financial support through a generous grant. Prof. Alladi Ramakrishnan was the Director of the Summer School and the entire organization as well as academic matters were left in the hands of the authorities of Matscience.

The school was inaugurated on the evening of 24 August 1964 by Dr S. Husain Zaheer, Director-General, CSIR. The academic sessions started from the morning of 25 August with four one-hour lectures a day. The Hon'ble Minister C. Subramaniam, patron of Matscience, visited the summer school and evinced keen interest in the lecture by the director on recent developments in high energy physics.

The summer school mainly consisted of invited lectures by seven foreign and eight Indian scientists. The foreign scientists who participated were Prof. R. Oehme, University of Chicago (USA); Prof. K. Symanzik, New York University (USA); Prof. E. R. Caianiello, Director, Institute for Theoretical Physics, Naples (Italy); Prof. W. Brenig, Max-Planck Institute (West Germany); Prof. F. Calogero, University of Rome (Italy); Dr A. Fujii, School of Science and Technology, Sophia University (Japan); and Dr J. Lukierski, University of Wroclaw (Poland). All of them were visiting scientists at Matscience. The invited Indian scientists were Prof. A. Ramakrishnan, Dr R. Vasudevan, Dr T. K. Radha, Dr N. R. Ranganathan and Dr K. Venkatesan (of Matscience), Dr V. Devanathan (Madras University), Prof. M. Venkataraman (Madras University, Madurai Centre), and Dr S. K. Srinivasan (Indian Institute of Technology, Madras).

The other participants at the summer school were mainly the research students of Matscience, lecturers from educational institutions in Madras, students from the Tata Institute of Fundamental Research, Bombay, and from the University of Roorkee, Roorkee. Besides these, a few scientists and research workers from educational institutions in Bangalore also attended the lectures regularly. The academic sessions were held in the new conference hall at the Madras Woodlands Hotel, Bangalore.

It was a very fortunate circumstance that this summer school was held immediately after the International Conference on High Energy Physics at Dubna, USSR, in which Prof. R. Oehme and Prof. A. Ramakrishnan participated. Among the various topics discussed at the Dubna conference, of particular interest is the reported violation of CP invariance and hence the violation also of time reversal (T) invariance in some weak interactions; the success of the SU_3 symmetry of the elementary particle interactions was also discussed at the conference. These topics were treated at great length in the summer school as some of the scientists at Matscience have done some interesting work relating to these problems which were discussed at Dubna. To mention a few, the calculation of the electric dipole moment of the nucleon which has acquired considerable importance in view of the violation of time reversal, and the work relating to origin of symmetries like SU_3 and charge independence of Yukawa interaction.

Some students reported on their work relating to scattering of particles from polarized targets and photoproduction of pions from complex nuclei in which there is considerable experimental interest at present. The students benefited considerably from the comments of the visiting scientists.

The other main topic on which there were several lectures in the summer school was Green's function formalism, both in elementary particle physics as well as in many-body systems, since some scientists at Matscience have used this formalism in their research work. These lectures focused attention on some of the unsolved problems in quantum field theory.

The summer school was given a good start with the lectures of Prof. Caianiello. He dealt with the basic problem of formulating renormalization in a manner which is mathematically rigorous using algorithms like pfaffians and hafnians. Only a few of the participants really managed to keep pace with this set of lectures, but all appreciated the tremendous display in combinatorics and were made aware of the difficult problems in renormalization that still exist.

The lectures of Prof. Symanzik were a fine treat in good mathematics and hence were very precise. He dealt with the many-particle structure of Green's functions using functional formalism. He discussed the advantages of formulating the problem in terms of retarded Green's functions instead of the usual causal ones. Some aspects of his lectures like the notion of ' double graph ' have left a deep impression. One of the interesting features of these two sets of lectures was the attempts made by both Prof. Caianiello and Prof. Symanzik to compare and comment on the two approaches, i.e. branching equations of the former and the coupled integral equations of the latter. Their comments were greatly helpful in the understanding of both the lectures.

One of the keenly awaited lectures at the summer school was that by Prof. Ramakrishnan on the recent developments in high energy physics incorporating some of the new results reported at the Dubna conference. He discussed in considerable detail the SU_3 symmetry which seems very successful in explaining the present structure of elementary particle spectrum. After presenting the famous experiment of $K_2^0 \rightarrow 2\pi$ decay which indicated the violation of CP invariance, he indicated the new possibilities in the theory of weak interactions. It was interesting to know that μ meson and electron behave identically as was shown by the determination of the fine structure constant using μ capture. He finally presented and discussed Schwinger's ideas on symmetries of elementary particles in relation to some of his own ideas in this field.

Dr Radha gave two lectures, one relating to her calculation (in collaboration with Meister) of the electric dipole moment of a nucleon assuming (1) a small violation of T invariance in the weak interactions of elementary particles and (2) that weak interactions are mediated by the intermediate vector mesons. In view of the discovery of the $K_2^\circ \rightarrow 2\pi$ decay (reported at the Dubna conference) and hence the possible violation of T invariance this work is of topical interest. Naturally there was a considerable discussion on the merits of this test. She indicated how the above ideas can be extended to the case of leptons and also outlined the further work of Feinberg and Mani on alternative methods of generating an electric dipole moment for the nucleons.

The second lecture was based on the research work of Schiff, Meister and Radha, which was also reported at the Dubna conference, on the determination of three-body wave functions of H^3 and He^3. The recent data on high energy electron scattering by H^3 and He^3, and the radiative capture of thermal neutrons by deuterium were used to estimate the probability of the state of mixed symmetry.

Prof. Oehme gave a series of twelve stimulating lectures on the strong and weak interactions of elementary particles. Under strong interactions he discussed the application of dispersion theory to high energy scattering. Until recently dispersion theory has been successful only in the low and medium energy regions. However, the unique interpolation of the physical partial wave amplitudes by an analytic function of the complex angular momentum variable has made it possible in principle to correlate the results of high energy experiments with our partial knowledge of low energy resonances and the forces in the crossed reaction. He discussed this aspect and also some of the latest developments in the field like the notion of moving branch cuts, etc., and the validity of the Mandelstam representation. He also gave four lectures on selected topics on weak interactions with particular reference to their underlying symmetries. Since the subjects are of topical interest, the lectures were marked by many discussions and most of the participants found it to be very useful.

A systematic series of five lectures on μ capture in light nuclei was given by Dr Fujii. He discussed the present status of both the experimental and theoretical aspects of μ capture. He suggested possible modifications that can be made in the calculations which are already being carried out by some of the scientists of Matscience.

Dr Calogero treated the audience to a novel approach called the phase method in scattering theory wherein differential equations are derived for the phase shifts of different partial waves themselves directly. These equations are first order differential equations of the Riccati type. The solution of this non-linear equation was obtained in an iterative fashion using variational techniques. The nuances of this method coupled with comparative tables of results computed for these phase shifts by solving Schrödinger equations under different approximations, presented by the lecturer in a clear and lucid manner, brought home to the audience the power and utility of these variational methods.

Two lectures on theories of particles with arbitrary spin based on the recent papers by Weinberg were given by Dr Venkatesan. In the first lecture he surveyed the various approaches pointing out the difficulties in each of them. After presenting Weinberg's work he discussed the group theoretic aspects of complex angular momentum and Regge poles which touched off an interesting discussion.

Dr Lukierski discussed various aspects of classical and quantum gauge transformations and obtained the commutation relations for Yang-Mills field. More than his lectures, his participation in various lectures roused interesting discussions.

Two interesting lectures were given by Prof. Brenig who joined the summer school in the last week. The first one dealt with the work of Migdal on the theory of finite nuclei using interacting quasi-particles. The success of Migdal's theory in explaining several properties of finite nuclei was a welcome information to the many-body theorists among the participants. The second lecture dealt with an important problem in many-body systems, i.e. lifetime of a quasi-particle.

Dr Vasudevan gave an interesting talk on Kubo's formalism which links up transport coefficients and equilibrium correlation functions of a many-body system. As he made a systematic derivation, even non-many-body theorists were able to appreciate the power of Kubo's formalism.

Dr Ranganathan presented some salient features of the recent programme which has been initiated by Martin and de Dominicis in the study of normal and superfluid systems. The purpose of the programme is to eliminate the bare potentials and formulate every physical quantity in terms of distribution functions which are the effects due to interactions, a procedure similar to renormalization. This renormalization is achieved naturally by means of Legendre transformation. An interesting feature of the programme is that one obtains stationary principle in terms of entropy.

In a very interesting survey Prof. Venkataraman discussed the various approaches to generalized functions.

Two lucid lectures on the applications of stochastic theory to some physical problems were delivered by Dr Srinivasan. The first one dealt with the explanation of shot effect using product densities introduced by Ramakrishnan and arrived at the correlations in shot noise. The novel feature of this work was his introduction of the non-Markovian feature which made a tremendous impression on the participants. In his second talk he presented his recent work with Dr Vasudevan on Barkhausen noise in ferromagnets where also the non-Markovian feature has to be invoked.

Dr Devanathan spoke on the photoproduction of charged pions from nuclei with special reference to some recent work in collaboration with Dr Ramachandran, the salient features of which were: (1) the cross-section for the nuclear process was obtained in an elegant form in which the many-body problem was separated out in terms of certain reduction factors and single nucleon transition probabilities the latter of which were expressed in a form where the shell model effects and the dependence on the basic amplitudes were clearly separated; and (2) the application of the above method of analysis in the reaction $^{60}Ni_{28}(\gamma,\pi^-)^{60}Cu_{29}$ led to a preference of the square well functions over the oscillator functions in the nuclear 2 p-shell.

The generalized Smushkevich principle was discussed by Mr Santhanam, who explicitly derived the charge independence of Yukawa interaction using this principle. He also deduced the SU_n invariance of the trilinear interaction between three multiplets of multiplicity n, n, (n^2-1). There was some discussion regarding the equivalence of Smushkevich principle and gauge invariance, and extension of this principle to arbitrary interactions.

Mr Ananthanarayanan spoke on some recent work in collaboration with Dr Ramachandran on the possibilities of using photoproduction and scattering of pions to study the structure of the H^3 and He^3 nuclei. The differential cross-section at 90° for scattering of positive pions on He^3 was found most sensitive to the admixture of the S-state of mixed symmetry.

Mr Umerjee discussed polarization phenomena in elastic electron-proton scattering with particular reference to (1) determination of the form factors of the neutron and (2) helicity of the electron in the final state of the processes. Since he reported almost complete polarization in back-scattered electrons, there was naturally a good discussion on understanding this result as well as on the possibility of using them.

The proceedings of the summer school are being edited and arrangements are being made to have the proceedings of the summer school published in the form of a book through a foreign press.

World Directory of Crystallographers

The International Union of Crystallography proposes to publish shortly the third edition of the *World directory of crystallographers*. The collection of the biographical information is being done through a questionnaire available from national sub-editors. For inclusion in the directory, a person should be a member of a national crystallographic organization, or have publications to his credit in the field of crystallography, or be a graduate student in the field of crystallography. Communications for further details and requests for copies of the questionnaire should be addressed to the Sub-editor for India, Dr K. Banerjee, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 32.

Comparison of Radiation Instruments

UNDER the auspices of the World Meteorological Organization (WMO), an international comparison of standard instruments used for the measurement of solar radiation was held at Davos-Platz in Switzerland during August-September 1964. The purpose of the comparison was to help ensure the comparability of meteorological radiation observations all over the world. This is of particular importance in connection with the world-wide meteorological observations being taken during the International Years of the Quiet Sun.

The first international comparison of working standard pyrheliometers was organized by WMO at Davos in 1959 soon after the International Geophysical Year (IGY) under the direction of Dr W. Mörikofer, Director of the Davos Observatory and Chairman of the former WMO Working Group on Radiation Measurement. The purpose of the first comparison was to make sure that two or three well-standardized pyrheliometers would be available on each continent, with which national working standards could be compared. The radiation instruments in each country used for routine radiation measurements would in turn be calibrated against the national working standard. Sixteen countries took part in the first comparisons, but mostly from Europe.

With the increase in the number of radiation stations during and after the IGY (they now number over 700) and the establishment of a number of observatories to serve as national and regional radiation centres, a Second International Comparison of Working Standard Pyrheliometers was organized, in order that all regional working standards at these centres could be recalibrated against primary reference standards. The following countries in which regional radiation centres, as officially designated are located, took part in the second international comparisons: Congo (Leopoldville), South Africa (Pretoria), Tunisia (Tunis), India (Poona), USA (Washington), Canada (Toronto), Australia (Melbourne), Sweden (Stockholm), Switzerland (Davos) and USSR (Leningrad).

Norway was permitted to attend as a special case. Japan, which has one of the two regional radiation centres in Asia (Tokyo), had earlier taken part in the Asian Regional Comparisons held at Poona during January 1964 and did not, therefore, take part in the Davos comparisons.

The number of participants was 11 and the number of instruments compared 19. Twenty-one scientists from 12 countries took part in the comparisons. The comparison was under the technical direction of Miss A. Mani of the India Meteorological Department, Chairman of the WMO Working Group on Radiation Instruments and Observations for General Use, assisted by Dr H. Wierzejewski of the Davos Observatory. All the local arrangements at Davos were under the direction of Dr Mörikofer, Director of the Davos Observatory.

Instruments Compared

Working standard radiation instruments used as national or regional standards are either the Ångström compensation pyrheliometer or the Abbot silver disc pyrheliometer. The silver disc pyrheliometer has been used as a secondary standard since 1903, with the Smithsonian water flow pyrheliometer as an absolute standard and with the readings of both these instruments expressed on the Smithsonian Scale 1913. The Ångström pyrheliometer has been used both as an absolute instrument and as a secondary standard during the last 50 years with the readings expressed on the Ångström scale (uncorrected). A difference of the order of 3·5 per cent was, however, known to exist between the two traditional scales. No attempt was made to devise a new single scale, till the advent of the IGY and the establishment of a world-wide network of meteorological radiation stations, when a new international scale, the International Pyrheliometric Scale 1956, was adopted by WMO incorporating both the original Ångström and Smithsonian scales. All meteorological radiation observations are now made on the IPS 1956.

The reference standard for the second international comparisons was one of the three original Stockholm standards, against which almost all the Ångström pyrheliometers in use all over the world were originally calibrated. The Stockholm standard, with two secondary reference standards at the Davos Observatory, is considered to represent the International Pyrheliometric Scale 1956, with a correction of 1·5 per cent to the original Ångström scale.

Comparison

The comparison was held at the Physikalisch-Meteorologisches Observatorium, Davos-Platz, Switzerland (1590 m. a.s.l.), from 24 August to 5 September 1964, at the invitation of Dr Mörikofer. The opening date of 24 August was selected for the convenience of participants attending the International Symposium on Atmospheric Radiation held at Leningrad from 5 to 17 August 1964. From the point of view of availability of the necessary facilities, viz. a standard group of reference instruments, experts experienced in international comparisons, workshop and laboratory facilities and favourable meteorological conditions with long, uninterrupted hours of sunshine and steady radiation intensities, Davos proved an excellent choice. And the success of the comparisons was in a large measure due to the superb arrangements made by Dr Mörikofer and his colleagues at the Davos Observatory.

Observing facilities and adequate space for the simultaneous comparison of 16 Ångström pyrheliometers and 2 silver disc pyrheliometers were provided on the two flat roofs of the Davos Observatory. Of the 19 instruments compared, 17 were of the Ångström and 2 of the silver disc types. Each

Ångström pyrheliometer requires a precision milliammeter, zero galvanometer and a resistance box as auxiliary equipment, and the silver disc pyrheliometer, an automatic timing device. The accuracy of the auxiliary equipment had been specified and the calibration of the milliammeters was checked every day with reference to a precision potentiometer and a standard cell. Despite the long distances over which most instruments had been transported and the very delicate nature of the instruments, no major defect was observed in any instrument and no major repairs were found necessary, obviously as a result of the excellent care taken in packing and expert handling during transport. Similarity and stability tests were also made to check the effect of transport on the pyrheliometric constants.

The weather was favourable throughout the two weeks of the comparisons, with exceptionally good observing conditions from 26 to 28 August and again from 2 to 4 September. Five hundred and fifty-two comparative observations were made on four days during the first week with 17 pyrheliometers and 456 observations on four days during the second week with 6 pyrheliometers, making a total of 1008 individual observations. The main comparisons with 17 pyrheliometers from 9 countries were made during the first week. USSR and Tunisia, who could not take part in first series due to late arrival of personnel and equipment, took part in the second series.

All measurements and calculations were made by individual participants, values of direct solar radiation for each series of observation being calculated the same day, using the old calibration constants and after applying corrections, if any, to the milliammeter readings. The ratio Q of the intensities of direct solar radiation obtained with the regional standards with those obtained with the main reference standards was computed and new calibration constants arrived at for each of the regional working standards. These new constants will, in future, be used for calculating values of solar and terrestrial radiation all over the world.

Seven of the regional working standards compared showed changes of the order of 0·5-1·8 per cent in their calibration constants, while seven showed no significant changes. Instruments with different apertures are open to different values of circumsolar radiation and are not truly comparable. The Davos comparisons showed that instruments with the same aperture conditions agree remarkably well. The changes in the calibration constants might, therefore, arise from the difference in sky conditions obtaining at Stockholm and Davos or in the different methods of calibration used at Stockholm and Davos. Or it may be due to a genuine change in the calibration factors themselves. These are now under study.

The main sources of disturbance were wind, cloud and haze on certain days of observation. The wind effect is serious in short tube instruments, and so is turbidity, even when clear sky conditions and steady solar intensities exist. The conditions of observations at Davos during the comparisons were, however, so good that with instruments having the same opening angle it was possible to obtain an accuracy of 0·25 per cent in the series of comparative observations.

Conclusion

The main aim of the Second Inter-regional Comparisons of Working Standard Pyrheliometers was the redetermination of the calibration constants of the regional radiation standards used at all major regional radiation centres in the world and this has been successfully accomplished. As a result of the long series of careful, systematic observations made and the perfect observing conditions existing at Davos, an accuracy hitherto not achieved in radiation measurements could be obtained.

The different radiation fluxes to and from the earth's surface are among the most important terms in the heat economy of the earth. Only with widely distributed, regular series of records of solar and terrestrial radiation components and the indispensable world-wide comparability of radiation instruments can comprehensive radiation climatologies be produced; and the daily and seasonal variations of the various radiation constituents of the general thermal budget be more precisely evaluated and their relationship with other meteorological elements better understood. The successful development of projects concerned with the practical utilization of solar energy, e.g. to improve agricultural yields and increase the capacity of the more arid regions of the world to support man, and the world-wide investigation of weather control and modification, also depends to a great extent on the acquisition of precise information of solar and terrestrial radiation on a world-wide scale.

Glycosides & Saponins: A Symposium

GLYCOSIDES as a class of compounds are widely distributed in nature and occur in plants as well as in microorganisms. Some of the compounds possess conspicuous physiological properties. It was, therefore, considered of interest to organize a symposium on glycosides and saponins jointly by Bengal Immunity Research Institute and the Council of Scientific & Industrial Research at Calcutta from 2 to 4 April 1964. It was presided over by Dr K. N. Bagchi (National Medical College, Calcutta). Dr U. P. Basu, Director, Bengal Immunity Research Institute, welcomed the delegates and Shri P. C. Sen, Chief Minister, West Bengal, inaugurated the symposium. Prof. S. Bose, FRS, National Professor, was the Guest-in-Chief. In all 23 papers including one from Czechoslovakia were read in the following three sections: (i) Chemistry presided over by Dr P. K. Bose (Bose Institute, Calcutta); (ii) Pharmacognosy presided over by Dr S. Prasad (Banaras Hindu University, Varanasi); and (iii) Pharmacology presided over by Dr R. B. Arora (All India Institute of Medical Sciences, New Delhi). In the chemistry section alone as many as 15 papers were presented dealing with the isolation and structure determination of glycosides and saponins, significant omissions being sulphur and nitrogen containing glycosides. Surprisingly there was only one paper in the whole of the symposium dealing with the biochemical aspects of glycosides.

In his special lecture on 'Scope and trend in modern pharmacognosy', Dr Prasad (Banaras Hindu University, Varanasi) emphasized the importance of pharmacognostical research in detecting adulteration and testing of drugs with the help of up-to-date methods. The need for setting up a pharmacognostical herbarium which could go a long way in correct and quick identification of plants of medicinal importance was stressed.

Chemistry

With the object of producing steroid hormones in the country, R. N. Chakraborty, D. Chakraborty, Sibani Dutta and M. N. Mitra (School of Tropical Medicine, Calcutta) have carried out an exhaustive chemical investigation of Indian plants for their steroid saponins content; steroid sapogenins could be converted into useful steroid hormones. As a result the following species of Indian Dioscorea, viz. *D. deltoidea*, *D. prazeri* (var. *glauca*), have been found to be a rich source for diosgenin. Using this it has been possible to prepare a large number of hormones. The other steroids which have been isolated are tigogenin and yuccagenin from *Cestrum nocturnum* (Fam. Solanaceae). In another paper, 'Enzymatic hydrolysis of steroid saponins', Chakraborty *et al.* discussed the action of enzymes, saponases, isolated from the juice of Agave leaves and also of keeping Dioscorea yams in water for a prolonged period. Though diosgenin was obtained by these procedures, the yield was lower than that expected on the basis of complete hydrolysis of the Dioscorea saponins into sapogenins and also the latter was found to be associated with other products, viz. smilagenone and epismilagenin. The action of water on the saponins from *C. nocturnum* was also reported.

In view of the economic importance of diosgenin, considerable attention is being paid to the development of economic and convenient methods for its isolation. Rabindra K. Basu (Smith Stainstreet & Co., Calcutta) in his paper 'Preparation of glycosides of Dioscorea' described an easy method for the isolation of diosgenin as its acetyl derivative. The same author also described a method, which can be exploited on a commercial scale, for the isolation of Senna glycosides by extraction with water. Structural investigations on the triterpenoid saponin, monnierin, isolated from *Bacopa monnieri* Wettst., and the triterpenoid glycoside, isothankuniside, from *Centella asiatica* Linn. were reported by Tapan Dutt and U. P. Basu (Bengal Immunity Research Institute, Calcutta). Complete hydrolysis of monnierin has been shown to give 3 molecules of arabinose (furanose type) and 1 molecule of glucose (pyranose type), and a triterpene aglycone. None of the sugars is present in a branched chain. Further structural investigations on the triterpene aglycone are in progress. Isothankuniside on acid hydrolysis was shown to give a new terpene acid, isothankunic acid, glucose and rhamnose.

As a result of a detailed chemical examination of *Bacopa monnieri* Wettst., N. Chatterji, R. P. Rastogi and M. L. Dhar (Central Drug Research Institute, Lucknow) have been able to isolate two saponins, bacoside A and bacoside B. Bacoside A on hydrolysis was shown to give four aglycones, bacogenin A_1, A_2, A_3 and A_4. On the basis of chemical, infrared and NMR studies on bacogenin A_1 and its diacetate, it has been concluded that bacogenin A_1 belongs to the class of tetracyclic triterpenoids. A partial formula for bacogenin A_1 could be written as 3,20-dihydroxy-10-hydroxymethyl-16-keto-dammar-24-ene. A tentative structure for bacoside A was also proposed. A. Polákova and Z. Čekan (Research Institute for Natural Drugs, Prague) in their paper 'A new glycoside from *Adonis vernalis* Linn.' gave the isolation of a new glycoside, m.p. 205-10°, besides the cardenolides adonitoxin, strophanthidin, adonitoxigenin-3-acetylrhamnoside, strophadogenin, vernadigin and 3-acetylstrophadogenin. The new glycoside has been assigned the structure, adonitoxigenin-2-acetylrhamnoside. The isolation of a new alkaloidal saponin, solakhasianin, from *Solanum khasianum* Clarke, was reported by P. C. Maiti and Sipra Mookherjee (Botanical Survey of India, Calcutta).

The saponin and sapogenins from various plants belonging to the family Leguminosae were discussed in detail by I. P. Varshney (Aligarh Muslim University, Aligarh). Most of them have been shown to belong to triterpenic group but a few plants yield steroidal genins. It was further observed that in various parts of the same or different plants same or different sapogenins are present. The nature of the genin has been found to vary in the same plant according to the climatic conditions and the place from where the plant has been collected. The isolation of two new sapogenins, proceric acid and acacic acid, both belonging to β-amyrin group, have been isolated and their structures determined. The paper on the constitution of barringtogenol C, a new terpenoid sapogenin from *Barringtonia acutangula* Gaertn., by A. K. Barua and Parul Chakrabarti (Bose Institute, Calcutta) dealt with the detailed study leading to the stereochemistry and constitution of the sapogenin as 3β,16α,21α,22β,28-pentahydroxyolean-12-ene.

Pharmacognosy

Four papers were presented in this section covering the following topics: distribution of saponins in angiosperms; pharmacognostical studies on the stem bark of *Ficus religiosa* Linn.; pharmacognosy of *Sapindus mukurossi* Gaertn. fruits; and some experiments in glycosidation in plants. B. C. Kundu and B. Gupta (Central Drug Research Institute, Lucknow) in their paper 'Distribution of saponins in angiosperms' gave the results of investigations on the available resources of saponins by chemotaxonomic studies. From the survey of the saponin bearing plants a list has been prepared from the data available from various sources. A modified arrangement of the system of classification of Hutchinson has been suggested, based on the presence of saponin as a criterion of affinity. In this modified classification, in a series of saponin containing orders, such orders where precise information regarding occurrence of saponin among their members is wanting, have also been included.

Ficus religiosa Linn. has been used in the indigenous system of medicine for a variety of ailments. Encouraging results obtained by the use of stem bark of *F. religiosa* in the treatment of asthma have led S. Prasad and R. B. Srivastava (Banaras Hindu University, Varanasi) to carry out pharmacognostical studies on the stem bark of this plant.

K. L. Khanna and C. K. Atal (Panjab University, Chandigarh) in their paper 'Some experiments in glycosidation in plants' confirmed the results of earlier workers about the ability of leaves to biosynthesize glycosides from phenols. Atal and Lamba (Panjab University, Chandigarh) also reported results of studies on the pharmacognosy of the fruits of *Sapindus mukurossi* Gaertn.

Pharmacology

In view of the earlier findings that peruvoside, a digitaloid glycoside, isolated from *Thevetia neriifolia* Juss., possesses cardiotonic activity equipotent to ouabain led Arora *et al.* (All India Institute of Medical Sciences, Delhi) to the determinations of therapeutic, irregularity and lethal doses of peruvoside in the denervated, isolated heart-lung preparation of dogs and also its subacute toxicity in the same species of animals. It was shown that continuous infusion of the drug affects the cardiac output, atrial pressures, heart rate and electrocardiogram. Rate of administration of peruvoside has been shown to have a marked effect on the therapeutic, irregularity and lethal dose of the drug. With higher rates of administration, the lethal dose was increased and there was decrease in experimental time. Peruvoside is shown to possess greater margin of safety as compared to other digitalis like preparations. It is further suggested that if chemical trials are conducted on human beings there is very high probability that this drug may replace digitalis which is only the sheetanchor for the treatment of congestive heart failure at present. M. L. Chatterjee and A. R. Roy (School of Tropical Medicine, Calcutta) in their paper reported the preliminary pharmacological studies on the two saponins from the leaves of *Cestrum diurnam* and *Cestrum nocturnum*. It was shown that both the saponins possess cardiotonic and cardiotoxic properties according to the dosages used. Structure-activity relationship in cardiac glycosides was discussed by M. M. Vohra and J. D. Kohli (Central Drug Research Institute, Lucknow). The influence of molecular structure on the activity of glycosides was discussed under the following: (i) influence of sugar moiety; (ii) influence of the aglycone part; and (iii) stereochemistry of the molecule. Tapan Dutta and U. P. Basu (Bengal Immunity Research Institute, Calcutta) presented a paper on 'Antifertility studies with crude extract and isolated products of *Centella asiatica* Linn. (Urb)' in which a detailed screening, though of a preliminary nature, was described.

S. S. SAKSENA

Molecular Force Fields

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A THOROUGH and systematic analysis of the vast amount of experimental data that have accumulated from the investigations of the vibrational spectra of polyatomic molecules is of considerable interest to the molecular spectroscopist. One of the main objects of study of the vibrational spectra of polyatomic molecules is the investigation of the nature of the forces holding the nuclei in a polyatomic molecule to their equilibrium positions. Most of the Raman and infrared transitions represent the fundamental vibration frequencies of the molecules involved in the scattering and absorption processes respectively. A correlation of these frequencies, as observed in the Raman and infrared spectra, may be made with the molecular structure from a knowledge of the characteristic modes of oscillation of the molecules. The magnitudes of the vibrational frequencies are determined by specific force fields appropriate to the various molecules.

In any normal coordinate analysis of a molecule there are $\Sigma n(n+1)/2$ independent quadratic potential energy constants where n is the number of vibrations of each symmetry type. Therefore, the number of constants is almost always impractically large compared to the number of vibrations. Hence for any practical application, approximations must necessarily have to be made.

Central Force Field

One such approximation is Dennison's[1] central force field. Dennison expressed the potential energy as a pure quadratic function of the change Q_i of the distance l_i between the nuclei. In terms of the central force coordinates, the potential energy is expressed as

$$2V = \Sigma b_{ii} Q_i^2$$

which postulates only forces along lines joining pairs of atoms. This would be true if the molecule were held by ionic interactions only. Also, this type of force yields only diagonal terms in the force constant matrix when the internal coordinate system is the complete set of interatomic distances[2,3]. As such this approximation is not satisfactory.

Valence Force Field

An approximation which is somewhat better than the central force field and is more compatible with ideas concerning interatomic forces is the valence force field[4]. Here, the forces considered are those which resist stretching or compression of valence bonds or oppose angular deformation or torsion. This excludes the forces between non-bonded atoms. The potential energy (V) is expressed as

$$2V = K\Sigma Q_i^2 + K_\delta \Sigma \delta^2$$

where Q_i is the change in bond length and δ is the change in bond angle, K is the stretching force constant and K_δ is the bending force constant.

Although this method is a slight improvement over the central force field approximation, the simple valence force field treatment often gives only approximate values for the constants. The number of force constants is usually less than the number of frequencies. The force constants can be computed from some of the frequencies and the remaining frequencies used for checks[2,3]. This simple picture is very useful in assigning observed spectral frequencies to modes of vibration. It provides a rough idea of bonds.

Orbital Valence Force Field

Heath and Linnett[5] have found that the simple valence force field is inapplicable to explain the out-of-plane vibrations of planar molecules. They have suggested a modified form of valence force field known as the orbital valence force field involving a three-constant potential function. The orbital valence force field gives a picture of angular distortion in the molecule which is in accordance with modern views on directed valency.

In order to derive this field, it is assumed that the bond forming orbitals of an atom X are at definite angles to each other and a most stable bond is produced when one of these orbitals overlaps the bond forming orbitals of another atom Y to the maximum extent possible. If now Y is displaced perpendicular to the bond, a force will be set up tending to resolve it to the most stable position. For the vibrations to be simple harmonic, the restoring force must be proportional to the displacement. The potential energy (V) is expressed as

$$\begin{aligned}2V = {} & 2B'\Sigma\Delta r_{ij} + K_1\Sigma\Delta r_{ij}^2 + K'_\beta\Sigma\Delta\beta_{ij}^2 \\ & -2B\underset{jk}{\Sigma}\Delta R_{jk} + 2A\underset{jk}{\Sigma}\Delta R_{jk}^2\end{aligned}$$

where i represents the central atom and j, k, etc., the outer atoms. Δr_{ij} is the increase in bond length r_{ij} and ΔR_{jk} is the increase in the distance between non-bonded atoms j and k. $\Delta\beta$ is the angular displacement. B', K_1, K'_β, B and A are constants. The second and third terms are the orbital valence force field terms. The fourth and fifth are those which represent the repulsion between the non-bonded atoms[6,7].

Urey-Bradley Force Field

The molecular force field postulated by Urey and Bradley[8] is a better approximation for the forces in polyatomic molecules. The Urey-Bradley type of potential function contains both force constants related to changes in the distances between non-bonded atoms and force constants associated with changes in bond lengths and bond angles. The Urey-Bradley field requires only a few parameters to describe the potential energy completely. This force field contains no quadratic cross terms as such, but they are expressed in terms of both the forces between non-bonded atoms. Shimanouchi *et al.*[9] have shown the general validity of this type of potential force field in the case of derivatives of methane and other molecules. Furthermore, Overend and Scherer[10] have demonstrated the transferability of Urey-Bradley force constants in carbonyl halides, methyl halides and silyl halides.

The Urey-Bradley field type of potential function, in general, is expressed as

$$\begin{aligned} V = & \sum_i K'_i r_i \Delta r_i + \tfrac{1}{2} K_i (\Delta r_i)^2 \\ & + \sum_{i<j} H'_{ij} r_{ij}^2 \Delta \alpha_{ij} + \tfrac{1}{2} H_{ij} (r_{ij} \Delta \alpha_{ij})^2 \\ & + \sum_{i<j} F'_{ij} q_{ij} \Delta q_{ij} + \tfrac{1}{2} F_{ij} (\Delta q_{ij})^2 \end{aligned}$$

where r's are the bond lengths, α's the bond angles, q's the distances between atoms not bonded directly and r_{ij} represents $(r_i r_j)^{1/2}$. K', K, H', H, F' and F are the force constants, F and F' being the repulsion constants between non-bonded atoms[11-24].

General Force Field

The simple force fields being inadequate for a correct description of the fundamental vibrations of molecules, modified force fields[25,26] which include the valence force fields plus a few judiciously chosen interaction constants account for the effect on the stiffness of a bond due to distortion in others. However, the judicious choice of these constants is a matter of great difficulty in any but the simplest of molecules. Wilson's group theoretical method[27] of evaluating the potential constants includes such interaction terms.

As an example, the most general quadratic potential function as it is applied to the case of bent symmetrical XY_2 type molecules can be expressed as

$$\begin{aligned} 2V = & f_d(\Delta d_1^2 + \Delta d_2^2) + f_\alpha d^2 (\Delta \alpha)^2 \\ & + 2 f_{dd} (\Delta d_1)(\Delta d_2) + 2 f_{d\alpha} d (\Delta d)(\Delta \alpha) \end{aligned}$$

where Δd_1 and Δd_2 are changes in bond lengths, $\Delta\alpha$ is the change in bond angle, f_d and f_α are the stretching and bending force constants respectively, and f_{dd} and $f_{d\alpha}$ are the interaction constants.

There are also certain practical data which enable the determination of as precise a potential energy function for the molecule as permissible, e.g. the data on isotopic molecules and the additional relations they provide. Based upon a reasonable assumption that the interaction constants between widely separated parts of a large molecule are small, one may transfer potential energy constants from one molecule to another with similar bond environs. The rotational distortion and Coriolis coupling constants also will be very useful in the normal coordinate treatments.

Anharmonicity Correction

From a knowledge of the vibrational frequencies in the molecule containing hydrogen and its deuterium substituent, corrections to be applied to the observed fundamentals as a result of anharmonicity can be estimated by the method suggested by Dennison[28].

The vibration frequencies of isotopic molecules are related by the product rule[29]. If ω_i and ν_i are the corrected and observed wave numbers, then

$$\omega_i = \nu_i (1 + x_{ii})$$

where $\nu_i x_{ii}$ is the correction due to anharmonicity.

The corresponding quantities ω_i^* and ν_i^* for the isotopic molecule obey the equation

$$\omega_i^* = \nu_i^* \left(1 + x_{ii} \frac{\omega_i^*}{\omega_i}\right) \cong \nu_i^* \left(1 + x_{ii} \frac{\nu_i^*}{\nu_i}\right)$$

The assumption implies that the anharmonicity correction varies nearly as the square of the wave number. Assuming that the potential constants are not altered by substitution, it can be written that

$$\frac{\omega_i^{*2}}{\omega_i^2} = \frac{|F|^D |G|^D}{|F|^H |G|^H} = \frac{|G|^D}{|G|^H}$$

where $|G|^H$ and $|G|^D$ are obtained from the G matrix elements. Substituting the values of G matrix elements and the known frequencies the correction factors x_{ii} and $x_{ii}(\nu_i^*/\nu_i)$ can be obtained. Using these values all the frequencies can be corrected.

Solution of Secular Equation

Normal coordinate treatment — In the secular equation obtained by formulating the potential and the kinetic energy for the vibration of a molecule, corresponding to a given solution λ_K of the secular equation, there is a normal mode of vibration of frequency $\lambda_K^{1/2}/2\pi$. So the problem of analysing the molecular vibrations is one of setting up the secular equation, using a proper set of coordinates.

For that purpose, one may think of the normal coordinates Q_K associated with each normal mode of vibration, so that potential energy representation involves no cross products but only squares of Q (Ref. 30, 31). Or one may use the mass-adjusted Cartesian displacement coordinates, or any system of coordinates in terms of which the kinetic and potential energies are homogeneous quadratic forms in the velocities and the coordinates. Also, one may introduce the 'internal coordinates', which describe the internal configuration of the molecule without regard for its position as a whole in space, thereby excluding the coordinates for translations and rotations. There is thus a reduction in the size of the secular equation.

But these procedures are too inadequate to be useful for molecules of even moderate size considering the troublesome steps involved in the solution of the secular equation. One of the most powerful tools in simplifying the treatment of larger molecules is the use of the molecular symmetry in factoring the secular equation. This is effected by the use of the symmetry coordinates introduced by Wilson[27] and Wilson *et al.*[32]. The application of this method is described in detail by Meister and Cleveland[33].

F-G matrix method — The changes in the interatomic distances or in the angles between chemical bonds, or both, can be used to provide a set of $3N$-6 (or $3N$-5 in the case of linear molecules) internal coordinates where N is the number of atoms in the molecule. These coordinates are unaffected by the translations or rotation of the molecule as a whole and are particularly important because they provide the most physically significant set for use in describing the potential energy of the molecule. To factorize the secular equation to the maximum possible extent, one has to set up linear combinations of the above internal coordinates. These linear combinations will be the symmetry coordinates. There are several ways of constructing these symmetry coordinates. One convenient way would be to use equivalent internal coordinates. Equivalent internal coordinates are those that are exchanged by the symmetry operations of the molecules.

Such linear combinations should be orthonormal and transform according to the character of the type of vibration they represent.

If they are of the form

$$R_j = U_{jk} r_k \qquad \ldots(1)$$

where R_j is the jth symmetry coordinate ($j = 1, 2, \ldots. 3N$-6). U_{jk} is the coefficient of the kth internal coordinate, r_k is the kth internal coordinate and the summation extends over all of the equivalent internal coordinates; one may represent them in the matrix notation as

$$R = U_r \qquad \ldots(2)$$

For the symmetry coordinates to be orthogonal, it is necessary that

$$U_{jk} U_{lk} = 0 \qquad \ldots(3)$$

where j and l refer to two different symmetry coordinates, and for normalization

$$(U_{jk})^2 = 1 \qquad \ldots(4)$$

The property of the transformation may be verified for non-degenerate and degenerate vibrations by considering the linear combinations obtained as a result of any symmetry operation on the R's. The rules have been illustrated by Meister and Cleveland[33] in specific cases.

F matrix — The elements of the potential energy matrices can be obtained if one writes the F matrix by assuming a harmonic potential energy function. One can write the potential energy V in the matrix notation as

$$2V = r'fr = R'FR \qquad \ldots(5)$$

where r' and R' are the transposes of r and R respectively, and $R = U_r$. Since the R_j's are orthonormal, $U^{-1} = U'$. Eq. (5) may, therefore, be written as

$$R'(UfU')R = R'FR \qquad \ldots(6)$$

whence

$$F = UfU' \qquad \ldots(7)$$

Eq. (7) gives the F matrix in terms of U and f.

For the cases where there are redundant coordinates, Gold *et al.*[34] have also shown that

$$f = \tilde{U}FU \qquad \ldots(8)$$

The above equations will, therefore, correlate the symmetry force constants with the valence force constants for a molecule.

G matrix — Wilson has shown that the elements of the kinetic energy matrices can be obtained from the equation

$$G_{jl} = \sum_p \mu_p g_p S_j^{(t)} S_l^{(t)} \qquad \ldots(9)$$

in the case of non-degenerate vibrations, and from

$$G_{jl} = \frac{1}{d} \sum_p \mu_p g_p [S_{ja}^{(t)}.S_{la}^{(t)} + S_{jb}^{(t)}.S_{lb}^{(t)} + \ldots] \qquad \ldots(10)$$

for degenerate vibrations, where $S_j^{(t)}$, $S_l^{(t)}$ are the S vectors for the atom t for the jth and lth symmetry coordinates respectively; g_p refers to the number of equivalent atoms in a set p; μ_p is the reciprocal mass of the typical atom t; d is the degree of degeneracy of the vibration; and S_{ja}, S_{jb} refer to the S vectors obtained by using the U's appearing in R_{ja} and R_{jb} respectively.

The S vectors are given by

$$S_j^{(t)} = \sum_k U_{jk} S_{kt} \qquad \ldots(11)$$

The summations in Eqs. (9), (10) and (11) extend over all the atoms of a molecule.

Having obtained the F and G elements, one can write the secular equation in the form

$$|FG - E\lambda| = 0 \qquad \ldots(12)$$

where E is a unit matrix. The above matrix splits up into as many blocks of submatrices as there are symmetry types and each block can be expanded in the form of an algebraic equation.

Wilson's *F-G* Matrix Method: Examples

Potential constants of SO_3 molecule and SO_4 ion — The vibrational frequencies of sulphur trioxide (SO_3) were reported by Gerding and Lecomte[35] and recently by Khachkuruzov[36] on the basis of a planar model having a symmetry D_{3h}. The sulphate ion is having a tetrahedral symmetry and the frequencies are given in Landolt-Börnstein tables[37]. The potential constants of these have been evaluated by many workers using different types of potential function. The forces between the non-bonded atoms are not directly accounted for in a valence force field potential function, whereas they are treated as major constants in a Urey-Bradley potential function. Making use of an entirely different procedure, Heath and Linnett[5,38] have obtained the repulsion constant between the non-bonded atoms along with the major constants. In this investigation valence force field potential functions containing all interactions are used. An additional term is introduced to account for the force between the non-bonded oxygen atoms. The constants are evaluated using Wilson's *F-G* matrix method. The internal coordinates and choice of the symmetry coordinates are the same as used by Sundaram[39].

The orthonormalized symmetry coordinates of SO_3 molecule are:

A_1' type

$$R_1 = (\Delta d_1 + \Delta d_2 + \Delta d_3)/\sqrt{3}$$

E_1 type

$$\begin{aligned} R_{2a} &= (2\Delta d_1-\Delta d_2-\Delta d_3)/\sqrt{6} \\ R_{2b} &= (\Delta d_2-\Delta d_3)/\sqrt{2} \\ R_{3a} &= (2\Delta\alpha_1-\Delta\alpha_2-\Delta\alpha_3)/\sqrt{6} \\ R_{3b} &= (\Delta\alpha_2-\Delta\alpha_3)/\sqrt{2} \end{aligned}$$

A''_2

$$R_4 = \Delta\Upsilon$$

and $R = (\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3)/\sqrt{3}$

$\equiv 0$ is the redundant coordinate

In the internal coordinates, Δd_1, Δd_2 and Δd_3 are the changes in the interbond distances; $\Delta\alpha_1$, $\Delta\alpha_2$ and $\Delta\alpha_3$, the changes in the interbond angles; and $\Delta\gamma$, the change in the angle caused by the motion of the sulphur atom out of the plane of the oxygen atoms.

The orthonormalized symmetry coordinates of SO_4 ion are:

A_1 type

$$\begin{aligned} R_1 &= (\Delta d_1+\Delta d_2+\Delta d_3+\Delta d_4)/2 \\ R &= (\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}+\Delta\alpha_{41}+\Delta\alpha_{42} \\ &\quad +\Delta\alpha_{43})/\sqrt{6} \equiv 0 \text{ (Redundant)} \end{aligned}$$

E type

$$\begin{aligned} R_{2a} &= (2\Delta\alpha_{12}-\Delta\alpha_{23}-\Delta\alpha_{31}-\Delta\alpha_{41} \\ &\quad -\Delta\alpha_{42}+2\Delta\alpha_{43})/\sqrt{12} \\ R_{2b} &= (\Delta\alpha_{41}-\Delta\alpha_{31}+\Delta\alpha_{23}-\Delta\alpha_{42})/2 \end{aligned}$$

F_2 type

$$\begin{aligned} R_{3a} &= (2\Delta\alpha_{12}-\Delta\alpha_{23}-\Delta\alpha_{31}+\Delta\alpha_{41} \\ &\quad +\Delta\alpha_{42}-2\Delta\alpha_{43})/\sqrt{12} \\ R_{3b} &= (\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}-\Delta\alpha_{41} \\ &\quad -\Delta\alpha_{42}-\Delta\alpha_{43})/\sqrt{6} \\ R_{3c} &= (\Delta\alpha_{23}-\Delta\alpha_{31}-\Delta\alpha_{41}+\Delta\alpha_{42})/2 \\ R_{4a} &= (\Delta d_1+\Delta d_2-2\Delta d_3)/\sqrt{6} \\ R_{4b} &= (\Delta d_1+\Delta d_2+\Delta d_3-3\Delta d_4)/\sqrt{12} \\ R_{4c} &= (\Delta d_2-\Delta d_1)/\sqrt{2} \end{aligned}$$

where Δd_1, Δd_2, Δd_3 and Δd_4 are the changes in the interbond distances and $\Delta\alpha_{12}$, $\Delta\alpha_{23}$, $\Delta\alpha_{31}$, $\Delta\alpha_{41}$, $\Delta\alpha_{42}$, $\Delta\alpha_{43}$ are the changes in the interbond angles.

A general quadratic potential function used in the case of SO_3 molecule is given below:

$$\begin{aligned} 2V &= f_d(\Delta d_1^2+\Delta d_2^2+\Delta d_3^2)+d^2 f_\alpha(\Delta\alpha_1^2+\Delta\alpha_2^2+\Delta\alpha_3^2) \\ &\quad +2f_{dd}[(\Delta d_1)(\Delta d_2)+(\Delta d_2)(\Delta d_3)+(\Delta d_3)(\Delta d_1)] \\ &\quad +2df_{d\alpha}[\Delta d_1(\Delta\alpha_1+\Delta\alpha_3)+\Delta d_2(\Delta\alpha_2+\Delta\alpha_1) \\ &\qquad +\Delta d_3(\Delta\alpha_2+\Delta\alpha_3)] \\ &\quad +2d^2 f_{\alpha\alpha}[(\Delta\alpha_1)(\Delta\alpha_2)+(\Delta\alpha_2)(\Delta\alpha_3)+(\Delta\alpha_3)(\Delta\alpha_1)] \\ &\quad +2df'_{d\alpha}[(\Delta d_1)(\Delta\alpha_2)+(\Delta d_2)(\Delta\alpha_3)+(\Delta d_3)(\Delta\alpha_1)] \\ &\quad +f_q[\Delta q_1^2+\Delta q_2^2+\Delta q_3^2]+d^2 f_r[\Delta r]^2 \end{aligned}$$

where f_d is the S—O stretching force constant; f_α, the in-plane angular deformation constant; f_{dd}, the interaction constant between the two distances; $f_{d\alpha}$, the interaction constant between the distance and the neighbouring angle; $f'_{d\alpha}$, the interaction constant between the distance and the angle opposite to it; $f_{\alpha\alpha}$, the interaction constant between the two angles; f_q, the non-bonded constant between one oxygen and the rest of the oxygen atoms; and f_r, the out-of-plane bending constant.

A general quadratic potential function for SO_4 ion may be written as:

$$\begin{aligned} 2V &= f_d(\Delta d_1^2+\Delta d_2^2+\Delta d_3^2+\Delta d_4^2) \\ &\quad +d^2 f_\alpha(\Delta\alpha_{12}^2+\Delta\alpha_{23}^2+\Delta\alpha_{31}^2+\Delta\alpha_{41}^2+\Delta\alpha_{42}^2+\Delta\alpha_{43}^2) \\ &\quad +2d^2 f_{\alpha\alpha}[\Delta\alpha_{12}(\Delta\alpha_{23}+\Delta\alpha_{31}+\Delta\alpha_{41}+\Delta\alpha_{42}) \\ &\qquad +\Delta\alpha_{23}(\Delta\alpha_{31}+\Delta\alpha_{42}+\Delta\alpha_{43}) \\ &\qquad +\Delta\alpha_{31}(\Delta\alpha_{41}+\Delta\alpha_{43}) \\ &\qquad +\Delta\alpha_{41}(\Delta\alpha_{42}+\Delta\alpha_{43}) \\ &\qquad +\Delta\alpha_{42}(\Delta\alpha_{43})] \\ &\quad +2d^2 f'_{\alpha\alpha}(\Delta\alpha_{12}\Delta\alpha_{43}+\Delta\alpha_{23}\Delta\alpha_{41}+\Delta\alpha_{31}\Delta\alpha_{42}) \\ &\quad +2f_{dd}[\Delta d_1(\Delta d_2+\Delta d_3+\Delta d_4)+\Delta d_2(\Delta d_3+\Delta d_4) \\ &\qquad +\Delta d_3(\Delta d_4)] \\ &\quad +2df_{d\alpha}[\Delta d_1(\Delta\alpha_{12}+\Delta\alpha_{31}+\Delta\alpha_{41}) \\ &\qquad +\Delta d_2(\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{42}) \\ &\qquad +\Delta d_3(\Delta\alpha_{23}+\Delta\alpha_{31}+\Delta\alpha_{43}) \\ &\qquad +\Delta d_4(\Delta\alpha_{41}+\Delta\alpha_{42}+\Delta\alpha_{43})] \\ &\quad +2df'_{d\alpha}[\Delta d_1(\Delta\alpha_{23}+\Delta\alpha_{42}+\Delta\alpha_{43}) \\ &\qquad +\Delta d_2(\Delta\alpha_{31}+\Delta\alpha_{41}+\Delta\alpha_{43}) \\ &\qquad +\Delta d_3(\Delta\alpha_{12}+\Delta\alpha_{41}+\Delta\alpha_{42}) \\ &\qquad +\Delta d_4(\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31})] \\ &\quad +f_q(\Delta q_{12}^2+\Delta q_{23}^2+\Delta q_{31}^2+\Delta q_{41}^2+\Delta q_{42}^2+\Delta q_{43}^2) \end{aligned}$$

where the notation has the same significance as in the case of SO_3 molecule.

Making use of the additional term $f_q(\Delta_q)^2$ in the potential energy function, the F matrix elements are modified using the procedure adopted by Lovell *et al.*[40] and are given below:

SO_3 Molecule

For A'_1 species

$$[F_{11}] = [f_d+2f_{dd}+4A_0^2 f_q]$$

For E'_1 species

$$\begin{bmatrix} F_{22} & F_{23} \\ F_{32} & F_{33} \end{bmatrix} = \begin{bmatrix} f_d-f_{dd}+A_0^2 f_q & \frac{1}{2}(df_{\alpha\alpha}-df'_{d\alpha}+A_0B_0f_q) \\ & d^2f_\alpha+d^2f_{\alpha\alpha}+B_0^2f_q \end{bmatrix}$$

For A''_2 species

$$[F_{44}] = [\delta^2 f_r]$$

where f_d is the S—O stretching constant; f_α, the O—S—O bending constant; f_q, the constant between the non-bonded oxygen atoms; f_r, the out-of-plane constant, and others are interactions.

$$A_0 = \frac{d}{q}(1-\cos\alpha),\ B_0 = \frac{d^2}{q}\sin\alpha \text{ and } q = \sqrt{2(1-\cos\alpha)}$$

SO_4 Ion

For A'_1 species

$$[F_{11}] = [f_d+3f_{dd}+6A_0^2 f_q]$$

For E species

$$[F_{22}] = [d^2(f_\alpha-2f_{\alpha\alpha}+f'_{\alpha\alpha})+B_0^2 f_q]$$

For F species

$$\begin{bmatrix} F_{33} & F_{34} \\ F_{43} & F_{44} \end{bmatrix} = \begin{bmatrix} \begin{matrix} d^2(f_\alpha-f'_{\alpha\alpha}) \\ +B_0^2 f_q \end{matrix} & \begin{matrix} d\sqrt{2}(f_{d\alpha}-f'_{\alpha\alpha}) \\ +\sqrt{2}A_0B_0f_q \end{matrix} \\ & f_d-f_{dd}+2A_0^2 f_q \end{bmatrix}$$

The constants are having the same significance as in the case of SO_3 molecule.

The kinetic energy matrices are:

For SO_3 Molecule

$$[G_{11}] = \mu_o$$

$$\begin{bmatrix} G_{22} & G_{23} \\ G_{32} & G_{33} \end{bmatrix} = \begin{bmatrix} \mu_o + \frac{3\mu_s}{2} & -\frac{3\sqrt{3}\mu_s}{4d} \\ & \frac{3[\mu_s + 3\mu_o/2)]}{d^2} \end{bmatrix}$$

$$[G_{44}] = \frac{\mu_o + 3\mu_s}{d^2}$$

For SO_4 Ion

$$[G_{11}] = \mu_o$$

$$[G_{22}] = \frac{3\mu_o}{d^2}$$

$$\begin{bmatrix} G_{33} & G_{34} \\ G_{43} & G_{44} \end{bmatrix} = \begin{bmatrix} \frac{2\mu_o + (16/3)\mu_s}{d^2} & -\frac{8\mu_s}{3d} \\ & \mu_o + \frac{4}{3}\mu_s \end{bmatrix}$$

where μ_o and μ_s are the reciprocal masses of oxygen and sulphur respectively.

In both cases the constants are first obtained by neglecting f_q. In the case of SO_4 ion, the large number of constants occurring in the F matrix are equated to the corresponding values obtained in the square matrix $u'Fu$ and the following relations are obtained:

$$f_d = \frac{F_{11}+3F_{44}}{4};\ d^2f_\alpha = \frac{F_{22}}{3} + \frac{F_{33}}{2};\ f_{dd} = \frac{F_{11}-F_{44}}{4};$$

$$df_{d\alpha} = \frac{F_{34}}{\sqrt{8}};\quad df'_{d\alpha} = -\frac{F_{34}}{\sqrt{8}};\quad d^2f_{\alpha\alpha} = -\frac{F_{22}}{6};$$

and

$$d^2f'_{\alpha\alpha} = \frac{F_{22}}{3} - \frac{F_{33}}{2}$$

The non-bonded constants are obtained by neglecting a few interaction constants. For the SO_3 molecule, the calculations are made for two assignments and the values of these constants are given in Table 1 and those for SO_4 ion are given in Table 2.

The following general observations may be made from the results reported in Tables 1 and 2. The S—O stretching constant is found to have a low value in SO_4 ion as compared to that for SO_3 molecule. The low value in the case of SO_4 ion may be attributed to the ionic forces in the radical. This conclusion may be further substantiated by the large value of f_q in SO_4 ion and a comparatively low value in SO_3 molecule.

In the case of SO_3 molecule the out-of-plane constant f_r is found to be higher than the value obtained by Pistorius which is due to his wrong choice of the out-of-plane frequency.

In cases where the interaction constants are high (SO_4 ion), the introduction of the non-bonded forces alters the major constants and a Urey-Bradley type potential function appears to be most suited. The bending constants are appreciably altered by the non-bonded forces, whereas the stretching constants are less affected.

Coriolis Coupling and Rotational Distortion

Two general methods may be used to improve the reliability of the potential energy constants. In cases where the rotational structure of the bonds is resolvable, more useful information can be obtained from the rotational distortion and the Coriolis constants. Kivelson[42], Polo and Wilson[43] and Pierce[44] have calculated precise potential energy constants in some molecules using the vibrational data obtained for isotopic molecules and the microwave rotational spectral data. A systematic account of the rotational

TABLE 1 — FREQUENCIES, PARAMETERS AND POTENTIAL CONSTANTS OF SO_3 MOLECULE[41]

Species	Frequency assignments cm.$^{-1}$		Parameters	Potential constants, 10^5 dynes/cm.						Basis of calculation
	Gerding and Lecomte[35]	Khachkuruzov[36]		f_d	f_{dd}	$f_\alpha - f_{\alpha\alpha}$	$f_{d\alpha}$	$f_{d\alpha} - f'_{d\alpha}$	f_q	
A	1068	1069	S—O=1·45 A.	10·138	0·168	0·542	0·492	1·514	—	A
E'_1	530	440	$\alpha_1=\alpha_2=\alpha_3$	10·138	—	0·488	—	—	0·216	B
	1333	1333	$=120°$							
				9·989	0·399	0·370	0·412	1·514	—	C
A''_1	653	652		9·192	—	0·237	—	—	0·531	D

Basis of calculation: A, assignments of Gerding and Lecomte[35] without taking into account the effect of f_q; B, assignments of Gerding and Lecomte[35] including effect of f_q; C, assignments of Khachkuruzov[36] without taking into account the effect of f_q; and D, assignments of Khachkuruzov[36] including effect of f_q.

TABLE 2 — FREQUENCIES, PARAMETERS AND POTENTIAL CONSTANTS OF SO_4 ION[41]

Species	Frequencies cm.$^{-1}$	Parameters	Potential constants, 10^5 dynes/cm.										Basis of calculation
			f_d	f_α	$f_\alpha - f'_{\alpha\alpha}$	f_q	f_{dd}	$f_{\alpha\alpha}$	$f'_{\alpha\alpha}$	$f_{d\alpha}$	$f'_{d\alpha}$	$f_{d\alpha}+f'_{d\alpha}$	
A_1	983	S—O= 1·51 A.	7·424	0·718	—	—	0·563	−0·106	−0·293	0·145	−0·145	—	A
E	450	α=109°28	5·573	—	0·590	1·179	−0·391	—	—	—	—	0·173	B
F	611 1105												

Basis of calculation: A, without taking into account the effect of f_q; and B, including effect of f_q.

distortion in polyatomic molecules has been given by Kivelson and Wilson[45]. Examples of the application of the Coriolis constants in defining the force fields may be found in the work of Dennison[28] and of Hansen and Dennison[46]. Meal and Polo[47] have discussed the problem of setting up the Coriolis constant matrices in any normal coordinate treatment.

Applications of Force Fields

A few applications of the knowledge of the molecular force fields are: (i) Fundamental vibrational frequencies for isotopic molecules and partially isotopically substituted molecules can be calculated from a knowledge of these fields. These data are particularly useful when the spectrum of the molecule cannot be easily obtained and may be used for computing the thermodynamic properties of the molecules. (ii) Bond orders and bond moments and their derivatives can be obtained from a knowledge of the potential energy constants. (iii) Amplitudes of vibrations can be evaluated which can be used in the interpretation of the electron diffraction studies. The method of doing this has been explained by Morino and coworkers[48]. (iv) Calculation of the rotational distortion constants from vibrational force constants provides very valuable data for the analysis of the rotational spectra, particularly in the microwave region. (v) Calculation of the interatomic distances can also be made using the empirical rules of Badger[49] and Gordy[50]. These calculations, though approximate, compare favourably with the observed values as well as those obtained from covalent radii. (vi) The study of the force constants of some characteristic bonds and bond angles in molecules may reveal the nature of the forces holding the atoms together and the electronic structure of the molecules.

In the following sections some of these applications have been illustrated.

Bond Forces and Bond Orders

Gordy[50] has put forward an empirical relation for the bond stretching force constant K in terms of the bond order N, bond length d and the electronegativities (x_A and x_B) of the bonded atoms. This relation has been found to hold good for a large number of diatomic and simple polyatomic molecules in their ground states. The bond order N represents the effective number of covalent or electrovalent bonds acting between the two atoms considered. The empirical relation $K = 1{\cdot}67N(x_A x_B/d^2)^{3/4}+0{\cdot}30$ can be used with known stretching constants to predict the bond orders.

In this investigation, an attempt has been made, under the direction of the author, to calculate the bond orders for different types of molecules using the K values obtained on the basis of a Urey-Bradley force field. The electronegativities x_A and x_B of the atoms used in the calculation were taken from Gordy's data. The bond orders for the different bonds in some molecules evaluated during this investigation[51,52] are listed in Table 3.

Characteristic Bonds and Their Force Constants

The comparison of the different force constants of different molecules with similar groups and of the different force constants in a given molecule is very important because such a comparison throws light on the nature of the forces holding the atoms together, or, in other words, on the electronic structure of the molecules. If the restoring force between two atoms is the same in one molecule as in another, one would conclude that the electronic structure of the bond is at least very similar in the two cases. Conversely, if one knows that the electronic structure is the same, one would expect the same force constants. On the basis of an elementary theory of valence one would expect the C—H bond to have essentially the same electronic structure and, therefore, the same force constant in different molecules and similarly for the $C=O$, $C\equiv N$, and other bonds. This is indeed observed in many cases discussed here. However,

TABLE 3 — BOND ORDERS FOR VARIOUS BONDS

Bond	Molecule	Bond distance A.	K 10^5 dynes/cm.	Bond order (N)
C−H or C−D	CH_2	1·08	4·686	0·87
	$HCOF$ $DCOF$	1·10	4·286	0·83
	CF_3H CF_3D	1·094	4·634	0·84
	CBr_3H_3 CBr_3D_3	1·093	4·857	0·88
	CH_3D CHD_3	1·1	4·568	0·85
	H_2CCO	1·075	4·526	0·85
	CH_3CN	1·112	4·552	0·84
	CH_3NC	1·094	4·607	0·83
	C_3H_4	1·06	4·629	0·80
C=C	C_3O_2	1·28	9·032	1·86
C−C	CH_3CN	1·4582	5·130	1·25
C≡N	CH_3CN	1·1572	17·248	2·76
C−N	CH_3NC	1·427	5·130	1·08
N−C	CH_3NC	1·167	16·246	2·63
C=O	$HNCO$	1·171	15·34	2·28
	$HCOF$ $DCOF$	1·18	11·837	1·78
	COH_2 COD_2	1·18	12·61	1·85
	C_3O_2	1·19	15·55	2·32
	H_2CCO	1·16	14·507	2·13
	BH_3CO BD_3CO	1·131	17·543	2·30
C−F	CF_2	1·36	5·729	0·91
	CF_4	1·38	5·134	0·83
	CF_3H CF_3D	1·329	5·325	0·82
N−H or N−D	HN_3	1·021	5·637	0·83
	DN_3	1·021	5·679	0·83
	$HNCO$	0·987	6·412	0·79
	$HNCS$	1·013	6·387	0·98
	NH_2D	1·014	6·105	0·88
	NH_2D	1·014	6·247	0·90
	NHD_2	1·014	6·173	0·89
	NHD_2	1·014	6·197	0·90
S=O	SOF_2	1·412	9·812	1·88
	$SOCl_2$	1·45	9·285	1·85
	$SOBr_2$	1·45	8·151	1·62

on closer examination, it is found that this invariance of force constants holds exactly only if the bond is in similar surroundings. For the bond bending force constants, the condition of similar surroundings is still more critical. It is not enough that the same type of bond (single, double or triple) be adjacent to the one considered; the atoms at the other end of the adjacent bond must also be the same. The force constants of several characteristic bonds and bond angles have been obtained and reported in earlier papers by the author and his collaborators[11-24, 53-74].

The force constants obtained for some characteristic bonds are listed in Table 4.

The following conclusions may be drawn from the results presented in Table 4: (1) The C—H bond in the molecules studied is in similar surroundings. The C—H stretching force constant has approximately a constant value of the order of $4 \cdot 8 \times 10^5$ dynes/cm. (2) The C=O stretching force constants depend on the nature of the environment. (3) The carbon-halogen stretching constant decreases as the higher member of the halogen group is substituted. (4) The S=O stretching force constant in thionyl halides behaves in a peculiar way. The stretching constant shows a decrease in value as one passes from lower to higher member of the halogen group. It may be due to the fact that the S=O stretching force constant increases as the electronegativity of the groups on sulphur increases.

TABLE 4 — FORCE CONSTANTS FOR SOME CHARACTERISTIC BONDS

Bond	Molecule	Bond distance A.	Force constant (K) 10^5 dynes/cm.
C−H	CH_3D CHD_3	1·1	4·880
	CF_3H	1·094	4·634
	CBr_3H	1·093	4·857
	CH_3CN	1·112	4·552
	CH_3NC	1·094	4·607
C−D	CH_3D	1·1	4·568
	CD_3H	1·1	4·431
	CF_3D	1·094	4·634
	CBr_3D	1·093	4·857
C−C	CH_3CN	1·4582	5·130
C=C	C_3O_2	1·28	9·032
C=C	H_2CCO D_2CCO	1·315	10·050
C=C	C_3H_4	1·340	9·372
C−N	CH_3NC	1·427	5·13
N=C	HNCO	1·207	13·303
N=C	HNCS	1·216	13·303
C≡N	CH_3CN	1·1572	17·248
N≡C	CH_3NC	1·167	16·246
C=O	HNCO	1·171	15·34
	HCOF DCOF	1·18	11·837
	COH_2 COD_2	1·18	12·61
	C_3O_2	1·19	15·55
	H_2CCO D_2CCO	1·16	14·507
	BH_3CO BD_3CO	1·131	17·543
C−F	CF_2	1·36	5·729
	CF_4	1·38	5·134
	CF_3H CF_3D	1·329	5·325
C−Cl	CCl_2	1·77	2·272
	CCl_3F	1·77	2·088
C−Br	CBr_2	1·91	1·919
	CBr_3F	1·91	1·513
	CBr_3H CBr_3D	1·91	1·513
N−H	HNCO	0·987	6·412
	HNCS	1·013	6·387
	NH_2D	1·014	6·105
	NHD_2	1·014	6·173
N−D	NH_2D	1·014	6·247
	NHD_2	1·014	6·197
S=O	SOF_2	1·412	9·812
	$SOCl_2$	1·45	9·285
	$SOBr_2$	1·45	8·151

Forces between Non-bonded Atoms

The Urey-Bradley type of potential function enables one to calculate the force constant related to changes in the distance between non-bonded atoms. Values of these repulsion constants in the case of certain pairs of atoms are listed in Table 5.

The correlation between the repulsion constant and the distance between the non-bonded atoms (Table 5) shows that the repulsion constant decreases as the distance between the non-bonded atoms increases and it is of the Van der Waals type being inversely proportional to the *n*th power of the separation distance where *n* ranges between 4 and 6. It is an interesting observation that the repulsion constants in H—H and D—D are generally negative.

Force Constants and Dipole Moments

Langseth and Møller[75] have suggested that there may be a certain simple connection between the force constants of some bonds involving hydrogen and ionic refractions of the atoms to which the hydrogen is bonded. An approximate formula for simple hydrogen bonds has been derived by Møller[76] which correlates the dipole moments of H-bond with the corresponding stretching force constant, bond length and ionic refraction.

$$\mu_{ij} = 1 \cdot 8 d_{ij} \left[1 - 0 \cdot 131 \left(\frac{8 \cdot 8}{d_{ij}} - K_{ij}\right)^{1/2} A_j^{1/2}\right] \text{ debyes}$$

where μ_{ij} is the dipole moment of the X—H bond; d_{ij}, the bond length in A.; K_{ij}, the stretching force constant in 10^5 dynes/cm.; and A_j, the ionic refraction in cm.^{3}.

The dipole moments of some X—H bonds have been calculated from the X—H stretching force constants obtained on the basis of a Urey-Bradley potential force field[51,52]. The calculated and experimental[77] values of the dipole moments are given in Table 6 along with the values of the bond force constants and ionic refraction[78] of the atom to which H is bonded.

It has been shown by Smith[79] that for symmetrical tetrahedral molecules the atom polarization A^P is given by

$$A^P = \frac{16\pi N\mu_i^2}{9}\left(\frac{1}{R^2K_s}+\frac{1}{K_b}\right)$$

where N is the Avogadro number; μ_i, the dipole moment; R, the internuclear distance; K_s and K_b, the stretching and bending force constants respectively.

The bond moments for CF_4, SiH_4, SiF_4 and $GeCl_4$ are calculated using the Urey-Bradley force constants[52] and the values are presented in Table 7. The A^P values used in this calculation are the same as those given by Smith[79].

TABLE 5 — FORCES BETWEEN NON-BONDED ATOMS

Non-bonded atoms	Molecule	Distance A.	Repulsion constant 10^5 dynes/cm.
H−H	H_2O	1·516	−0·1568
	CH_2	1·791	−0·0663
	H_2S	1·935	−0·0380
	NH_4	1·656	0·0840
	SiH_4	2·334	0·0270
	PH_4	2·401	−0·0249
	GeH_4	2·455	−0·0240
D−D	D_2O	1·524	−0·1724
	D_2S	1·948	−0·1008
O−O	NO_2	1·865	1·2260
	NO_2^-	2·085	1·1190
	NO_2^+	2·193	0·8973
	PO_4	2·422	0·7347
	SO_2	2·528	0·4594
	ClO_2	2·561	0·3185
	SiO_4	2·564	0·5295
	OsO_4	2·613	0·5101
	CrO_4	2·645	0·5040
	SeO_4	2·678	0·3423
	IO_4	2·874	0·2259
F−F	NF_3	2·137	1·1070
	CF_4	2·254	0·9912
	PF_3	2·39	0·6220
	SiF_4	2·458	0·4803
	AsF_3	2·57	0·4310
Cl−Cl	CCl_4	2·87	0·6500
	CCl_3-CCl_3	2·87	0·6500
	$CHCl_2$-COCl	2·87	0·6500
	CCl_2	2·935	0·5714
	Cl_2O	3·069	0·4483
	SCl_2	3·130	0·3930
	$GeCl_4$	3·397	0·2667
	$ZrCl_4$	3·806	0·1331
	$HfCl_4$	3·936	0·0825
	$AlCl_4$	4·197	0·0573
Br−Br	C_2Br_4	3·12	0·5000
	CBr_3-CBr_3	3·12	0·5000
	BBr_3	3·25	0·4080
	$SOBr_2$	3·374	0·2410
	$SiBr_4$	3·51	0·2300
	$GeBr_4$	3·707	0·0861
	$GaBr_4$	3·843	0·0654
	$TeBr_4$	3·968	0·0568
I−I	HfI_4	4·490	0·0375
	InI_4	4·496	0·0330

The direction of the dipole moment of the C—H bond as obtained here is opposite to that calculated by Coulson[78] but is in conformity with that indicated by Møller[76]. In general, the agreement between the calculated and experimental bond moments, except in the case of N—H bond, is satisfactory, considering the empirical nature of the formula used and the uncertainties inherent in the ionic refractions.

Mean Amplitudes of Vibration

If the instantaneous intramolecular distance between an arbitrary pair of atoms be denoted by R and the equilibrium distance by R_e, the root-mean-square deviation

$$U = [\overline{(R-R_e)^2}]^{1/2}$$

will be called the mean amplitude of vibration and its square (U^2) the mean-square amplitude of vibration. The importance of mean amplitudes of vibration in molecular structure studies will be understood from the following statements. As is well known, the rigid model of a polyatomic molecule of given symmetry in its equilibrium position is defined by a certain number of parameters, i.e. interatomic distances and occasionally some interbond angles. To define the actual non-rigid molecular model, an additional set of parameters is required. For this purpose the mean amplitudes of vibration are highly suitable. A precise knowledge of some mean amplitudes of vibration of a molecule may serve as

TABLE 6 — DIPOLE MOMENTS OF X—H BONDS

Bond	Molecule	d_{ij} A.	K_{ij} 10^5 dynes/cm.	A_j cm.^{3}	μ_{ij}, debyes	
					Calc.	Exp.
OH	H_2O	0·958	8·472	4·06	1·341	1·51
SH	H_2S	1·345	3·967	15·0	0·449	0·68
SeH	H_2Se	1·47	3·198	17·3	0·238	0·3
NH	HN_3	1·021	5·637	7·0	0·747	1·31
NH	HNCO	0·987	6·412	7·0	0·802	—
NH	HNCS	1·013	6·387	7·0	0·864	—
NH	NH_2D	1·014	6·105	7·0	0·810	—
NH	NHD_2	1·014	6·173	7·0	0·824	—
PH	PH_4	1·47	3·233	18·0	0·206	0·36
CH	CH_2	1·08	4·586	12·0	0·279	0·4
CH	HCOF	1·1	4·286	12·0	0·249	—
CH	CF_3H	1·094	4·634	12·0	0·319	—
CH	CBr_3H	1·093	4·857	12·0	0·371	—
CH	CH_3D and CHD_3	1·1	4·880	12·0	0·393	—
CH	H_2CCO	1·075	4·526	12·0	0·255	—
CH	CH_3CN	1·112	4·552	12·0	0·336	—
CH	CH_3NC	1·094	4·607	12·0	0·313	—
CH	C_3H_4	1·06	4·629	12·0	0·248	—

TABLE 7 — DIPOLE MOMENTS IN TETRAHEDRAL MOLECULES

Molecule	A^P	R A.	K_s	K_b	μ_i, debyes (Calc.)
CF_4	2·86	1·38	5·134	0·3342	1·6440
SiH_4	1·79	1·4	2·712	0·0270	0·2241
SiF_4	5·46	1·56	5·201	0·0656	0·3652
$GeCl_4$	6·5	2·1	2·207	0·0186	0·6205

additional information to the normal frequencies for determination of force constants of molecules.

Mean amplitudes of vibration are determined by the two largely different methods of electron diffraction and molecular spectroscopy. There is, however, no theoretical foundation for the practice of referring to the mean amplitudes of vibration evaluated from electron diffraction data as 'observed' and to that evaluated from spectroscopical data as 'calculated'. The mean amplitudes of vibration are not directly observed by either of the methods, but are obtained from complicated computations from the measured and interpreted experimental data.

The computations of mean amplitudes of vibration from spectroscopic data are based on the vibrational frequencies as obtained from the assignment of observed frequencies in the infrared and Raman effect.

Cyvin's secular equation method[80] makes it possible to establish relations between the mean-square amplitude quantities and the normal frequencies of a polyatomic molecule.

The elements of the mean-square amplitude matrix are obtained by solving the secular equation

$$|\Sigma G^{-1} - \Delta E| = 0 \qquad \ldots(13)$$

where G^{-1} is the inverse kinetic energy matrix and the values of Δ are given by the relation

$$\Delta_K = \left(\frac{h}{8\pi^2 \nu_K}\right) \coth \left(\frac{h\nu_K}{2kT}\right) \qquad \ldots(14)$$

In Eq. (14), ν_K is the normal frequency, h is the Planck's constant, k the Boltzmann's constant and T the absolute temperature.

If the coordinates S are chosen as a set of symmetry coordinates, the mean-square amplitude matrix will have a diagonalized form identical with the energy matrices, depending on molecular symmetry. Hence the new secular Eq. (13) will factorize in the same manner as the ordinary secular equation $|FG - E\lambda| = 0$. If the symmetry coordinates S are found by Wilson's method as an orthogonal transformation of a set of internal coordinates denoted by q then we have

$$S = Rq;\ q = R'S \qquad \ldots(15)$$

R being an orthogonal matrix.

The relations connecting the symmetrized matrix Σ and the mean-square amplitude quantities σ of the internal coordinates and non-bonded distances can be obtained as follows.

A set of bonded and non-bonded interatomic distance deviations (r) can be related to the set of internal coordinates q by the expression

$$r = Uq \qquad \ldots(16)$$

where the matrix U is assumed to be known from the geometry of the molecule under consideration. If r is related to the set of symmetry coordinates S by

$$r = VS \qquad \ldots(17)$$

Then

$$V = UR' \qquad \ldots(18)$$

Here R' is the transpose of the orthogonal matrix of transformation from internal coordinates to symmetry coordinates. The elements of matrix σ can be obtained from

$$\sigma = V\Sigma V' \qquad \ldots(19)$$

Of all the elements of the σ matrix, the important ones are σ_r and σ_r^* related to the bonded and non-bonded interatomic distances respectively where

$$\sigma_r = \langle r^2 \rangle \quad \text{and} \quad \sigma_r^* = \langle r^{*2} \rangle$$

The mean amplitudes of vibration in the case of CF_2 molecule are obtained as detailed in the following.

The fundamental frequencies of CF_2 are: $\nu_1 = 1079$, $\nu_2 = 532$ and $\nu_3 = 1262$ cm.$^{-1}$ and $\alpha = 110°$.

The mean-square amplitudes (in A.^{2}) for CF_2 at 300°K. (Rajalakshmi, K. V., unpublished work) are given below:

$\Sigma_1 = 0{\cdot}001901$, $\Sigma_2 = 0{\cdot}008702$, $\Sigma_{12} = -0{\cdot}001420$, $\Sigma_3 = 0{\cdot}002205$, $\sigma = 0{\cdot}002053$, $\sigma' = -0{\cdot}000152$, $\tau = 0{\cdot}008702$, $\rho = -0{\cdot}001004$, $\sigma^* = 0{\cdot}003466$ and $\sigma'^* = 0{\cdot}000981$

Of all the quantities given above, σ and σ^* are the most important ones representing the bonded and non-bonded distances respectively.

The mean amplitudes of vibration for the bonded and non-bonded distances are given by $U_{C-F} = \sigma^{1/2}$ and $U_{F-F} = (\sigma^*)^{1/2}$. They are

$$U_{C-F} = 0{\cdot}045311 \text{ A.}$$

$$U_{F-F} = 0{\cdot}058878 \text{ A.}$$

These results will prove very useful in the interpretation of the electron diffraction studies on these molecules.

Thermodynamic Properties

One of the important applications of the study of the vibrational spectra of a polyatomic molecule is the calculation of the thermodynamic properties such as heat content, free energy, entropy and heat capacity. Such calculations are possible if all the fundamental vibrational wave numbers and their degeneracies are known. The determination of the thermodynamic properties for a molecule has great practical importance since it is often difficult and sometimes impossible to measure these quantities experimentally. Furthermore, in some cases the calculated values even surpass the accuracy of thermochemical measurements.

The energy of a molecular system may be treated as the sum of the energies of the translational, rotational, vibrational, electronic and nuclear spin motions. The electronic state has been taken as the ground state. The nuclear spin energy has been neglected since it is much smaller than the translational, rotational or vibrational energies. The calculations are all based on a rigid rotor, harmonic oscillator model with no interaction between vibrational and rotational energies. On the basis of these assumptions the following relations were obtained:

$$S^\circ_{tr} + S^\circ_r = 2{\cdot}2870\ (8 \log T + 3 \log M + \log I_{xx} I_{yy} I_{zz} - 2 \log \sigma) - 7{\cdot}6965$$

$$-(F^\circ_{tr} + F^\circ_r - E^\circ_o)/T = S^\circ_{tr} + S^\circ_r - 7{\cdot}9459$$

and

$$(C^\circ_p)_{tr} + (C^\circ_p)_r = (H^\circ_{tr} + H^\circ_r - E^\circ_o)/T = 7{\cdot}9459$$

where S is the entropy; F, the free energy (in cal./mole); C_p, the heat capacity at constant pressure; H, the heat content (in cal./mole); E_o°, the energy of one mole of a perfect gas at 0°K.; T, the temperature (in °K.); $I_{xx}.I_{yy}.I_{zz}$, the product of the principal moments of inertia in (*amu* A.^{2})^3; and M, the molecular weight. The subscripts *tr* and *r* refer to translational and rotational motions respectively. The symmetry number σ is the number of indistinguishable positions into which a molecule can be turned by simple rotations.

The vibrational contributions to C_p, H, F and S corresponding to values of (1·4387 × wave number/T) are evaluated by use of the tables prepared by Taylor and Glasstone[81] and Pitzer[82]. For any particular thermodynamic property under consideration, for each value of (1·4387 × wave number/T), the value is read from the table, and multiplied by the degeneracy of the fundamental. Then all the vibrational contributions are summed for the particular thermodynamic property. Values for C_p, H and F are read directly from the tables, while the contribution to S is the sum of the vibrational contributions of the free energy and the heat content. The vibrational contributions are then added to the translational and rotational contributions to give the values of the entropy, free energy, heat content and heat capacity. Values of the frequencies and molecular parameters for three molecules, viz. GeH_4, $GeCl_4$ and $GeBr_4$, are given in Table 8 and the thermodynamic properties of these molecules calculated[52] using the above relations are listed in Table 9.

TABLE 8 — FREQUENCIES AND MOLECULAR PARAMETERS OF GeH_4, $GeCl_4$ AND $GeBr_4$

Molecule	Internuclear distance A.	Frequencies, cm.$^{-1}$			
		A' type σ_1	E type σ_2	F_2 type	
				σ_3	σ_4
GeH_4	1·53	1990	832	2110	933
$GeCl_4$	2·08	397	132	451	328
$GeBr_4$	2·297	234	78	171	111

TABLE 9 — CALCULATED VALUES OF THE THERMODYNAMIC PROPERTIES OF GeH_4, $GeCl_4$ AND $GeBr_4$ MOLECULES

(Thermodynamic properties are in cal./deg./mole)

T, °K.	$(H^\circ - E_0^\circ)/T$	$-(F^\circ - E_0^\circ)/T$	S°	C_p°
		GeH_4		
100	7·946	34·304	42·250	7·946
200	8·054	39·828	47·883	8·633
273·16	8·383	42·384	50·767	9·996
300	8·560	43·179	51·738	10·586
400	9·331	45·745	55·086	12·677
500	10·207	47·914	58·107	14·576
600	11·055	49·846	60·900	16·182
700	11·889	51·615	63·504	17·570
800	12·678	53·253	65·932	18·765
900	13·420	54·799	68·219	19·761
1000	14·472	56·760	71·231	20·792
		$GeCl_4$		
100	10·741	51·176	61·857	15·195
200	14·488	59·851	74·340	20·600
273·16	16·399	64·650	81·049	22·531
300	16·990	66·250	83·239	23·012
400	18·639	71·359	89·998	24·116
500	19·801	75·667	95·468	24·690
600	20·661	79·418	100·079	25·026
700	21·283	82·591	103·874	25·226
800	21·782	85·382	107·164	25·367
900	22·208	88·135	110·343	25·469
1000	22·509	90·304	112·813	25·529
		$GeBr_4$		
100	13·010	57·838	70·848	18·419
200	17·034	68·227	85·265	22·874
273·16	18·792	73·860	92·652	24·090
300	19·287	75·663	94·951	24·365
400	20·627	81·345	101·972	24·967
500	21·545	86·134	107·679	25·271
600	22·144	89·892	112·035	25·432
700	22·647	93·483	116·130	25·540
800	23·007	96·538	119·546	25·606
900	23·315	99·386	122·701	25·655
1000	23·541	101·800	125·341	25·687

Summary

The various force fields postulated for the study of vibrations of polyatomic molecules are briefly outlined. The method of evaluation of the force constants using the Wilson's *F-G* matrix method has been explained taking the case of SO_3 and SO_4 molecules as examples. The different factors to which attention has to be given for improving the accuracy of the potential constants are also indicated. Some important applications which include the evaluation of the bond forces and bond orders, force constants in relation to dipole moments, characteristic bonds and their force constants, non-bonded forces, mean amplitudes of vibration, and thermodynamic proties have been discussed with examples.

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Measurement of Gaseous Thermal Diffusion Factor by Trennschaukel

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A KNOWLEDGE of the gaseous thermal diffusion factor is basic to and useful in the solution of a variety of problems of both fundamental and applied nature. Its intimate relationship with the nature of intermolecular forces has been made use of in recent years by a number of workers[1-4] for deriving certain inferences which could not be drawn otherwise. In the design of isotope separation plants, based either on pure thermal diffusion[5-8] or along with chemical exchange[9-11], the values of the thermal factor, α_T, are needed. These interesting applications have led several workers[1,4,12-17] to improve and devise better techniques of measuring α_T and also to develop simpler and accurate theoretical expressions[18-28] for α_T to warrant proper interpretation of the experimental data.

Chapman and Enskog propounded a rigorous kinetic theory of thermal diffusion which has been well presented in treatises by Chapman and Cowling[18] and Hirschfelder *et al.*[29]. Since then several elementary theories[30] have been advanced to explain this phenomenon. According to rigorous theory the relation defining α_T is

$$\ln q(\infty) = \int_{T_1}^{T_2} \alpha_T \, d \ln T \qquad \ldots(1)$$

where

$$q(\infty) = \frac{X_2(\infty)\{1-X_1(\infty)\}}{X_1(\infty)\{1-X_2(\infty)\}}$$

is the separation factor, X represents the mole fraction of the lighter component, subscripts 1 and 2 refer to the two bulbs at temperatures T_1 and T_2 $(T_2>T_1)$ and ∞ to the steady state. For a particular system the value of α_T depends both on temperature and composition and, therefore, special methods are needed to evaluate it from Eq. (1). Because of the feeble composition dependence of α_T, and as the thermal separation is usually small, it is sufficiently accurate to assign the mean composition to the determined value of α_T. For temperature assignment two methods have been used. In one method an average value of the thermal diffusion factor, $\bar{\alpha}_T$, for the temperature range T_1 to T_2 is calculated from the expression

$$\bar{\alpha}_T = \ln q(\infty)/\ln (T_2/T_1) \qquad \ldots(2)$$

This average value is then identified with the actual value of α_T at some intermediate temperature[31,32] $\bar{T}$ between T_1 and T_2. The second method which is preferable consists in making a series of measurements at different values of T_2 and a fixed value of T_1 and then determining α_T by differentiation

$$\alpha_T = d \ln q(\infty)/d \ln (T_2/T_1),\ T_1 \text{ constant} \ \ldots(3)$$

so that α_T at any temperature T_2 is the slope of the $\ln q(\infty)$ versus $\ln (T_2/T_1)$ curve at the point corresponding to T_2. Eq. (3) gives comparatively unambiguous results than Eq. (2) and permits α_T to be determined over a larger temperature range, but it introduces considerable strain on the precision of the measurements because of the differentiation.

Chapman and Dootson[33] were the first to verify the phenomenon of thermal diffusion in a simple two-bulb apparatus. Since then this simple apparatus has been used by a number of workers with several improvements. The major difficulty with this method is the small thermal separation obtained which sensitively controls the accuracy attainable in the determination of α_T. To enhance the separation of the two-bulb apparatus, the multiple expansion technique[34-36] has been used. In this method after the steady state is reached one of the bulbs is evacuated and the contents of the other bulb are allowed to expand in the evacuated bulb and then thermally equilibrated. The net effect is that if five expansions are tried, the total separation is five-fold of the single elementary separation. Here, of course, it has been tacitly assumed that the thermal diffusion separation is independent of pressure, a fact which is supported by theory[37].

Another device for multiplying the elementary two-bulb separation developed by Clusius and Huber[38] is known as 'Trennschaukel' or 'swing-separator'. Since this pioneering work[38], several workers[39-45] have used this apparatus to measure α_T. Van der Waerden[46] has worked out the theory of this apparatus and has given expressions for the various design and correction factors. In view of the increasing prospect of applicability of this apparatus and the promise it offers for measuring α_T, it would be of interest to discuss the theory of this apparatus in a more physical way and essentially derive similar results though with a different approach.

The swing-separator (Fig. 1) consists of a number of identical suitable size vertical tubes arranged such that the bottom of one tube is suitably connected[47] with the top of the next tube by a capillary of suitable bore. The top ends of all the tubes are maintained at temperature T_2, while the bottom ends are at temperature T_1 such that $T_2>T_1$, to avoid the possibility of any convection. The top of the first tube is connected to the bottom of the last tube via some sort of gas pump which pushes and pulls the gas as a whole through the entire assembly. Such an arrangement and operation is intended to secure equality of concentration between the top end of one bulb with the bottom end of the preceding tube, with the result that if the whole assembly contains N tubes the difference in concentration of a component between the top end of the first tube and the bottom end of the last tube will be N times the separation obtained in a single tube. In the following sections the various criteria which

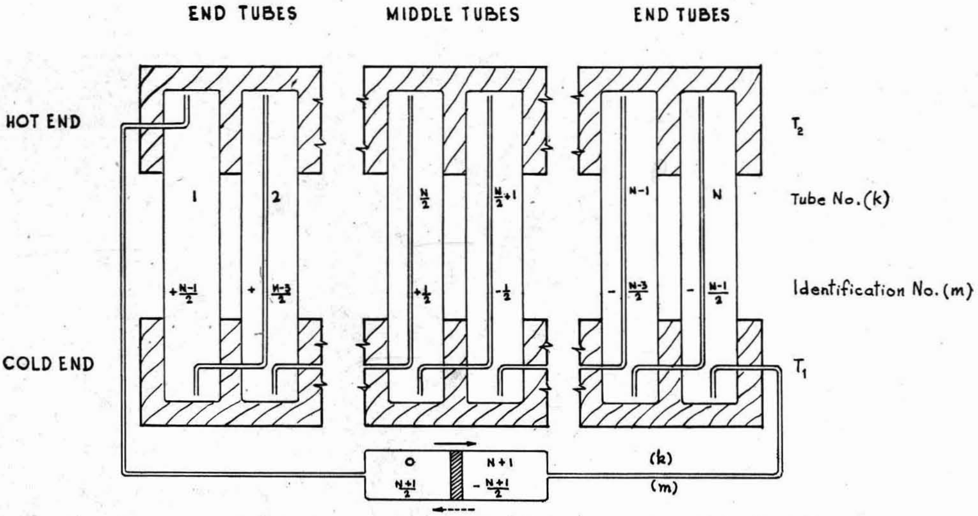

Fig. 1 — Schematic representation of a trennschaukel consisting of an even number of tubes [→ indicates the direction of piston movement in the first half cycle and - - - → that in the other half cycle]

can lead to the ideal operation of a trennschaukel are derived and the various correction factors which appear because of the non-fulfilment of the ideal geometry required have been calculated.

Separation Factor for a Trennschaukel

At the steady state let $X_k(\infty)$ and $X^k(\infty)$ represent the mole fraction of the lighter component in the kth tube at the bottom and top ends respectively. Then the separation of the lighter component in the kth tube, $S_k(\infty)$, is given by

$$S_k(\infty) = X^k(\infty) - X_k(\infty) \qquad \text{...(4)}$$

and the total separation in the system consisting of N tubes will be given by

$$\underset{(1\rightarrow N)}{S(\infty)} = [X^1(\infty)-X_1(\infty)]+[X^2(\infty)-X_2(\infty)] + \ldots\ldots + [X^N(\infty)-X_N(\infty)] \qquad \text{...(5)}$$

Since

$$X^{k+1}(\infty) = X_k(\infty), \text{ where } k = 1, 2 \ldots (N-1) \qquad \text{...(6)}$$

therefore,

$$\underset{(1\rightarrow N)}{S(\infty)} = [X^1(\infty)-X_N(\infty)] \qquad \text{...(7)}$$

The expression for the flux density of the lighter component, $\vec{J}$, under the effect of a temperature gradient is[1]

$$\vec{J} = -nD\,[\text{grad}\,X + X(1-X)\alpha_T\,\text{grad}\ln T] \qquad \text{...(8)}$$

Here D is the concentration diffusion coefficient and n, the total number of both the types of molecules per unit volume. At the steady state $\vec{J} = 0$ and integration of Eq. (8), say for the kth tube, gives

$$\int_{X_k(\infty)}^{X^k(\infty)} \frac{dX}{X(1-X)} = -\int_{T_1}^{T_2} (\alpha_T)_k\, d\ln T \qquad \text{...(9)}$$

or

$$\overline{(\alpha_T)_k} = \ln q_k(\infty)/\ln (T_2/T_1) \qquad \text{...(10)}$$

where

$$q_k(\infty) = \frac{X^k(\infty)\{1-X_k(\infty)\}}{X_k(\infty)\{1-X^k(\infty)\}} \qquad \text{...(11)}$$

However, for the trennschaukel unit as a whole consisting of N tubes, Eq. (10) gives

$$\sum_{k=1}^{N} \overline{(\alpha_T)_k} = \sum_{k=1}^{N} \ln q_k(\infty)/\ln (T_2/T_1) \qquad \text{...(12)}$$

Rigorously speaking, α_T depends feebly on composition and as such its value will vary from tube to tube, but as the change in average composition is small, α_T can be assumed to be constant and same for all the tubes. Consistent with this approximation,

$$\bar{\alpha}_T = \frac{1}{N}\frac{\ln Q(\infty)}{\ln (T_2/T_1)} \qquad \text{...(13)}$$

If α_T is composition dependent $\bar{\alpha}_T$ may be identified with the average of α_T values of the various individual separating tubes. Here, the overall separation factor, $Q(\infty)$, is given by

$$Q(\infty) = \frac{X^1(\infty)\{1-X_N(\infty)\}}{X_N(\infty)\{1-X^1(\infty)\}} \qquad \text{...(14)}$$

Eq. (13) shows how separation is multiplied in a trennschaukel.

An alternative solution of Eq. (8) has been suggested by Moran and Watson[39] which holds rigorously in those cases where the product $X(1-X)$ remains essentially constant before and after the separation. In this case instead of Eq. (10), the following equation is obtained:

$$\overline{(\alpha_T)_k} = \frac{S_k(\infty)}{[X(\infty)\{1-X(\infty)\}]_k}\cdot\frac{1}{\ln (T_2/T_1)} \qquad \text{...(15)}$$

An elaboration of Eq. (15) for the case of a trennschaukel has been given by Saxena *et al.*[3].

For an assembly of N tubes Eq. (15) gives

$$\frac{S_1(\infty)}{[X(\infty)\{1-X(\infty)\}]_1} = \frac{S_2(\infty)}{[X(\infty)\{1-X(\infty)\}]_2} = \ldots. = \frac{S_N(\infty)}{[X(\infty)\{1-X(\infty)\}]_N} = \bar{\alpha}_T \ln (T_2/T_1) \quad \ldots(16)$$

where the subscripts refer to the number of the tube. From Eq. (16) we get

$$\frac{S_1(\infty)+S_2(\infty)+\ldots\ldots\ldots+S_N(\infty)}{[X(\infty)\{1-X(\infty)\}]_1+[X(\infty)\{1-X(\infty)\}]_2+\ldots\ldots+[X(\infty)\{1-X(\infty)\}]_N} = \bar{\alpha}_T \ln (T_2/T_1) \quad \ldots(17)$$

As the composition of the bottom end of each tube is the same as the top end of the next tube, the numerator of the left side of Eq. (17) will be equal to the difference in composition between the top end of the first tube and the bottom end of the last tube, i.e. $\underset{(1\rightarrow N)}{S(\infty)}$. Also, if it is assumed that

$$[X(\infty)\{1-X(\infty)\}]_1+[X(\infty)\{1-X(\infty)\}]_2+\ldots\ldots+[X(\infty)\{1-X(\infty)\}]_N = N[X(1-X)]_{\text{initial}} \quad \ldots(18)$$

Eq. (17) reduces to

$$\frac{\underset{(1\rightarrow N)}{S(\infty)}}{N[X(1-X)]_{\text{initial}}} = \bar{\alpha}_T \ln (T_2/T_1) \quad \ldots(19)$$

In actual practice, $X(1-X)$ changes from one tube to the next, though in most cases the difference may be negligible. If, however, it is assumed that $X(1-X)$ varies in such a way that the difference of $X(1-X)$ values between the two consecutive tubes is constant, the left side of Eq. (18) can be summed accurately so that

$$[X(\infty)\{1-X(\infty)\}]_1+[X(\infty)\{1-X(\infty)\}]_2+\ldots\ldots+[X(\infty)\{1-X(\infty)\}]_N = \tfrac{1}{2}N\Big[[X(\infty)\{1-X(\infty)\}]_1+[X(\infty)\{1-X(\infty)\}]_N\Big] \quad \ldots(20)$$

For any other type of variation Eq. (20) will not be exact.

It is interesting to note that $\bar{\alpha}_T$ calculated from Eqs. (13) and (19) bears the following simple relationship

$$[\bar{\alpha}_T]_Q = [\bar{\alpha}_T]_S \left[1+\frac{1}{12}\frac{\Big[\underset{(1\rightarrow N)}{S(\infty)}\Big]^2}{\{X(1-X)\}^2_{\text{initial}}} \times\{1-3X(1-X)\} \right]_{\text{initial}} \quad \ldots(21)$$

In deriving Eq. (21) it has been assumed that the two bulbs share the separation equally, which requires the system to be symmetrical about the middle section of each main tube. Eq. (21) shows that the values of $\bar{\alpha}_T$ in the case of a trennschaukel calculated by two different ways can have appreciable difference as compared to the corresponding change for the two-bulb apparatus.

Relaxation Time for a Trennschaukel

The theory of approach to the steady state for a two-bulb convection-free thermal diffusion apparatus has been developed by Saxena and Mason[48]. On the basis of this theory it is easy to see that for most of the trennschaukel geometries used so far the time required to attain the steady state thermal separation is very small[3]. This is mainly because in trennschaukel the tube connecting the two bulbs is much wider as compared to the two-bulb apparatus where it is preferable to have a narrow tube of small volume. In a trennschaukel the approach to steady state is governed by the mechanical transport which equalizes the composition of the two bulbs across the connecting capillary. The relaxation time of a trennschaukel is related to the total time required in this mechanical mixing which is brought about by the to and fro motion of the gas as a whole. An expression for the relaxation time is derived below. For this derivation, the general approach is essentially that of Van der Waerden[46] with several notable differences.

In Fig. 2 the continuous curve represents the concentration profile of the lighter component in a trennschaukel consisting of an even number of tubes. The profile is always symmetrical about the middle

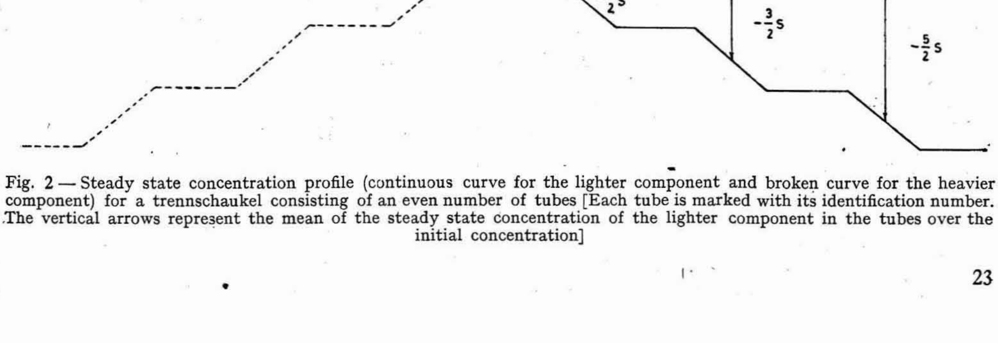

Fig. 2 — Steady state concentration profile (continuous curve for the lighter component and broken curve for the heavier component) for a trennschaukel consisting of an even number of tubes [Each tube is marked with its identification number. The vertical arrows represent the mean of the steady state concentration of the lighter component in the tubes over the initial concentration]

point of the central connecting tube, except that on the right side of this point the composition of the lighter component is increasing as we move away while it is decreasing on the left side. It is this fact which ultimately leads to an enrichment in a trennschaukel. The concentration profile of the heavier component is also shown in Fig. 2 (dotted lines) and is seen to be the mirror image of the concentration profile of the lighter component about the symmetry axis. For a trennschaukel assembly of an odd number of tubes the situation is similar except that the point of symmetry now lies on the middle of the central main tube instead of the connecting capillary.

In the following treatment, besides assuming that the thermal diffusion relaxation time in the main tube is small compared to the relaxation time of the trennschaukel, it has also been assumed that the process of concentration diffusion in the main tubes is very fast. This implies that as the gas composition in the end bulb changes because of the gas movement, it takes no time in redistributing itself by the process of normal diffusion. This will be true if the time for this process is small compared to the period of gas movement. Thus the following two assumptions are justified: (i) the rate of diffusion is infinite in the main tubes, and (ii) the thermal separation is small and α_T can be taken to be independent of composition in this range. Because of these assumptions it is reasonable to assume that the concentration difference of a component between the top and bottom ends of a tube, S, will be the same at all times. This gives

$$X^k(t)-X_k(t) = S_k \qquad \ldots(22)$$

where k can take values from 1 through N. Further S_k will be the same for all tubes and since its value does not vary with time,

$$X^k(\infty)-X_k(\infty) = S_k \equiv S_k(\infty) \qquad \ldots(23)$$

$X^k(\infty)$ refers to the steady state value of X^k. On introducing the two new variables,

$$X^k(t) = X^k(\infty)-X^k(t) \qquad \ldots(24)$$

$$X_k(t) = X_k(\infty)-X_k(t) \qquad \ldots(25)$$

Combining the last two equations,

$$\{X^k(\infty)-X_k(\infty)\}-\{X^k(t)-X_k(t)\}=X^k(t)-X_k(t) \ldots(26)$$

Because of Eqs. (22) and (23), the left side of Eq. (26) is zero so that

$$X^k(t) = X_k(t) \equiv X(k,\ t) \qquad \ldots(27)$$

Let us now consider a particular tube k and assume that in the first half cycle the gas flows from the kth to $(k-1)$th tube. If during this period the volume of the gas displaced is $2A$, the number of molecules of the lighter component that will be transported from kth to $(k-1)$th tube will be $2AnX^k(t)$, while the transport from $(k+1)$th to the kth tube will be $2AnX^{k+1}(t)$. Similarly, in the next half cycle the number of the lighter molecules that are transported from $(k-1)$th to kth tube is $2AnX_{k-1}(t)$ and that transported from kth to $(k+1)$th tube is $2AnX_k(t)$. Therefore, the net number of lighter molecules that are retained in the kth tube during a cycle is

$$G_k = 2An[X^{k+1}(t)-X_k(t)-X^k(t)+X_{k-1}(t)] \ldots(28)$$

or in terms of X, Eq. (28) can be written as

$$G_k = -2An[X\{(k+1),\ t\}-2X(k,\ t)+X\{(k-1),\ t)\}] \qquad \ldots(29)$$

If the period of oscillation is t_p for the average rate of enrichment in the kth tube,

$$G_k/t_p = -\frac{2An}{t_p}[X\{(k+1),\ t\}-2X(k,\ t)+X\{(k-1),\ t\}]$$
$$\equiv \dot{X}(k,\ t)nV \qquad \ldots(30)$$

where V is the volume of the main tube.

It has been mentioned earlier that the concentration profile of a trennschaukel is antisymmetrical about the middle point irrespective of the fact whether it consists of an even or odd number of tubes. Based on this antisymmetric property each tube is numbered by its identification number, m, such that it is zero for the middle point of the central tube, and for any particular tube k it is related with N such that $m = [(N+1)/2]-k$. Here it is implied that the volumes on either side of the piston of the gas pump have identification numbers $\pm (N+1)/2$ corresponding to tube number $k=0$ and $(N+1)$ respectively. These identification numbers have the physical significance that at the steady state the average mole fraction of a component in a separating tube with identification number m departs from its initial value by mS.

Similarly, if V' is the mean volume of the gas on either side of the piston of the pump connecting the two end tubes of the trennschaukel, for the rate of enrichment in these parts

$$\dot{X}\left\{\frac{N+1}{2},\ t\right\} = \frac{2A}{V't_p}\left[X\left(\frac{N+1}{2},\ t\right) - X\left(\frac{N-1}{2},\ t\right)\right] \qquad \ldots(31)$$

$$\dot{X}\left\{-\frac{N+1}{2},\ t\right\} = \frac{2A}{V't_p}\left[-X\left(-\frac{N-1}{2},\ t\right) + X\left(-\frac{N+1}{2},\ t\right)\right] \qquad \ldots(32)$$

The solution of the above differential equations must also satisfy the following relations which correspond to $t = 0$:

$$X\ (m,\ 0) = mS \qquad \ldots(33)$$

$$X\left\{\frac{N+1}{2},\ 0\right\} = \frac{NS}{2} \qquad \ldots(34)$$

$$X\left\{-\frac{N+1}{2},\ 0\right\} = -\frac{NS}{2} \qquad \ldots(35)$$

and the condition of antisymmetry, viz.

$$X(-m,\ t) = -X(m,\ t) \qquad \ldots(36)$$

In arriving at Eqs. (34) and (35) it is further assumed that the compositions of the two extreme end bulbs are in equilibrium with the composition of the gas present in the corresponding sides of the piston of the gas pump.

Following Van der Waerden[46], the solution of Eq. (30) can be written as

$$X(m,\ t) = Ce^{im\nu}\,e^{-bt} \qquad \ldots(37)$$

where ν and b are the constants to be evaluated from the conditions of Eqs. (33)-(35). Substitution of Eq. (37) in Eq. (30) yields the following relation between ν and b:

$$b = \{2A/Vt_p\}\{4\sin^2(\nu/2)\} \qquad \ldots(38)$$

It follows from Eq. (36) that only the sine function in Eq. (37) should be retained so that

$$X(m, t) = C \sin m\nu \exp(-bt) \qquad \ldots(39)$$

Substituting $k = (N+1)/2$ in Eq. (30) and equating the value of $\dot{X}\{(N+1)/2, t\}$ thus obtained with that from Eq. (31) we get

$$-\frac{2A}{Vt_p}\left[X\left(\frac{N+3}{2}, t\right)-2X\left(\frac{N+1}{2}, t\right)+X\left(\frac{N-1}{2}, t\right)\right] = \frac{2A}{V't_p}\left[X\left(\frac{N+1}{2}, t\right)-X\left(\frac{N-1}{2}, t\right)\right] \qquad \ldots(40)$$

Combining Eqs. (39) and (40),

$$\frac{V'}{V}\cos\left(\frac{N+2}{2}\right)\nu+\left(1-\frac{V'}{V}\right)\cos\frac{N}{2}\nu = 0 \qquad \ldots(41)$$

Solution of Eq. (41) is not straightforward for arbitrary values of (V'/V), but it can be easily solved for the specific values 0, $\frac{1}{2}$ and 1. ν can then be estimated for any arbitrary value by interpolation. For $(V'/V) = 0$, we have

$$\cos\frac{N}{2}\nu = 0 \qquad \ldots(42)$$

or

$$\nu = \frac{\pi}{N}, \frac{3\pi}{N} \qquad \ldots(43)$$

for $(V'/V) = \frac{1}{2}$, Eq. (41) becomes

$$\cos\frac{N+1}{2}\nu\cos\frac{\nu}{2} = 0 \qquad \ldots(44)$$

or

$$\nu = \frac{\pi}{N+1}, \frac{3\pi}{N+1}, \ldots\ldots \qquad \ldots(45)$$

and for $(V'/V) = 1$, we get

$$\cos\frac{N+2}{2}\nu = 0 \qquad \ldots(46)$$

or

$$\nu = \frac{\pi}{N+2}, \frac{3\pi}{N+2}, \ldots\ldots \qquad \ldots(47)$$

All the three sets of possible values of ν given by Eqs. (43), (45) and (47) can be represented by the following general relation:

$$\nu = \frac{\pi}{N+2(V'/V)}, \frac{3\pi}{N+2(V'/V)}, \frac{5\pi}{N+2(V'/V)}, \ldots\ldots \qquad \ldots(48)$$

and this equation may be used as an interpolation formula for intermediate values of (V'/V).

The general solution of Eq. (30) may now be written as

$$X(m, t) = C_1 \sin(m\nu_1)\exp(-b_1t) + C_3 \sin(m\nu_3)\exp(-b_3t) +, \ldots \qquad \ldots(49)$$

where $\nu_1, \nu_3, \ldots\ldots$ are the values of ν taken from Eq. (48) in order. The values of $b_1, b_3, \ldots\ldots$ are obtained from Eq. (38) by substituting these values of $\nu_1, \nu_3, \ldots\ldots$ respectively.

If N is sufficiently large, ν will be small and hence Eq. (38) can be approximated as follows:

$$b_1 \simeq \left\{\frac{\pi}{N+2(V'/V)}\right\}^2 \frac{2A}{Vt_p}$$
$$b_3 = 9b_1;\ b_5 = 25b_1 \qquad \ldots(50)$$

Eq. (50) indicates that the values of b_i increase rapidly with i and the contribution of the terms other than the first in the series for $X(m, t)$, Eq. (49), will become negligible after a short interval. Thus, to a first approximation we may write

$$X_1(m, t) = C_1 \sin m\nu_1 \exp(-b_1t) \qquad \ldots(51)$$

The relaxation time, τ, will, therefore, be given by

$$\tau = \frac{1}{b_1} \simeq \frac{Vt_p}{2A}\left\{\frac{N+2(V'/V)}{\pi}\right\}^2 \qquad \ldots(52)$$

Thus, the relaxation time is directly proportional to the volume of a main tube, the periodic time of the gas swing, and approximately to the square of the number of tubes used. It is also inversely proportional to the volume of the gas displaced in each swing. The increase in the value of the ratio, (V'/V), also tends to increase the value of τ.

In the above treatment of the relaxation time an infinitely fast diffusion in the main tubes has been assumed. In practice, this condition does not hold rigorously and hence the relaxation time increases. The change in τ due to a finite rate of diffusion is next estimated. Eq. (8) can be rewritten as

$$\vec{J} = -nD\left[\text{grad}\,X(t) - \frac{X(t)\{1-X(t)\}}{X(\infty)\{1-X(\infty)\}}\text{grad}\,X(\infty)\right] \qquad \ldots(53)$$

As already mentioned the change of concentration in trennschaukel operation is usually small, so that

$$X(t)\{1-X(t)\} \simeq X(\infty)\{1-X(\infty)\} \qquad \ldots(54)$$

Eq. (53), therefore, assumes the following form for the kth tube:

$$\vec{J}_k = nD\ \text{grad}\ \{X(\infty)-X(t)\}_k \qquad \ldots(55)$$

Eq. (55) can be integrated along the length of the tube, L, to get the average current density $<J_k>$av and hence the relation

$$X^k(\infty)-X_k(\infty) = X^k(t)-X_k(t)+<J_k>\text{av}\left(\frac{t_D}{V}\right) \qquad \ldots(56)$$

Here,

$$<J_k>\text{av} = \frac{1}{L}\int_0^L J_k dz \qquad \ldots(57)$$

and t_D, the diffusion time, is given by

$$t_D = L^2/D \qquad \ldots(58)$$

The average value of the current density can also be determined by considering the average transport that is taking place through the two connecting capillaries on both the sides of the main tube under consideration during a cycle, i.e.

$$<J_k>\text{av} = \frac{A}{t_p}\left[X^k(t)-X_{k-1}(t)+X^{k+1}(t)-X_k(t)\right] \qquad \ldots(59)$$

Here the various $X(t)$ values are the average values over the period t_p. Substituting the value $<J_k>$av from Eq. (59) into Eq. (56) and rearranging the terms we get

$$\begin{aligned} X^k(\infty)-X_k(\infty) &= \left[X^k(t)+\frac{At_D}{Vt_p}\{X^k(t)-X_{k-1}(t)\}\right] \\ &\quad -\left[X_k(t)+\frac{At_D}{Vt_p}\{X_k(t)-X^{k+1}(t)\}\right] \\ &\equiv X^k(t)-X_k(t) \qquad \ldots(60) \end{aligned}$$

where X^k and X_k are the effective concentrations at the top and bottom ends of the kth tube. In a similar manner it can be shown that for the $(k+1)$th tube

$$\begin{aligned} & X^{k+1}(\infty)-X_{k+1}(\infty) \\ &= \left[X^{k+1}(t)+\frac{At_D}{Vt_p}\{X^{k+1}(t)-X_k(t)\}\right] \\ &\quad -\left[X_{k+1}(t)+\frac{At_D}{Vt_p}\{X_{k+1}(t)-X^{k+2}(t)\}\right] \\ &\equiv X^{k+1}(t)-X_{k+1}(t) \qquad \ldots(61) \end{aligned}$$

From Eqs. (60) and (61),

$$X^{k+1}(t)-X_k(t)=(1+2At_D/Vt_p)[X^{k+1}(t)-X_k(t)] \quad \ldots(62)$$

Thus, for a finite rate of diffusion the concentration difference across a capillary is smaller by a factor $(1+2At_D/Vt_p)$. This reduces the transport per cycle and consequently increases the relaxation time proportionately. The corrected relaxation time is, therefore, given by

$$\tau' = (1+2At_D/Vt_p)\tau \qquad \ldots(63)$$

The important point to note in the correction factor, which appears because of the finite rate of diffusion, is that if $t_p<t_D$ the relaxation time τ' will increase. The physical reason for this is that even if the gas is swung rapidly it does not get enough time to uniformly disperse itself in the main tubes, with the result that shortening of t_p does not help in reducing τ'.

Decay in Amplitude of the Gas Swing towards the Central Tube

In trennschaukel operation a certain mass of the gas is transferred through the capillaries in one direction in the first half cycle and in the opposite direction in the next half cycle. As the flow of gas through the capillaries needs a pressure gradient across them, the exchange of gas in the middle tubes will be less than in the end tubes. If the bore of the connecting capillaries is not properly chosen it is possible that the pressure drop may be so large that in the middle tubes there is practically no exchange of gas. This will reduce the overall separation and hence the evaluated α_T value will be smaller than the actual one. An investigation of this effect is necessary for proper designing of trennschaukels and has been attempted in the following paragraphs.

The change in density, ρ, of a perfect gas is very simply related with the change in pressure, p, by the following relation:

$$\rho = \frac{M}{RT}\,p = fp \qquad \ldots(64)$$

where M is the molecular weight; T, the temperature; and R, the gas constant. Due to the periodic mass motion of the gas the density in each tube also varies with the same period. The situation is somewhat analogous to that of the stationary sound waves. The middle point of the trennschaukel assembly forms the node for density variation while the two ends form antinodes. This implies that the density variation, ρ, in the main tubes which are equidistant from the middle point is the same, but the phase on one side differs from that on the other side by 180°. Let us designate the instantaneous deviations from the initial value of the density and pressure by ρ and p respectively. Then for the tube with identification number m we have from Eq. (64)

$$\rho_m = fp_m \qquad \ldots(65)$$

The value of f is approximately constant for all the tubes. Using Poiseuille's law and Eq. (65) the mass of gas, σ, transferred at a particular instant from a tube with identification number m to that with $(m+1)$ can be represented as

$$\frac{d\sigma}{dt}(m\rightarrow m+1) = \frac{E'}{f}\,(\rho_m-\rho_{m+1}) \qquad \ldots(66)$$

and

$$E' = \pi r^4(d_m+d_{m+1})/16\eta l \qquad \ldots(67)$$

where d_m represents the density of the gas in a tube with identification number m; η, the viscosity of the gas; and l and r are the length and the radius of a connecting capillary respectively. Similarly, the rate of the mass of the gas transferred from a tube with identification number $(m-1)$ to that with identification number m is

$$\frac{d\sigma}{dt}(m-1\rightarrow m) = \frac{E''}{f}\,(\rho_{m-1}-\rho_m) \qquad \ldots(68)$$

where

$$E'' = \pi r^4(d_{m-1}+d_m)/16\eta l \qquad \ldots(69)$$

It is reasonable to take $E''=E'=E$ and consequently from Eqs. (66) and (68) it follows that

$$V\,\frac{d\rho_m}{dt} = \frac{E}{f}\,(\rho_{m-1}-2\rho_m+\rho_{m+1}) \qquad \ldots(70)$$

or

$$\epsilon\dot{\rho}_m = \rho_{m-1}-2\rho_m+\rho_{m+1} \qquad \ldots(71)$$

where $(Vf/E)=\epsilon$ and $\dot{\rho}_m$ is the rate of change of density in a tube with identification number m. The form of the differential Eq. (71) is the same as due to Van der Waerden[46], except that the variable here is the change in density of a particular tube instead of the gas mass transported. Further, at the two ends we have

$$\rho_{\left(\frac{N+1}{2}\right)} = \rho_{\left(\frac{N+1}{2}\right)}(\max)\,e^{i\omega t} = -\rho_{-\left(\frac{N+1}{2}\right)} \qquad \ldots(72)$$

where $\rho_{\left(\frac{N+1}{2}\right)}(\max)$ is the maximum change in the density of the gas contained on either side of the piston of the gas pump which swings the gas back and forth with an angular velocity ω and t refers to time. Eq. (71) may be written as

$$\rho(m,\,t) = \rho_m(\max)\,e^{i(\omega t-\phi_m)} \equiv \rho(m)e^{i\omega t} \qquad \ldots(73)$$

where $\rho(m)\equiv\rho_m(\max)\,e^{-i\phi_m}$, and ϕ_m represents the phase of the oscillating column in the tube with identification number m with respect to the phase of the end tube having identification number $(N+1)/2$. ρ as well as ϕ obey the following antisymmetry conditions:

$$\rho(m, t) = -\rho(-m, t) \qquad \ldots(74)$$

and

$$\phi_{-m} = -\phi_m \qquad \ldots(75)$$

Substitution of Eq. (73) in Eq. (71) and the use of Eq. (72) yields

$$\epsilon i\omega\rho(m) = \rho(m-1)-2\rho(m)+\rho(m+1) \qquad \ldots(76)$$

For the two ends we have from Eqs. (72) and (74)

$$\rho_{-\left(\frac{N+1}{2}\right)}(\max) = -\rho_{\left(\frac{N+1}{2}\right)}(\max) \qquad \ldots(77)$$

The general solution of Eq. (76) is

$$\rho(m) = C_1e^{\alpha m}+C_2e^{-\alpha m} \qquad \ldots(78)$$

Eq. (78) on substitution in Eq. (76) yields

$$2+i\epsilon\omega = e^{\alpha}-e^{-\alpha} \qquad \ldots(79)$$

The two constants C_1 and C_2 can be evaluated with the help of Eq. (77) and the following expression is obtained:

$$\rho(m) = \rho_{\left(\frac{N+1}{2}\right)}(\max)\,\frac{\sinh \alpha m}{\sinh (N+1)\alpha/2} \qquad \ldots(80)$$

Because ϵ is a small quantity, Eq. (79) demands that α must also be small and hence on expanding e^{α} and $e^{-\alpha}$ we get

$$i\epsilon\omega = \alpha^2+\alpha^4/12+\ldots \qquad \ldots(81)$$

The value of α is to be determined by the method of successive approximations, i.e.

$$\alpha^2 = i\epsilon\omega-\tfrac{1}{2}(i\epsilon\omega)^2+\ldots \qquad \ldots(82)$$

Since α is small Eq. (8) can be expanded in powers of α whence we get

$$\rho(m) = \frac{2m\rho_{\left(\frac{N+1}{2}\right)}(\max)}{(N+1)}\times$$

$$\left[\frac{1+m^2\alpha^2/3!+m^4\alpha^4/5\,!+\ldots\ldots}{1+\left\{\frac{(N+1)\alpha}{2}\right\}^2\Big/3\,!+\left\{\frac{(N+1)\alpha}{2}\right\}^4\Big/5\,!+\ldots}\right] \ldots(83)$$

In Eq. (83) for $m = 0$, $\rho(0) = 0$, which of course is correct, for at the middle point of the trennschaukel there is no change in the density. Eq. (83) is differentiated with respect to m and the resulting expression is evaluated at $m = 0$ and $m = (N+1)/2$. From this the amplitude of the gas mass transported at the middle tube, σ_0 (max), can be written in terms of the gas mass transported in the end tubes, $\sigma_{\left(\frac{N+1}{2}\right)}$ (max), as

$$\sigma_0(\max) = \sigma_{\left(\frac{N+1}{2}\right)}(\max)\left[1-\frac{1}{192}(N+1)^4\epsilon^2\omega^2\right] \ldots(84)$$

Eq. (84) shows that as we go from the ends to the middle portion of the trennschaukel the amplitude of the mass-transfer falls by $0{\cdot}521(N+1)^4\epsilon^2\omega^2$ per cent. Depending upon the values of N, ϵ and ω, this correction may be sufficiently large in certain cases thereby causing either insufficient or no mixing at all in the middle tubes. As already stated the effect of this decay in amplitude is to lower the experimental α_T values.

Decrease in Separation due to Thermal Diffusion in the Capillaries

At the steady state there is no concentration gradient along the capillaries connecting the main tubes but there is a temperature gradient. This gives rise to thermal diffusion effect which causes the lighter component to move in a direction opposite to that due to the trennschaukel operation as a whole. The change in composition of the end bulbs on this account is calculated hereunder.

Considering a particular connecting capillary, say cth, we have $\partial X_c(\infty)/\partial z \simeq 0$, and, therefore, from Eq. (8) for the flux density we get

$$\vec{J}_c = nD\alpha_T\,X_c(\infty)[1-X_c(\infty)]\frac{\partial}{\partial z}\ln T \qquad \ldots(85)$$

where $\vec{J}_c$ is the value of $\vec{J}$ in the connecting capillary and its direction is opposite to that of $\vec{J}$. The average molar current in a capillary tube, $\langle I_c\rangle$av, is defined as

$$\langle\vec{I}_c\rangle\,\mathrm{av} = \frac{1}{l}\int_0^l \frac{\vec{J}_cA_c}{n\mathrm{V}_c}\,dz \qquad \ldots(86)$$

where A_c is the cross-section of the capillary tube of volume V_c. Combining Eqs. (85) and (86) we get

$$\langle\vec{I}_c\rangle\,\mathrm{av} = \frac{A_cD\alpha_T}{V_cl}X_c(\infty)\{1-X_c(\infty)\}\ln\frac{T_2}{T_1} \qquad \ldots(87)$$

Further from Eq. (15) we have

$$S \simeq \alpha_TX_c(\infty)\{1-X_c(\infty)\}\ln(T_2/T_1) \qquad \ldots(88)$$

where S is the maximum separation in any main tube. Dividing Eq. (87) by Eq. (88),

$$\langle\vec{I}_c\rangle\,\mathrm{av} = \frac{A_cD}{V_cl}\,S \qquad \ldots(89)$$

This molecular transport will enrich the hot bulb on one side of the capillary with the lighter component, and the mechanical movement on the other hand will effectively transport the lighter component in the opposite direction. The current due to the latter effect can be calculated as follows:

If it is assumed that under the combined effect of thermal diffusion and mechanical gas movement there is a small difference in concentration, δS, across the capillary tube then the average molar current through it during a period is

$$\langle\vec{I'_c}\rangle\,\mathrm{av} = \frac{\delta S.2A}{V_ct_p} \qquad \ldots(90)$$

In the equilibrium condition the two values of the molar current given by Eqs. (89) and (90) must be equal so that

$$\delta S = \frac{t_p}{t_D}\cdot\frac{A_cl}{2A}\cdot S \qquad \ldots(91)$$

Eq. (91) should be used as a guide for choosing the sizes of the various components of a trennschaukel and t_p, such that δS is small in comparison with S; the same implication is involved in Eq. (85).

Enhancement in Separation due to Mass Displacement of the Gas

When the gas columns are pushed upwards, the amount of the lighter component transported towards the positive direction from the top bulb is $2AnS$. Similarly, in the other half cycle when the gas columns are pulled downwards, an equal amount of the heavier component is transported in the negative direction. The latter implies that during this half period also there is a transport of an equal amount of lighter component in the positive direction. Hence, during a complete cycle the mechanical motion of the gas generates in the main tubes a net molar current of the lighter component in the positive direction of magnitude $4AS/Vt_p$. Here an important assumption has been made, viz. $t_D \ll t_p$, and, therefore, this analysis will hold only for systems having large values of D.

At the steady state during a cycle there should be no transport of any component in any direction and hence this mechanical transport of the lighter component in the positive direction must be balanced by the transport of an equal amount of the lighter component in the negative direction. The transport of the lighter component in the negative direction is possible only if there is a concentration gradient of the lighter component in the positive direction. This gradient is independent and is in excess of the gradient which results from the normal thermal diffusion. Assuming that the excess separation needed for counterbalancing the mechanical transport of the lighter component in the positive direction is $\delta S'$, the flux of the lighter component in the negative direction is given by

$$\vec{J} = nD\delta S'/L_e \qquad \ldots(92)$$

where L_e is the effective length of a main tube across which the temperature gradient exists. Therefore, the total molar current of the lighter component through the tube is

$$\langle \vec{I'} \rangle \text{av} = \frac{JA_m}{nV} = A_m D\delta S'/VL_e \qquad \ldots(93)$$

where A_m is the cross-sectional area of the main tube. At the steady state for no net transport the two average molar currents must be equal, i.e.

$$4AS/t_p = A_m D\delta S'/L_e \qquad \ldots(94)$$

or

$$\delta S' = \frac{4AS}{t_p}\,\frac{L_e}{A_m D} \qquad \ldots(95)$$

This result will be valid only if $2A \ll A_m L_e$, because otherwise the displacement of the gas will be large and it will not be able to acquire the temperature of the wall which is involved in the above derivation.

In the above treatment it has been assumed that the rate of diffusion is very large in the main tubes. In actual practice, this requirement may not be fulfilled and hence the enhancement in separation calculated from the approximate Eq. (95) gives only an upper limit. Van der Waerden[46] has given a more general treatment which does not involve such assumptions. According to his treatment we get

$$\delta S' = \left[\frac{\{\sin 3r \cos 3r\,(1-2s) \sinh 3r\,(1-2s) \cosh 3r\} - \{\sin 3r\,(1-2s) \cos 3r \sinh 3r \cosh 3r\,(1-2s)\}}{(\sin 3r \cosh 3r)^2 + (\cos 3r \sinh 3r)^2}\right] S \qquad \ldots(96)$$

where

$$r = \frac{1}{6}\left(\frac{\pi t_D}{t_p}\right)^{1/2} \qquad \ldots(97)$$

and s is the ratio of the length of either of the bulbs to the total length of the main tube.

Corrections and Their Magnitudes for Various Trennschaukels Used for Measurements

In the previous sections all the important corrections associated with the trennschaukel operation and calculable on simple physical basis have been considered. There are, however, several other effects which may have appreciable contribution to the final separation. It is, therefore, equally important to consider the design and operation of trennschaukel so that the contribution of these effects is minimized and brought to a negligible level for obtaining reliable values of α_T.

Trennschaukel is essentially a dynamic system in which the gas is moved back and forth as a whole and it is presumed that this does not upset the temperature and concentration distribution. In actual practice, the gas movement perturbs these distributions and proper considerations are essential to reduce them. When the gas jets are released in the end bulbs, they cause vortex motion in the gas columns which mix the gas and alter the concentration distribution. These jets release gas at a different temperature than that of the bulb, and this may lower or raise the effective temperature of the bulb as the case may be. As shown by Saxena and Joshi[47] the net consequence of this is to lower the α_T values. The mechanical movement of the gas column as a whole in the main tubes may cause a difference in the temperature of a horizontal gas layer and the wall with which it is in contact. To reduce these objectionable features which are hard to calculate theoretically it is essential that t_p should be kept large, the temperature of the two end bulbs should not be much different and the volume of the end bulbs should be large as compared to the amount of gas which is moved back and forth. Some of these corrections will have less pronounced effects if the gas and the material of the tubes used in construction have large thermal conductivity values. It is also important that all the tubes are vertical.

The magnitudes of some of the important corrections for the various trennschaukels used by different workers so far have been estimated and the results are given in Table 1. In the calculation of these corrections the pertinent geometrical constants given in the respective papers have been used. In the case of Moran and Watson's data[39] the decrease in separation due to thermal diffusion in capillaries is pronounced for the case of helium and more so at high temperatures which is obviously due to the higher values of the diffusion coefficients

TABLE 1 — DATA ON CORRECTION FACTOR FOR DIFFERENT TRENNSCHAUKELS

Correction factor	Moran and Watson[39]			Saxena *et al.*[3]		Van der Valk and de Vries[41,42]
	Kr (250°K.)	He (600°K.)	He (300°K.)	Ne (200°K.)	He (250°K.)	He (600°K.)
Decrease in S due to thermal diffusion*, % [Eq. (91)]	0·3	19	6	0·2	1·0	5·3
Enhancement in S due to mass motion, % [Eqs. (96) and (97)]	0·5	0·1	0·04	—	0·04	0·3
Decay in amplitude of central tube relative to end tubes, % [Eq. (84)]		1		33		9

*D values used in these calculations are at 1 atm. pressure.

at such temperatures. This is also one of the reasons other than already given by Saxena and Joshi[47] for expecting the values of Moran and Watson to be lower than the actual values. The magnitudes of the various corrections associated with the trennschaukel measurements of Saxena *et al.*[3] seem to be within reasonable limits. Though the decay in amplitude of the gas swing in the central tube relative to the end tubes is 33 per cent, yet its effect on the separation or α_T will not be appreciable. It is interesting to note that in the measurements of Van der Valk and de Vries[41] on helium, none of the corrections assume any appreciable magnitude. For this case the decrease in separation due to thermal diffusion in the capillaries is also within reasonable limits as contrasted with the trennschaukel of Moran and Watson[39]. The reason for this difference lies in the narrower size of the capillary used by Van der Valk and de Vries[41,42] in their trennschaukel construction.

Recently, Watson *et al.*[45] have reported the α_T values for He and Ne at low temperatures by a carefully designed four-tube trennschaukel. Most of the corrections are negligible for this trennschaukel except the effect of back thermal diffusion through the capillaries, as still they have used capillaries of 1·5 mm. internal diameter. Calculations reveal that α_T values on this account will be low by as much as about 15 per cent at 312°K. and by about 5 per cent at 136°K. for helium. The large value of D for helium under the operating pressure of 15 cm. is also partly responsible for enhancing the magnitude of this correction. Thus, the correct α_T values may exhibit a much different temperature dependence than that given by the values reported by Watson *et al.*[45].

As already stated, Watson and coworkers have used Eq. (19) to evaluate α_T as an alternative to Eq. (13). Calculations performed on the basis of Eq. (21) with a view to estimating the error on this account reveal that the difference is negligible. The maximum contribution is found in the case of Moran and Watson's data[39], but here also the magnitude is small, e.g. it is only 0·6 per cent for helium at 233°K.

This study suggests that α_T measurements be done for several larger values of t_p and the correct α_T value be obtained by back extrapolation of the straight line plot of α_T versus t_p, for $t_p = 0$. It is, however, advisable to keep the value of t_p comparatively small, viz. of the order of t_D, in the beginning with a view to keeping τ small, and then t_p may be adjusted for the desired large value. The preference to larger t_p values is because then most of the corrections assume negligible magnitude and the only important correction due to thermal diffusion in the capillaries becomes directly proportional to t_p. An experimental investigation planned on these lines will be highly useful in establishing this technique.

Summary

Various methods for measuring the thermal diffusion factor of gas mixtures, α_T, have been reviewed. In view of the increasing prospects and utility of trennschaukel for measuring α_T, certain aspects which are pertinent for its design and optimum performance have been considered in detail. While Van der Waerden has described the theory of this apparatus, the present review presents an alternative treatment which is more physical and brief in the derivation of certain corrections. The magnitudes of the important corrections for the different trennschaukels used so far have also been considered and a procedure for evaluating α_T accurately is suggested.

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Genes & Their Expression*

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THE term 'gene' is defined as the unit of physical element which can be transmitted from parents to the offspring. Early in the twentieth century, when the science of genetics began with Mendel's work, genes were endowed with a few characteristics. For example, they should be able to duplicate and their character should be pretty stable. If this character is altered for some reason or other, then the altered character should also be stable and transmitted from generation to generation. As years passed by and considerable knowledge accumulated in genetics, the 'gene' has been subdivided into subunits as recons, mutons, cistrons, etc. In this article, the mode of expression of the hereditary material is discussed. The Symposium on Synthesis and Structure of Macromolecules, held at Cold Spring Harbor last year[1], has provided much useful information on this subject.

Throughout the middle of the nineteenth century, i.e. before the momentous discovery of Mendel, people were interested in locating the hereditary material within a cell. Early in the twentieth century, Sutton demonstrated that the chromosomes contain the genes. Even a few years ago, biochemists were investigating the protein part of the chromosomes in their search for the gene. Eventually, however, it was observed that a particular kind of nucleic acid, deoxyribonucleic acid (DNA), is a constant part of the chromosomes which possesses the properties required by the genes. That DNA is the genetic material has been confirmed by the interesting experiments on transformation. When DNA is extracted from one strain of Pneumococcus, purified to a high degree and then introduced into another strain, the recipient organism develops some of the characters of the donor[2].

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Abbreviations used: ATP, adenosine triphosphate; GTP, guanidine triphosphate; CTP, cytosine triphosphate; and UTP, uridine triphosphate.

Further evidence in favour of the genetic role of DNA has come from the studies made by Zinder and Lederberg[3], Hershey and Chase[4], and others who have demonstrated that when a bacterial virus infects a host, the virus injects its DNA into the host cell, but the empty protein coat surrounding the DNA remains outside. Similarly, in the case of the RNA-containing plant virus, the tobacco mosaic virus (TMV), it has been shown by separating RNA and the protein parts that it is the nucleic acid and not the protein which has the infectivity[5,6]. It is now well established that DNA is the genetic material. The phenotypic expression of the genetic material, DNA, is mediated by enzymes which are proteins. The missing link between the two macromolecules, DNA and the protein, was discovered following the early observation made by Volkin and Astrachan[7] who showed that after T2 or T4 infection there is synthesis of a class of RNA which is complementary to T2 or T4 DNA respectively. Later, it was found that not only in the case of viral-infected cells but also in every living cell there is a small fraction of RNA which has the base composition complementary to that of the DNA. The term ' messenger RNA ' was coined by Jacob and Monod[8] for this class of RNA. This means that this particular type of RNA carries the genetic information from the hereditary material DNA to the site of protein synthesis in order to synthesize the enzymes, the agents for phenotypic expression. All the above observations and assumptions gained a firm foothold with the discovery of the enzyme RNA polymerase (cf. review by Burma[9]). The following scheme shows the reaction catalysed by RNA polymerase:

$$\text{nATP}+\text{nGTP}+\text{nCTP}+\text{nUTP}+\text{DNA} \xrightleftharpoons{\text{RNA polymerase}} (\text{pApGpUpC})\text{n}+\text{nPP}+\text{DNA}$$

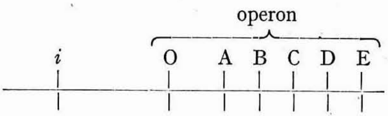
where U = uracil; A = adenine; C = cytosine; G, guanine; T = thymine. This enzyme requires DNA as primer and makes RNA complementary to the primer.

The biochemical reactions starting from DNA to protein can be divided into the following two steps:

$$\text{(i) DNA} \xrightarrow{\text{Transcription I}} \text{RNA}$$

$$\text{(ii) RNA} \xrightarrow{\text{Transcription II}} \text{Protein}$$

Does DNA contain the informations for making proteins only? If that is so, the cell will be nothing but a mess of enzymes working in a random fashion. But if we analyse a few experimental observations it will appear that this is not the case. For example, *Lactobacillus plantarum* when grown on glucose does not possess the enzymes required for the utilization of L-arabinose, i.e. L-arabinose isomerase, L-ribulokinase, etc. But when the same organism is grown on arabinose all the enzymes required for arabinose metabolism are produced within the cell. So the DNA of *L. plantarum* must have all the informations for making the enzymes but normally they are not expressed. In this institute studies are being carried out on the induction and repression of some of the enzymes in *L. plantarum*[10-12]. Considerable amount of genetic and biochemical work has been carried out to explore the regulatory mechanism operating within a cell. Most of the work was done with the enzyme β-galactosidase which made *Escherichia coli* famous along with a group of scientists. As a result of a series of brilliant experiments done by Jacob, Monod and their associates, we have now learnt that DNA contains (a) structural genes which have the information for the amino acid sequences of the enzymes, (b) regulatory genes which regulate the function of the structural genes through another type of genes, and (c) the operator genes. To describe in a more explicit way, suppose the following is a part of the genome of *Esch. coli*, where A, B, C, D, E represent a number of structural genes:



Usually the structural genes for a series of enzymes in a biochemical pathway are situated close to each other. At one end of that series lies the operator gene denoted as 'O'. The operator gene acts as a switch to on or off the transcription for the series of enzymes. The activity of the operator gene is controlled by the regulator gene (or genes) named as '*i*' gene. Normally the product of the '*i*' gene which is known as repressor combines with the operator and blocks its function, i.e. keeps it in off position. When an inducer is added which may be a substrate for the enzyme, the inducer reacts with the '*i*' gene product. The repressor now cannot combine with the operator and hence cannot turn it off and the enzyme synthesis starts. Recently, it has been suggested by Jacob and Monod[13] that the operator gene may not be a separate gene. It may be the end of a series of structural genes from which the reading of the whole genome starts. Under this condition, blockage of the operator means that the reading of the whole genome cannot start.

What is the nature of the repressor? It is a product of the DNA, the genetic material. Is it a protein or a nucleic acid? The fact that the repressor for β-galactosidase can be produced even in the presence of chloramphenicol or 5-methyl tryptophan[14] which are specific inhibitors of protein synthesis aroused the suspicion a few years ago that repressors may not be protein in nature. But recently genetic evidences are in favour of the idea that the repressors may be protein in nature. Garen and Garen[15] as well as Jacob and his group[16] have shown that suppressor mutations which affect some structural genes also affect the regulatory genes. This indirect evidence indicates that the regulator genes also produce proteins. Novick[17] has provided more conclusive evidences in favour of the protein nature of the repressors. He isolated a few mutants in which β-galactosidase can be induced when the cells are grown at 37°C., i.e. the repressor is produced and is active at this temperature. The same cell behaves as a constitutive mutant when grown at 45°C. This thermosensitivity indicates that either the repressor itself or the repressor producing mechanism or both are thermolabile. Kinetic experiments have proved that repressor molecules are thermolabile in some mutants and in some others the repressor producing machinery is sensitive to higher temperature. If the repressor is labile at 45°C., then protein is the most probable candidate to act as the repressor. But it must be remembered that up till now there is no definitive evidence regarding the nature of the repressor.

The repressor is assumed to have a structural 'fit' with the operator gene. Monod *et al.*[18] have proposed a hypothesis on the mechanism of action of the regulator genes. The repressor is thought to be a protein molecule and it has two sites; one binds with the operator and the other binds with the effector which is either the inducer or the repressor. Normally, i.e. when there is no inducer within a cell, the repressor binds with the operator. But when inducer combines with the effector site the protein molecule undergoes allosteric transition. The three-dimensional configuration is changed in such a way that it can no more bind with the operator. Besides the genetic control there is also another efficient control system operating within a cell. This is the control at the cytoplasmic level. In a series of biochemical reactions the product of the pathway is known to inhibit the activity of the first enzyme. These feedback inhibitions can also be explained by allosteric transition of the protein molecule. In a very recent article Stent[19] has elaborated some of the ideas of Bruce and Hartman[1] and has proposed an operator-less operon. Transfer RNAs of a rarer class and representing alternate codes might regulate the reading of the genome. Enzymes responsible for altering the structure of these RNAs might act as repressors.

The repressor plays a unique role in the regulation of growth and other biological activity. In normal cell both structural as well as regulator genes are active, hence there is growth but in a regulated fashion, whereas in case of cancerous tissue there are structural messages but no regulatory information which result in unregulated growth. Even in the case of cellular differentiation the repressors play an important role. Histones, which combine with the DNA of the chromatin forming nucleoprotein, are considered as the repressors[20,21]. It has been shown by Huang and Bonner[20] that free chromatin can carry out DNA synthesis, whereas the nucleoprotein of the chromatin cannot. The histones by combining with a portion of the genome of a cell can stop the expression of those genes. Thus, repressors can explain ' why does a liver cell behave like a liver cell and the pancreatic cell functions like a pancreatic cell, though both the cells contain the same genetic material '. Bonner and his group[22] have demonstrated a beautiful example of regulation by the repressor, the histone. The protein globulin is produced only in the embryo and not in the other parts of the pea seedling. When chromatin was isolated from different parts of pea seedling in order to study *in vitro*, it was found that only the chromatin isolated from the embryo can carry out globulin synthesis. Now, if histone is removed from the chromatin then the chromatin from any other part of the cell also carries out globulin synthesis. This proves definitely that all the cells have the potentiality of making globulin, but histones do not allow those genes to be expressed except in the embryo. Allfrey *et al.*[21], working with the mammalian system, have also provided evidences that histones inhibit DNA-dependent RNA synthesis.

Thus we know that DNA contains information for both regulatory and structural genes and that the repressors, the products of the regulatory genes, control the activity of the structural genes. We also know that DNA is a double-stranded structure and one strand is complementary to the other. How from this double-stranded DNA are the single-stranded messenger RNAs (M-RNA) formed ? Is M-RNA formed complementary to both the strands ? In that case the two types of messenger RNAs produced in a cell will be different and of complementary type. This presents a little confusing situation for the cell as it has to decide which one is the correct message. Or, could it be that of the two strands of DNA one strand is transcribed ? Inequality in the amounts of G and C contents of M-RNA[7,23] led to the suspicion that the M-RNA formed may not be complementary to both the strands. Yankofsky and Spiegelman[24] showed that ribosomal RNA of *Esch. coli* hybridized with *Esch. coli* DNA. So the origin of ribosomal RNA is on DNA. Again, the base composition analysis of ribosomal RNA shows that G is not equal to C, and this tempts one to suggest that most probably one strand of DNA is involved in transcription. This type of study in the case of virus ϕX174 was quite interesting. The virus ϕX174 has single-stranded DNA. Upon infecting the host, it first produces the complementary strand of its own DNA and becomes double-stranded. This double-stranded form is called the replicating form. It has been shown by Spiegelman and his coworkers[25] that ϕXRNA hybridized only with the double-stranded replicating form and not with the mature single-stranded DNA, indicating that it can hybridize with that strand of DNA which is complementary to the single-stranded form of the virus. This means that not the single-stranded DNA of mature ϕX174 but the strand complementary to that contains the genetic information. The same contention was proved by Guild and Robinson[26] who showed that of the two strands of pneumococcal DNA one strand is much more effective in transformation. They separated the two pneumococcal strands in caesium chloride solution at *p*H 12 and carried out transformation experiments with both the samples. There was no lag in phenotypic expression in the case of low GT containing fraction, whereas in the other fraction it took about 45 min. to have the same rate as obtained by the former fraction. This time is little more than one generation time which suggests that the strand has to be duplicated before message can be translated. Genetic evidences have also been provided by Champe and Benzer[27] which indicate that only one strand can make effective messenger. But we know that under *in vitro* conditions both the strands are duplicated with the help of RNA polymerase. Thus it appears that the control is not operating under *in vitro* conditions. At least the specificity does not lie with the enzyme. Bresler *et al.*[28], however, are of the opinion that both the strands of DNA may be effective in production of messengers even under *in vivo* conditions.

Let us now consider another interesting aspect regarding the mode of genetic expression. Genetic analysis of the frequency of recombination suggested long time ago that the genetic material, at least in case of bacteria and viruses, should be circular, but until Kleinschmidt *et al.*[29] from USA and Cairns[30] from Australia provided electron microscopic pictures of circular DNA, no direct evidence was available in favour of this. They opened the cell very gently by treating it with lysozyme. Cairns[30] has proposed a model for duplication of the circular DNA. According to this model the circularity of DNA is not interrupted at all during duplication and at the end of duplication two intact circles are formed. Hayashi *et al.*[31] eventually showed that even under *in vitro* conditions when double-stranded circular DNA is used as a primer along with DNAse-free RNA polymerase the RNA synthesized is the copy of one of the strands as evident from the nearest neighbour frequency analysis and also from hybridization experiments. But when the template is not circular both the strands are copied. The deciding factor is perhaps the intactness and the circularity of the DNA.

It is known that the primary structure of a protein is determined by the base sequence of the DNA. It is quite reasonable to speculate that there should be a colinearity between the base sequence of the DNA and the amino acid sequence of the protein. Yanofsky *et al.*[32] as well as Brenner and his coworkers[33] have shown definitive evidences for the existence of such colinearity. They have mapped different mutants and analysed the defects in the amino acid sequences. The results agreed nicely with the colinearity concept.

The other question which has been raised and partially answered is regarding the polycistronic nature of the messenger RNAs. From the genetic material DNA a number of messenger RNAs must be produced complementary to different regions of the genome. The problem may be posed as follows: How long are these messenger RNAs? Are separate messenger RNAs produced for different cistrons? Evidences have been provided by Kiho and Rich[34] and others[1] that M-RNA can be polycistronic, i.e. it may contain messages for more than one cistron. The next obvious question which arises is whether a polycistronic messenger RNA will catalyse the synthesis of all the proteins at the same rate. Again evidences for this have come from Spiegelman's laboratory. Working with RNA containing phage MS $\phi 2$, Ohtaka and Spiegelman[35] have demonstrated that in the case of polycistronic M-RNA, the timing as well as the rates of syntheses of different proteins are independent of each other, i.e. there is a control at the level of translation of message from M-RNA as well.

It is obvious from the above review that in past one or two years we have been able to learn a lot about the mode of genetic expression, but we are still far off from understanding the mechanism of expression and its regulation to the fullest extent.

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Hormones & Enzymes

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HORMONES have been found to produce a change (i) in enzyme activities, (ii) in the synthesis of enzyme by enzyme induction, and (iii) in the formation of apoenzymes. Enzymes are concerned in the synthesis, degradation and inactivation of hormones. The mechanism of action of some hormones on the target organs seems to be mediated through enzymes. Although interest in the subject of interrelations between hormones and enzymes exists amongst scientific workers in this field and considerable research on the problem has been carried out, we are still in the dark about the actual mechanism by which one influences the other. Attempts are made in this review to indicate the influence of different endocrine organs on specific enzyme systems.

Glucose-6-phosphate Dehydrogenase and 6-Phosphogluconate Dehydrogenase

These two key enzymes are necessary for the initiation of carbohydrate metabolism through the hexose-monophosphate shunt pathway.

Thyroid — Hyperthyroidism enhances the glucose-6-phosphate dehydrogenase activity of erythrocytes and liver. When hypophysectomized rats are injected with thyroxin, 5 µg./day for 10 days, there is an increase in the 6-phosphogluconate dehydrogenase activity of the liver, whereas there is no change in glucose-6-phosphate dehydrogenase activity. When the dose of thyroxin is increased to 70 µg./day and the hormone injected for 14 days, both these enzyme activities are found increased[1].

Glucose-6-phosphate dehydrogenase activity in the erythrocytes has been studied in a group of patients with various thyroid disorders. Significant variations in the enzyme activity have been observed to follow other thyroid function tests[2].

Patients suffering from thyrotoxicosis have elevated enzyme levels averaging 232 enzyme units per 100 ml. erythrocytes, the levels in normal persons being 137 enzyme units per 100 ml. erythrocytes. None of the patients was anaemic and had normal reticulocyte count. Administration of thyroxine and triiodothyronine to a normal subject has been associated with a rapid increase in glucose-6-phosphate dehydrogenase level. The mechanism for this change, however, is uncertain[3].

Glucose-6-phosphate dehydrogenase and 6-phosphogluconate dehydrogenase activities in the liver of rats have been found to increase when the animals are fed thyroid. Glucose phosphate isomerase, phospho-fructokinase and aldolase were not affected. Phosphoglucomutase activity was decreased[4].

Adrenal cortex — In rats fed a commercial low-salt diet, the zona glomerulosa has been found to increase from 10 per cent of total width of the adrenal cortex to 20 per cent in 2 weeks and to 30 per cent in 3 weeks; no further increase is observed after 10 weeks. The wide glomerulosa shows a striking increase in glucose-6-phosphate dehydrogenase activity which persists up to the 10th week[5].

When the adrenal cortex of rats is stimulated by cold stress, glucose-6-phosphate dehydrogenase activity of the gland does not vary in distribution or intensity, but remains concentrated in the reticular and fascicular zone. Glycogen in the normal rat adrenals, although distributed in the same areas as the enzymes, gets depleted rapidly by stress. This depletion is much more rapid than the response of lipid to stress. Glycogenolysis initiated by ACTH possibly provides the substrate for glucose-6-phosphate dehydrogenase, thus setting into motion the initial steps in the pentose phosphate pathway of carbohydrate metabolism. This provides energy and TPNH required for steroid synthesis and results in the utilization of cortical lipid stores[6].

Four TPN-linked dehydrogenases have been studied in the adrenal glands of women undergoing bilateral adrenalectomy for advanced breast cancer. The four enzymes have been localized almost exclusively in the soluble part of the cell sap. A marked increase in glucose-6-phosphate dehydrogenase activity is observed after injecting corticotropin, but the increase is not parallel to the concomitant increase in the weight of the adrenal gland. After injection of corticotropin, the distribution of glucose-6-phosphate is mainly in the middle third of the cortex, while before injection the distribution is uniform[7].

Ovary — The hexose monophosphate shunt pathway has been found to be greatly accelerated in liver slices on administration of stilbestrol at a level of 25-100 µg. daily. The glycolytic pathway is not affected and there is a concomitant increase in the synthesis of lipid from glucose-1-C^{14}. The body weight decreases more than the liver weight and the ratio of liver weight to body weight in the treated group actually increases. This indicates that the total metabolic activity of the hexose monophosphate shunt pathway of the liver per body weight is far greater than the control[8].

When diethylstilbestrol is equilibrated with glucose-6-phosphate dehydrogenase, it lowers the extent of reduction of TPN added subsequently to the mixture. Stilbestrol and hexestrol and other estrogenic compounds inhibit the removal of hydrogen from glucose-6-phosphate by binding with the TPN-accepting sites on the dehydrogenase apoenzyme. If this competition for TPN sites takes place in the adrenal, then the decreased availability of TPNH would restrict corticoid synthesis. It has been possible to increase the synthesis of corticosteroids from an adrenal homogenate when the supply of TPNH is increased[9]. In view of the inhibitory effect of estrogen on the enzyme glucose-6-phosphate dehydrogenase prepared from adrenal cortex tissue, it is possible that adrenal cortex may be a primary site for the action of estrogen and analogous compounds. The pituitary is able to compensate for the inhibition by increasing its corticotropin. The amount of circulating corticotropin actually increases[10]. However, since hexose monophasphate shunt acitivity also increases in liver, there is also an increasing possibility of inactivation of corticoids by reduction.

Pituitary — Enzymes belonging to the hexose monophosphate shunt are stimulated in the testes of rats by chorionic gonadotrophin[11].

Pancreas — Insulin seems to play a role, either directly or otherwise, in the operation of the pentose phosphate pathway of glucose metabolism. A decreased activity of this pathway in diabetes[12] and in diabetic rats[13] has been reported. There are evidences indicative of insulin primarily affecting TPN/TPNH system[14]. Insulin might stimulate processes utilizing TPNH such as fatty acid synthesis leading to increased operation of pentose phosphate pathway by efficient regeneration of TPN. There are evidences to suggest that reoxidation of TPNH is a rate limiting step in the operation of this pathway[15,16]. The effect of insulin in increasing the hepatic glucose-6-phosphate dehydrogenase activity of scorbutic guinea-pigs has been reported[17]. In scurvy the secretion of insulin is diminished.

Glucose-6-phosphatase

The activity of glucose-6-phosphatase, an enzyme involved in hepatic glucose production, has been found to be influenced by various hormones.

Adrenal gland — Glucose-6-phosphate activity in liver is markedly increased when rats are injected with cortisone or hydrocortisone. This is accompanied by elevated blood sugar levels and marked liver glycogen deposition. Adrenal cortex, therefore, seems to play a role in the physiological maintenance and regulation of this enzyme[18]. Liver glucose-6-phosphatase activity is decreased in fasted adrenalectomized rats as compared to normal fasted controls[19]. Adrenalectomy in alloxan diabetic rats returned increased liver glucose-6-phosphatase activity to normal levels[20]. It has been observed that glucose-6-phosphate activity of cell-free liver homogenate is not influenced by the addition of corticosterone even in high concentration. Corticosterone influences gluconeogenesis which in turn increases the substrate level of glucose-6-phosphate in the liver and induces increased glucose-6-phosphatase level[20].

Pituitary gland — In 24 hr fasted hypophysectomized animals the decrease in the liver glucose-6-phosphatase activity has been found to parallel the decreased blood sugar level. Administration of growth hormone to hypophysectomized rats has been reported to restore the hepatic glucose-6-phosphatase activity to normal. Growth hormone when administered to normal rats doubled the liver glucose-6-phosphatase activity[21].

A striking increase in glucose-6-phosphatase activity per gram of liver has been observed in ACTH-secreting tumour bearing mice as compared to normal mice[22]. This indicated that ACTH at least in part probably controlled the activity of this enzyme.

Pancreas — An increased glucose-6-phosphatase activity is observed in the livers of human diabetics as compared to non-diabetics[23]. Glucose-6-phosphatase activity of alloxan diabetic rats has been found to be higher than that of normal rats[24] and insulin administration lowers the increased enzyme activity to normal values. Adrenalectomy of alloxan diabetic rats has been found to restore the activity of the enzyme to normal levels[20]. An increase in the glucose-6-phosphatase activity of the liver has been observed in scorbutic guinea-pigs which suffered from hypoinsulinism[25]. An increase in glucose-6-phosphatase activity does not markedly alter the relative rates of metabolism of glucose-6-phosphate via the Embden-Meyerhof and phosphogluconate oxidation pathways.

Injection of glucagon has been found to almost double the liver glucose-6-phosphatase activity in normal rats[21].

Thyroid gland — An increase in hepatic glucose-6-phosphatase has been observed in animals made thyrotoxic by the injection of thyroxin over a period of several days[26]. An increase in glucose-6-phosphatase activity in thyrotoxicosis suggests that this system may be accelerated and thus contribute to an overall decreased cellular efficiency of energy utilization.

The observation that hypophysectomy causes a more profound decrease in liver glucose-6-phosphatase activity than does adrenalectomy[27] indicates that the decreased hepatic glucose-6-phosphatase activity in hypophysectomized animals cannot be attributed solely to decreased or the absence of adrenocortical activity. Since thyroxin will also cause an increase in glucose-6-phosphatase activity it is possible that the effect of hypophysectomy on hepatic glucose-6-phosphatase activity is mediated through at least two endocrine organs, the adrenal cortex and the thyroid gland.

Ovary and testes — Female rats which have 40 per cent less glucose-6-phosphatase in the liver than do male rats, when injected with 10 mg. of testosterone propionate for a period of 14 days, have been found to possess glucose-6-phosphatase activity of liver almost to the same level as in normal males[28].

Hormones concerned in the homeostasis of blood sugar level affect glucose-6-phosphatase activity of the liver in a similar manner.

Carbonic anhydrase — Carbonic anhydrase is present in significant concentration in the rabbit endometrium. Variations in its concentration has been related quantitatively to progestational hormone activity[29]. A bioassay method of progestin depending on the concentration of carbonic anhydrase in rabbit endometrium has been developed[30]. Carbonic anhydrase is present also in the uterus of the rat and the mouse. But the response of oestrogens and progesterone on the carbonic anhydrase concentration varies in different species.

Rabbit — Studying the carbonic anhydrase concentration of different tissues of rabbits before and after progesterone administration, it has been observed that there is a remarkable increase in endometrial enzyme activity without any significant change in the enzyme concentration in the adrenals, kidney, liver and blood[31]. The enzyme concentration is increased five-fold from the 2nd day to the 5th day, maintained through the 8th day, and declined to a minimum level on the 24th day of pregnancy[32]. The role of the enzyme on the uterine endometrium is not clear. The enzyme might play a role in the blastocyte implantation and maintenance. Progesterone-treated rabbits when injected with estrogens have been found to exhibit diminished carbonic anhydrase activity of the endometrium. In the matured rabbit, ovariectomy leads to a decrease in uterine carbonic anhydrase[33].

Rat — In the adult rat carbonic anhydrase content of the uterus is increased after ovariectomy. Total enzyme concentration in the uterus does not change[34]. The increased concentration is reduced by estrogen administration and unaffected by progesterone administration[35,36]. The change in the concentration of carbonic anhydrase might be explained by the effect of these hormones on the weight of the uterus. In male rat the concentration of the enzyme in the seminal vesicles is six times that observed in the ventral prostate when the animal is immature[34].

Mouse — Uterine carbonic anhydrase concentration in the mouse is maximal at oestrus and minimal at dioestrus. In the mouse estrogen stimulates uterine carbonic anhydrase. The injection of progesterone leads to a decrease in the enzyme concentration[35].

Mammary gland — Mammary tissue from several species has been analysed for carbonic anhydrase activity. Highest enzyme activity has been observed in actively lactating postpartum tissue from rats and mice. Mammary tissue from cows and rabbits is not very active[37].

Glutamic-oxalacetic Transaminase and Glutamic-pyruvic Transaminase

Thyroid — In thiouracil-fed rats, in which the ovarian reactivity to gonadotrophin stimulation is enhanced, the stimulating effect of serum gonadotrophin on GOT activity is markedly enhanced[38]. The activity of serum GOT and GPT under the influence of thyroxin has been determined in rat serum. Injection of 3-5 mg. per animal has been found to enhance the enzyme activity as a function of time, the increase being greater after 5 hr. With approximately physiological doses, 0·01 mg. per animal, an increase in activity is also noted. This indicates a direct influence of the thyroid hormone on the protein metabolism[39].

Parathyroid — Injection of parathormone, 60 Collip units per day for 5 days, has been reported to increase serum GOT from 45·5 to 92·7 and serum GPT from 38·8 to 70·3.

Testis — Oral administration of 30 mg. of methyl testosterone to patients has been found to cause an increase in the serum GOT and GPT activity in a few days and from normal to pathological levels in most cases. After the initial rise, the elevated enzyme activity returns rapidly to the normal level even when the treatment is continued. Administration of testosterone propionate by intramuscular injection or oral administration in a 25 mg. dose for the same period does not, however, produce any change in the serum enzyme activity[40].

Serum gonadotrophin — The response of ovarian and uterine GOT activity to serum gonadotrophin treatment at various ages of the developing rat has been studied. The greatest response, 62 per cent increase in ovary and 75 per cent increase in the uterus, has been found at the ages of 31-33 days. Growth hormone and estrogen administration causes an increase in ovarian weight with no rise in GOT. The action of gonadotrophin on GOT in the ovary seems to be specific. Oestrone, testosterone and progesterone, which have a stimulating activity on the immature rat uterus, induce increased GOT activity in this organ. Growth hormone also stimulates growth of the uterus but reduces its GOT activity, indicating a difference between the growth promoting action of growth hormone and of the sex hormone on the uterus. As the GOT stimulating effect of serum gonadotrophin was induced in hypophysectomized rats, it is concluded that this effect is not mediated by the hypophysis[41].

Tyrosine-α-ketoglutarate Transaminase

Thyroid — Tyrosine-α-ketoglutarate transaminase has been found in small amounts in the thyroid gland of rats. The activity (expressed as μmoles of *p*-hydroxyphenyl pyruvic acid formed from tyrosine per gram of fresh weight of tissue) was 2·9 units in the glands of healthy rats. This content is 2-6 per cent of that found per gram of liver. In the thyroid glands of thyroxin-treated animals the activity of the enzyme is similar to that of the untreated controls. The rate of degradation of tyrosine by the thyroid is relatively stable, and this stands out in contrast with the fluctuations often observed in liver[42].

Adrenal cortex — Induction of hepatic tyrosine-α-ketoglutarate transaminase by graded amounts of hydrocortisone has been shown to be substantially modified by changes in the thyroid status. In thyroxin-treated rats, the enzyme is induced only by very large doses of hydrocortisone, while in hypothyroid animals the enzyme is maximally induced by relatively small doses of hydrocortisone. After an intraperitoneal injection of hydrocortisone-1,2-H^3, the ratio of hydrocortisone metabolites to hydrocortisone present in liver has been found to be 3 times as great in hyperthyroid animals as in the controls. Thyroxine seems to minimize the action of hydrocortisone as an inducer of hepatic tyrosine transaminase by increasing the rate of steroid degradation[43].

Cortisol produces a 3-fold increase in tyrosine transaminase in the isolated perfused rat liver. There is no evidence to show that cortisol metabolites have any effect on the enzyme activity in the isolated liver. The increased enzyme activity in cortisol-treated rats is reported to be due to the direct effect of steroids on liver[44].

Kynurenine aminotransferase and aspartate aminotransferase — The phosphate esters of estradiol and stilbestrol compete with pyridoxal 5-phosphate for the apoenzyme in the reconstitution reaction of 2-pyridoxal phosphate dependent enzymes, namely kynurenine aminotransferase and aspartate aminotransferase. The esters, however, are without action on the enzymic transamination itself. The phosphate esters act as inhibitors of the combination of apoaminotransferase with coenzyme[45].

Dehydrogenases

Glutamic dehydrogenase — The rate of reduction of DPN by crystalline glutamic dehydrogenase has been found to increase by the addition of corticosterone or progesterone at concentrations of $10^{-6}M$ or $10^{-8}M$. No increase in rate could be demonstrated when these steroids are added to comparable systems of malic, lactic or alcohol dehydrogenase, which transfers hydrogen to side 1 of the pyridine nucleotide or with α-glycerophosphate or glyceraldehyde-3-phosphate dehydrogenase which transfer hydrogen to side 2 of the purine nucleotide[46].

C_{19}-Steroid dehydrogenase — Homogenates of the seminal vesicles and prostate of the rat and guinea-pig, and the prostate of the dog and man have been found to interconvert testosterone and androstenedione with the use of DPN (DPNH) and TPN (TPNH) as coenzymes. The reductase activity of TPNH system has been found to be more effective than the DPNH system for all animal species. Androsterone and small amounts of epiandrosterone also are formed by dog prostate by the DPNH and TPNH systems respectively. The formation of androsterone by the DPNH-linked dehydrogenase and epiandrosterone by the TPNH system provides a hypothesis for the necessity of two specific enzyme systems for the synthesis of C_{19}-steroids. The results indicate the following sequence of reactions. Androstenedione serves as an intermediate pool from which the end products, androsterone and epiandrosterone, can be formed. The regulation of the size of the androstenedione pool could conceivably be by end product inhibition of the specific 17β-hydroxy-C_{19}-steroid dehydrogenase. The presence of the C_{19}-steroid dehydrogenase in the respective target tissue is a secondary mechanism to regulate the concentration of specific steroids by converting the circulating hormone to the form most suitable for the action of the necessary elements in the particular cell. The relatively high activity in the liver and kidney could function as the primary mechanism to maintain homeostasis of these steroids[47].

Δ^5-3β-Hydroxysteroid dehydrogenase — In maturing rats, ovarian Δ^5-3β-hydroxysteroid dehydrogenase activity is low at the initial ovulation period (5 weeks) and increases to a peak in 9-10 weeks which is significantly above the adult (98 days) level. Values for the above three ages were 14·3, 20·4 and 12·5 μg./min./mg. N. Histological studies have been correlated with the enzyme assays[48].

Incubation of homogenized bovine adrenal glands with 3β,21-dihydroxy-Δ^5-pregene-20-one and 3β,17α, 21-dihydroxy-Δ^5-pregene-20-one has been found to give rise to desoxycorticosterone and desoxyhydrocorticosterone respectively. This indicates that 3β-hydroxysteroid dehydrogenase system is also operative on steroids with 3β-hydroxy-Δ^5-pregene-one structure after hydroxylation at position C_{17}, C_{21} or both[49].

α-Glycerophosphate dehydrogenase — Mitochondria of rat liver and kidney have been found to oxidize α-glycerophosphate 3-5 times more when the rats are given dried thyroid. Much smaller increases occur in the rates of oxidation of succinate, choline and glutamate and the rate of oxidation of β-hydroxybutyrate decreases. The rate of oxidation of α-glycerophosphate increases to a peak after 10 days or more rapidly when thyroid hormones are injected. Withdrawal of dried thyroid from the diet has been found to restore α-glycerophosphate dehydrogenase activity to the normal level in 10 days. When protein synthesis is blocked by ethionine in the diet, thyroid has been found to have only a slight effect on α-glycerophosphate dehydrogenase activity. It is concluded that new protein synthesis is required for increased dehydrogenase. Thyroid hormone may regulate electron transport between pyridine nucleotides and the cytochrome system of the mitochondria[50].

Malic dehydrogenase — Malic dehydrogenase activity has been investigated in 10 healthy subjects, 11 patients with hypothyroidism and 10 patients with hyperthyroid Grave's disease. Serum PBI has been determined in each case and compared with serum malic dehydrogenase level. The highest level of the enzyme occurred in myxoedema. In hyperthyroid Grave's disease serum malic dehydrogenase is elevated (55-75 units) which could be grouped between that of normal control (25-40 units) and of hypothyroid patients (82-225 units)[51].

Succinic, malic and isocitric dehydrogenases in the ovaries of immature and mature normal and serum gonadotrophin injected rats have been studied. The QO_2 of these enzymes are markedly enhanced in the gonadotrophin injected rats of both age groups, except in the case of succinic dehydrogenase in the ovary of immature rats, when a non-significant decrease is noted. It is concluded that in the mature rat ovary, gonadotrophin administration stimulates the activity of all the dehydrogenases of the citric acid cycle, whereas in the immature rat ovary, at least the isocitric and malic dehydrogenases are thus stimulated[52].

In vitro, thyroxin has been found to enhance the oxidation of succinate and inhibit the oxidation of malate. The response is similar to that observed in the myocardium of the rat. Following *in vivo* administration of thyroxin, no enhancement of succinate oxidation could be demonstrated, whereas malate oxidation is slightly stimulated. Succinoxidase response indicates a manifestation of the action of the thyroid hormone and its relationship to the deiodination of thyroxin[53].

Phosphatases

Ovary — After administration of progesterone for a prolonged period to ovariectomized newts (*Triturus pyrobogaster*), the growth of the oviduct has not been found to be stimulated, but the cytoplasm of the epithelial cells of the oviduct exhibits a strong histochemical reaction of alkaline phosphatase[54].

Parathyroid — Woolly monkeys (*Lagothrise humboldt*) suffering from chronic hyperparathyroidism have been found to possess high levels of alkaline phosphatase in the femora. Histologically high alkaline phosphatase is associated with poor mineralization of the bone and osteitis fibrosa. The level of acid phosphatases present is 1/20th to 1/100th of the amount of alkaline phosphatases[55].

Serum alkaline phosphatase in rats, injected with 60 Collip units of parathormone for 5 days, has been found to increase on from 1·92 to 4·75 and alkaline phosphate from 0·41 to 1·12 units[56].

Adrenals — Forcibly fed rats have been found to exhibit a higher content of alkaline phosphatase in the intestinal wall than those freely fed; the values are lower after adrenalectomy, but the difference in favour of the forcibly fed persists. The fall is large only in freely fed rats which eat less after adrenalectomy and is, therefore, ascribed to underfeeding[57].

Phosphorylase

Epinephrine — An intraperitoneal injection of adrenaline into spayed rats, treated with estradiol benzoate 48 hr earlier, has been found to decrease uterine phosphorylation *a* (active) activity and glycogen content. The restoration of enzyme activity to the normal levels occurs abruptly between the 2nd and 3rd hour, but the recovery of glycogen levels is gradual and is attained approximately by the 8th hr. A study of sprayed rats treated with estradiol and adrenaline concurrently, and also given additional adrenaline at intervals for 6 hr has shown that adrenaline inhibits the effect of estradiol to increase uterine weight, phosphorylase *a* activity and glycogen deposition. The action is possibly due to vasoconstricting action of adrenaline on the uterine blood vessels[58].

Estrogens — The splitting activity of phosphorylase and the activity of the phosphoglucomutase in the ovariectomized rat liver are considerably diminished in the presence of oestrogens, specially synthetic ones. The synthesizing activity of phosphorylase remains unaffected by the presence of oestrone and its synthetic analogues. It is possible that synthetic estrogens promote a greater increase in glycogen content of liver than does estrone, because they prevent its amylolysis and phosphorolysis as well as conversion of Cori ester into glucose-6-phosphate[59].

Hyaluronidase

Insulin — Intravenous injection of insulin and hyaluronidase in dogs has been reported to cause a greater decrease in blood sugar level than when insulin alone is injected[60].

Oxytocin — The intracellular material of the epithelium of the frog bladder gives a positive staining response for mucopolysaccharides, but bovine testicular hyaluronidase inhibitor of 53 K decreases the response of the bladder to oxytocin without affecting the normal rate of sodium transport. Hydrocortisone but not aldosterone has also been reported to exhibit reduced response to oxytocin. Both hydrocortisone and 53 K are only effective when placed on the serosal side of the bladder[61].

Vasopressin — Rat kidney slices inactivate 8-arginine vasopressin 1·23 times as fast as 8-lysine vasopressin and 2·14 times as fast as 2-phenylalanine-8-lysine vasopressin. The rate of inactivation is dependent upon the initial concentration of these peptides, i.e. 8-11 μg./ml. There is a positive correlation between the apparent first order rate constants of these vasopressins and their pressure potency per mg. peptide. 8-Arginine vasopressin is not inactivated by hyaluronidase, but rat kidney slices inactivate 8-arginine vasopressin 1·25 times faster when testicular hyaluronidase is present. Slices of rat kidney, taken 7 days after bilateral adrenalectomy, inactivate 8-arginine vasopressin at the same rate as those taken from normal animals. Hydrocortisone sodium succinate does not affect the rate of 8-arginine vasopressin inactivation by normal rat kidney slices, but there is no increase in the rate of inactivation when hyaluronidase, 8-arginine vasopressin and hydrocortisone sodium succinate are incubated together with normal rat kidney slices[61].

Bovine testicular hyaluronidase, when injected intravenously into hydrated, ethanol-anaesthetized rats, has been reported to cause increased excretion of the enzyme in the urine and antidiuresis. The significance of this finding is the possible role of hyaluronidase in the mechanism of action of the antidiuretic hormone[62].

Peroxidase

Thyroid — The action of a purified peroxidase, myeloperoxidase, on diiodotyrosine has been investigated in the presence of glucose and glucose oxidase as a hydrogen peroxide generating system. Thyroxine has been identified as one of the reaction products. The incubation of diiodotyrosine with the cell-free thyroid particular preparation under similar conditions also leads to the formation of thyroxine. The involvement of a thyroid peroxidase in the synthesis of thyroxine from diiodotyrosine by the thyroid particular preparation under the conditions employed in the study has been suggested[63].

Ribonuclease

Thyroid — Human serum ribonuclease has been found to be significantly elevated in the sera of hyperthyroid patients as compared with sera from normal and myxoedematous individuals. Administration of thyroid hormone to patients with myxoedema has been reported to cause a prompt elevation of serum ribonuclease activity and the enzyme levels in hyperthyroid patients are reduced to normal when adequate treatment is instituted[64].

Histaminase

ACTH, hydrocortisone sodium succinate, cortisone acetate, prednisolone-21-phosphate and oestradiol valerianate promote the histaminase activity *in vitro*, while desoxycorticosterone, thyroid gland preparation, testosterone and 17-α-hydroxyprogesterone capronate inhibit the enzyme activity. Administration of ACTH, hydrocortisone, cortisone, and prednisolone increases the tissue histaminase content in rabbit, rat and guinea-pig, while thyroid hormone, testosterone, oestradiol and 17-α-hydroxyprogesterone have no effect. Following extirpation of the pituitary in rats or of the adrenals in rabbits, tissue histaminase level decreases. After extirpation of the thyroid or testis in rabbits, it tends to increase, while reverse is the case after ovariectomy[65].

Proteinases and Amino Acid Activating Enzymes

Ovaries — Levels of proteinase activity in saline extracts of pooled ovaries from rats in oestrus and dioestrus have been found to be significantly higher than those from rats which are immature but pseudopregnant, or in late pregnancy, when tested at *p*H 4 or *p*H 8 (Ref. 66).

Androgens — Castration of adult male guinea-pigs has been reported to produce a gradual decrease in the specific activity of the amino acid activating enzymes of the seminal vesicles to approximately 40 per cent of the normal in about 40 days. Administration of testosterone, testosterone propionate or androsten-17β-ol-3-one gradually restores the specific activity of the enzymes, but a higher dose of the androgen than that required to restore the tissue weight is needed. The enzyme activities of the prostate and temporal muscle are not altered by castration or androgen administration. The use of groups or individual amino acids as substrates in the enzyme reaction has been found to give the same pattern of responses as when a mixture of 17 amino acids is used as the substrate[67].

Tryptophane Pyrrolase

Cortisone injection produces a significant increase in tryptophane pyrrolase activity in rat liver[68]. The reaction catalysed by tryptophane pyrrolase is the oxidation of tryptophane by molecular oxygen, resulting in the rupture of the pyrrole ring of tryptophane yielding formylkynurenine as the reaction product. Formylkynurenine undergoes further metabolic conversion to nicotinic acid. The reaction catalysed by tryptophane pyrrolase is the first enzymatic step in the metabolic pathway leading to the formation of the pyridine nucleotide coenzymes DPN and TPN. The role of beef adrenocortical extract, hydrocortisone and DOCA in the substrate induced increase in hepatic tryptophane pyrrolase activity has been investigated in the adrenalectomized rat. Removal of the adrenals has been shown to diminish the ability of the liver to form tryptophane pyrrolase following tryptophane injection. Under conditions, in which hydrocortisone and adrenocortical extract do not act as inducers, it has been demonstrated that they permit the quantitative response of enzyme activity to substrate administration to return to normal; DOCA has been found to be ineffective. The results are interpreted as an example of the 'permissive action of the adrenocortical secretory product'[69]. Cortisol produces a threefold increase in tryptophane pyrrolase activity in the isolated perfused rat liver. There is no evidence to indicate that the cortisol metabolite has any effect on the enzyme activities in isolated liver. This suggests that increased enzyme activity in cortisol-treated rats is due to the direct effect of the steroid on liver[44].

Increased levels of tryptophane pyrrolase activity of liver following parenteral administration of either tryptophane or cortisone (substrate or hormone-induced elevation of tryptophane pyrrolase activity) may be due to (a) accelerated rate of synthesis of the enzyme protein, (b) stabilization of the enzyme molecule *in vivo* resulting in its accumulation, and (c) activation of pre-existing enzyme resulting in increased catalytic efficiency without augmentation in the number of enzyme protein molecules.

The tryptophane-induced elevation of rat liver tryptophane pyrrolase activity *in vivo* is associated with two consecutive processes: (a) saturation of the endogenous apotryptophane pyrrolase with its heme cofactor and (b) an increase in the amount of the protein moiety or the enzyme system which can be determined by immunological titration. Process (b) is inhibited by the administration of puromycin (an inhibitor of protein synthesis) but not by that of actinomycin (an inhibitor of RNA synthesis). The induction of tryptophane pyrrolase by cortisone involves process (b) alone and is inhibited by puromycin as well as actinomycin. These agents also inhibit the cortisone-induced elevation of the level of liver tyrosine-α-ketoglutarate transaminase. The results suggest a basic difference between the mechanism of substrate and hormone-induced stimulation of enzyme synthesis[70].

DPN and TPN Coenzymes

In the induced synthesis of DPN by parenteral injection of nicotinamide, injection of insulin or ACTH has been found to interfere with the process, resulting in a decrease in DPN content. The hormone action has been related to the mechanism of increased turnover of the DPN molecule. Whether the hormones act by increasing the rate of DPN turnover or whether an activating effect is exerted on DPN-splitting enzymes cannot be decided from the present state of our knowledge[71].

Changes in the levels of DPN and DPNH have been studied in the liver of normal, growth hormone-treated normal, insulin-treated normal, diabetic and growth hormone-treated diabetic rats with periods of hormone treatment ranging from 1 hr to 7 days. Growth hormone has little effect on the DPN of normal rats but increases the level of DPNH. Insulin increases both the DPN and DPNH, the latter to a greater extent. Diabetes causes a profound fall in DPNH, but this can be completely restored in 1 hr by the injection of growth hormone[72].

DPN, DPNH, TPN and TPNH contents of liver and diaphragm have been determined in control, diabetic and fasting rats, and in rats subjected to treatment with growth hormone, thyroxin and thiouracil. Total DPN contents of the liver are markedly reduced in alloxan diabetes and after 48 hr starvation. A decrease is also observed after thyroxin treatment. Striking increases in total DPN contents of liver are, on the contrary, found after treatment with a crystalline growth hormone preparation. Total liver TPN (principally TPNH) contents are strikingly reduced as a result of thyroxin treatment, although thiouracil produces no significant changes. Alteration in diaphragm coenzyme contents are less striking than those found in liver. The DPN/DPNH quotient of rat liver is significantly reduced in alloxan diabetes. It is suggested that hormone may directly or indirectly regulate the synthesis of both DPN and TPN[73].

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REVIEWS

EXPERIMENTAL FLUID MECHANICS by P. Bradshaw (Pergamon Press Ltd, Oxford), 1964. Pp. xii+210. Price 20*s*.

This book has been published under the auspices of the Thermodynamics and Fluid Mechanics Division of the Commonwealth and International Library of Science, Technology, Engineering and Liberal Studies and primarily addressed to mechanical and aeronautical engineering students in their undergraduate studies. It is also of value to chemical engineering students. Research workers in the field of fluid mechanics will find it very interesting and useful.

The book is divided into seven chapters. The introductory first chapter is devoted to the equations of motion and the different flow regimes. In the second chapter the various experimental tunnels and test rigs are described. Chapters 3, 4 and 5 respectively cover the measurements of fluid velocity and shear stress, pressure and force, and position. In the sixth chapter the different flow visualization techniques and their interpretation have been discussed. The last chapter deals with planning of experiments, report writing and analysis of some test reports. This last section is perhaps the most valuable and interesting part of the book inasmuch as several published research reports have been critically examined to expose general principles of experimentation, report writing and demonstration of the practical use of measurement techniques described in the book.

A few exercises have been given at the end of the first six chapters and answers to the exercises have been given at the end.

The book is well written and is particularly valuable to those who contemplate specializing in experimental fluid dynamics. The theoretical and experimental aspects of the subject have been given in clear and precise language and the reader should have no difficulty in following the book and, therefore, it should be of interest to all those who have to study fluid mechanics.

N. R. KULOOR

MECHANISMS FOR THE GENERATION OF PLANE CURVES by I. I. Artoboleveskii; translated from the Russian by R. D. Wills (Pergamon Press Ltd, Oxford), 1964. Pp. xv+278. Price 84*s*.

It is really very refreshing to discover a book on the mechanisms for the generation of plane curves. It fills a badly felt need for such a comprehensive book and both the author and others responsible for bringing out the English edition deserve congratulations.

This book, a translation from a Russian book, deals with the theory and synthesis of mechanisms with kinematic linkages for the exact generation of a desired motion. It is well known that the problems of constructing mechanisms of generating plane curves can be solved by any analytical or geometrical method, but unfortunately the mechanisms obtained are so complicated and contain so many links that the above methods limit their utility in actual practice.

In this monograph, the author presents the so-called geometro-algebraic method of generating plane curves based on his own theory and research work and on the established theories of plane curves. The book has been written presupposing some background in analytical geometry and kinematics from the readers. There are seven chapters and each chapter contains a list of references.

The first chapter is devoted to the general considerations for generating curves by centrode and trajectory pairs and with three-link, five-link and six-link kinematic chains. The second chapter deals with the utilization of kinematic properties, similarity properties, inversion properties, pedal curve properties of kinematic chains and the utilization of properties of individual forms of transformation mechanisms for the generation of algebraic and transcendental curves and for synthesizing mechanisms. Mechanisms for the generation of straight lines and circles using inversors are expounded in the third chapter. The fourth chapter deals with the theory and synthesis of mechanisms for the generation of ellipses, hyperbolas and parabolas. The theory and synthesis of mechanisms for the generations of third degree curves of cissoid type, focal type, verser type and certain special types are examined in the fifth chapter. The sixth chapter is devoted to the theory and synthesis of mechanisms for the generation of fourth degree curves of the conchoidal type, volute type, leaf type, polyzonal type, curves with nodes which touch one another and some other particular types of curves. The seventh chapter deals with the theory and synthesis of mechanisms for the generation of certain curves of a degree higher than the fourth, like cycloidal curves, pedals of cycloidal curves, curves associated with cycloidal curves, conchoid and Roulette type curves and some other particular form of curves. Connecting rod curves of sixth and higher degree and other curves of higher degree are not examined in this chapter. The book concludes, with references, with an outline of the development of the theory of mechanisms for the generation of curves. An index is given at the end of the book.

The way in which the text is presented is rather straightforward and obscure and the majority of the illustrations are irritating. There do appear a number of trivial errors and a few misprints. The translation is too literal. It will increase the utility of the book if an introductory chapter on analytical geometry and kinematics is added.

Yet, the above few inevitable remarks certainly do not detract from the real value of the book which will be a great boon to those confronted by the problem of designing mechanisms for desired plane curves.

R. N. SINGHAL

A GUIDE BOOK TO MATHEMATICS FOR TECHNOLOGISTS AND ENGINEERS by I. N. Bronshtein & K. A. Semendayer; translated from the Russian by

Jan Jaworowski & Michael N. Bleicher (Pergamon Press Ltd, Oxford), 1964. Pp. 783. Price £ 7

The book, as the title suggests, is essentially an excellent guide book of mathematics to technologists and engineers. The chapters and sections cover such a wide spectrum that it is impossible to do more than mention them by title. The book is divided into six parts: Part I (pp. 19-130) gives tables and graphs; Part II (pp. 133-233) deals with algebra and theory of equations, plane and solid figures and trigonometry; Part III (pp. 235-314) consists of analytic geometry of two and three dimensions and differential geometry of plane and space curves and of surfaces; Part IV (pp. 315-584) outlines foundations of mathematical analysis with a brief account of numbers, sequences, differential and integral calculus, ordinary and partial differential equations with Riemann's method applied to Cauchy problem of hyperbolic type, Green's method to boundary value problems and other methods; Part V (pp. 585-742) presents supplementary chapters on analysis and comprises functions of complex variables with conformal mapping, vector calculus, calculus of variations, integral equations and Fourier series; and Part VI (pp. 743-771) introduces to the reader foundations of the theory of probability, theory of errors and interpolation.

The book is written in a lucid style and arrangement of sections though not perfect is a careful development. The individual sections are provided with a number of problems illustrating the grasp of the method used. The reviewer, however, receives an impression of a little vagueness and lack of analytical vigour and sometimes fundamental concept. Derivations of the formulae are often not made but cited. Though the qualitative theoretical side is much abridged because of large number of fields covered in the book, their treatment, though expertly done, is rather brief. As the book is designed mainly to meet the need of engineers and technologists looking for a survey of different mathematical tools, the reviewer believes that the objective has been fully achieved. Besides that, the demands made on the mathematical knowledge of the reader are modest. Upper undergraduates or students at the early years of postgraduate study of engineering as well as those who have already finished their studies will use the book with great profit. The book is hence recommended to a wide group of readers. A cheaper edition of the book is suggested for Indian readers.

D. N. MITRA

NON-STEADY FLAME PROPAGATION edited by George H. Markstein (Pergamon Press Ltd, Oxford), 1964. Pp. x+328. Price £ 5 10*s*

The present monograph is an authoritative account of the progress achieved in the field of non-steady combustion, finding an increased application in industrial as well as jet propulsion units, and as such is of great interest to the research workers in this field.

In the first chapter, the author gives an introduction to the non-steady flame phenomenon, its importance and application. The non-linear character of the flame phenomenon poses a great problem to the proper analysis of the process and to the economic sizing of the combustion chamber. The author considers that the linearized analysis in spite of its limitations is valuable as a first step towards understanding the complicated phenomenon of flame propagation.

The second chapter deals with the theory of steady flame propagation. Two theoretical approaches towards the solution of flame phenomenon such as independent treatment of fluid dynamics from flame zone and interaction of flame front on flow are outlined. The effect of transport process on the flame propagation as enunciated by Bubnoff and later by Lewis and Elbe is explained in the light of selective diffusion.

The next chapter includes detailed linearized analysis of small perturbations on flow field and flame shape. The problems discussed here refer to the solution of the homogeneous flame response equation with perturbations arising simultaneously and also to the forced response under the influence of upstream shear flow disturbances. A mathematical analysis of the flow field, boundary conditions at the flame front and the linearized equation of the flame front response has been represented. While discussing the problem of the dependence of burning velocity on flame shape and flow field, special reference is made to the ' Darrieus-Landau model ' and ' Markstein model '. The role of selective diffusion and other properties of the combustible mixture on the process of flame propagation has been discussed in the Ekhaus analysis.

In Chapter 4 the author mentions about the flame front instability, which is of two types—spontaneous and artificial. The spontaneous instability comes into play and is controlled by fluid dynamics process as well as by selective diffusion, whereas the artificial instability is created by external disturbances of acoustic, vibratory and shock wave nature.

Chapter 5 deals with the mechanism of flame propagation in closed chambers and tubes with different boundary conditions. The different phases of flame propagation, the phenomenon of flame deceleration and influence of different parameters on the flame shape are analysed.

Chapters 6, 7 and 8 analyse the interesting phenomenon of oscillatory combustion, which is finding a wide application in domestic, industrial and space appliances. The conception of ignition delay and Rayleigh's criterion are introduced to account for the combustion oscillations with different theoretical approaches to the problem such as linearized treatment, method of dimension analysis and physical model. Different methods of obtaining the organ-pipe acoustic oscillations are outlined with a reference to solid propellent units and transverse acoustic oscillation, which is becoming increasingly important in recent years.

Finally it should be added that a detailed discussion on turbulent flame propagation and the design methods of combustion chambers, which is rather hurriedly covered in the book, would have been a matter of much appreciation.

D. BHADURI

ELECTROMAGNETIC SCATTERING edited by Milton Kerker (Pergamon Press Ltd, Oxford), 1963. Pp. xii+592. Price £ 7

This volume is a collection of 40 papers presented at the Interdisciplinary Conference on Electromagnetic

Scattering, held at Clarkson College, Potsdam, New York. It deals with the scattering of electromagnetic radiation by particles and by inhomogeneities as well as the application of this phenomenon to various scientific discipline.

Part 1, ' Particle scattering ', considers the scattering by non-homogeneous and by irregularly shaped particles. In this section, Ikeda extends the Rayleigh-Gauss theory in a treatment of the scattering of an electromagnetic vector wave by a non-conducting particle. Heller formulates the practically important expressions derived from the Mie theory and follows it by a discussion of the phenomena in scattering which may be used for particle size determination.

Part 2, ' Light scattering in the atmosphere and space ', is concerned with the determination by light scattering of the particle size distribution by laboratory aerosols and hydrosols of atmospheric, interplanetary and interstellar aerosols. Deirmendjian computes the angular scattering and polarization properties of polydispersed systems of non-absorbing and partially absorbing spheres using the complete Mie series. Bullrich presents the results of calculation of the spectral scattering functions and polarization functions for a scattering volume of turbid air.

The scattering by hydrometeors and by inhomogeneities in the atmosphere is dealt with in Part 3, ' Microwave and radiowave scattering in the atmosphere '.

A section is devoted to the light scattering by solutions of macromolecules and by electrolyte solutions. Benoit begins with a review of the theoretical interpretation of light scattering results in the field of dilute solutions of high polymers and discusses its application to solutions of block copolymers. An excellent account of the light scattering by non-Gaussian macromolecular coils is given by Peterlin.

Part 5, ' Light scattering and molecular forces ', is concerned with the scattering by liquid mixtures, macromolecular solutions, semiconductors, glasses and polymeric films. A method for the calculation of the persistence length and the range of molecular forces in polymer solutions is elegantly developed by Debye. The importance of absolute intensity measurements in small-angle X-ray studies for attributing the electron densities and consequently, the mass densities to the geometrical structures is clearly demonstrated by Kratky.

The final section of this book deals with multiple scattering. This refers to the situation in which particles can still be recognized as individual scatterers but give rise to mathematically complicated results because each particle in turn contributes to the radiation field incident on the other. Some fields in which such problems occur are meteorology, astronomy and neutron diffusion; representatives of each have contributed to this section.

In a short review such as this, it is not possible to mention all the papers, but it is hoped that enough has been said to illustrate the scope and quality of this book. The volume is well printed on excellent paper and the editor and publisher must be congratulated on its excellent get-up. A few mistakes that are found in the book must, however, be mentioned for correction in a future edition. On page 292, relation (12) has to begin with $1/\nu_0$ and not $1/\partial\nu$. On page 296, the second term within the brackets of formula (15) should read $\sin^2 u/u^2$. On page 340, the right-hand side of formula (8) must be $K'[\partial n/\partial C_2]^2$, etc. On the same page, the relation given in the last line has to read $\tau = (16\pi/3)R_{90}$. These minor criticisms do not detract from the value of the book. On the other hand, its wide scope makes it an essential acquisition for any library.

S. Subramanian

Structure Analysis by Electron Diffraction

by B. K. Vainshtein; translated from the Russian by E. Feigl & J. A. Spink (Pergamon Press Ltd, Oxford), 1964. Pp. ix+420. Price £5

Prof. Vainshtein (Director, Institute of Crystallography, USSR Academy of Sciences) is a well-known figure in the field of electron diffraction and has contributed much to the application of this method for the elucidation of crystal structures. It is, therefore, very gratifying to see his book translated into English and made available to a much wider audience.

The book contains a systematic presentation of the theory and practice of crystal structure analysis by electron diffraction, without touching upon other applications of electron diffraction. The specific features connected with the scattering of electrons by crystals is considered in detail and compared to those of scattering of X-rays. The geometry of the electron diffraction pattern is considered in a separate chapter and this is followed by another detailed chapter on the intensities of the reflections from an ideal single crystal, from mosaic crystals, textured films, polycrystalline films, and so on. The application of Fourier methods in electron diffraction is considered briefly and followed by an account of some typical structure determinations. It is pointed out that hydrogen atoms are much more easily located by electron diffraction than by X-ray diffraction. Some of the results so obtained, as for instance in diketopiperazine, are very striking.

The author has clearly made out a case for a more systematic application of electron diffraction methods in structure analysis. Although the original Russian edition appeared in 1956, the later work has also been included in the English edition. This book is sure to remain as the standard reference book on the subject for years to come.

G. N. Ramachandran

Organic Chemistry — An Introductory Course

by H. Lowther (Pergamon Press Ltd, Oxford), 1964. Pp. ix+197. Price 20s.

This little book is based upon the author's thirty-two years' experience as a teacher and is the result of his desire to write a text-book of organic chemistry for beginners, which ' whilst keeping the new developments in view concentrates on stating the basic principles and reactions clearly and concisely '. On the whole the author has succeeded in achieving this aim.

The book is divided into twenty chapters. The subject is introduced by a discussion of the essential features of organic compounds, structures of simpler molecules (illustrated by photographs of models) and typical reactions which they undergo. This chapter also deals with some basic manipulations of organic chemistry. Each of the other chapters is concerned with compounds of a specific functional type. Similar treatment has been used to describe the aromatic compounds. There are two short sections which seek to acquaint the student with compounds of biological importance and typical organic chemical industries. Analysis of organic compounds, and derivation of empirical, molecular and structural formulae are discussed in a separate chapter towards the end. Finally, a short section is devoted to consideration of physico-chemical principles which are necessary for an intelligent grasp of organic chemistry. A selection of exercises at the end is intended to guide the student's study of the subject.

There is a need for books of this type which enable the beginner to understand the fundamental principles without burdening him with too much of detail. The standard of printing and get-up of the book are high usually associated with Pergamon Press publications. The only difficulty in the way to its wide use might be its price.

V.V.S.

The International Encyclopaedia of Physical Chemistry and Chemical Physics: Vol. 1 — Application of Neutron Diffraction in Chemistry by G. E. Bacon (Pergamon Press Ltd, Oxford), 1963. Pp. xi+141. Price 42*s*

This book can be said to be a supplement to Prof. Bacon's first book on neutron diffraction and embodies in it the contributions which this new technique has made in the solution of various problems in chemistry. All the latest results have been incorporated, including those on hydrogen bonding in inorganic systems. The book has been very cogently written, the subject matter well classified and illustrated with neat figures and diagrams. Pertinent references to original papers are given at the end of each chapter.

To understand the book, some knowledge of crystallography and X-ray diffraction methods is essential. X-ray and neutron crystallography are very similar and the author has taken pains to compare the two techniques and bring out clearly the superiority of neutron diffraction over the X-ray methods in locating light atoms like hydrogen in the presence of heavier atoms (Chapters 2 and 3) and also in the study of systems containing very heavy elements like uranium and thorium (Chapter 4). In Chapter 5, the author has dealt with the metal hydrides and the ammonium compounds. Chapter 6 deals with neutron diffraction of compounds containing neighbouring elements which cannot be easily distinguished by X-rays but often lend themselves to neutron diffraction techniques as their neutron scattering amplitudes are considerably different. The last two chapters deal with magnetic materials, and liquids and gases.

In spite of the fact that, in India, the intense neutron sources are located in Bombay, the book will be found useful to teachers in physical chemistry in all universities and to research workers in crystallography all over the country.

J. Shankar

Mass Spectrometry edited by Charles A. McDowell (McGraw-Hill Book Co. Inc., New York), 1963. Pp. x+639. Price $ 20.00

This is a comprehensive book dealing with all aspects of mass spectrometry and is, therefore, a welcome addition to the many others which deal with a few specialized aspects only. The individual chapters have been written by experts in the field.

The chapter 'Types of mass spectrometers' gives a good review of the progress in instrument design which has taken place since the first one was built, while the chapter 'Mass spectrometry in research' deals with the types of problems that this technique can handle. These chapters are thus excellent introductions to the beginners in mass spectrometry.

Chapters 4, 5 and 6, dealing with ion sources, ion optics and electronic techniques, are largely useful to those who wish to build mass spectrometers of their own. The following chapter on high resolution mass spectrometers brings the instrumental techniques up to date.

Chapter 8 on vacuum techniques is well written. Certain things, such as the working of a vacuum pump, could have been taken for granted, while more information on the type of valves suitable for isolating the ion source from the analyser tube, and high temperature valves would have been more pertinent.

The chapter on isotope abundance measurements has been well written and includes isotope effect studies, reaction mechanism, geochemical studies — C^{12}/C^{13}, O^{16}/O^{18} and S^{32}/S^{34} measurements, etc. Mineral age determination by lead isotope, argon-potassium and rubedium-strontium methods has not found place in detailed discussion. Similarly, hydrogen-deuterium determination has not been dealt with. The last three chapters dealing with applications in the study of free radicals, ionization and dissociation of molecules and ion molecule reactions are very informative.

The book is not free from printing errors; for example, on page 46, line 5, 'helium' of mass 20 and 22 instead of 'neon'. On page 598, in equation 13.16 the denominator should be $E_r^{1/2}$ and not $E_r^{-1/2}$. On the same page, the kinetic energy is given as $2m_p\bar{v}^2$ instead of $1/2m_p\bar{v}^2$, which makes equation 13.17 also erroneous.

The only serious omission is a chapter on the use of mass spectrometry in structure determination. On the whole the book is well written and illustrated. The bibliography at the end of each chapter is extensive and up to date and the book will be useful to a wide spectrum of scientists.

J. Shankar

Theory and Structure of Complex Compounds edited by B. Jezowska-Trzebiatowska (Pergamon Press Ltd, Oxford), 1964. Pp. xii+707. Price £ 6

The book is a collection of eighty-seven papers which were presented at a symposium held in Wroclaw, Poland, from 15 to 19 June 1962. The preface to the book has been written by the editor in which she draws pointed attention to the importance of symposia which bring about a 'synthesis of what is being born, created and what happens in the solitude of scientific laboratories in the whole world'. The contributors are from many lands with a big majority from Poland and other East European countries.

The papers cover a wide range of topics in co-ordination chemistry, but the main emphasis appears to be on the review articles describing the applications of various physico-chemical techniques like absorption spectra, refractometry, magnetic moments, Massbauer effect, polarography and chronoamperometry to the determination of nature and stability of various complex ion forming systems. Notable amongst these reviews and articles of sustaining interest are: (i) the role of oxygen in coordination compounds by B. Jezowska-Trzebiatowska; (ii) chemistry and photo-chemistry of iron and manganese pyrophyrins by Calvin *et al.*; (iii) structure of fluoroarsenates by L. Kolditz; (iv) optical rotatory dispersion of asymmetric complex compounds by S. Kirschner and co-workers; (v) kinetics and mechanism of substitution reactions by F. Basolo; and (vi) coordination polymerization in metal alkoxides by D. C. Bradley.

Rest of the articles are generally brief reviews of the work of the authors; most of this was either already published elsewhere or has been published during the last two years since the symposium was held. The practice followed by some of the international congresses of coordination chemistry to publish the main plenary lectures in the form of a book and the other papers only in the form of abstracts appears to be of better practical utility.

The paper, printing and layout of the book are superb; the book is particularly free from printing errors and the editorial staff as well as printers are to be congratulated for the excellent job they have accomplished.

R. C. MEHROTRA

EXPERIMENTAL METHODS IN GAS REACTIONS by H. Melville & B. G. Gowenlock (Macmillan & Co. Ltd, London), 1964. Pp. viii + 464. Price 84*s*.

This volume is a revised version of the original book by Farkas and Melville and has been improved in various ways. First, much of the earlier material has been expanded and has been better illustrated by diagrams. Secondly, a considerable effort has been made to include almost a complete account of the up-to-date techniques employed in gas kinetics. Thirdly, the book is better organized and contains extensive bibliography for the benefit of the reader. For convenience and usefulness of a concise volume, the object seems to have been to emphasize only the necessary descriptions and working procedure of the various techniques, since detailed accounts can be available in the references cited. The presentation is elegant and the language is simple to follow. The material is systematically arranged.

The book is not only useful for studies in gas kinetics but is very instructive and inspiring for an experimentalist initiating a new research programme, to introduce new or modified techniques in solving his problems. The main utility of this volume lies in that various alternative techniques for a particular process have been made available. In my opinion, this book should be a welcome addition to libraries in research institutions and as a reference book in research laboratories making use of vacuum techniques. I am sure all experimentalists in physics and chemistry, particularly those interested in gas kinetics, owe a debt of gratitude to the authors for their immensely useful service rendered to facilitate accurate experimental measurements. This volume, undoubtedly, contains a wealth of information and is, therefore, an outstanding contribution.

M. L. LAKHANPAL

IR THEORY AND PRACTICE OF INFRARED SPECTROSCOPY by H. A. Szymanski with a chapter on instrumentation by N. L. Alpert (Plenum Press Inc., New York), 1964. Pp. xiv+375. Price $ 15.00

This book by Szymanski is intended to cover all the aspects of infrared spectroscopy from basic theory to latest applications. The theory is covered nicely for a beginner. The chapter on instruments by Alpert is adequate. For an excellent review on instrumental aspects, the book by Potts is probably the best. Sampling techniques have been reviewed in sufficient detail for those mainly interested in practical applications. The real weak point of the book is the lack of sufficient information on spectra-structure correlations. Practically no attempt has been made to discuss the elucidation of structures of molecules of importance to organic, inorganic or biological chemists. The reader will have to consult the books by Bellamy and Rao for a detailed discussion of spectra-structure correlations. Quantitative analysis forms the material of a chapter and is discussed in fair detail.

The book has several figures, charts and tables which will be of value. References to the literature are rather limited compared to other books and treatises on the subject. Considering the general title of the book, the author has not done justice to the subject matter. The book is much too expensive — $ 15.00 for a book of 375 pages. The get-up of the book, however, is fine.

C. N. R. RAO

SAMPLING SYSTEMS THEORY AND ITS APPLICATION: Vols. 1 & 2, by Ya. Z. Tsypkin (Pergamon Press Ltd, Oxford), 1964. Pp. xvi+742. Price £ 5 each

These two volumes are a welcome addition to the literature in English on this subject. Although only recently translated, they were originally published in Russia in 1958; however, despite the delay of 5 years they are still topical.

The author takes considerable pains to discuss the principles of sampling systems in an integrated manner; much of the literature in this field has been restricted either to pulse communication systems or to sampled data control systems. Although the distinction between open loop and closed loop systems has of necessity been retained in these two books, the theory presented is common to both.

The author commences with a chapter in which he attempts a number of definitions. It is regrettable that instead of clarifying the issues, this will certainly cause confusion to anyone who is not already well familiar with this field. One might have wished the author to have used those familiar words: 'This chapter may be omitted on a first reading.' If the reader is not now too discouraged by the complexity of the problem he will find his further reading greatly rewarding. A wide variety of practical systems are discussed to give a suitable engineering background to the ensuing theoretical material; these examples are selected from both the field of communication and control engineering.

As the title of this text states, this is a book on theory and one must not be disappointed that hereafter it is almost entirely mathematical. A very comprehensive section follows giving the principles of the discrete Laplace transformation and its relationship to finite difference equations. This is conducted in a rigorous mathematical manner although the author frequently resorts to specific graphical illustrations to demonstrate the significance of the results; this is of considerable value for the engineer who is usually more interested in the end product of a mathematical manipulation than in the rigour or sophistication of the derivation of the result.

In subsequent chapters the application of the discrete Laplace transform to both open loop and closed loop systems is illustrated. In particular, the application to the problem of the response of open loop systems to stochastic signals is considered.

This book may be strongly recommended as a comprehensive volume on the use of the discrete Laplace transformation in the analysis of pulse systems.

ROBERT KING

AUTOMATION OF CONTINUOUS PRODUCTION PROCESSES by V. L. Lossiyerskii & L. G. Pliskin; translated from the Russian by R. P. Froqui (Pergamon Press Ltd, Oxford), 1964. Pp. viii+118. Price 42*s*.

Around two hundred years ago, we had the beginnings of an industrial revolution, which introduced machines to lessen the toil and to quicken the methods of production. With technical progress, the lines of production expanded and machines got integrated into one another. A natural outgrowth of this was the development of self-regulatory machines through a feedback system, which processed data and performed control functions. This is automation, which is now augering a second industrial revolution in the world.

The authors of the book under review discuss mainly the principles which should govern any decision on automatization. The economic basis for this, as discussed in Chapter 1, is obviously the minimization of the ex-factory cost of output. An analysis of the structure of costs generally pinpoints the areas where mechanization is desirable.

The statistical characteristics of the limits within which inputs, outputs and process conditions may vary define the parameters for automation of a continuous production system. A detailed study of their magnitudes and tolerances indicates the type of regulatory mechanism, which would be required for a feedback system. The time rates of the production processes in relation to the operating time required for their regulation decide on the nature of the instrument sensitivity, which is essential for automation control. Proceeding from this analysis in Chapter 2, the authors elaborate in Chapter 3 on the structures of some typical multi-point control systems in the metallurgical and chemical processes. However, disturbing influences may upset primary controls. Authors discuss this aspect in Chapter 4 and opine on the feasibility of a supplementary control device or a cascade type of regulation. This could be based on compensating for or suppressing such disturbances as well as their likely effects on the system of production. Integrated automatic controls could be devised by quantitative analysis of the range within which such disturbances generally occur and a feedback system could be then designed for optimal self-regulation.

The authors appear to be concerned only with production engineering and its amenability to automation. Types and levels of automation depend primarily upon cost minimization. Their economic analysis is of a very limited nature and restricted only to some intra-firm details. Inter-industrial repercussions through changes in relative costs of inputs or shifts in their substitutability have been overlooked. The broader impact of automation on the national output, employment and growth has also not been discussed. These are obviously the limitations of any specialist, and within them the book has been admirably well conceived. Some more illustrative examples of metallurgical and chemical processes, with indications of appropriate automatic devices, would have further helped the reader's ' imagineering '.

The discussions being mostly abstract, the style has become very terse. In many instances, sentences have become much involved and this has obscured understanding. In places, it looks like an attempt at ' transliteration ' rather than ' translation '. Obviously, the translation editor has yet to learn his lessons on the differences between the peculiar modes of Russian and English expressions. In spite of it all, however, this book would be a valuable addition to any library on production engineering.

S. S. WAGLE

PHOTOCHEMISTRY OF PROTEINS AND NUCLEIC ACIDS by A. D. McLaren & D. Shugar (Pergamon Press Ltd, Oxford), 1964. Pp. ix+450. Price £ 5

As a part of the series on ' Modern Trends in Physiological Sciences ' the book deserves special mention not only because there has been tremendous development in our knowledge regarding the proteins and nucleic acids but also due to the fact that our knowledge in photochemistry of these have just started to expand. The authors in the introduction have justified the publication of this volume not as a monograph and in the actual coverage they have definitely gone beyond the limits of photochemistry. It is difficult to draw a sharp line of demarcation between photobiology and photochemistry, but the book under review may be considered more in the former area than in the latter.

The chapters on the principles of photochemistry and the absorption and luminescence spectra of nucleoproteins and their components have been carefully written and will be extremely useful not only to the beginners but also to the research workers interested in the photochemistry of the macromolecules. With their own experiences in the area the authors have elaborated in detail the effect of ultraviolet light on amino acids, proteins, etc., and photochemistry of purine and pyrimidine derivatives. Unfortunately, however, in spite of the extensive kinetic studies the mechanism of action of the photosensitized reactions involving macromolecules is still somewhat obscure. Actually this has led to the gradually increasing attention towards photobiology. The discussion in case of nucleic acids and polynucleotides is very good, but some of the observations made are controversial, as expected. The last chapter of the book 'Some selected topics in photobiology' and the appendix 'Some techniques in photochemistry' appear to serve a special purpose at least for the beginners. But the critical examination of the two chapters reveals that they could have been nicely knit into the actual text without being dealt with separately. This would have helped to illustrate the major discussion.

The treatment as a whole, however, is elaborative and the references collected are exhaustive, if not complete. In spite of the detailed treatment of diverse areas of chemistry and biology the book is practically free from errors. However, after all the good impressions and the help obtained in theory and practice the reader may wonder at the end 'Why did the authors intrude in so many areas of biology which are not pertinent to the main theme of this well-planned guide book?' Yet nobody will deny the importance and usefulness of this authoritative treatment.

D.P.B.

ADVANCES IN ORGANIC GEOCHEMISTRY: Monograph No. 15 — Earth Science Series (Pergamon Press Ltd, Oxford), 1964. Pp. ix+488. Price £ 6

The monograph compiles an array of 39 impressive papers on different branches of organic geochemistry including a group of articles on analytical techniques. The origin, accumulation and subsequent transformation of organic material as well as its molecular nature as they occur in petroleum, coal, water, sediments, etc., are intriguing problems in organic geochemistry. The present monograph records experimental results and interesting views of a number of eminent workers on some specific aspects of such problems.

The general outline of the monograph seems not very orderly. Grouping of similar topics is rare. More than one language is used in publishing the papers.

A few papers discuss about two very fascinating subjects, namely (i) oil genesis and (ii) cosmological history of carbonaceous meteorites.

With a lot of evidences to its support the organic theory of oil fails to offer convincing explanations for a number of facts connected with oil genesis; such a case history is presented from southern Norway where oil occurs in vesicles in dolerite.

The possibility of existence of life in extraterrestrial objects is discussed, based on laboratory data on carbonaceous meteorites. Disagreement in the views expressed by different authors unfolds the complexity of the problem. Further studies are obviously warranted.

Geochemical criteria are suggested as an aid in reconstructing palaeogeography and palaeo-temperature of sedimentary basins. Such criteria in themselves are not always diagnostic, but integration of these with other geological and geophysical evidences would help in understanding the depositional history of the past sediments.

Analytical techniques for surface geochemical prospecting and detecting promising oil/gas bearing horizons through geochemical indices during actual drilling are discussed. Of the two techniques the latter is more promising since similar techniques are in common use in oil-well drilling. Data obtained through the former technique, from relatively favourable area for geochemical survey, are not convincing. Suggested means to reduce interference in such determinations are not supported by additional data.

Papers dealing with the changes of oil properties through migration and mechanism of oil accumulation in anticlines are presented, based on the studies made on laboratory model experiments. Simulating natural geological conditions in laboratories is difficult. Applications of such knowledge for solutions of field problems would have been more convincing had the authors been able to cite more field examples in support of their views.

Isolations and identifications of different types of organic compounds from samples like sediments, rocks, coal, water, etc., as well as the microbial modifications of many organic compounds are discussed. Accumulation of more such data on organic substances of samples of different geologic ages would aid in better understanding of their geochemical significance.

In general, the monograph contains a wealth of information, with many a hint for future lines of approach, on a number of intriguing problems of organic geochemistry. The section dealing with the analytical techniques relating to specific determinations has added much practical value to the monograph. Therefore, the monograph will greatly benefit those who are engaged in research on organic geochemistry.

S. N. BHATTACHARYA

ENGINEERING UNITS AND PHYSICAL QUANTITIES by H. S. Hvistendahl (Macmillan & Co. Ltd, London), 1964. Pp. viii+132. Price 25*s*.

According to the author, this book is intended for 'engineers, physicists and students of these subjects throughout the world'. Of late, the subject of 'Units' is demanding more and more attention for a specialized treatment or a course of lectures. This is evident from publications like the book under review (first published in 1964); *A dictionary of scientific units* (*including dimensionless numbers and scales*) by H. G. Jerrard and D. B. McNeill (Chapman & Hall Ltd, London, 1963); and the reviewer's own book, *A guide to metric system* (Asia Publishing House, Bombay, 1961).

The book under review gives a fairly lucid account of the different units used in mechanical and electrical engineering: their origin, evolution and present basis, their nomenclature and symbols according to the latest international agreements and the conversion factors among them. It covers all the units and measures used by engineers: British, American and Metric.

The recent trend all over the world, including India, is the adoption of the MKSA (Metre-Kilogram-Second-Ampere) system. This is shortly going to be merged into the 'System Internationale des

Unites', as per the latest resolution of the Conference Generale des Poids et Measures (CGPM), and the International Organization for Standardization (ISO), in 1960 and 1961.

The book contains 8 chapters, besides a section on reference and the index. The contents of the first eight chapters (pp. 1-117) are: (i) Definitions and basic principles; (ii) Quantity calculus, quantity arithmetic and conversion of units; (iii) Systems of units; (iv) The units of heat and thermodynamics; (v) The units of electricity and magnetism; (vi) Dimensional analysis and the laws of similitude; (vii) Conversion factors (tables); and (viii) Vector calculus, symbols and notation.

A study of the above chapter headings reveals that, after a review of the 'Definitions and basic principles' of units in general, the author proceeds to the survey of the different systems of units and the problem of interconversion. It specifically deals with units in 'Heat and thermodynamics' and 'Electricity and magnetism' in two separate chapters. Then it proceeds to cover such allied topics as the 'Dimensional analysis', 'Vector calculus', and symbols and notations used in it.

The chapter on 'Vector calculus' in a book on 'Units' is unusual but all the same welcome as this chapter deals with symbols for vector quantities, addition, subtraction and product of vectors, area as a vector quantity, the gradient, the divergent, the curl or rotation — concepts so essential for the students of advanced engineering or physics.

From pages 97 to 116, in all 34 very useful conversion tables for all branches of engineering are given. Some of them are of such specialized nature as: centrifugal pump specific speeds; dynamic moment of inertia, spring stiffness rate, energy or enthalpy per unit mass, value of the universal gas constant (R_0), entropy; rate of heat liberation/unit volume; thermal conductivity; radiation coefficient; and dynamic viscosity and kinematic viscosity.

In section 9 under 'References' the author lists 76 references (papers and books) on the subject of units published all over the world. The index, comprising 4 pages, adds to the utility of the book for ready reference.

The author, being an executive of a leading British engineering firm and a full member of three British engineering institutions and one American institution, with 40 years' experience with British and continental firms in commerce and industry, has been able to write the present work authoritatively with such a wide background. He deserves the gratitude of both engineers and scientists for the wealth and variety of information presented by him in the text and tables in this modest volume.

The reviewer has no hesitation in recommending the book to all libraries in science or engineering faculty, or to their advanced students. It should be an essential reference book for all colleges hereafter. The get-up of the book is excellent. Only the price of 25*s*. is high for the average Indian student to purchase individually.

The reviewer, being an electrical and electronics engineer, particularly misses a good treatment of the 'Rationalization', now so common in all published literature in electrical engineering and electronics as well as in 'Electricity and magnetism' in physics. This should really deserve a separate chapter, at least in the next edition.

V. V. L. RAO

PUBLICATIONS RECEIVED

THE PLANET EARTH edited by D. R. Bates (Pergamon Press Ltd, Oxford), 1964. Pp. vii+370. Price 42*s*.

PROGRESS IN BORON CHEMISTRY: Vol. 1, edited by H. Steinberg & A. L. McCloskey (Pergamon Press Ltd, Oxford), 1964. Pp. vii+487. Price £ 7

SPECTROSCOPY AND PHOTOCHEMISTRY OF URANYL COMPOUNDS — International series of monographs on nuclear energy, Vol. 1, by Eugene Rabinowitch & R. L. Belford (Pergamon Press Ltd, Oxford), 1964. Pp. x+370. Price 80*s*.

FATIGUE RESISTANCE OF MATERIAL AND METAL STRUCTURAL PARTS edited by A. Buch (Pergamon Press Ltd, Oxford), 1964. Pp. viii+312. Price 100*s*.

ADVANCES IN BIOLOGY OF SKIN: Vol. 5 — WOUND HEALING edited by William Montagna & Rupert E. Ballingham (Pergamon Press Ltd, Oxford), 1964. Pp. xvi+254. Price £ 5

METHODS OF ENZYMATIC ANALYSIS edited by Hans-Ulrich Bergmeyer (Academic Press Inc., New York), 1963. Pp. xxiii+1064. Price $ 30.00

ANALYSIS OF ANCIENT METALS — International series of monographs on analytical chemistry, Vol. 19, by Earle R. Caley (Pergamon Press Ltd, Oxford), 1964. Pp. xi+173. Price 70*s*.

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

HEAT ENGINES AND APPLIED THERMODYNAMICS by N. C. Dey (Asia Publishing House, Bombay), 1964. Pp. xv+443. Price Rs 26.00

HIGH TEMPERATURES IN AERONAUTICS — International series of monographs in aeronautics and astronautics, Vol. 15, edited by Carlo Ferrari (Pergamon Press Ltd, Oxford), 1964. Pp. xiii +446. Price £ 5 5*s*.

THE BIOCHEMISTRY OF POLIOMYELITIS VIRUSES by Ernest Kovacs (Pergamon Press Ltd, Oxford), 1964. Pp. xii+272. Price 70*s*.

WATER AND SOLUTE-WATER INTERACTIONS by J. Lee Kavanan (Holden-Day Inc., San Francisco), 1964. Pp. 101. Price $ 5.50

ADVANCES IN ORGANOMETALLIC CHEMISTRY: Vol. 1, edited by F. G. A. Stone & Robert West (Academic Press Inc., New York), 1964. Pp. xi +334. Price $ 11.00

SYMPOSIUM ON FOODS: PROTEINS AND THEIR REACTIONS edited by H. W. Schultz (AVI Publishing Co. Inc., Westport, Connecticut), 1964. Pp. x+472. Price $ 3.50

POLYCYCLIC HYDROCARBONS: Vols. 1 & 2, by E. Clar (Academic Press Inc., New York, and Springer-Verlag, Berlin), 1964. Pp. Vol. 1, xxvii+487; Vol. 2, lvi+487. Price Vol. 1, DM 70; Vol. 2, DM 128

REACTION KINETICS: Vol. 1 — HOMOGENEOUS GAS REACTIONS; Vol. 2 — REACTIONS IN SOLUTIONS by Keith J. Laidler (Pergamon Press Ltd, Oxford), 1963. Pp. Vol. 1, x+136; Vol. 2, x+232. Price 30*s*. each

NOTES & NEWS

International cooperative investigation of the tropical Atlantic Ocean

Preliminary results of the international cooperative investigation of the tropical Atlantic have been announced at the third session of the Intergovernmental Oceanographic Commission meeting held during 10-19 June 1964 in Paris. One of the significant results reported is the confirmation of the existence of an ' underwater river ', flowing eastward in the Atlantic along the Equator at a speed of about 3 miles/hr. The investigation of the tropical Atlantic took place during the winter phase from February to April 1963, when 14 ships from seven countries ran north-south transects across the Equator from South America to Africa. It was also confirmed during summer that the current continued to flow and it appeared to oscillate in a zone 100 miles north and 100 miles south of the Equator at depths between 100 and 200 ft.

The investigations carried out during summer made use of a new technique in which the observed data from a vessel were sent directly to the National Oceanographic Data Centre in Washington via a communications satellite in fixed orbit over the north-east coast of Brazil. The data so received at the centre are processed by a computer and any inaccuracy in taking the measurement is pointed out to the people aboard the ship by a return message from the centre in about ½ hr. This is a significant improvement since previously there was no way of detecting the errors in measurement till the completion of the voyage by the vessel. During the third and final phase of the tropical Atlantic investigation, currents in the Gulf of Guinea east of Canary Islands were studied and evidence for a westerly current flow of high salinity water was found. Another major project undertaken along with these studies is the Guinean trawling survey in which two chartered French trawlers sailed on 63 transects at right angles to the coast over the continental shelf south of the Sahara [*Press Release No.* 2517, *from UNESCO, Paris, dated* 19 *June* 1964].

Theory of supernova collapse: Need for revision

A rocket launched on 7 July 1964 by the US Naval Research Laboratories has returned to earth with evidence against the existing theory regarding the collapse of a supernova. Hence, it becomes necessary to revise the existing theory about the sudden blazing of a star to a supernova, releasing in 1 sec. energy comparable to the sun's normal output for a billion years. According to the present theory, when such a super explosion occurs, a neutron star so dense that each cubic inch weighs about a billion tons is left behind. A neutron star radiates only a ten-billionth of the visible light put forth by the sun, but it is ten billion times brighter than the sun in pouring out X-rays.

The rocket was launched to investigate the X-ray radiations coming from the Crab Nebula, which is one of the most thoroughly studied of supernova remnants. It is known to have exploded on 4 July 1054, when it suddenly appeared on the sky with a brightness exceeding that of Venus. The visible nebulous material is the expanding wreckage of the supernova, a gas shell expanding at 780 miles/sec. Last year investigations showed that the Crab Nebula was a strong source of X-rays. The instruments in the rocket were designed to determine whether or not a neutron star left from the supernova explosion was the source of these X-rays. The Crab Nebula was scanned during the time when the moon passed between the source and the rocket's instruments. If the X-rays had been coming from the Crab Nebula, their intensity would have dropped abruptly as the moon cut them off. The observations made showed that the falloff was slow, which means that the X-rays are coming from an extended source and not a neutron star. It is felt that the X-ray source could be an extremely hot gas having a temperature of 10-20 million degrees. This observation makes it necessary to revise the existing theory regarding the supernova. One of the views expressed is that the Crab Nebula supernova may have involved the explosion of the entire star. The extended source of extremely hot gas may be the remains of the star's core [*Sci. Newslett.*, **86** (1964), 53].

Gas lenses for laser beams

Gas lenses that show promise for guiding laser beams in pipes for communication over long distances have been developed at the Bell Telephone Laboratories (BTL), New York. These lenses, which use variations in the refractive indices of gases to guide light, do not reflect or absorb light as much as conventional optical components. A long gas lens, or series of lenses, can confine a laser beam to a path near the centre of a pipe. In a straight pipe, the lens need not be strong because it must only compensate for the small natural spreading of the laser beam. In curved sections of a pipe, the light beam normally would travel in a straight line. However, as the centre of the pipe curves away from the beam's path, the beam encounters gas of decreasing refractive index. This region acts like a prism, deflecting the light beam in the direction of the pipe's curvature. These gas lenses take advantage of the well-known phenomenon that light rays curve towards regions of high refractive index. The lens structure for continuously focusing light is obtained by controlling variations in the refractive index of transparent gases due to thermal expansion, flow and diffusion. One lens structure consists of a gas-filled pipe. Inside the pipe running through its centre, a spiralling coil or helix is kept a few degrees warmer than the pipe. The helix heats the gas and sets up non-turbulent convection currents that cause the gas to concentrate in the centre of the pipe. The index of refraction of the gas being proportional to the density, the light beam is focused. In the second type of lens, two gases with different refractive indices flow together continuously from opposite directions into a mixing chamber. The gases meet, mix together and are drawn out of the chamber. The rate of gas flow and the chamber's shape create a symmetrically curved boundary region where the two gases meet. The light beam passes through the mixing chamber and is focused in this region.

These and other types of gas lenses currently being investigated at the BTL represent a basically new approach to the guiding of light beams over long distances. Further development is expected to lead to systems for focusing a laser beam for use in long-range communications [*News from Bell Telephone Laboratories, release dated* 23 *July* 1964].

A new microwave variable time delay technique

A new technique for varying the time delay in the case of microwaves has been developed at the US Air Force Rome Air Development Centre, New York. The technique makes use of the principle of varying the velocity of an electron beam which is modulated by the signal frequency to which the time delay is to be given. In the device developed, an electron beam leaving the cathode is accelerated by a voltage V_a applied to a helix. The signal frequency is also fed into the input helix. Thus the electron beam is modulated by the input signal which is to be delayed. On leaving the helix the electron beam is further accelerated or decelerated by a voltage V_b along the drift region of the device. The beam moves through the drift region of the device at its new velocity and gives up the modulating signal to an output helix placed before the collector. The time taken for the signal to travel from the input helix to the output helix depends upon V_a and V_b and the length of the drift region. For a drift region of 6 in. and a change in V_b of 300 V. a variable time of 23 nanosec. was obtained. The device is inherently a broad band one, which makes it particularly attractive. A further advantage is that a gain of 20-30 db. can be obtained. Further work for increasing the length of the variable delay time is in progress. When this is accomplished, the technique should prove to be of considerable value in the sophisticated signal processing systems which are rapidly becoming an essential part of radio astronomy and radar work [*New Scientist*, **23** (1964), 335].

A novel preparation of organic iodides

A new process involving the direct interaction of the appropriate alcohol or ether with elementary iodine in the presence of a small quantity of diborane or other boron hydride has been found to give organic iodides in high yield at ambient temperature. Hydrogen is evolved in the reaction and oxygen is replaced by iodine. Thus methyl iodide can be produced from methyl alcohol and also from any methyl ether, such as anisole. These reactions have been expressed by a general expression which may be written

$$6ROR'+3I_2+B_2H_6 \rightarrow 6RI+2B(OR')_3+3H_2$$

where R = alkyl or substituted alkyl and R' = H or alkyl or aryl or any other organic radical. The reaction is very widely applicable and almost any aliphatic or alicyclic iodide may be made by a suitable choice of alcohol or ether as starting material. Ethers may be symmetric, asymmetric, aliphatic, aromatic or cyclic such as tetrahydrofuran. Of the numerous compounds tested, difficulties have so far been encountered only with diphenyl ether and alcohols with their hydroxyl groups vicinal to a halogen atom.

Cyclic ethers, among which are included epoxides, do not give iodides in single stage, but an iodinated boric ester from which the organic iodo compound is immediately liberated on hydrolysis. When more than one hydroxyl or etheric oxygen atom is available in the molecule, iodination may occur at each site, but with a limited amount of iodine a selectivity may be manifested.

A most interesting feature of these reactions is the small quantity of diborane required to convert a large quantity of iodine. For small-scale preparation it is convenient to mix the anhydrous alcohol or ether with the appropriate quantity of iodine in a large flask fitted with a removable vacuum tap. The air is swept out by nitrogen, which is then pumped out to a low pressure by means of a rotary oil pump, an operation which may entail a prior freezing of the organic reactant where there is appreciable volatility. Diborane is now admitted to the flask to a pressure not exceeding 200 mm. after which the tap is closed and the contents of the flask allowed to warm up. Reaction usually commences well below the room temperature and in most cases is complete within a few minutes. Slow rotation of the flask is helpful and reduces the time required [*Chem. & Ind.*, (1964), 1582].

Structure and function of iron-flavoproteins

Xanthine oxidase, an iron-flavoprotein, was discovered about sixty years ago, and has been obtained in an essentially homogeneous and crystalline form [Avis, P. U., Bergel, F. & Shoster, K. V., *Nature, Lond.*, **173** (1954), 1230]. Although the physiological function of this enzyme is not clear [Bray, R. S., *Enzymes*, vol. 7, edited by P. D. Boyer, H. A. Lardy & K. Myrback (Academic Press Inc., New York), 1963, 533], work on the mechanism of action of this enzyme and other iron-flavoproteins like rabbit liver aldehyde oxidase, dihydroorotic dehydrogenase was stimulated by the suggestion [Green, D. E., *Inorganic nitrogen metabolism*, edited by W. S. McElroy & B. Glass (Johns Hopkins University Press, Baltimore), 1956, 574] that these serve as convenient models for the study of mitochondrial electron transport sequence.

In a recent paper, Handler and his associates [Handler, P., Rajagopalan, K. V. & Aleman, V., *Fed. Proc.*, **23** (1964), 30] have presented the results of studies carried out on the role of metals, particularly non-heme iron, in the internal electron transport system of bovine milk xanthine oxidase, rabbit liver aldehyde oxidase and dihydroorotic dehydrogenase. A unique feature of these enzymes is the formation of an oxygen-free radical, the superoxide anion, O^-. Accompanying this is the appearance of sulphite autoxidation and chemiluminescence when luminol and dimethyl-bis-acrylidin are present in the mixture along with the substrate and oxygen. The occurrence of the oxygen-free radical is suggested by the absolute requirement for oxygen for the reduction of cytochrome *c*. The involvement of iron in this process is indicated by the fact that the flavoproteins that do not contain iron (e.g. microsomal TPNH cytochrome *c* reductase) do not show a requirement for oxygen.

Following the observation made earlier by Beinert *et al.* [Beinert, H., Heinen, W. & Palmer, G., *Enzyme models and enzyme structure, Brookhaven Symp. Biol.*, **15** (1962), 229] that the non-heme component of mitochondria when reduced with appropriate substrate produces a characteristic EPR signals at $g_1 = 1{\cdot}94$, Handler *et al.* in collaboration with Beinert have studied the non-heme iron, molybdenum and flavin of aldehyde oxidase. Judging from the signal heights, molybdenum and flavin were located on the substrate end of the electron transport sequence. The presence of secanol or triton-X 100 did not affect the appearance of signal due to molybdenum and flavin; and secanol delayed the appearance of the signal due to iron, while triton prevented the appearance of the signal.

In addition, spectrophotometric studies were carried out to obtain independent characterization of the iron component. When the absorbance at 450 and 550 mμ was correlated with the flavin content of these enzymes, the presence of an additional chromophore absorbing at these wavelengths was indicated. Flavoproteins that do not contain iron did not show any difference in absorbance at these wavelengths. The spectrum of the chromophore was obtained by subtracting the spectrum of an equivalent amount of FAD and by difference spectra, i.e. spectra of enzyme minus spectra of FAD. Treatment with methanol releases the flavin from aldehyde oxidase and treatment with methanol-ethanol mixture releases the flavin from xanthine oxidase. The resultant flavin-free iron-containing protein had a striking similarity to the difference spectra of the two enzymes [Rajagopalan, K. V. & Handler, P., *J. biol. Chem.*, **239** (1964), 1509]. The following pathway of electron transport in aldehyde oxidase has been suggested on the basis of spectral and EPR evidence:

$$\text{Substrate} \rightarrow \overset{\text{Mo}^{6+}}{\underset{-\text{S}-\text{S}-}{+}} \rightarrow \text{FAD} \rightarrow$$
$$\text{CoQ} \rightarrow \text{Fe} \rightarrow \text{O}_2$$

N. APPAJI RAO

Phytochrome: A protein controlling plant growth and development

Many aspects of plant growth and development are controlled by light intensity and daily duration of light and night. The remarkable similarity in the action spectra of the effect of light on seed germination, flowering, etiolation, plastid development, etc., indicates that these diverse expressions of plant growth and development have a common point of control and that the same reversible photochromic pigment acts as the photoreceptor in all these responses [Siegelman, H. W. & Hendricks, S. B., *Advanc. Enzymol.*, **26** (1964), 1]. The active protein, phytochrome, has been isolated and shown to exist in two photoreversible forms with absorption maxima at 660 mμ (P_{660}) and 730 mμ (P_{730}) respectively, with P_{730} as the active form. P_{730} reverts to P_{660} spontaneously in darkness or effectively on irradiation as indicated below:

$$P_{600} \underset{730\ \text{m}\mu}{\overset{660\ \text{m}\mu}{\rightleftharpoons}} P_{730}$$

The rate of reversion of P_{730} to P_{660} appears to be an important factor in photoperiodism. It has been reported earlier that photoreversibility is destroyed by urea, acid, tryptic digestion or heating to 60°C.

Recently, the protein has been purified 60-fold from oat seedlings, with a purity of 30 per cent [Siegelman, H. W. & Firer, E. M., *Biochemistry*, **3** (1964), 418]. The molecular weight calculated from ultracentrifugation data has been found to range from 90,000 to 150,000.

Though the chromophore of phytochrome has not yet been hydrolysed from the protein it has been suggested earlier to be a bilidiene or bilitriene based primarily on the close resemblance of its absorption to that of allophycocyanin. A *cis-trans* or *lactam-lactim* isomerization of the chromophore would account for the existence of the two forms.

At the biochemical level, the active form of the pigment, P_{730}, has been suggested to be involved in the synthesis of the phloroglucinol ring of anthocyanins and in seed germination by helping fatty acid degradation.— C. K. RAMAKRISHNA KURUP

Role of inhibitors in elucidation of enzyme mechanisms

Carbonates, sulphonates and phosphates inhibit proteases and esterases. The mechanism of catalysis is represented as follows:

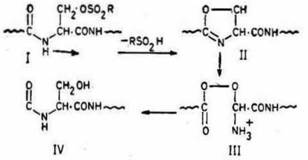
$$E + S \underset{K_2}{\overset{K_1}{\leftrightharpoons}} E.S \overset{K_3}{\rightarrow} E' + P_1 \overset{K_4}{\rightarrow} E + P_2$$

where E is the enzyme; S, substrate; $E.S$, enzyme substrate complex; E', acyl enzyme; P_1, alcoholic product; and P_2, acid product. The enzyme forms a reversible complex with the substrate forming the acyl enzyme and releases the alcoholic product. The acyl enzyme is later hydrolysed to enzyme and acid product. The inhibitor transfers its acyl group to the enzyme in a manner analogous to that of substrates, but the acyl enzyme now formed is either slowly hydrolysed or not at all.

A. M. Gold and D. Fahrney [*Biochemistry*, **3** (1964), 783] have obtained a phenylmethanesulphonyl-chymotrypsin (PMS-chymotrypsin) by reacting the enzyme with phenylmethanesulphonyl fluoride. The reaction has 1: 1 stoichiometry over a range of concentration and during the reaction a protein is released. The kinetic studies indicate the formation of a dissociable PMSF-enzyme complex, prior to the formation of PMS-enzyme as indicated below:

$$E{:} + RSO_2F \rightleftharpoons E{:} - RSO_2F \rightarrow$$
$$E^+ - SO_2R + F^-$$

The sulphonylation reaction has been shown to take place in the active site of the enzyme. The evidences obtained by the authors suggest that the hydroxyl group of serine at the active site is involved in the reaction. The sulphonyl enzyme is stable indefinitely in aqueous solution between *p*H 3 and 9. In the presence of 8*M* urea, protein loses the sulphonyl group between pH 2 and 8·5, but regains the catalytic activity only at pH 8·5. In the absence of urea at 40°C., the PMS-enzyme desulphonylates below pH 3·0 and above pH 9·0. The desulphonylated product obtained at pH 2, and at 40°C., does not show any enzymic activity. However, when the desulphonylated enzyme is allowed to stand at pH 7, it regains the esterase activity spontaneously. The following mechanism of desulphonylation is suggested:

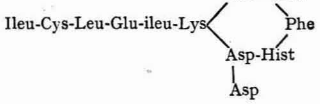


Desulphonylation of PMS-enzyme (I) leads first to the formation of an oxazoline complex (II), which is hydrolysed to the corresponding 'O'-acyl serine derivative (III) which is stable at low pH and does not show any esterase activity (product obtained on desulphonylation at pH 2·0 and at 40°C.). However, at neutral or alkaline pH, this compound undergoes a change (O-N acyl shift) to reform itself into original peptide structure (IV). The reactivated chymotrypsin has been shown to possess 60-70 per cent of its original activity.

The above results establish the formation of enzyme substrate complex and the mode of the inhibitory action of the inhibitors. In another report by H. P. Matzer and J. B. Wilson [*Biochemistry*, **3** (1964), 926] the results of studies on the action of methylphenylcarbonyl chloride, diphenylcarbonyl chloride and their fluoride analogues on choline esterases, chymotrypsin and trypsin are presented. It has been found that fluorides whose rate constants are 5-160 times greater than those of chlorides are more potent inhibitors. The reactivity of organic halogen compounds was I > Br > Cl > F. In acyl halogen derivatives also usually the fluorides were least reactive. The order of reactivity of halogen derivatives is reversed under two special circumstances, viz. (i) nucleophilic tetrahedral complex formations and (ii) electrophylic catalysis. The above phenomenon has been explained on the basis of hydrolysis of benzoyl fluoride and benzoyl chloride in acid, neutral and alkaline conditions. Benzoyl fluoride hydrolysis is efficiently acid catalysed. In neutral solution benzoyl chloride is hydrolysed 50-100 times faster than benzoyl fluoride, but in alkaline medium the reactivity is reversed and benzoyl fluoride is hydrolysed 40 per cent faster than benzoyl chloride. The authors attribute the increased reactivity of benzoyl fluoride in alkaline medium to the operation of nucleophilic tetrahedral complex formation (the nucleophilic unit such as OH^- group of the reagent attacks the carbonium ion and the electrophilic unit of the reagent attacks the negative halogen atom resulting in a tetrahedral complex), and in acid medium due to the operation of electrophilic catalysis (the electrophobic hydrogen ion forms a stronger hydrogen bond with the electronegative halogen atom). The reactivity of fluoride inhibitors is far greater than could be accounted for by the nucleophilic tetrahedral complex forma tion. Hence, it is concluded that the electrophilic mechanism offers a better explanation for the catalytic activity of hydrolytic enzymes.— P. A. KUMAR & T. S. ANANTHA SAMY

Biosynthesis of bacitracin

The polypeptide antibiotics provide excellent models for the study of protein biosynthesis. The presence of D-amino acids and occurrence of unusual peptide linkages add interest to the problem. The bacitracins are a group of polypeptide antibiotics produced by a strain of *Bacillus licheniformis*. Bacitracin A, the major peptide, is composed of 12 α-amino acids with 9 α-peptide linkages, a thiazolene ring, and two unusual peptide linkages, one incorporating the ε-amino group of lysine and the other the β-carboxy group of aspartic acid.



Protoplasts and protoplast membrane systems from a strain of *B. subtilis* were shown by T. Aida [*J. agric. chem. Soc. Japan*, **36** (1962), 724, 793, 797] to form bacitracin-like antibiotics. It was also found that ATP, hexose diphosphate, glutamic acid, aspartic acid and cysteine have a stimulating effect on antibiotic formation. J. E. Snoke [*J. Bact.*, **81** (1961), 986] showed that the formation of bacitracin by protoplasts of *B. licheniforma* was dependent upon six amino acids including cysteine and was stimulated by glucose. K. Shimura, T. Sasaki and K. Sugawara [*Biochem. biophys. Acta*, **86** (1964), 46] have now studied the biosynthesis of bacitracin in a cell-free system, from a strain of *B. licheniformis* (ATCC 10716). A sonic extract of the cells was fractionated into a heavy precipitate, a light precipitate and a supernatant fraction. The formation of the antibiotic occurred on incubation with the purified light precipitate fraction and was markedly decreased on omitting the amino acid mixture, and was not stimulated by ATP. The antibiotic production decreased greatly in the absence of cysteine. The single omission of the other amino acids in bacitracin did not greatly affect the antibiotic produced; isoleucine increased the antibiotic production only when added together with cysteine. The light precipitate fraction produced three antibiotic materials with R_f values lower than that of bacitracin, but on the addition of the supernatant fraction an antibiotic material having the same R_f as that of bacitracin was produced. The supernatant fraction probably catalyses the reaction to completion from precursor peptides. The antibiotic was found to incorporate S^{35}-cysteine and C^{14}-isoleucine actively but C^{14}-lysine, which is contained in the cyclic part of the bacitracin, gets incorporated very slowly. It is explained that the formation of the antibiotic proceeds together with a concomitant incorporation of cysteine and isoleucine but not of lysine. Probably the reaction in this system is mainly composed of the addition of cysteine and isoleucine through peptides bonding to a peptide precursor conferring on it antibiotic property. The isolation of the peptide precursors currently being attempted by these workers would establish the pathway of the biosynthesis of this antibiotic.— S. L. N. RAO

Progress Reports

US National Bureau of Standards

The varied activities and achievements during the year 1963 of the Bureau, which is the main agency responsible for developing and maintaining the national standards of physical measurement and making available to science, industry and commerce suitable calibration services, are recorded in its latest annual report. During the year, the Bureau's efforts were directed to facing the demands of a rapidly expanding technology, particularly in the fields of nuclear and space sciences and electronics. Consequently, considerable research effort was devoted to the extension of precise standards and measurement techniques to new areas of science and technology and to new accuracies. In the major area of physical measurement the activities covered the following broad divisions: (i) basic measurement standards, (ii) engineering measurement standards, (iii) standard reference data, and (iv) standard reference materials. An idea of the magnitude of the Bureau's programme can be had from the following statistics: Over 75,000 calibrations involving a total cost of over $ 2 million were performed for government and industry (New services during the year included calibration of microwave noise sources at 9-11·0 Gc/s. and power calibration of bolometer-coupler units). The Bureau distributed 72,074 samples of standard materials valued at $ 551,264. About 600 different standard materials were being made available; those added during the year included radioactive standards I^{125} and Ce^{139}, 2 polystyrene molecular weight standards, 5 portland cement standards, a standard soda-lime silica glass and various alloys for spectroscopic standardization. The number of publications during the year totalled 1122 papers and documents, besides about 420 classified and unclassified reports.

A number of data centres, which together formed the National Standard Reference Data System, established during the year, for compilation and storage of critically evaluated data, were operated in fields like chemical thermodynamics, atomic transition probabilities, atomic cross-sections, ceramic phase equilibria and cryogenics; useful bibliographies were compiled and literature searches were made.

The Bureau continued to conduct a broad programme of exploratory or background research in the physical sciences. Direct visual observations have been made of the phase transitions and other changes occurring in a variety of polymers subjected to ultrahigh pressures (10^6 lb./sq. in.). These observations assist in determining and defining the interatomic forces and perturbing effects of neighbouring atoms on one another. From a programme of studies on crystal growth mechanisms, it was found that at very low temperatures, large crystals of rare gases (in which the intermolecular forces are so weak that they crystallize at very low temperatures) may be prepared and studied with many of the techniques used at higher temperatures on other substances. Thus argon and krypton crystals were grown at temperatures near their triple points, viz. 84°K. and 116°K. The properties and growth characteristics of these crystals were found to be easily correlated with the theoretical predictions. Study of the properties of coordination polymers formed by combining the ligand *bis*-(8-hydroxy-5-quinolyl)-methane with divalent manganese, cobalt, nickel, copper and zinc, which are important in the fabrication of missile and rocket components, has led to a better understanding of the mechanism governing the polymer decomposition and may be of particular use in predicting the thermal behaviour of coordinated systems when only a minimum of experimental data are available.

Notable achievements in the field of basic measurement standards were: (i) the demonstration of the successful use of a helium-neon laser source for measuring interferometrically long distances (up to 200 m.) to a high accuracy; (ii) a 200 W. quartz-iodine lamp which operates without auxiliary optics and provides relatively high spectral irradiances which will provide a new standard for spectral irradiance to which space vehicles will be subjected; (iii) development of standards and measurement techniques in the high pressure range; (iv) a new differential transfer standard for measuring a.c. voltages at a.f. frequencies, permitting greater speed and high accuracy (1 in 10^5); and (v) a permanent adjustable standard of magnetic susceptibility incorporated into a bridge of high accuracy and sensitivity, and apparatus to determine absolute susceptibilities down to liquid helium temperatures.

In the field of standard reference data, studies on the absorption properties of neon and argon resulted in the discovery of new atomic energy levels in these gases. These findings were confirmed from observations on energy losses of electrons scattered by the gases and from theoretical studies of their ultraviolet absorption properties. A microwave spectrometer which can be operated at temperatures up to 1000°C. fabricated at the Bureau permitted the extension of powerful microwave techniques to the identification and structure determination of molecules and radicals that are present in high temperature systems. Spectra for such molecules as aluminium monofluoride and aluminium monochloride which are important constituents in rocket combustion systems have been detected and analysed. Using ultrahigh resolution techniques to determine the rotational fine structure of the infrared absorption spectrum of carbon suboxide (C_3O_2) in the 3 μ region, conclusive evidence that C_3O_2 is a straight-chain molecule consisting of 3 carbon atoms with an oxygen atom at each end, was obtained. This resolved a scientific controversy of thirty years' standing.

In the area of engineering measurement standards, the feasibility of employing computer programmes for speed and accuracy in micrographic analyses of alloys was demonstrated and their usefulness in areas like petrography, microbiology and astronomy also was suggested. A new 3-terminal dielectric cell was completed and used for the precise determination (with an error not greater than 200 in 10^6 in the 100 c/s. to 50 kc/s.

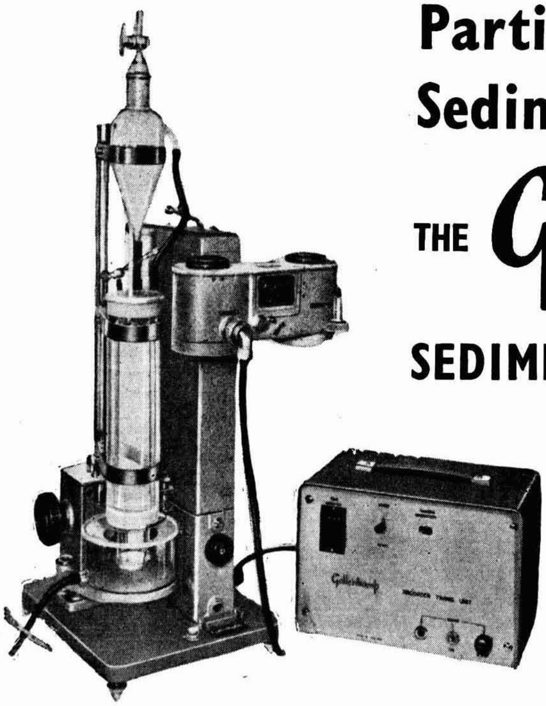
frequency range) of the dielectric constant by the two-fluid method. A scheme of colour tests for identifying antioxidants commonly used in styrene butadene synthetic rubbers was developed. The certainty of distinguishing between similar colours obtained with a single test was overcome in this procedure.

In the domain of developing new standard reference materials, a technique known as 'dielectric cryometry', which permits the use of relatively small samples (4-10 ml.), was devised for precise determination of purity. From studies of phase changes in silica metal oxide systems, a new method of producing glasses having a controllable degree of light scattering was developed. These glasses are being evaluated as turbidity standards to replace the less durable plastic and liquid standards now in use. A new scale of *p*H, designated as *p*H*, for methanol-water and ethanol-water media was shown to be practical and procedures were designed for assigning standard values of *p*H* to reference solutions. The *p*H* determined experimentally bears a simple relation to dissociation constants and other thermodynamic quantities in the same medium and hence should have wide applications in many branches of chemistry and biology.

Under the special central missions' programme, ground-based studies of the equatorial ionosphere were carried out at the Jicamarca (Peru) Observatory using the scatter radar technique with the purpose of obtaining the electron density distribution with height up to 6000 miles above the earth's surface. The information obtained from the measurements of the synchrotron radiation resulting from nuclear detonations above Johnston Island is expected to help improve our understanding of the physics of the upper atmosphere. The scope of the research activity in the field of data processing systems included new components for computer circuitry, studies of the properties of component materials used and development of techniques for extending automated procedures to the processing of scientific information. The building research programme covered subjects like the reactions taking place in concrete upon and after setting, fire control, heat transfer in structures, metallic building materials and properties of asphalts. Experimental results were obtained which support the colloidal theory of asphalt.

FORTHCOMING INTERNATIONAL SCIENTIFIC CONFERENCES, 1965

Date	*Conference*	*Place*
8-10 March	Second International Calibration Conference	Leipzig
8-11 March	Second International Industrial Lubrication Symposium	London
22-26 March	International Symposium on the Physics and Chemistry of Fusion	Salzburg
5-10 April	First International Nuclear Exhibition and Conference	Brighton
21-23 April	International Conference on Non-linear Magnetics	Washington D.C.
21 April to 2 May	Thirty-sixth International Congress of Industrial Chemistry	Paris
26-30 April	International Congress on Combustion Engines	Montreal
24 May to 1 June	International Conference on Cloud Physics	Tokyo and Sapporo
8-11 June	International Carbon-14 and Tritium Dating Conference	Washington D.C.
9-11 June	International Rubber Conference	Munich
11-20 June	Seventh International Aeronautical Congress	Paris
14-17 June	International Powder Metallurgy Conference	New York
21-23 June	International Meeting on Fuel Cells Research	Brussels
25-28 June	International Symposium on Modern Methods of Analytical Chemistry	Baton Rouge, La.
28 June to 1 July	International Colloquium on the Physical, Chemical and Nuclear Properties of Refractory Materials	Paris
28 June to 2 July	Third International Vacuum Congress	Stuttgart
2-9 July	Twenty-third Conference of the International Union of Pure & Applied Chemistry	Paris
12-16 July	Fourth International Mining Congress	London
August	International Mendel Memorial Symposium, including Discussion of the Mechanism of Mutations Brought about by Radiation	Brno
3-7 August	Fourth International Conference of the Physics of Electronic and Atomic Collisions	Quebec
16-21 August	International Congress on Electron Diffraction and the Nature of Defects in Crystals	Melbourne
22-27 August	International Symposium on Microchemical Techniques	University Park, Pa.
25-28 August	Fifth International Seaweed Symposium	Halifax
25 August to 1 September	Third International Symposium on Fluorine Chemistry	Munich
27 August to 4 September	Seventh International Conference on Ionization Phenomena in Gases	Belgrade
29 August to 1 September	Sixth International Conference on Medical Electronics and Biological Engineering	Tokyo
1-5 September	Thirteenth International Conference on Nuclear Magnetic Resonance and Relaxation in Solids	Louvain
1-9 September	Twenty-third International Congress of Physiological Sciences	Tokyo
7-12 September	Twenty-fourth International Congress on Pharmaceutical Sciences	Amsterdam
7-14 September	International Congress of Acoustics	Liége
8-10 September	International Congress of Medical Physics	Yorkshire
8-15 September	Sixth International Society of Soil Mechanics and Foundation Engineering	Montreal
13-18 September	Thirty-second International Foundry Congress	Warsaw
14 September to 1 October	Fourteenth International Congress of Technology	Turin
24-25 September	International Symposium on Surface Activity and the Microbial Cell	London
24-27 September	International Symposium on Oxy-Compounds of the Transition Elements in the Solid State	Bordeaux
September	Fifth International Aerosol Congress	Milan



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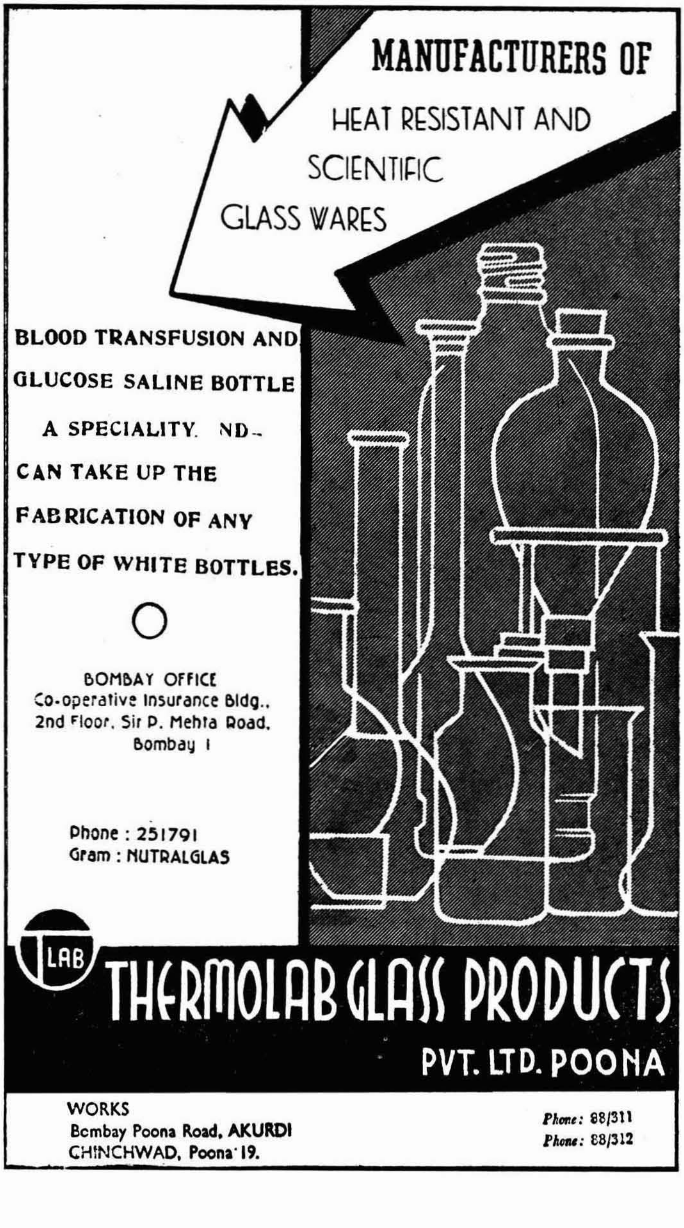

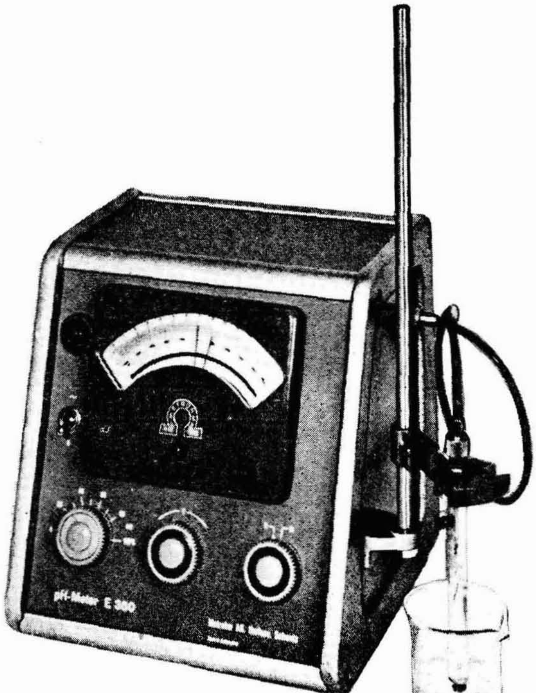
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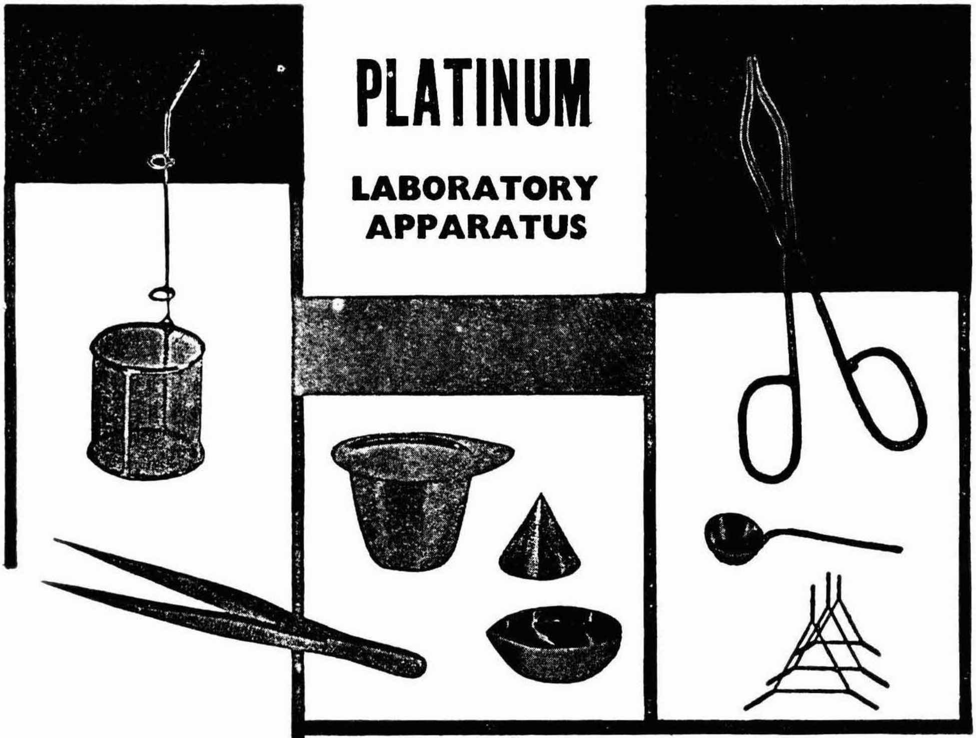

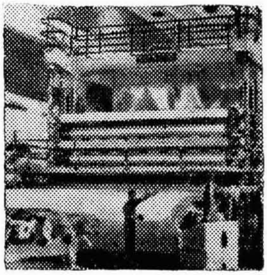

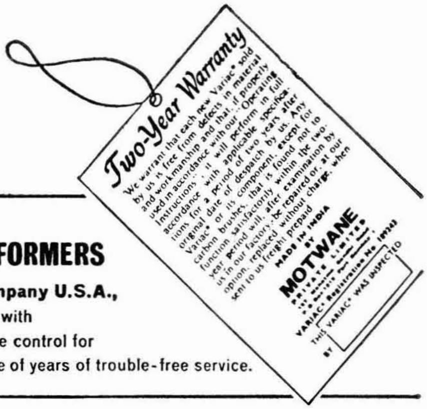

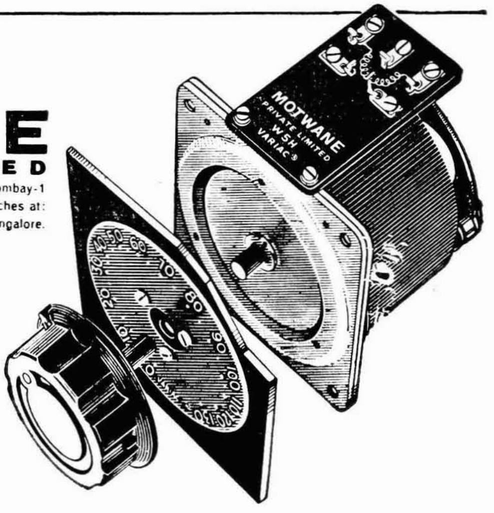
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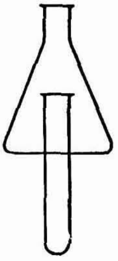

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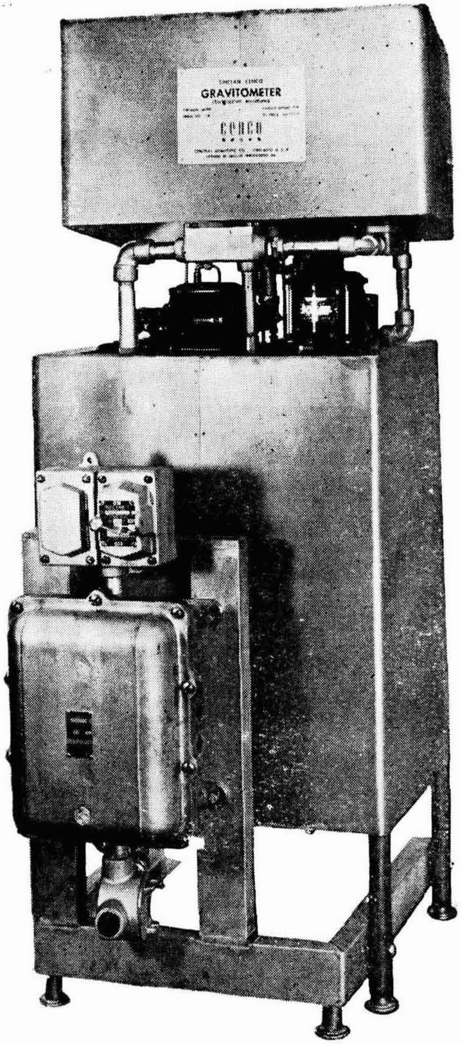

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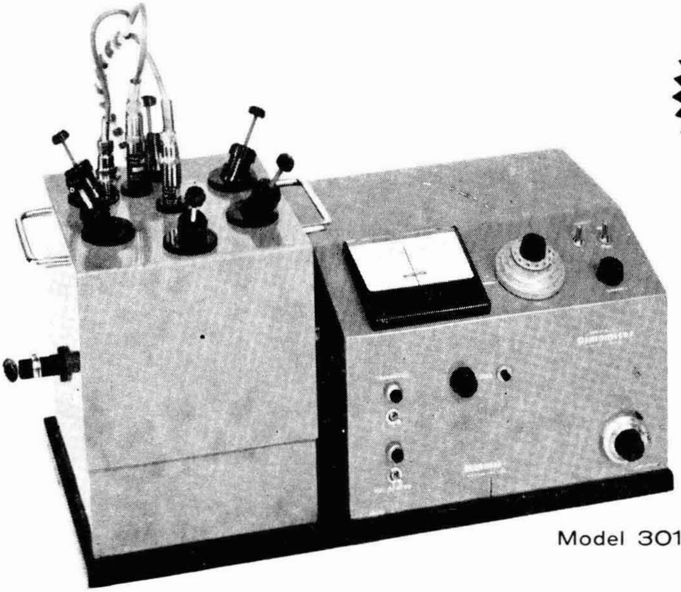

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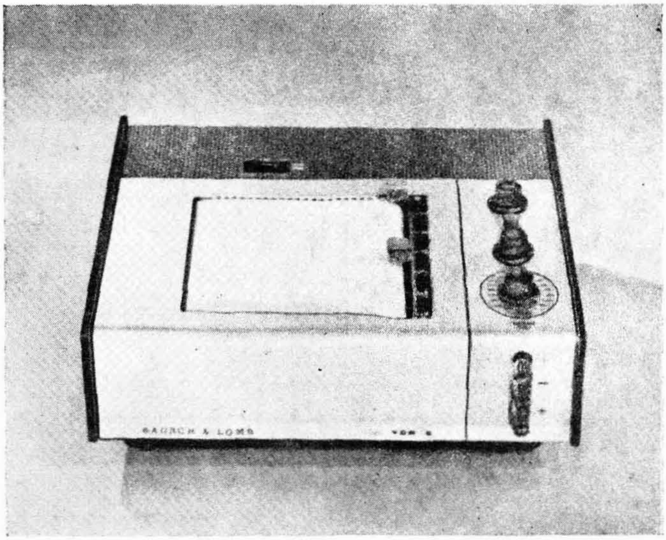

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