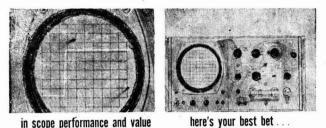
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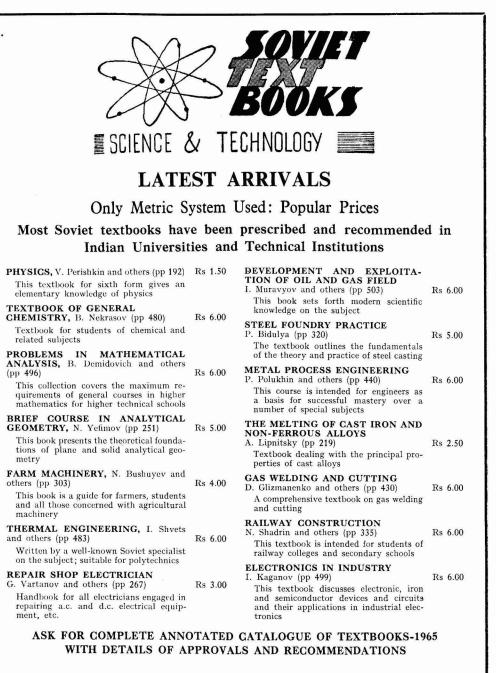
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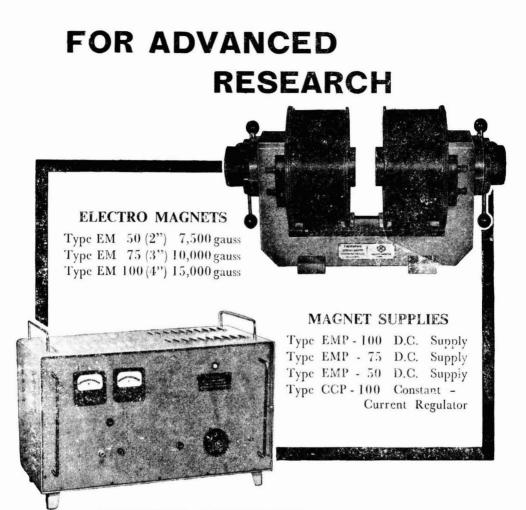
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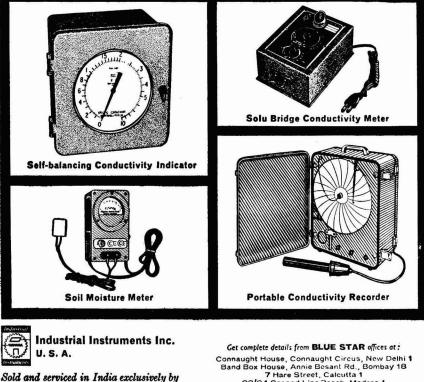
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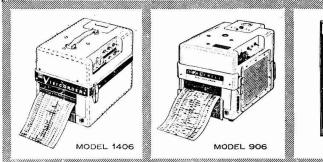


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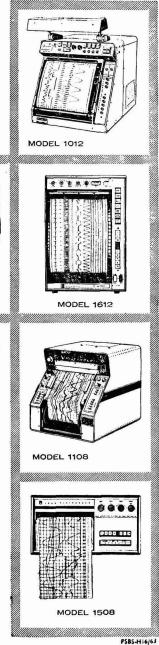
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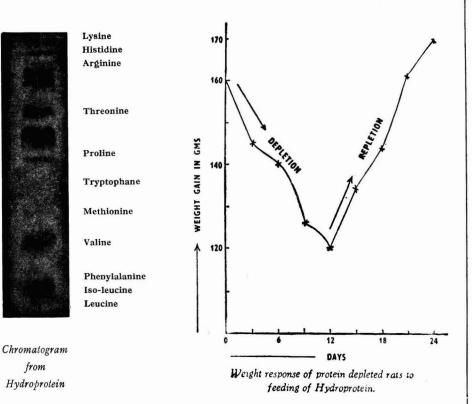
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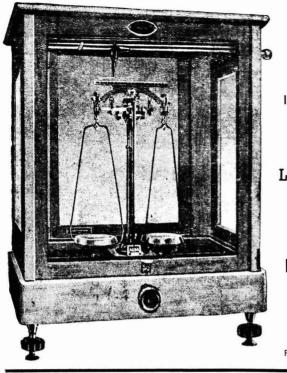
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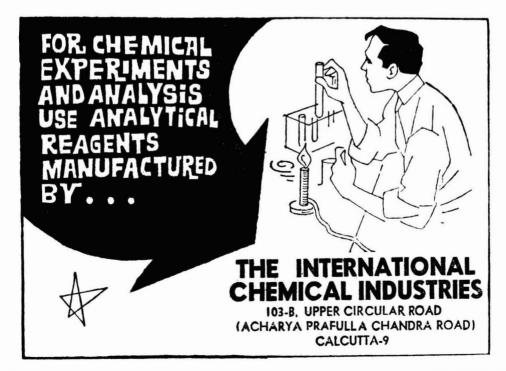
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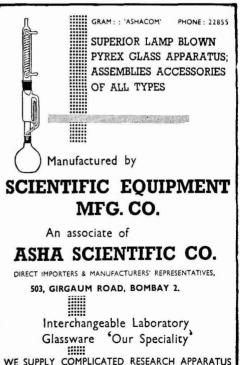
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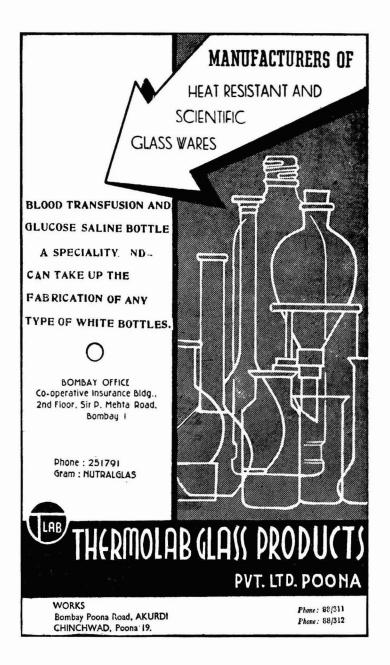
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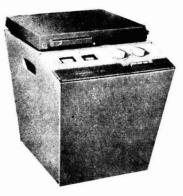
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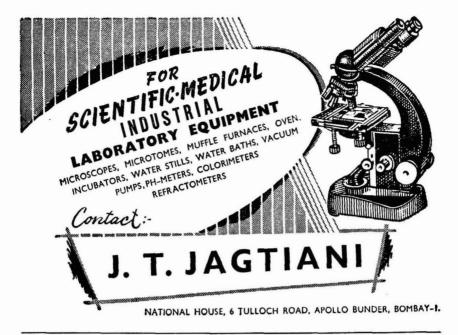


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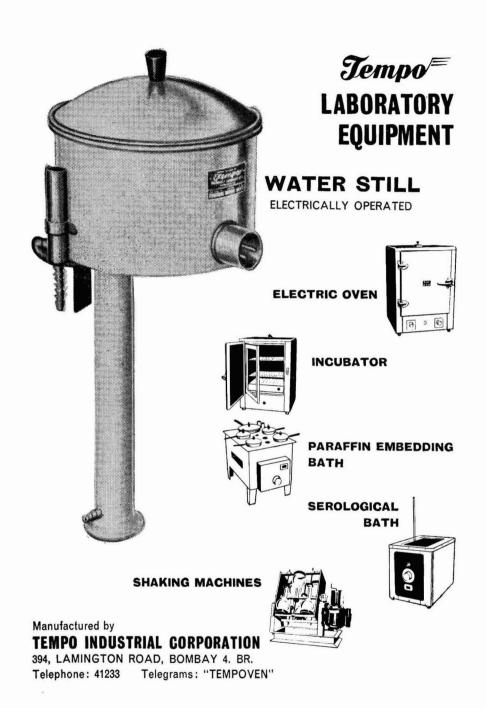
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Current Topics

Project Oriented Research Programmes in CSIR Laboratories

 $\mathbf{I}_{\mathrm{Governing}}^{\mathrm{N}}$ 1955, the Special Committee set up by the Governing Body of the Council of Scientific & Industrial Research (CSIR) under the chairmanship of late Dr J. C. Ghosh reviewing the scientific effort of CSIR laboratories made the following basic recommendation in regard to the research programmes of the laboratories. "We are of the opinion that at present scientific effort in the national laboratories is spread over too large an area. To produce concrete results it is essential that each laboratory (apart from a very small number of ad hoc problems or what can better be called opportunity problems) should take up only a few projects of basic importance and concentrate on them. The major research progamme of each laboratory should be formulated in terms of projects and not in terms of divisions." The Third Reviewing Committee of CSIR (1964) in its report has also observed "that the programmes of the CSIR laboratories should be mainly concerned with applied research and its related basic research. They should be framed in the context of the country's plans for industrial and economic development. The programmes should be made up of well-defined projects with clear objectives and the applied research projects should be time targeted and should not extend beyond a period of 3-5 years."

In pursuance of these recommendations the Governing Body of CSIR directed the CSIR laboratories to orient their research programmes with specific objectives and time targets. In accordance with this directive the CSIR laboratories have drawn up a list of projects keeping in view the present national emergency and the needs of defence requirements in particular. The acute foreign exchange position and the need to make the country self-sufficient in food have also been taken into consideration in formulating the research projects. The projects numbering 1536 have been grouped under the following heads: Defence oriented (96); Import substitution/elimination (158); Industrial technology (877); Food and agricultural products (180); and Basic objective (225). Pilot plants numbering 170 are listed and grouped under the first four heads, the break-up being 5, 68, 82 and 15 respectively.

A careful scrutiny of the projects listed under various heads indicates that while defence oriented projects should necessarily receive a high priority, there is need to work out priorities in the case of projects listed under other heads. Efforts must be concentrated on those projects which in general will help industrial effort, effect substantial saving in foreign exchange or earn foreign exchange and help in the development of products which will find immediate use as substitutes for imported products. For example, under import substitution/elimination, projects such as manufacture of carbon tetrachloride and chloroform from methane, manufacture of calcium hypophosphite, development of different types of refractories, hard and soft ferrites, substitutes for imported raw materials for special types of glass articles, development of light metal alloys, ferroalloys, nickel-free alloys, manganese bearing brasses, etc., appear to be more urgent than others. Similarly, in the case of projects under industrial technology, which form the biggest group, there is considerable scope for further selection of projects. Many projects appear to be long-range ones, and it may be worth while to concentrate on short-term (3-5 years) projects. The projects listed under the other two heads also can stand further screening, and even the basic objective research projects could be made more selective. The basic aim should be to select projects and assign priorities to them keeping in view the present national emergency, and the immediate needs and requirements of the country as will be laid down in the Fourth Five Year Plan programmes.

Information & Liaison Cell for Small Scale Industries

AN Information and Liaison Cell for Small Scale Industries has been set up by the Council of Scientific & Industrial Research (CSIR) as part of the Industrial Liaison and Extension Services Unit at its headquarters in New Delhi with a view to providing technical guidance and help to small-scale industries in the country in solving their problems and organizing follow-up of projects taken up by CSIR on their behalf. This step fulfils a great need and should promote better and closer liaison between CSIR laboratories and the small-scale industries.

The main objectives of the Cell are: (i) to compile information regarding research projects worked out by CSIR laboratories which are of interest to smallscale industries; (ii) to strengthen liaison and cooperation with small-scale industries and organizations representing them, and assist them in solving their technical problems for which facilities do not exist either with the industry or the Small Scale Industries Service Institutes which may act as a forum for channelizing such problems of the small-scale industries to CSIR for solution; and (iii) in cooperation with small-scale industries and the organizations representing them to undertake collection, compilation and dissemination of technical information which may interest small-scale industries. Specifically, the Cell will render the following services to small-scale industries: (i) it will receive enquiries from small-scale industrial units or organizations representing them, and organizations, private or government, dealing with small-scale industries; (ii) enquiries which are of a technical nature will be disposed off with the help of information available with the Cell or the party will be put in touch with the appropriate laboratory for obtaining necessary information, and the Cell will arrange for the follow-up; and (iii) enquiries which are not of a technical nature will be referred to appropriate organizations.

The setting up of the Information and Liaison Ccll for Small Scale Industries is a much needed measure and it should go a long way in making the small-scale industrial units in the country more research conscious, and to adopt modern and improved method not only to increase their production in qualitative and quantitative terms but also bring down the cost of production. Feeding of nascent information on recent developments would also enable the small-scale industrial units to expand their production in terms of variety, and to do this the Cell should provide such information, carefully selected and oriented to meet the needs of an industry, on a continuing basis.

It may be worth while to follow the example of the Office of the International Cooperation Administration in USA which handles a sizeable number of enquiries from small-scale industrial units to encourage them to make use of facilities and services offered by the Cell. All enquiries as far as possible must be dealt with and disposed off directly by the Cell itself, and not passed on to some other organization for necessary action. The help the Cell provides must be direct and positive. Above all, every effort should be made to dispose off the enquiries expeditiously and the party kept informed of the progress being made. This is essential to elicit the response of the industries in an increasing measure.

In handling the enquiries also, the procedure followed by the Office of the International Cooperation Administration may be adopted. A limit

may be set in respect of the cost incurred in dealing with an enquiry and providing a report which may involve information search and/or laboratory investigation. If the cost involved is below this limit, no change may be made. If the cost of providing a project report, involving laboratory work, exceeds the cost limit set, the party should be given an idea of the cost. This is necessary if the small-scale industrial units are to be encouraged and persuaded to take advantage of the services and facilities offered by the Cell and the CSIR laboratories. The CSIR could even consider establishing a 'research facility' for groups of related small-scale industries in appropriate laboratories where the technical personnel from the small-scale industrial units could go and work under the guidance and direction of experts and work out solutions for their problems free of charge. This is being done in a few of the laboratories but could be extended to other laboratories which are not specifically industry based. Testing facilities may also be arranged for on a nominal charge or free of charge. In short, the Information and Liaison Cell must act as a cooperative industrial research association in respect of smallscale industries with research facilities in appropriate CSIR laboratories. These additional facilities will not only make the small-scale industries more receptive to the idea of making use of the services offered but also help them to organize themselves better and in a more rational way than at present.

There are over 80,000 small-scale industrial units in the country and the services which the Information and Liaison Cell wants to render them calls for a tremendous effort in many directions. The task is indeed formidable in view of the variety of enquiries and problems that will come up for solution. It is essential that the Cell is efficiently and properly organized with suitable and adequate technical staff to cope with the demands that will be made on it.

Organization & Management of Industrial Research*

TN my talk today, I am dealing with some aspects of organization and management of industrial research. My emphasis is on industrial research and not on research in general. It is true that it is no longer possible to make a rigid distinction between pure or fundamental and applied or industrial research. All fundamental research in course of time finds application and industrial research itself throws up problems necessitating fundamental research. Thus essentially the difference between the two is in respect of the time lag — how soon the results attained find application in processes or products of industrial or agricultural development or human welfare.

Expenditure on Research

The role of scientific and industrial research as an instrument of industrial and economic development is universally recognized. To be effective the quantum of research must have a minimum threshold potential. Unless investment in research is at least of this minimum order, it will not be able to make an impact on the economy. In the case of India, we estimate that an investment of 1 per cent of the national income must be made industrial research coming next (24 per cent), and then defence (12 per cent). Expenditure on agricultural research including veterinary and animal husbandry was 14 per cent and geology and mineral surveys accounted for a bare 7 per cent of the total expenditure.

The distribution of expenditure in various sectors² is shown in Table 2.

It is obvious from Table 2 that mineral surveys and agricultural research would need greater resources and effort.

Planning of Industrial Research

I do not agree with those who say that research cannot and should not be planned. Planning is more or less equally necessary for both types of research, pure and applied. Whereas greater freedom of operation, greater free-play of ideas and investigations to satisfy intellectual curiosity are possible in the case of fundamental research, applied research must be directed to goals set for attainment of specified objectives without digressing too much to what may look as promising offshoots. Applied research is also required to provide answers and offer solutions within specified time limits

TABLE 1- PER CAPITA RESEARCH EXPENDITURE AND PER CAPITA NATIONAL INCOME IN VARIOUS COUNTRIES

Country	Year	Expenditure on scientific research million rupees	Population millions	Per capita research expenditure Rs	Per capita national income Rs	Research expenditure per cent of national income
USA	1961-62	71580	174	410	14190	2.9
UK	1961-62	8467	52	162	6010	2.7
Sweden	1961-62	1088	7.4	146	8649	1.7
China	1960	2000	669	3.00		
Australia	1958-59	400	9.9	40	5780	0.70
Norway	1958	124	3.5	35	4540	0.70
Yugoslavia	1958	76	18	4.20	1810	0.22
USSR	1958-59	20700	209	99	3303	3.00
India	1961-62	469	440	1.07	334	0.32

on civilian research. In 1960, China spent almost four times on scientific research as compared to India and may be spending much more at present. Comparative position of the expenditure on scientific research in various countries in terms of per capita research expenditure and per capita national income¹ is given in Table 1.

Distribution of National Research Effort

It is worth while examining how the national investment in India on research is distributed. In 1962-63, out of Rs 42 crores spent on research, the largest percentage of investment (about 26 per cent) was on atomic energy, scientific and

 TABLE 2 -- PERCENTAGE DISTRIBUTION OF CENTRAL

 GOVERNMENT EXPENDITURE ON DIFFERENT SECTORS OF

 SCIENTIFIC RESEARCH DURING 1962-63

Sectors	Million rupees	Percentage
Agricultural research	46.90	11.06
Veterinary and animal husbandry research	12.63	2.98
Medical and public health research	24.37	5.75
Scientific and industrial research	101.82	24.02
Geological survey and mines	29.06	6.85
Atomic energy	109.79	25.90
Irrigation and power	15.36	3.63
Economics and statistics	20.52	4.84
Archaeological exploration, archi-		
ves and anthropological surveys	3.37	0.79
Railways	7.73	1.82
Defence	52.40	12.36

^{*}Talk delivered by Dr S. Husain Zaheer, Director General, Scientific & Industrial Research, New Delhi, at Srinagar on 15 July 1965 at a meeting of the All India Management Association.

to meet user demands and to avoid being outdone by rival competition. The examples of war-time developments such as nuclear power, missiles, etc., show that more rapid achievements can result from definite objectives than years of scientific research without definite goals, though the results could be applied years after. This is particularly significant in revolutionizing a nation's industrial economy.

Industrial Research and the User

Industrial or applied research by its very nature has to have a close relation with its user. In UK, USA, Germany, etc., a large number of industries do their own research. In Britain nearly 60 per cent of the total expenditure on research is met by the industries themselves. In India and the less developed countries, in general, where industry is vet to come into its own and develop research consciousness, the responsibility for research effort and expenditure primarily lies with the State. In the seminar organized in Beirut in 1964 by the United Nations Centre for Industrial Development dealing with industrial research institutes in the developing countries, it was universally recognized that unless the governments in these countries bear the major share for financing industrial research, both research and development would suffer.

It is a peculiar paradox that creative research of high quality can only be carried out when it is not encumbered or pressurized by the day-to-day demands from the user. Hence most of the industrial enterprises which undertake research make deliberate efforts to insulate their research institutions from the day-to-day demands of their production departments. On the other hand, industrial research must be in close contact with the user in order to have impact on itself of the industry's needs and requirements and to help speedy utilization. The government-sponsored research institutes and laboratories have the requisite conditions for creative research but lack close contact with the user industries in the public or private sectors. That is where need arises for closer liaison and collaboration in various forms with the departments responsible for industrial development and planning and with the industrial sectors themselves.

Industrial Research and National Planning

India has accepted planning as a technique for balanced industrial and economic development. Unfortunately, research up till now has had no living contact with the processes of industrial development or planning. The departments responsible for research and industrial development and planning have functioned more or less independently without any relation to each other's existence. Till recently the Directorate General of Technical Development and the Ministry of Industry had very little contact with the Council of Scientific & Industrial Research (CSIR) or its laboratories. The research programmes of laboratories hardly bore any impact of the plans for industrial development or the needs or requirements of the industries. The programmes in the laboratories were based upon what the scientists or the directors

considered to be useful and not on any reliable data from the planning departments or the industry.

The Third Reviewing Committee of the CSIR under the Chairmanship of Dr A. Ramaswami Mudaliar, while referring to this major lacuna in the organization of industrial research in this country, drew attention to the lack of contact with the departments of planning and those responsible for industrial developments as follows:

"Fortunately India has a highly developed organization, the Planning Commission and a number of government departments to put its Plans into action. The field of work covered by the Council of Scientific and Industrial Research would benefit in many ways by a closer liaison with the Directorate General of Technical Development and the Ministry of Industry. There are many directions in which CSIR can closely cooperate with other organizations, but the links with the departments and ministries responsible for planning and setting out, and execution of policies for industrial development are of paramount importance. The extent of effort required, purposeful direction of industrial research as an aid to industrial development and the long-range planning of research in national perspective would need the close association of CSIR with these departments in the framing of its programmes."

Industrial Research Organizations

Council of Scientific & Industrial Research and the National Laboratories

In India, the major effort (about 90 per cent) for industrial research is by the State-sponsored institutes which derive almost their entire finances from the Central Government sources. The States have invested to some extent in agricultural research and animal husbandry but have not interested themselves in technological and industrial research. Private industry has also not taken up industrial research as a means of its advancement and growth, and has depended far too much on research carried out in the laboratories of their foreign collaborators. Indirectly the indigenous industry finances, and quite heavily, research effort of foreign interests and becomes increasingly more dependent on them. There are some notable exceptions like the Shri Ram Institute for Industrial Research, Tata Research Enterprises, Atul Drugs, Amar Dye-Chem. and Kelkar & Co. Subsidies of some foreign companies also take up some developmental research, such as the Hindustan Lever, Associated Cement Companies, Metal Box of India, CIBA, Imperial Chemical Industries and Firestone Rubber Co., but the effort is far too little to be significant.

The State effort has been in the shape of major national laboratories, some thirty in number, in important fields, such as drugs and chemicals, leather, metallurgy, engineering, fuels, petroleum, glass and ceramics, roads, buildings, instrumentation and electronics, oceanography and biology, and public health engineering. All the laboratories are well equipped and staffed with highly qualified scientists and technical personnel and have extensive laboratory, pilot plant, instrumentation and

ORGANIZATION & MANAGEMENT OF INDUSTRIAL RESEARCH

Year Research Mu institutes		Museums	Scientific and	Budget	Staff strength	
		technical organs	rupees	Scientists and technologists	Total employees	
1954-55	14		4	21.6757	550	2993
1955-56	15		4	27.4868	570	3038
1956-57	17	-	4	30.9060	702	4680
1957-58	18		4	36.5836	846	5475
1958-59	19	_	4	47.2507	1080	6422
1959-60	22	1	4	59.1780	1354	7309
1960-61	24	1	4	68.7759	1557	8305
1961-62	26	1	4	81.2830	1793	9478
1962-63	27	2	5	95.8275	2134	10865
1963-64	27	2	8	117.5000	2435	11319

TABLE 3 - GROWTH OF CSIR ACTIVITIES: LABORATORIES AND INSTITUTES

TABLE 4 -- GROWTH OF CSIR ACTIVITIES: SCIENTISTS' POOL, FELLOWSHIPS AND SCHEMES.

Year	Research fellowships*			Resea	arch schemes*	Scientists' pool [†]		
	Senior	Junior	Total	No.	Expenditure million rupees	No.	Expenditure million rupees	
1955-56				139	0.384698		_	
1956-57				228	1.302449			
1957-58		2	2	380	1.543601		(
1958-59	19	43	62	332	2.109396			
1959-60	46	132	178	383	2.868230	197		
1960-61	84	209	393	419	3.173011	360	0.0192	
1961-62	114	376	490	398	2.688732	887	0.2724	
1962-63	101	364	465	460	2.546138	1280	0.9648	
1963-64	353	1212	1565	518	2.570771	2119	1.7960	
1964-65	368	1087	1455	562	4.780230	2795	2.7647	

library facilities. Even though full use has not yet been made by the industry in the public or private sector, these national institutes have already contributed in a significant manner to the industrial development and growth of the Indian economy. The growth of the activities of CSIR is shown in Tables 3 and 4.

Cooperative Research Associations

Another useful method of bringing research and industry closer is the organization of cooperative research associations wherein the user industry is provided financial and organizational assistance to set up research institutes. Although a significant portion (up to 50 per cent) of the funds are provided by the State, the control of the research association vests in a council consisting of the representatives of industry. The principle of cooperative research which was enunciated in UK in 1950 is now universally accepted as a form of organization which has drawn the industry into research with great benefit to the industry and the national economy. Even industries which have research organizations of their own join the cooperative research association since it helps them with their general problems. Sectors of industry which cannot afford to organize research at their own benefit the most. Thus although a large number of the British iron and steel firms have their

own research departments, the British Iron & Steel Cooperative Research Association is one of the most powerful research organizations of which most of the British steel firms are members. Cooperative research associations exist in France, Norway, Sweden, Germany, Belgium and a number of other countries. Of late, cooperative research associations have also started accepting problems of particular interest to individual industries and giving back the results on preferential terms to the sponsoring industry. In India, some industries have been assisted by CSIR in setting up research organizations of their own. Textile industry has three institutes, the tea, the plywood, paints, rubber, silk and art silk have one each. The control and management of the institutes rest with the industry. Efforts are afoot by CSIR to set up research institutions for automobile, paper and pulp, radio and electronics, instruments, cables, and textile machinery industries. The progress of cooperative research associations is shown in Table 5.

Data for Research Planning

There are two types of information which are essential for research planning. The first is the information about the industrial plans and future requirements. For this, data about the industries set up or proposed to be set up, licensed capacity,

Cooperative research association	Year of establishment	Industry served	CSIR financial support million rupees				
			1961-62	1962-63	1963-64		
Ahmedabad Textile Industry's Research Association, Ahmedabad	1947	Cotton textile	0.6740	0.5217	0.6340		
South India Textile Research Association, Coimbatore	1956	do	0.2480	0.5140	0.2675		
Silk and Art Silk Mills Research Association, Bombay	1957	Art silk	0.2196	0.2178	0.2400		
Indian Rubber Mfrs Research Association, Calcutta	1959	Rubber	0.0032	0.0120	0.0071		
Bombay Textile Research Association, Bombay	1960	Cotton textile	0.4176	0.4440	0.4208		
Indian Plywood Industries Research Association, Bangalore	1960	Plywood		0.0200	0.1530		
Indian Paint Research Association, Calcutta	1962	Paint	-		_		
Tea Research Institute, Toklai (Assam)	1963	Tea			0.2000		
		Total	1.5624	1.7295	1.9224		

TABLE 5 - CSIR SUPPORT TO COOPERATIVE RESEARCH ASSOCIATIONS

the level of technology and economics, the processes and know-how employed by them is essential. Data on extent, nature and source of imports and exports, the countries of import and to whom exports are directed, the requirements of standardization and quality of goods would be required. These data are not readily available. It is only recently that statistics about the production in different industries are being properly maintained. Even now information on the raw materials, the processes used, efficiency of production, equipment, the standards and quality of the product, the economics of production in the various industries is not easily available. The system of classification of imports and exports which groups together a large variety of items under a single clause makes it of no value for the purposes of research programming. If the research programmes in the research institutes have to be related to the industrial needs of the country, the detailed data would be needed to form the basis of research programming.

I may mention another aspect which is of great concern to the industrial research organizations in this country. Most of the industries in the country have been set up in financial and technical collaboration with entrepreneurs overseas. The collaboration agreements have served to exclude the Indian research institutions or scientific personnel from any contacts with processes or products manufactured by them. The Indian industrialist thus pays and pays heavily for research carried out elsewhere. By this I do not mean that the country should not permit the inflow of advanced technology or know-how from abroad. The Indian industry has yet to generate a sense of pride in itself and to appreciate the urgency for generating self-dependence in the field of technology. This is a matter of national policy which has a direct impact on the organization of industrial research. The level of interflow between the countries must be brought to a level which restores a proper balance in the field of technology.

The other type of data required is internal data on industrial research. The Survey and Planning of Scientific Research Unit of CSIR has been engaged on studies on the expenditure on research and investment of resources in different sectors of the Indian economy. Their studies have shown that a larger part of resources are being invested in the fields of atomic energy and the scientific and industrial research, while sectors on surveys, agricultural research, animal husbandry and health are being poorly financed. This imbalance must be corrected. They have also studied the growth rate for proper and healthy development in scientific research. The country's investment in scientific research is far too meagre to enable it to make an impact on and effective contribution to the country's development. The projected investment during the Fourth Five Year $\rm Plan^1$ is shown in Table 6. We have found that the growth rate of 20-25 per cent is essential for the healthy growth and development of scientific research in the national laboratories. We have also studied that after out-growing their optimum, the laboratories must give rise to sister institutions for reasons of efficiency. We have calculated expenditure per scientist in the laboratorics, investment in pilot plants, libraries, apparatus and equipment, etc. Till recently no data were available about the expenditure, availability of technical manpower and their relationship with the country's plans for scientific and industrial development. We give the highest importance to these data for a rational organization of scientific research in the country.

Autonomy of Research Organizations

Although industrial research is also carried out by the institutes of technology and the departments of technology in the universities, but by way of investment and volume of research undertaken, CSIR is the major organization in the field of industrial research. The orientation of research

Sector of research	Projection of expenditure in the year					Total expen-	Percentage
	1966-67	1967-68	1968-69	1969-70	1970-71	diture during 1966-67 to 1970-71	of total
Central Government (other than rail- ways, defence and universities)							
Recurring	566.2	655.1	759.8	880.0	1023.5	3884.6	43.7
Capital	277.2	316.5	369.4	377.2	400.0	1690.3	19.0
Defence							
Recurring	69.0	79.4	91.3	104.9	120.7	465.3	5.2
Capital	50.0	55.0	60.0	70.0	80.0	315.0	3.5
Railways	14.0	16.2	18.8	21.8	25.3	96.1	1.1
State Governments (besides univer- sities)	94.6	115.1	141.2	174.0	215-9	740.8	8.3
Universities (from Central and State Governments)	46.0	58.3	73.8	93.1	116.8	388.0	4.4
Organized industries (for research associations)	193.4	223.1	258.0	299.5	343.1	1317.1	14.8
Total	1260.4	1518.7	1772.3	2020-5	2325.3	8897.2	100.0

TABLE 6 — PROJECTION OF TOTAL INVESTMENT FOR SCIENTIFIC AND TECHNOLOGICAL RESEARCH AND DEVELOPMENT DURING THE FOURTH FIVE YEAR PLAN (Figures are in million funces)

work will be further directed in keeping with the recommendation of the Third Reviewing Committee of CSIR so that 80 per cent of the research effort of the national laboratories should be applied or industrial research.

CSIR is an autonomous body and this autonomy gives it a great flexibility and capacity for functioning unencumbered by the rules and procedures of the government departments. Its flexibility enables it to initiate activity for industrial research in any field that it may feel necessary. The Research Committees under the Board of Scientific & Industrial Research make proposals on the setting up of newer research institutions and the recent proposals include the setting up of an Institute of Occanography, an Institute for the Paper Industry, a National Institute for Electrical Engineering and Packaging Research.

Technical Orientation of CSIR Headquarters

The Council of Scientific & Industrial Research has recently initiated measures for a technical orientation of its work at the Headquarters. The Headquarters at New Delhi is expected to coordinate and administer the work of highly specialized industrial research institutions in keeping with the overall policies of the organization. This can only be achieved with a corps of technical personnel and technical sections at the Headquarters who should be responsible for coordination or gathering of technical information and data. The purely administrative set-up up till now functioned in accordance with the rules and procedures of a normal government department and was hardly capable of understanding or appreciating the needs of research institutions. This created serious diffi-culties in functioning. The following technical units have been set up: (i) Research Coordination, Industrial Liaison and Extension Services Unit; (ii) Survey and Planning of Scientific Research Unit; (iii) National Register for Scientific and Technical Personnel; (iv) Defence Coordination

Unit; and (v) Central Design and Engineering Unit.

Up-to-date data about the work, personnel, scientific and research requirements, and other information regarding the various institutions under CSIR is now maintained at the Headquarters. Efforts are made to assist the laboratories in their relations with the industrial and planning departments of the government. Giving a technical orientation to administration and coordinating function is a major step in research management. The Headquarters, through technical groups, also endeavours to pinpoint and delineate areas of importance needing research. Information on these is passed on to the laboratories.

Autonomy of Laboratories

The autonomy of CSIR organization is passed on to the laboratories who are autonomous in functioning within their budgets. The Executive Councils and the directors of the laboratories have almost complete powers to frame research programmes, staff requirements and budget allotments to the extent of their budget provision.

Project Orientation of Research Programmes

Effort is made that research in these organizations does not rest on vague and general schemes. With the help of the Headquarters and the scientists and industrialists on the scientific advisory committees and Executive Councils of the laboratories, such areas of research are chosen as are of importance. These areas are studied for identification of the problems which are in turn formulated into research projects. Each research project has a clearly defined objective, indicates the resources required by way of scientific and technical personnel, equipment, foreign exchange and has a tentative time target for the completion of the work. Each project has a team leader who coordinates the interdisciplinary approach required for the execution of the project. The Executive Councils

and the Research Committees make a periodic review of these projects and keep a watch on their progress. It is expected that no project may last for more than 3-5 years. Effort is made to get the user industry or the user government department to take interest in the progress of the research project. Most of the research passes through different phases of laboratory and bench scale investigations, pilot plant, prototype plant and, at times, semi-commercial and commercial production. Demonstrations of pilot plants or semicommercial plants are made to convince the industry about the technical and economic feasibility of the process. Projects are chosen keeping in view the resources available, the promise of gainful results and the importance of the subject. A list of priorities helps to allot the resources and drop projects which may not show progress.

Research as an Industry

A number of laboratories are large establishments — some of them employing more than 1000 persons. At least 14 of the national laboratories employ more than 500 persons and have budgets exceeding Rs 10 lakhs recurring. The total investment in the CSIR up till now exceeds Rs 200 crores. Although the Indian effort in industrial research is insignificant as compared to the more advanced countries and the total annual expenditure on industrial research (about Rs 10 crores) does not even compare with that spent by a firm like CIBA, still it is a significant investment when compared to the general economic level of the country.

Considering the size of the laboratories, the scientific and technical personnel required, one would say that management of these laboratories is in no way less specialized than the management of an industry. In certain ways it is more difficult since it involves dealing with scientists who can be a very touchy and sensitive lot. It is the task of the director of research that while he carefully plans, distributes and husbands the resources of the institution with a view to concentrating them on the projects of maximum promise, still he sees that the creative scientist does not feel frustrated and the projects which are of emotional attach-ment to him are given sufficient encouragement. The director is also faced with innumerable problems of scientific and technical personnel, running of the pilot plants, supply of raw materials, housing, import of equipment and chemicals and books from abroad, drawing up of the budgets and sanctioning expenditure. He is thus running an establishment in which his managerial and administrative capabilities would be taxed to the maximum. He needs tact and firmness where required. Research management is as much a science as it is an art. In advanced countries, scientists with technical background who show administrative ability are drawn into research management which has become a specialized field with its own techniques, methodology and journals, reference books and literature.

Industrial Research and Economics

Economic criteria and evaluation are applicable to industrial research which has come to be recognized as an investment in the industrial development and is thought of in terms of the returns it is capable of making. The factors which judge the success of an industry are to some extent applicable to judging the results of an industrial research establishment. Judging by these stan-dards, industrial research in India has yet to make its mark. The only plea that can be entered is that it is only now that industrial research in India has come to maturity. A recent study carried out by the Survey and Planning Unit, CSIR, showed that a saving of Rs 22 crores in respect of foreign exchange has been made by way of developing substitutes for imported products and increasing production and developing processes for those items which would otherwise have to be imported. This is not a very impressive figure but there are numerous intangibles by way of contributions which cannot be accounted for. The setting up of washeries by the Central Fuel Research Institute, the optical glass unit at the Central Glass & Ceramic Research Institute, the carbon blocks and brushes and carbon based products of National Physical Laboratory, the activated carbon plant at the Hyderabad Laboratory and development of knowhow for television receivers and signal generators by the Central Electronics Engineering Research Institute are significant examples of contribution whose effect can be indirectly computed.

In the developing countries it is essential that the field of industrial research is not confined to laboratory and bench scale investigations only but is stepped up to pilot plant, prototype and even commercial scale units. The setting up of these units not only involves laboratory and technological studies but also economic studies, design and engineering, and even collection of sociological data and market surveys, etc. All these would come in the ambit of industrial research. It is the task of research management to organize research from laboratory stage to their successful exploitation. Research management as a specialized skill is yet to be developed in India. An effort in that direction has been made by us by organizing the biannual conference of the Directors of National Laboratories where experience of administration and organization of scientific and industrial research is exchanged and problems facing the laboratories discussed and solutions evolved. In due course research management is bound to take the shape of a specialized activity in this country also.

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International Symposium on the Impact of Mendelism on Agriculture, Biology & Medicine

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• ENETICS is one of the youngest sciences and **T** has gained importance in biology, medicine and allied applied sciences. Several hybrid disciplines like biophysics, molecular biology, etc., have emerged in recent years to probe into the architecture of genetic material. At the last international congress of biochemistry held in the United States in 1964, the chemistry of genetic material dominated the sessions. In India, the science of genetics has received little encouragement inasmuch that there is not even a single university which has a chair for genetics. It was, therefore, most appropriate to focus the attention of the scientists and the government to this lacuna in Indian science and the Third International Sympo-sium on the Impact of Mendelism on Agriculture, Biology and Medicine, organized by the Indian Society of Genetics and Plant Breeding, did this to a great extent. This symposium was organized by the society to commemorate the successful completion of 25 years of its existence and the centenary year of the publication of Mendel's work, which was first read in February 1865 at Brüno. About 400 geneticists, and plant and animal breeders from India and other countries attended this symposium, which was held from 15 to 20 February 1965. The symposium was financially supported by the Indian Council of Agricultural Research, Council of Scientific & Industrial Research, Department of Atomic Energy, the University Grants Commission, the Rockefeller Foundation and the International Union of Biological Sciences. Five days were devoted to scientific sessions and one day was devoted to an excursion to the experimental fields of the Division of Botany, IARI, and histori-cal places in and around Delhi. Forty-five papers were read in 11 sessions. There were four evening lectures: (1) Mutations and Problems of Viability by Prof. Gustafsson, Forest Research Institute, Stockholm, Sweden; (2) Malthus and Mendel by Dr M. S. Swaminathan, Indian Agricultural Research Institute (IARI), New Delhi; (3) The Genetic Code by Dr O. Siddiqi, Tata Institute of Fundamental Research, Bombay; and (4) The Organization and Integration of Agricultural Research by Dr R. F. Chandler, International Rice Research Institute (IRRI), Manila, Philippines. The symposium concluded with a variety programme, the highlight of which was a scientific ballet on the 'Secrets of Life' which was an interesting piece of experiment in depicting the structure of DNA and its function through the medium of a ballet.

Mendelism and Evolution

The first scientific session was devoted to Mendelism and Evolution and opened with the paper of A. Muntzing (Institute of Genetics, Lund, Sweden)

titled 'On the origin and evolution of cultivated plants'. Prof. Muntzing discussed the role of genetic recombination, selection, mutation and polyploidy in the evolution of cultivated forms in nature and pointed out the usefulness of induced mutations as a new and important plant breeding method. Prof. Muntzing struck a note of warning in view of the threatening over-population of the world and emphasized that the occurrence of a rational basic research is an absolutely necessary condition for rapid and far-reaching improvements of our cultivated plants. Prof. H. Kihara (National Institute of Genetics, Misima, Japan) spoke on the ' Factors affecting the evolution of common wheat ' and pinpointed three factors which have steered common wheat (Triticum aestivum) in its evolutionary course: (1) Cross incompatibility and hybrid sterility in interspecific hybridization, (2) Alien cytoplasm, and (3) Gene interaction. Prof. Kihara also referred to the extensive gene analysis which has been carried out due to the advantage of having many different strains of emmer wheat (AABB) and Aegilops squarrosa (DD) on one hand and many synthesized wheats on the other. The con-cluding paper of the session 'Mendelism and evolution' was presented by Dr M. S. Swaminathan (IARI, New Delhi) who, in his talk 'The origin of macro- from micromutations and factors governing the direction of micromutational changes', proposed a new system of classification for different types of mutations, viz. micromutations, visible mutations, macromutations and systemic mutations. Taking the Q locus in bread wheat as an example, Dr Swaminathan described how a series of micromutational events can get transformed into a macroor systemic mutation, and discussed the significance of such mutations in studies of plant geography and origin.

Genetics and Plant Breeding

Seventeen papers were presented under Genetics and Plant Breeding and 3 full sessions were devoted to it. Dr F. J. Wellhausen (Rockefeller Foundation, Mexico) opened the first session with a talk on the 'Origin and breeding of maize', and presented data to postulate that domestication of maize in the Tehuacan Valley of Mexico began as early as 3000 B.C. and that many primitive varieties including Teosinte have played a part in the genetic constitution of high yielding modern races of maize in Mexico. About breeding of maize he presented data on inter- and intra-racial crosses which suggest that the degree of heterosis in intervariety crosses depends on diversity of varieties crossed and that new races much higher in yield potential can be formed by blending certain germ plasm complexes. Dr Wellhausen emphasized the need of re-evaluating the simple mass selection technique of maize improvement and said that the possibilities of further improvement of maize through an exploitation of the germ plasm reserves available seem exceedingly great.

Dr N. L. Dhawan (IARI) discussed the role of cytoplasm in the manifestation of heterosis and other quantitative traits in maize. He postulated that in the evolutionary differentiation of the races of maize, there has been a process of divergence in the nuclear genes as well as the plasmagenes and the inhibitory cytoplasm has perhaps also played a role as an isolating mechanism. Dr K. O. Rachie (Rockefeller Foundation, IARI, New Delhi) drew the attention of the audience to the vast unexplored features of millets and the potentialities of Sorghum, Pennisetum and minor millets in solving the food problem of the countries of the world where the population and food needs are expanding rapidly. Dr D. S. Athwal (Punjab Agricultural University, Ludhiana) presented data to show how the breeding work in Pennisetum typhoides can be expedited by taking the help of male sterile lines and by growing two to three crops a year. Dr L. R. House and Shri N. Ganga Prasada Rao (IARI, New Delhi) also advocated the use of F1 hybrids and male sterile lines for increasing the yields of Sorghum. Dr A. B. Joshi (IARI, New Delhi) referred to the slow progress that has been achieved by the breeding methodology in self-fertilizing crops and advocated more dynamic breeding programmes, based on information on genetics of yield and its component characters. Dr R. G. Anderson (Rockefeller Foundation, Delhi) gave a talk on 'Some major milestones in genetics and plant breeding for rust resistance in wheat' and presented a historical sketch of the basic studies in genetics, cytogenetics and plant breeding for rust resistance. Dr Anderson pointed out that there is immediate need for collecting the fast disappearing sources of natural variation in countries where land races are now grown. The potato crop was dealt with by Dr Pushkarnath (Central Potato Research Institute, Simla) who discussed the recent trends in potato breeding in India, in production breeding where there has been a shift from seedling raising, and selection and clonal maintenance in the high hills to regionalization of breeding in the plains. Regarding resistance breeding, Dr Pushkarnath observed that breeding for field immunity is a worthwhile goal for the plains.

The third and final session on Genetics and Plant Breeding started with the paper of Dr H. F. Robinson (North Carolina, USA) titled 'Quantitative genetics in relation to breeding on the Centennial of Mendelism', who devoted his paper to the components of genetic variance and their relationships in breeding. The status of information on additive genetic variance, dominance variance, epistatic variance and the implication of level of dominance was discussed by Dr Robinson with major emphasis on the experimental results with maize. The second paper on 'Biometrical genetics' was presented by Dr B. R. Murty (IARI, New Delhi) who examined the nature of genetic divergence as assessed by statistical distance and canonical analysis and its relationship

to the components of genetic variation in some outbreeding, self-pollinated and material with variable degree of outbreeding for some components of yield and characters related to fitness. Dr H. M. Beachell (IRRI, Philippines) described the hybridization work that is in progress in IRRI designed to combine into single strains desirable plant and grain characteristics from different varieties in rice. Another paper from IRRI, Philippines, was that of Dr T. T. Chang who spoke on the 'Need for genetic investigations to assist rice breeding in tropical Asia'. The important topics which Dr Chang discussed were resistance to lodging, resistance to important diseases and insects, nature and effects of intervarietal hybrid sterility and possible synthesis of cytosterility to utilize heterosis. Dr Chang stressed the urgent need for additional genetic information on economic traits to help rice breeders achieve rapid advances in varietal improvement.

Cytogenetics

One session was devoted to cytogenetics which opened with the paper of Dr D. N. De (Indian Institute of Technology, Kharagpur) titled 'Organizational pattern of the chromosome'. Dr De said that the modern techniques of electron microscopy have shown that a chromosome is composed solely of fine fibres, whereas X-ray irradiation and autoradiographic studies have strongly indicated that it is composed of two functional units before chromosome replication. A chromosome model was proposed by him in which non-basic proteins had a structural role. Dr H. K. Jain (IARI, New Delhi), who spoke on 'Chromosomal regulation of nucleolar synthesis', came to the conclusion, based on his work on the analyses of the incorporation of tritium labelled precursors of RNA in disomic and trisomic individuals, that nucleolar synthesis is closely correlated with other synthetic activities associated with chromosomal reproduction and condensation. Prof. A. Abraham (University of Kerala, Trivandrum), talking about the cytology of endosperm in coconut, recorded that with increasing maturity the proportion of triploid nuclei decreases and the proportion of nuclei with higher level of ploidy increases. 'Genomic differentiation in Oryza' was dealt with by Dr S. V. S. Shastry (IARI, New Delhi) who analysed the genomic constitution of some diploid and tetraploid species of Oryza and discussed chromosomal pairing in allogenomic hybrids, where depending upon the genomic constitution of the parents pairing is suppressed either by desynapsis or by timing imbalance in condensation and migration of chromosomes. Dr E. K. Janaki Ammal (Regional Research Laboratory, Jammu Tawi) discussed the results of a cytological survey of several hexaploid genera belonging to different families of flowering plants and reported regular pairing in them. She conjectured the presence of genes for controlling diploid behaviour in these hexaploids as has been discovered in the case of a hexaploid like wheat.

Mutations in Higher Plants

The session began with the paper of Dr A. T. Natarajan (IARI, New Delhi) on 'Chromosome

breakage in relation to induced mutagenesis in barley'. Dr Natarajan, on the basis of his studies with several mutagenic agents and other compounds possessing the chromosome breaking ability in diploid barley, reported that all mutagenic agents induce chromosome breaks, but all chromosome breaking agents do not induce mutations. Dr Natarajan further stated that by appropriate manipulation of pre-, post- and conditions during treatment chromosome breakage or mutations can be allowed to dominate. Dr D. C. Joshua (Atomic Energy Establishment, Trombay, Bombay) reported about percentage of translocation heterozygotes, frequency of interchanges and mutation rate in japonica and indica rices and their hybrids after irradiation with gamma rays. Shri S. S. Rajan (IARI, New Delhi) presented data which indicated that Sesamum orientale when subjected to a second dose of irradiation shows comparatively less damage than when exposed for the first time.

Human and Animal Genetics

The first paper in this session was presented by Dr L. D. Sanghvi (Indian Cancer Research Centre, Bombay) on consanguineous marriages in Andhra Pradesh and their bearing on the genetic effects of inbreeding in man. He said that such studies could possibly differentiate loci which are maintained by mutation from the ones which are maintained by selective advantage of the heterozygote. Dr O. S. Reddi (Osmania University, Hyderabad) reported about the production of translocations in the spermatogonia of mice after X-radiation, which has bearing on the genetic damage and the hazards of ionizing radiations. Dr Sushil Kumar (IARI, New Delhi) reported a significantly higher frequency of gene for hypertrichosis of the ear pinnae in the Punjabi people as compared to those of east and south-east of India, and in a Tibetan sample the frequency of this *He allele* appeared to be very low. He presented data to show that the frequency of this gene could be used as an anthropological marker which confirmed the anthropometric studies of northern, western and eastern people of India and Mongoloids of Tibetan origin. Dr C. R. Balakrishnan (National Dairy Research Institute, Karnal), with the help of standard electrophoresis apparatus, has collected information on haemeglobin polymorphism in Indian cattle. Dr G. B. Deodikar (Central Bee Research & Training Institute, Poona) considered phylogenetic data of some diploid and tetraploid species of Apis and its bearing on the problem of breeding improved stock of honey bees. Dr E. I. Ambrose (Chester Beatty Research Institute, London) wound up the session with his paper 'The use of cell surface markers for cytogenetic studies on mammalian cell'. Dr Ambrose said that recent physico-chemical and immunological studies have provided evidence for the presence of a mosaic structure composed of phospholipids mucopolysaccharides and proteins. Many of the biological phenomena associated with cellular specificity are dependent on substances localized on this surface mosaic which helps in investigations of so-called somatic mutations and viral transformations.

Biochemical and Molecular Genetics

This was the last topic of the fascinating and latest field in the science of genetics under which five papers were presented opening with the paper of Dr R. N. Singh (Banaras Hindu University, Varanasi) who reported evidence for the occurrence of mutation and genetic recombination in blue-green algae, after exposure to different muta-gens. Dr G. P. Kalle (Atomic Energy Establish-ment, Trombay, Bombay) reported a new type of mutant in *Escherichia coli* which determines resistance to ultraviolet. Dr G. W. Notani (Tata Institute of Fundamental Research, Bombay) presented data which indicated that f2 specific proteins can be synthesized by f2 RNA in vitro. Miss K. Pandharipande of the same institute, working on a male specific bacteriophage f1, reported the isolation of several host dependent and temperature sensitive mutants after treatment with nitrous acid, hydroxylamine and ethyl methanesulphonate. They also presented data about several mixed infection experiments with single and double mutants. Dr S. Sarkar, presenting the third paper from Tata Institute of Fundamental Research, spoke on 'βgalactosidase forming capacity in repressed and derepressed cells of *Esch. coli*'. Studying the decay of the enzyme forming capacity in constitutive strains and comparing this with inducible strains he concluded that mRNA is unstable and that repressor possibly acts at transcriptional level.

In addition to the above-mentioned sessions where papers were presented in different fields, one session was arranged for group discussion on Mutation, Cereal breeding and Biometrical genetics. in which the interested audience also participated in the short lectures about their work and the discussions which followed. One session was devoted to 'Teaching of Genetics and Plant Breeding' in which almost all the speakers pointed out the inadequacy in teaching genetics and plant breeding in the universities and recommended that more attention should be paid to this important subject which has a bearing on the food production of a country, more so of India which is dependent to a large extent on imports for its food requirements.

Summer School in Analytical Techniques in Biochemistry

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THE Review Committee on Biochemistry of the University Grants Commission had suggested organizing summer schools in analytical techniques in biochemistry to overcome the disparity in standards among the several universities and institutions, and the generally inadequate training in analytical methods and instrumentations in biochemistry. To implement this recommendation, a Summer School in Biochemistry was organized in the Department of Biochemistry, Indian Institute of Science, in June 1963. In continuation of this programme, a Summer School in Analytical Techniques in Biochemistry was similarly held during May-June 1965 in this department under the direction of Prof. P. S. Sarma.

In his inaugural address Prof. S. Dhawan, Director, Indian Institute of Science, reiterated the need for such summer schools and promised help, encouragement and the facilities at the institute for this and future efforts in the organization of such schools annually. He also emphasized the need for interdisciplinary collaboration in the planning of summer schools covering related areas of science and technology so that better returns could be obtained for the investment made in research by the country. He pointed out the necessity for critical self-evaluation of the benefits from such a training and suggested to the trainces to write back at a later date their impressions with a view to future improvement. Prof. P. S. Sarma then outlined briefly the objectives of the summer school and emphasized that the summer school was intended to impart a general training in several biochemical techniques and not for specializing in anyone of them. Moreover, he indicated that the teachers and students who have learnt new techniques should go back and impart it to their colleagues, thereby increasing the utility of these summer schools.

Thirty-two trainees from 32 universities and research institutions were selected from a large number of applicants. The trainees were either working towards a doctoral degree or were teachers in biochemistry and allied sciences. A representative from an industrial laboratory was also selected. Thirteen teachers were drawn from the Department of Biochemistry and the Laboratory of Pharmacology of the Indian Institute of Science and one each from the Dental Wing, Madras Medical College, and the Cancer Research Centre, Madras. The course consisted of one lecture in the morning by one of the teachers followed by two three-hour sessions of laboratory demonstrations. The experiments were designed to acquaint the trainees with the techniques most frequently used and the common instruments generally employed in biochemical research. Starting the lecture series with a talk on the 'Biochemical concepts of the living cell', Prof. P. S. Sarma emphasized the importance of analytical techniques in biochemical research by saying that the best part of an investigator's time is rightly taken up in separations, fractionations, isolations and purifications. Later, discussing the mechanisms of transmission of the hereditary characteristics by DNA, he sounded a note of caution that the entire concept of coding is almost getting out of hand.

Dr J. Ganguly spoke on the intracellular localization of enzymes highlighting the pitfalls and the precautions to be taken in obtaining cell components in an uncontaminated condition. He also described the biochemical parameters of these cell organelles. Analytical methods in carbohydrate chemistry with special emphasis on the chemical principles involved in their analyses were discussed by Dr P. L. Narasimha Rao. Dr T. K. Virupaksha discussed in critical detail the principles and application of electrophoresis-free and -zone in the separation of charged macromolecules, such as proteins. Dr N. Appaji Rao highlighted the general methods available for the assay of water-soluble vitamins, with special reference to riboflavin. The principles of chemical, microbiological and coenzymatic assay of vitamins and coenzymes were discussed with their limitations and advantages. The theoretical principles underlying column chromatography, with special reference to amino acids were elucidated by Dr P. J. Vithayathil. The role of automation in amino acid analysis was also discussed. Dr S. Mahadevan described the various techniques available for the end-group analysis of proteins, with special reference to the FDNB technique of Sanger. The successful use of these techniques in the sequence analysis of peptides and proteins was discussed. Dr H. R. Cama spoke on the analysis of fat-soluble vitamins with reference to the principles of spectrophotometry and the use of the 3-point correction method for the assay of vitamin A. The chemical analysis of lipids was described by Dr T. Ramasarma. The uses of reverse-phase and thin-layer chromatography in lipid separations were highlighted.

The recent advances in the techniques of biochemical genetics were expounded by Dr T. Ramakrishnan. These techniques have been responsible for the opening up of new and exciting frontiers in biology. Dr E. Raghupathy described the isolation of single cells from animal tissues through a trypsinization procedure. He discussed the application of this procedure in understanding the metabolism of the thyroid gland. Dr C. S. Vaidyanathan spoke on handling plants for biochemical work and the precautions to be taken in the isolation of plant organelles such as chloroplasts. Speaking on the assay of hormones, Dr N. R. Moudgal enumerated the general chemical and biological methods available for the assay of a number of hormones. $D_F S. C.$ Pillai presented in detail the work carried out on the understanding of the role of protozoa in sewage purification. The significance of these mechanisms in the purification of wastes was brought to the attention of the participants. Dr V. M. Sivaramakrishnan highlighted the principles and precautions to be observed in the handling of radioactive tracers and the use of autoradiography in biochemical analysis. He also discussed the use of the various types of counting equipment commonly available to the biochemist. Winding up the lecture series, Dr P. J. Vithayathil spoke on the importance of the maintenance of research records and on the errors commonly encountered therein.

During the first two weeks the following techniques were demonstrated by the participating teachers: isolation of cell components by differential centrifugation and chemical analysis of lipids (Dr J. Ganguly); chemical analysis of carbohydrates and thinlayer and reverse-phase chromatography (Dr T. Ramasarma); assay of water-soluble vitamins and circular paper chromatography of flavin nucleotides (Dr N. Appaji Rao); different methods for the estimation of proteins, glycerol and formaldehyde (Dr T. K. Virupaksha); principles of buffers, paper electrophoresis and amino acid analysis (Dr P. J. Vithayathil); use of the microscope, staining techniques and assay of antibiotics (Dr P. L. Narasimha Rao); some operations such as adrenalectomy and ovariectomy, and immunochemical analysis of proteins (Dr N. R. Moudgal); estimation of phosphate and end-group analysis of proteins (Dr S. Mahadevan); chemical and bacterial analysis of water and sewage and microbiological assay of vitamin B12 (Dr S. C. Pillai); techniques in biochemical genetics (Dr T. Ramakrishnan); calibration of manometers and manometry and enzyme assays (Dr C. S. Vaidyanathan); use of tracers and counting equipment (Dr V. M. Sivaramakrishnan); analysis of trace elements, such as copper, manganese and iron (Dr P. S. Sarma); analysis of carotenoids and fat-soluble vitamins and agar-gel and movingboundary electrophoresis (Dr H. R. Cama); and isolation of cells from tissues by trypsinization procedures (Dr E. Raghupathy).

One of the suggestions at the last Summer School in Analytical Techniques held in 1963 was that the trainees should spend some time in learning, a little more thoroughly, a few techniques used during the investigation of a research problem. Implementing this suggestion, during the last week, the trainees in batches of six were assigned special problems in one of the following five fields: (i) proteins, (ii) microbiology, (iii) vitamins and enzymes, (iv) lipids, and (v) tracer technique, analysis of trace elements and immunochemical analysis of proteins. Assignment to the various groups was made, as far as possible, according to trainee's preference, but due consideration was given to the learning of a new technique.

As in the previous years, the summer school with this ambitious programme of training was undoubtedly strenuous and the shortage of time was felt by the teachers and the trainees alike. Although the organization and implementation of the training drew heavily on both the personnel and facilities in the department, the research students and staff of the department gave unstintingly their time and resources. It will be worth while in the future to organize a separate laboratory completely equipped to impart such a training in analytical techniques in biochemistry.

Tenth Congress on Theoretical & Applied Mechanics

The Tenth Congress on Theoretical and Applied Mechanics will be held at the Indian Institute of Technology, Madras, during 20-24 December 1965 under the presidentship of Prof. B. R. Seth. Research papers can be contributed on any of the following subjects: Elasticity, plasticity and rheology; Fluid mechanics (aerodynamics and hydrodynamics); Mechanics of solids (ballistics, vibration, friction and lubrication); Statistical mechanics, thermodynamics and heat transfer; Mathematics of physics and statistics; Experimental techniques; and Computation methods. Papers accompanied by 3 copies of abstracts should reach Dr M. K. Jain, Secretary-Treasurer, the Indian Society of Theoretical and Applied Mechanics, Indian Institute of Technology, New Delhi, by 15 November 1965.

Unilateral Conductivity of the First Class Oxide Films

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XIDE films produced by the electrochemical method^{1,2} on the surface of the so-called valve metals (i.e. aluminium, tantalum, niobium, zirconium, titanium, etc.) may be divided into two classes^{2,3}. The first class oxide films are not porous and possess high denisty (of the order of 3.2 g./cm.3). They are comparatively very thin (not thicker than 1 micron) and can be produced by electrochemical oxidation of metal in suitable weak (i.e. not able to dissolve the generated oxide) electrolytes. The second class oxide films are porous and of lower density (of the order of 2.5 g./cm.³) but are thicker (5-10 microns up to several millimetres) than the first class oxide films. They are produced by electrochemical oxidation in strong electrolytes capable of dissolving the oxide partially. The first class oxide films are mainly used in various oxide (i.e. electrolytic, oxide-semiconductor and metaloxide) capacitors2-6, and the second class oxide films find use in heat resistant electrical insulation, chemical protective coatings, etc.1,2.

Basic Unilateral Conductivity Data

It is well known that oxide films of the first class possess distinctly the property of unilateral electrical conductivity^{1,2,6,7}. If the oxidized metal is made the anode, and if its potential is not higher than the potential required for film formation, the electrical resistance of the oxide film is large and only a little current leaks through it. On the contrary, when the oxidized metal is made the cathode, the resistance of the oxide film is little. Because of this property, the simplest, common electrolytic capacitors are polar and operate reliably only if connected in one definite direction relative to the source of direct voltage.

The theory of unilateral conductivity of the oxide films has been elaborated by many investigators during the past 60 years, starting from the time of electrolytic rectifier invented by Mitkevich⁸ in 1901. Valve metal-oxide films-liquid electrolyte systems were the first to be investigated and the rectifying properties of the oxide films were explained mainly on the basis of the processes occurring on the oxide-electrolyte boundary and in the microscopic pores of the film. In recent years, unilateral conductivity was discovered in oxide-semiconductor and metal-oxide capacitors, i.e. in such cases where the second electrode is not an electrolyte but a semiconductor or even a solid metal. New experimental facts together with the development of solid state physics necessitated the need for new explanations of the phenomenon of unilateral conductivity of oxide films, and different aspects of this phenomenon had to be investigated and elucidated. Some of the basic ideas of the nature of oxide films on valve metals are considered in the following paragraph.

Theoretical Consideration of Unilateral Conductivity

When a valve metal (e.g. aluminium) without the oxide film on its surface is immersed in a liquid electrolyte and made the anode, then oxygen will be generated on its surface and a thin layer of aluminium oxide will be formed. Due to the thinness of this oxide layer, a very strong electric field acts on the film; the intensity of this electric field is of the order of 106-107 V./cm. even when low voltage is maintained between aluminium and the electrolyte. Under the influence of electric field forces, negative oxygen ions will be moving through the oxide layer in the direction of aluminium and positive aluminium ions in the opposite direction, so that the thickness of the oxide film goes on increasing. This process continues up to the moment when the growing oxide film, across which a constant formation voltage is applied, decreases the electric field intensity to such an extent that the force of this field is insufficient for the escape of metal ions through the film. As a result, no ionic electric current passes through the oxide film and the film thickness ceases to increase.

The non-uniformity in the concentration of ions in the oxide film is inevitable during the process of film generation⁷. The concentration of oxygen ions is maximum in the oxide layer on the outer surface of the film and it is possible to observe the variation in the composition of aluminium oxide with increase in oxygen concentration. The composition of the oxide film at this stage may be written as Al₂O_{3+p}. With the removal of the oxide film, the oxygen ion concentration on the outer surface of the metal drops, but the concentration of aluminium ions must rise and reach a maximum level at the metal surface. Hence, in the deep layers of the oxide film, the deviation in the composition of the oxide film from the stoichiometric composition may be written as Al2+0O3. Between these two layers of non-stoichiometric oxide composition is an intermediate layer with exact stoichiometric composition Al₂O₃. Aluminium ions, whose dimension is 2.6 times smaller than that of oxygen ions, diffuse more easily than oxygen ions. It is, therefore, obvious that the stoichiometric oxide layer is situated not in the very middle of the oxide film but it is shifted in the direction of the electrolyte surface (Fig. 1).

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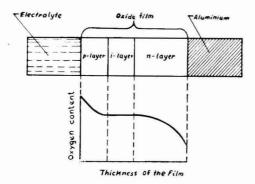


Fig. 1 -- Dependence of oxygen content of oxide film on the distance separating the valve metal (aluminium) from the electrolyte (schematic)

It is known that aluminium oxide containing surplus of oxygen behaves like a semiconductor with hole conductivity (p-type semiconductor), and when it contains surplus of aluminium it behaves like a semiconductor with electronic conductivity (n-type semiconductor). Consequently, in the generated oxide film, p-n junction (with intermediate intrinsic layer of stoichiometric oxide, i.e. p-i-n junction) must be created. This is one of the main reasons for the unilateral conductivity of oxide films.

It is to be expected that if the current in the conductive direction passes through oxide film for a long period, the concentration of ions will change and the junction will be partially destroyed. Finally, the whole film will be transformed into n-type semiconductor having some surplus aluminium ions. The destruction of p-n junction may be observed by heating the oxide film, because by heating the concentration of oxygen ions in the film is decreased. Analogously, hydrogen ions must transform the film into n-type semiconductor.

If the oxidized aluminium with destroyed p-n junction is made the anode, the junction will be restored gradually but only when oxygen ions have access to the film surface. These considerations have been confirmed by numerous experiments7,9-12.

When an oxidized metal is immersed in a liquid electrolyte, it reveals its unilateral conductivity more clearly than in the dry state. In the wet state, the rectifying coefficient (the ratio of the current in conductive direction to the current in non-conductive direction) reaches a value of 5000-50,000, whereas in the dry state this coefficient is only 10-100. This may be explained as due to the abundant supply of oxygen and hydrogen ions from the electrolyte, and also by the existence of defects and small channels in the film.

When the oxidized metal, immersed in a liquid electrolyte, is made the cathode, the resistance of the oxide film drops sharply because of the rapid destruction of p-n junction and the formation of n-type semiconductor having little resistivity, expansion of defective spots of the film, and pulling of electrolyte into the film pores. In this case, the directions of the action of electrostatic and electro-osmotic forces coincide. The resistance of oxidized metal in the conductive direction is considerably lower in the electrolyte than in the dry state.

When the oxidized metal, immersed in a fluid electrolyte, is made the anode, the resistance of the oxide film rises quickly because of the restoration of p-n junction, partial film formation in the defective spots and pushing out of the electrolyte from the pores. This may be explained as due to the electroosmotic and electrostatic forces acting in opposite directions. In this case, the electro-osmotic force is greater than the electrostatic force.

It is of interest to note that the second class oxide films of valve metals do not show unilateral conductivity in the dry state. The rectifying properties of these films, when immersed in a liquid electrolyte, are very poor. This may be explained mainly by the existence of the thin first class oxide film between the metal and the second class oxide film.

Summary

Oxide films formed on the surface of aluminium. tantalum, and other valve metals are of great technological interest and their properties deserve further detailed examination. First class oxide films (very thin and of comparatively high density) possess the property of unilateral electrical conductivity when the oxidized valve metal is connected cathodically. The theory of unilateral conductivity developed by the authors and described in the paper is based on (i) the existence of p-i-n junction in the semiconductor oxide film and (ii) the action of electrostatic and electro-osmotic forces in the defective spots (pores) of the oxide film when it is in contact with a liquid electrolyte.

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Theoretical Formulae for the Thermal Diffusion Factor of Binary Gas Mixtures

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CINCE the prediction of the phenomenon of **b** thermal diffusion in gases by Chapman¹ and Enskog², and its experimental verification by Chapman and Dootson³ several efforts have been made to measure the thermal diffusion factor, α_T , both for isotopic as well as non-isotopic gas mixtures. A knowledge of the binary thermal diffusion factor of a gas mixture is useful in various applications, e.g. in the design of thermal diffusion plants for the separation of stable isotopes, and other practical problems of design where one deals with gas flow under temperature gradients. The phenomenon of thermal diffusion has long been known for its sensitivity to the nature of intermolecular forces4-9 and consequently several attempts have been made in recent years in this direction. The accuracy of the conventional measurements of α_T with the two-bulb apparatus10 is improved by using a more sensitive microthermal conductivity gauge11,12. To get a more reliable value of α_T , systems involving a radiotracer gas have also been studied which incidentally also offer a sensitive detection system for the thermal separation¹³⁻¹⁷.

The approach to steady state in a two-bulb thermal diffusion apparatus has also been very carefully investigated^{13,18-21}. The results of diffusion and thermal diffusion coefficients thus obtained have made it possible to somewhat uniquely determine the nature of intermolecular force fields of some simple molecules²².

A new technique for measuring α_T by a 'trennschaukel' or 'swing-separator' has been introduced by Clusius and Huber²³ and since then the theory of this apparatus has been investigated in detail by Van der Waerden²⁴ and Saxena and Joshi²⁵. A number of workers have employed trennschaukel for α_T measurements²⁶⁻³⁴.

The theory of thermal diffusion columns³⁵⁻³⁷ has also been carefully re-examined by a few workers³⁸⁻⁴⁸. The experimental performance of the columns has been investigated⁴⁹⁻⁵² with the object of evaluating the elementary diffusion factors accurately and reliably from the cascaded separation in a column.

In all such applications a reliable and simple theoretical expression of α_T is the basic starting point. Rigorous expressions⁵³⁻⁵⁵ are unfortunately very complicated and lengthy. In recent years several attempts⁵⁶⁻⁶³ have been made to simplify the rigorous expressions without impairing the accuracy. The purpose of this article is to review all this work together and present, in a systematic way, the various approximate expressions for α_T with their limitations and accuracies. To demonstrate the criteria of application to actual mixtures, calculations are discussed for a few gas systems. This analysis thus enables us to make some general

conclusions and recommendations as regards the applicability of various α_T formulae. Some new formulae and several tabulations and simpler versions of the known rigorous formulae are given as an aid to numerical computation of α_T . The discussions are confined mostly to noble gas mixtures, as the theory rigorously applies to only such systems.

We shall further consider only the L-J (12-6) potential energy function which has proved very successful⁵³ in correlating and explaining the various properties of gases and easier to handle. As the accuracies of the various formulae are only weakly dependent upon the form of the potential the energy function, we have preferred this potential⁵³

$$\phi(r) = 4\epsilon [(r_0/r)^{12} - (r_0/r)^6] \qquad \dots (1)$$

$$= \epsilon [(r_m/r)^{12} - 2(r_m/r)^6] \qquad \dots (2)$$

Here $\phi(\mathbf{r})$ represents the interaction potential energy at a molecular separation \mathbf{r} , ϵ is the depth of the potential energy minimum, and \mathbf{r}_0 and \mathbf{r}_m are the values of \mathbf{r} for which the potential energy is zero and minimum respectively such that $\mathbf{r}_m = 2^k \mathbf{r}_0$.

Theoretical Formulae for a_T

The rigorous Chapman-Enskog theory expresses α_T as the ratio of infinite determinants which has been finally put in the form of an infinite series by two alternative approximation procedures, one due to Chapman and Cowling⁶⁴ and the other due to Kihara⁶⁵ further extended by Mason⁵⁴. The latter procedure is referred to as the Kihara-Mason approximation scheme. We thus get two sets of formulae which have different rates of convergence. For actual systems one considers both sets to find out which particular approximation procedure is preferable for expressing α_T . These α_T expressions are fairly lengthy and complicated, hence attempts have been made in recent years to simplify them. We shall now discuss all the rigorous as well as simpler formulae⁵⁷⁻⁶³ obtained by both the approxi-mation procedures. The simpler formulae mentioned earlier have been cast into a form which is more suitable for computation, and in addition some new formulae have been derived.

According to the Chapman-Cowling approximation scheme the *m*th approximation to α_T , $[\alpha_T]_m$, is^{64,66}

$$\begin{split} [\alpha_T]_m &= (5/2) [A_{00}^{(m)}]^{-1} [X_2^{-1} A_{01}^{(m)}] (M_1 + M_2) / 2M_1 \}^{\frac{1}{2}} \\ &+ X_1^{-1} A_{0-1}^{(m)} [(M_1 + M_2) / 2M_2]^{\frac{1}{2}}] \quad \dots (3) \end{split}$$

where $A^{(m)}$ represents a determinant of order (2m+1) whose general element is a_{ij} , i and j range from -m to +m including zero, $A_{ij}^{(m)}$ is a determinant obtained from $A^{(m)}$ by deleting the

row and column containing a_{ij} , and M_i and X_i are the molecular weight and the mole fraction of the ith component respectively. In this paper subscript 1 is used for the heavier component and 2 for the lighter component. The elements a_{ij} are complicated functions of X_{ij} , M_{ij} , the reduced collision integrals $\Omega_{ij}^{(l,n)^*}$, and r_m or r_0 . The explicit expressions for all the a_{ij} relevant up to $[\alpha_T]_3$ have already been worked out54,64,66. The present calculations are confined to the second approximation. The expressions for the corresponding a_{ij} are given in Appendix I. These a_{ij} expressions are somewhat different from the earlier ones and are also written in terms of a set of reduced quantities (A_{ii}^*, B_{ij}^*) C_{ij}^{*} , E_{ii}^{*} , F_{ii}^{*} , G_{ij}^{*} , H_{ij}^{*} , J_{ij}^{*} , K_{ij}^{*} and L_{ij}^{*}), which offer some convenience of interpolation as their variation with temperature is smaller than that of $\Omega_{ii}^{(l,n)^*}$. A tabulation of newly defined reduced quantities is given in Table 1 as a function of reduced temperature $(T^* = kT/\epsilon)$. For m = 1, Eq. (3) yields the first approximation to α_T which is very often written in the following more convenient form⁵³

$$[\mathbf{x}_{T_{2}}]_{1} = (6C_{12}^{\bullet} - 5) \frac{X_{1}S_{1} - X_{2}S_{2}}{X_{1}^{2}Q_{1} + X_{2}^{2}Q_{2} + X_{1}X_{2}Q_{12}} \quad \dots (4)$$

where

$$S_{1} = \frac{M_{1}}{M_{2}} \left(\frac{2M_{2}}{M_{1}+M_{2}}\right)^{4} Z_{11} - \frac{4M_{1}M_{2}A_{12}^{*}}{(M_{1}-M_{2})^{2}} - \frac{15M_{2}(M_{2}-M_{1})}{2(M_{1}+M_{2})^{2}} \dots (5)$$

$$Q_{1} = \frac{2}{M_{2}(M_{1}+M_{2})} \binom{2M_{2}}{M_{1}+M_{2}} \overset{1}{Z}_{11} [\{(5/2)-(6/5)B_{12}^{*}\}M_{1}^{2} + 3M_{2}^{2} + (8/5)M_{1}M_{2}A_{12}^{*}] \dots (6)$$

$$Q_{12} = 15 \binom{M_1 - M_2}{M_1 + M_2}^2 \binom{5}{2} - \frac{6}{5} B_{12}^* + \frac{4M_1M_2A_{12}^*}{(M_1 + M_2)^2} \times \left(11 - \frac{12}{5} B_{12}^*\right) + \frac{8(M_1 + M_2)}{5(M_1M_2)^4} Z_{11} Z_{22} \dots (7)$$

$$\begin{split} A_{12}^{\bullet} &= \Omega_{12}^{(2,2)*} / \Omega_{12}^{(1,1)*}, \quad B_{12}^{\bullet} &= (5\Omega_{12}^{(1,2)*} - 4\Omega_{12}^{(1,3)*}) / \Omega_{12}^{(1,1)*} \\ C_{12}^{\bullet} &= \Omega_{12}^{(1,2)*} / \Omega_{12}^{(1,1)*} \text{ and } Z_{ii} &= \Omega_{ii}^{(2,2)*} \sigma_{ii}^2 / \Omega_{12}^{(1,1)*} \sigma_{12}^2 \quad \dots (8) \end{split}$$

The expressions for S_2 and Q_2 are obtained from those of S_1 and Q_1 respectively by the interchange of subscripts. In these expressions σ refers to the characteristic distance parameter of the potential and thus is equal to r_0 for the *L-J* potential and r_m for the exp-six potential.

Eq. (3) gets considerably simplified if either of the two components is present in trace. Thus, if the heavier component is in trace we get⁵⁷ for the first two approximations to α_T

$$[\mathbf{z}_{T}]_{1}(X_{1} \rightarrow 0) = \frac{5}{2} \begin{bmatrix} a_{10} \begin{pmatrix} M_{1} + M_{2} \end{pmatrix}^{\frac{1}{2}} + \begin{pmatrix} a_{-10}a'_{11} - a_{10}a_{-11} \\ a'_{11}a''_{-1} \end{pmatrix} \\ \times \begin{pmatrix} M_{1} - M_{2} \\ 2M_{2} \end{pmatrix}^{\frac{1}{2}} = (6C_{12}^{*} - 5)(-S_{2}/Q_{2}) \quad \dots (9)$$

and

$$\begin{split} & [\mathbf{a}_{T}]_{2}(X_{1} \rightarrow 0) = \frac{5}{2} \binom{M_{1} + M_{2}}{2M_{1}}^{1} \binom{a_{10}}{a_{11}'} \binom{1 - \frac{a_{20}a_{12}'}{a_{10}a_{22}'}}{X_{11}' \binom{1}{a_{10}'} \binom{1}{a_{10}'} \binom{1}{a_{10}'} \binom{1}{a_{22}'} \times \binom{1 - \frac{a_{12}'}{a_{11}'} \binom{1}{a_{22}'} + \frac{5}{2} \binom{M_{1} + M_{2}}{2M_{2}}^{1} \binom{1}{a_{11}'} \binom{a_{12}' - a_{12}'}{a_{10}'} \binom{1}{a_{22}'} + \frac{3}{2} \binom{1}{a_{11}'} \binom{1}{a_{22}'} - \frac{a_{12}'}{a_{12}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} - \frac{1}{a_{12}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} \binom{1}{a_{12}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} \binom{1}{a_{12}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} \binom{1}{a_{12}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} \binom{1}{a_{12}'} \binom{1}{a_{11}'} \binom{1}{a_{22}'} \binom{1}{a_{22}'}$$

Similarly, if the lighter component is in trace we get⁵⁸

$$\begin{bmatrix} z_T \\ 1 \end{bmatrix}_1 (X_2 \to 0) = \frac{5}{2} \left[\left(\frac{M_1 + M_2}{2M_1} \right)^{\frac{3}{2}} \left(\frac{a_{10}a'_{-1-1} - a_{-10}a_{-11}}{a''_{11}a'_{-1-1}} \right) \\ + \frac{a_{-10}}{a'_{-1-1}} \left(\frac{M_1 + M_2}{2M_2} \right)^{\frac{1}{2}} \right] = (6C_{12}^* - 5)(S_1/Q_1) \dots (11)$$

and

$$\begin{split} [a_{T}]_{2}(X_{2} \rightarrow 0) &= \frac{5}{2} \left[\left(\frac{M_{1} + M_{2}}{2M_{1}} \right)^{\frac{1}{2}} \{ (a'_{-1-1}a'_{-2-2} - a'_{-1-2}^{2}) \\ &\times (a''_{11}a''_{22} - a''_{12}^{2})^{-1} \{ (a_{10}a''_{22} - a''_{12}a_{02})(a'_{-1-1}a'_{-2-2} - a'_{-1-2}^{2}) \\ &+ (a_{1-1}a''_{22} - a''_{12}a_{2-1})(a_{-20}a'_{-1-2} - a_{-10}a'_{-2-2}) \\ &+ (a_{1-2}a''_{22} - a''_{12}a_{2-2})(a_{-10}a'_{-1-2} - a_{-20}a'_{-1-1}) \} + \left(\frac{M_{1} + M_{2}}{2M_{2}} \right)^{\frac{1}{2}} \\ &\times \left(\frac{a_{-10}}{a'_{-1-1}} \right) \left(1 - \frac{a_{-20}a'_{-1-2}}{a_{-10}a'_{-2-2}} \right) \left(1 - \frac{a'_{-1-2}}{a'_{-1-1}a'_{-2-2}} \right)^{-1} \right] \dots (12) \end{split}$$

The Kihara-Mason approximation procedure leads to the following expressions^{54,65} for the first two approximations to α_T :

$$[x'_{T}]_{1} = (6C^{*}_{12} - 5) \frac{X_{1}S_{1} - X_{2}S_{2}}{X_{1}^{2}Q'_{1} + X_{2}^{2}Q'_{2} + X_{1}X_{2}Q'_{12}} \dots (13)$$

where

$$Q_{1}' = \frac{2}{M_{2}(M_{1} + M_{2})} \left(\frac{2M_{2}}{M_{1} - M_{2}}\right)^{\frac{1}{2}} Z_{11} \left[M_{1}^{2} + 3M_{2}^{2} + \frac{8}{5}M_{1}M_{2}A_{12}^{*}\right] \dots (14)$$

$$(M_{1} - M_{2})^{\frac{2}{2}} - 32M_{1}M_{2}A_{12}^{*}$$

$$Q_{12}' = 15 \left(\frac{M_1 - M_2}{M_1 + M_2}\right)^2 + \frac{32M_1M_2.4_{12}^*}{(M_1 + M_2)^2} - \frac{8(M_1 + M_2)}{5(M_1M_2)^4} Z_{11}Z_{22} \quad \dots (15)$$

and Q'_2 is obtained from Q'_1 by the interchange of subscripts.

$$[\alpha'_{T}]_{2} = [\alpha_{T}]_{1}(1+K_{1}) + K_{2} \qquad \dots (16)$$

where

$$K_1 = h_3 h_5 + h_4 h_{-6} + h_{-3} h_{-5} + h_{-4} h_6 \qquad \dots (17)$$

and

$$K_{2} = \frac{5}{2X_{1}} \left(\frac{M_{1} + M_{2}}{2M_{2}} \right)^{\frac{1}{2}} (h_{-1}h_{-5} + h_{1}h_{6} - h_{2}h_{4} + h_{-2}h_{3}) - \frac{5}{2X_{2}} \left(\frac{M_{1} + M_{2}}{2M_{1}} \right)^{\frac{1}{2}} (h_{1}h_{5} + h_{-1}h_{-6} - h_{-2}h_{-4} + h_{2}h_{-3}) \dots (18)$$

T_{ij}^*	L-J(12-6)	Modified 1	Buckingha	m (Exp-6)	potential	T^{\bullet}_{ij}	<i>IJ</i> (12-6)	Modified I	Buckinghat	n (Exp-6)	potential
.,	potential	α=12	a == 13	α=14	α=15		potential	α 12	x 13	α 14	α 15
		$E^{*}_{ij} = \Omega^{(2)}_{ij}$	$^{3)*}/\Omega_{ij}^{(2,2)*}$					$F^{ullet}_{ij}=\Omega^{(2,4)}_{ij}$	$^{(2,2)^{*}}/\Omega_{ij}^{(2,2)^{*}}$		
0.0		0.9166	0.9166	0.9166	0.9166	12.0		0.9121	0.9191	0.9257	0.9294
0.1		0-9181	0.9173	0.9176	0.9175	14.0		0.9119	0.9196	0.9254	0.9295
0.2	0.9102	0.9170	0.9202	0.9204	0.9200	16·0 18·0		0.9119 0.9119	C+9195 0-9200	0·9250 0·9247	0·9296 0·9295
0·3 0·4	0.8957	0·9064 0·8874	0·9105 0·8938	0·9122 0·8970	0·9136 0·9002	20.0	0.9351	0.9119	0.9200	0.9247	0.9295
0.5	0.8826	0.8733	0.8801	0.8841	0.8882	25.0		0.9120	0.9208	0.9239	0.9298
0.6	0.8746	0.8649	0.8714	0.8758	0.8801	30.0	0.9357	0.9125	0.9215	0.9237	0.9302
0.7	0.8705	0.8611	0.8671	0.8717	0.8760	35.0	0.0255	0.9131	0.9224	0.9240	0.9306
0·8 0·9	0·8702 0·8716	0-8504 0-8620	0.8661 0.8672	0.8706	0.8748	40·0 45·0	0.9355	0.9139 0.9144	0.9233 0.9242	0.9242 0.9245	0·9315 0·9321
1.0	0.8746	0.8650	0.8072	0·8717 0·8743	0.8757 0.8781	50.0	0.9356	0.9154	0.9252	0.9250	0.9328
1.0 1.2	0.8815	0.8728	0.8772	0.8813	0.8850	60.0	0.9361	0.9167	0.9269	0.9262	0.9342
1.4	0.8906	0.8815	0.8857	0.8892	0.8929	70.0	0.9355	0.9184	0.9284	0.9271	0.9355
1.6	0.8994	0.8898	0.8940	0.8970	0.9006	80.0	0.9356	0.9196	0.9301	0.9285	0.9370
1·8 2·0	0·9058 0·9132	0·8973 0·9040	0·9014 0·9080	0·9041 0·9105	0.9078	90-0 100-0	0-9359 0-9359	0.9210 0.9224	0·9314 0·9327	0.9296 0.9307	0-9380 0-9393
2.5	0.9259	0.9170	0.9210	0.9232	0-9140 0-9267	100 0	0 7557	0 7224	0 7.527	0 /30/	0 7575
3.0	0.9344	0.9260	0.9300	0.9322	0.9354			$G^{ullet}_{ij}=\Omega^{(1,4)}_{ij}$	$^{*}/\Omega^{(1,1)}^{*}$		
3.5	0.9409	0.9325	0.9362	0.9385	0.9417			i) i)	71)		
4.0	0.9459	0.9369	0.9406	0.9434	0.9464	0.0		0.7605	0.7605	0.7605	0.7605
5·0 6·0	0·9518 0·9555	0·9426 0·9457	0·9463 0·9493	0·9497 0·9532	0·9519 0·9551	0.1		0.7458	0.7488	0.7516	0.7516
7.0	0.9579	0.9474	0.9512	0.9553	0.9572	0·2 0·3	0.6544	0.6957 0.6439	0.7073	0·7154 0·6704	0·7207 0·6791
8.0	0.9596	0.9486	0.9522	0.9565	0.9584	0.4	0.6353	0.6202	0.6435	0.6477	0.6574
9.0	0.9605	0.9493	0.9530	0.9571	0.9590	0.5	0.6342	0.6154	0.6300	0.6425	0.6523
10.0	0.9612	0.9498	0.9535	0.9576	0.9594	0.6	0.6418	0.6210	0.6350	0.6473	0.6571
12·0 14·0		0.9500 0.9500	0.9538 0.9542	0-9579 0-9578	0.9599 0.9600	0.7	0.6534	0.6316	0.6451	0.6571	0.6665
16.0		0.9499	0.9542	0.9576	0.9602	0.8	0.6670 0.6813	0.6444 0.6577	0.6574 0.6705	0.6692 0.6820	0.6784 0.6910
18.0		0.9499	0.9545	0.9575	0.9602	1.0	0.6942	0.6712	0.6836	0.6949	0.7034
20.0	0.9634	0.9500	0.9547	0.9573	0.9601	1.2	0.7191	0.6957	0.7077	0.7184	0.7269
25.0	0.0(2)	0.9499	0.9549	0.9569	0.9602	1.4	0.7415	0.7168	0.7285	0.7388	0.7471
30·0 35·0	0.9636	0·9502 0·9504	0.9552 0.9556	0.9568	0.9604	1.6	0-7602	0.7346	0.7594	0.7560	0.7647
40.0	0.9638	0.9508	0.9550	0-9570 0-9570	0·9606 0·9610	1·8 2·0	0·7760 0·7892	0·7494 0·7618	0.7607 0.7732	0.7702 0.7822	0·7787 0·7907
45.0	0 7000	0.9510	0.9565	0.9570	0.9612	2.5	0.8146	0.7847	0.7960	0.8046	0.8135
50.0	0.9637	0.9514	0.9570	0.9573	0.9616	3.0	0.8315	0.8000	0.8115	0.8201	0.8287
60.0	0.9637	0.9521	0.9579	0.9578	0.9623	3.5	0.8436	0.8105	0.8221	0.8306	0.8393
70.0	0.9638	0.9531	0.9589	0.9582	0.9631	4.0	0.8529	0.8176	0.8295	0.8382	0.8471
80·0 90·0	0·9636 0·9635	0-9537 0-9546	0.9597 0.9603	0-9589 0-9597	0.9639 0.9643	5.0	0.8630	0.8262	0.8387	0.8479	0.8564
100.0	0.9640	0.9552	0.9611	0.9601	0.9651	6·0 7·0	0.8699 0.8732	0.8304 0.8322	0.8432 0.8457	0.8532	0-8618 0-8648
			0 /011	0 /001	0 /001	8.0	0.8759	0.8332	0.8469	0.8576	0.8663
		$F_{ij}^{\bullet} = \Omega_{ij}^{(2)}$	$^{(4)*}/\Omega_{ii}^{(2,2)*}$			9.0	0.8781	0.8330	0.8472	0.8584	0.8674
		·) ·)	1 1			10.0	0.8804	0.8326	0.8471	0.8587	0.8679
0.0		0.8555	0.8555	0.8555	0.8555	12.0		0.8315	0.8463	0.8586	0.8682
0.1		0.8588	0.8568	0.8572	0.8577	14·0 16·0		0.8299 0.8287	0.8456 0.8447	0.8581 0.8574	0.8683 0.8683
0·2 0·3	0.8377	0·8597 0·8270	0-8609 0-8359	0.8615 0.8397	0-8611 0-8434	18.0		0.8274	0.8440	0.8570	0.8680
0.4	0.8090	0.7939	0.8050	0.8111	0.8174	20.0	0.8817	0.8262	0.8430	0.8567	0.8681
0.5	0.7891	0.7736	0.7844	0.7913	0.7985	25.0	0.0014	0.8246	0.8420	0.8559	0.8682
0.6	0.7797	0.7642	0.7742	0.7816	0.7886	30.0	0.8841	0.8233	0.8416	0.8555	0.8686
0.7	0.7778	0.7624	0.7715	0.7789	0.7855	35·0 40·0	0.8836	0·8228 0·8226	0·8416 0·8419	0.8557 0.8563	0·8693 0·8702
0·8 0·9	0·7803 0·7857	0·7654 0·7710	0·7736 0·7788	0.7808 0.7857	0·7873 0·7917	45.0		0.8228	0.8424	0.8569	0.8702
1.0	0.7927	0.7783	0.7857	0.7922	0.7980	50.0	0.8833	0.8230	0.8432	0.8575	0.8723
1.2	0.8085	0.7942	0.8011	0.8069	0.8127	60.0	0.8829	0.8239	0.8445	0.8594	0.8745
1.4	0.8241	0.8100	0.8166	0.8217	0.8274	70.0	0.8833	0.8249	0.8464	0.8611	0.8765
1.6	0.8382	0.8242	0.8307	0.8351	0.8410	80·0 90·0	0.8832 0.8832	0.8268 0.8280	0.8482 0.8499	0.8631 0.8649	0.8786 0.8810
1·8 2·0	0·8501 0·8613	0·8364 0·8470	0·8429 0·8536	0.8469	0·8529 0·8631	100.0	0.8851	0.8280	0.8499	0.8649	0.8810
2.5	0.8811	0.8470	0.8536	0.8572 0.8770	0.8631						0 00000
3.0	0.8946	0.8804	0.8869	0.8907	0.8960			$H_{ij}^* = \Omega_{ij}^{(2,2)}$	$^{3)^{*}}/\Omega_{ii}^{(1,1)^{*}}$		
3.5	0.9041	0.8895	0.8958	0.9002	0.9052						
4.0	0.9113	0.8958	0.9022	0.9072	0.9117	0.0		0.9226	0-9226	0.9226	0.9226
5·0 6·0	0·9202 0·9254	0.9036	0.9098	0.9161	0.9197	0.1		0.9237	0.9307	0.9403	0.9405
7.0	0.9254	0·9074 0·9096	0.9138 0.9161	0-9208 0-9188	0.9240 0.9265	0·2 0·3	0.9523	0-9513 0-9727	0.9546 0.9736	0-9614 0-9787	0·9600 0·9771
8.0	0.9305	0.9098	0.9174	0.9246	0.9283	0.3	0.9523	0.9727	0.9736	0.9787	0.9817
9.0	0.9321	0.9115	0.9183	0.9254	0.9286	0.5	0.9642	0.9700	0.9740	0.9787	0.9794
10.0	0.9330	0.9120	0.9186	0.9257	0.9290	0.6	0.9622			0.9745	0.9759

TABLE 1 VALUES OF	RATIOS OF COLLISION	INTEGRALS WHIC	H OCCUR IN HIGH	ER APPROXIMATIONS TO XT
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T_{ij}^{\bullet}	L-J(12-6)	Modified I	Buckinghan	n (Exp-6)	potential	T^{*}_{ij}	L-J(12-6) potential	Modified E	Buckingha	n (Exp-6)	potentia
,	potential	a=12	x=13	a=14	α=15	9	potential	x=12	α=13	α=14	a=15
		$H_{ij}^{*} = 1$	$\Omega_{ij}^{(2,3)*} / \Omega_{ij}^{(1,5)}$	1)*				$J_{ij}^* = \Omega_{ij}^{(1,5)}$	$)^{*} / \Omega_{ij}^{(1,1)*}$		
$0.7 \\ 0.8$	0·9607 0·9609	0.9638	0.9672	0.9715	0.9730	35.0		0·7896 0·7897	0·8119 0·8126	0.8285	0.8450
0.9	0.9624	0·9631 0·9641	0.9660 0.9663	0·9700 0·9699	0·9714 0·9713	40.0	0.8605	0.7897	0.8126	0.8295	0.8462
1.0	0.9646	0.9663	0.9680	0.9710	0.9722	45·0 50·0	0.8606	0·7901 0·7906	0·8134 0·8143	0·8304 0·8312	0·8476 0·8489
1.2	0.9697	0.9728	0.9733	0.9754	0.9763	60.0	0.8600	0.7920	0.8163	0.8336	0.8518
1·4 1·6	0·9773 0·9846	0·9807 0·9889	0-9804 0-9881	0-9815 0-9879	0.9822	70.0	0.8607	0.7939	0.8186	0.8359	0.8544
1.8	0.9910	0.9889	0.9955	0.9879	0·9887 0·9953	80.0	0.8603	0.7958	0.8211	0.8383	0.8570
2.0	0.9981	1.0044	1.0027	1.0006	1.0014	90·0 100·0	0·8615 0·8638	0·7978 0·7997	0·8234 0·8255	0.8409 0.8430	0·8597 0·8621
2.5	1.0124	1.0207	1.0183	1.0143	1.0154	100 0	0 0000			00150	0 0021
3.0	1.0230 1.0316	1.0335	1.0306	1.0255	1.0264			$K_{ij}^{*}=\Omega_{ij}^{(3,3)}$	$)^{*} / \Omega_{ii}^{(1,1)^{*}}$		
3·5 4·0	1.0384	1·0437 1·0517	1.0404 1.0479	1.0348 1.0425	1.0355 1.0427	0.0				0.0417	0.0447
5.0	1.0476	1.0636	1.0593	1.0543	1.0532	0·0 0·1		0·9417 0·9302	0·9417 0·9329	0·9417 0·9369	0·9417 0·9390
6.0	1.0543	1.0719	1.0668	1.0625	1.0605	0.2		0.9179	0.9225	0.9269	0.9299
7.0	1.0588	1.0779	1.0727	1.0689	1.0659	0.3	0.8889	0.9038	0.9091	0.9133	0.9180
8·0 9·0	1·0624 1·0651	1·0830 1·0868	1.0768 1.0803	1·0736 1·0772	1.0698 1.0730	0.4	0.8888	0.8968	0.9019	0.9063	0.9115
10.0	1.0672	1.0900	1.0832	1.0803	1.0755	0·5 0·6	0.8903 0.8919	0.8942 0.8942	0·8991 0·8987	0·9034 0·9030	0.9086
12.0		1.0955	1.0879	1.0849	1.0796	0.0	0.8944	0.8957	0.9000	0.9030	0·9081 0·9090
14.0		1.1003	1.0923	1.0886	1.0825	0.8	0·8975 0·9025	0.8980	0.9022	0.9064	0.9108
$16.0 \\ 18.0$		1·1043 1·1080	1·0959 1·0992	$1.0914 \\ 1.0937$	1.0850 1.0872	0.9	0.9025	0.9012	0.9052	0.9092	0.9134
20.0	1.0783	1.1116	1.1025	1.0960	1.0890	1·0 1·2	0·9061 0·9144	0·9048 0·9124	0.9086	0.9124	0.9163
25.0		1.1200	1.1099	1.1007	1.0932	1.4	0.9227	0.9202	$0.9161 \\ 0.9238$	0·9195 0·9267	0·9230 0·9300
30.0	1.0831	1.1275	1.1167	1.1044	1.0968	1.6	0.9301	0.9275	0.9309	0.9334	0.9367
35·0 40·0	1.0864	1.1347	1.1230	1.1080	1.1003	1·8 2·0	0.9366	0.9344	0.9378	0.9397	0.9431
45.0	1.0004	1·1414 1·1476	1·1293 1·1351	1·1113 1·1142	1·1032 1·1062	2.0	0.9435	0.9406	0.9440	0.9453	0.9491
50.0	1.0890	1.1534	1.1405	1.1170	1.1088	2·5 3·0	0.9554	0.9540 0.9645	0·9570 0·9671	0-9570 0-9663	0.9616 0.9712
60.0	1.0910	1.1644	1.1503	1.1221	1.1137	3.5	0-9638 0-9708	0.9731	0.9752	0.9736	0.9789
70.0	1.0926	1.1748	1·1595 1·1677	1.1268	1·1182 1·1221	3·5 4·0	0.9755	0.9799	0.9814	0.9795	0.9847
80·0 90·0	1.0940 1.0949	1·1841 1·1924	1.1754	1·1311 1·1354	1.1257	5.0	0.9817	0.9904	0.9910	0.9884	0.9928
100.0	1.0967	1.2006	1.1822	1.1385	1.1292	6·0 7·0	0·9871 0·9897	0·9976 1·0028	0·9969 1·0012	0·9947 1·9993	0.9980
						8.0	0.9925	1.0066	1.0044	1.0029	1.0017 1.0039
		$J_{ii}^{\bullet} = \Omega_{ii}^{(1)}$	$^{,5)*}/\Omega_{ij}^{(1,1)*}$			9.0	0.9945	1.0095 1.0113	1.0068	1.0055	1.0062
						10·0 12·0	0.9955	1.0113	1.0086	1.0076	1.0075
0·0 0·1		0.7222	0·7222 0·7030	0.7222	0.7222	12.0		1·0145 1·0165	1.0114	1.0106	1.0101
0.2		0.6986 0.6292	0.6437	0·7067 0·6541	0.7068 0.6612	16.0		1.0177	1·0137 1·0153	1·0130 1·0147	1·0119 1·0134
0.3	0.5893	0.5759	0.5925	0.6057	0.6157	18.0		1.0185	1.0166	1.0163	1.0143
0.4	0.5761	0.5586	0.5747	0.5882	0.5990	20.0	0.9988	1.0193	1.0178	1.0176	1.0162
0-5 0-6	0-5830 0-5951	0.5606	0.5760	0.5895	0.6001	25·0 30·0	1.0018	1·0206 1·0211	1.0207	1.0205	1.0193
0.0	0.6110	0·5716 0·5865	0.5864 0.6009	0·5996 0·6138	0.6100 0.6238	35.0	1 0018	1.0217	1·0232 1·0256	1·0227 1·0248	1·0224 1·0256
0.8	0.6282	0.6025	0.6164	0.6292	0.6390	40.0	1.0060	1.0224	1.0283	1.0268	1.0284
0.9	0.6472	0.6185	0.6323	0.6447	0.6544	45.0		1.0232	1.0305	1.0286	1.0315
$1.0 \\ 1.2$	0.6608 0.6878	0.6338	0.6472 0.6743	0.6594 0.6859	0.6690	50·0 60·0	1.0057 1.0045	1·0234 1·0244	1·0328 1·0367	1.0304	1.0341
1.4	0.7125	0.6610 0.6840	0.6969	0.0839	0.6955 0.7177	70.0	1.0037	1.0260	1.0405	1.0337	1.0389 1.0435
1.6	0.7331	0.7030	0.7157	0.7266	0.7362	80.0	1.0059	1.0272	1.0442	1.0370 1.0398	1.0477
1.8	0.7487	0.7185	0.7314	0.7418	0.7516	90.0	1.0063	1.0279	1.0476	1.0426	1.0517
2.0	0.7649	0.7314	0.7445	0.7546	0.7644	100.0	1.0084	1.0289	1.0505	1.0448	1.0554
$2.5 \\ 3.0$	0·7910 0·8081	0.7552	0.7685 0.7841	0.7782	0.7883			r* 0(2.4	*/0(1.1)*		
3.5	0.8198	0.7695	0.7841	0.7941 0.8051	0.8042 0.8151			$L_{ij}^* = \Omega_{ij}^{(2,4)}$	(/ 12 _{ij}		
4.0	0.8293	0.7881	0.8022	0.8127	0.8228	0.0		0.8610	0.8610	0.8610	0.8610
5.0	0.8401	0.7963	0.8109	0.8222	0.8322	0.1		0.8642	0.8694	0.8782	0.8792
6·0 7·0	0·8476 0·8513	0.7997	0·8152 0·8171	0.8271	0.8371	0.2	0.07//	0.8917	0.8932	0.9001	0.8984
8.0	0.8538	0·8012 0·8016	0.8171	0-8296 0-8308	0·8400 0·8413	0·3 0·4	0·8766 0·8698	0.8874 0.8714	0.8937 0.8800	0-9010 0-8878	0.9020
9.0	0.8558	0.8010	0.8178	0.8313	0.8422	0.4	0.8620	0.8592	0.8800	0.8878	0.8913 0.8806
10.0	0.8585	0.8003	0.8174	0.8314	0.8424	0.6	0.8578	0.8537	0.8618	0.8698	0.8744
12.0		0.7986	0.8164	0.8309	0-8428	0.7	0.8584	0.8535	0.8606	0.8682	0.8726
14·0 16·0		0·7969 0·7953	0.8154 0.8145	0·8304 0·8297	0·8427 0·8426	0.8	0.8618	0.8567	0.8628	0.8698	0.8744
18.0		0.7933	0.8145	0.8297	0.8426	1.0	0·8674 0·8780	0.8624 0.8696	0.8680 0.8742	0·8742 0·8798	0-8780 0-8837
20.0	0.8590	0.7929	0.8128	0.8288	0.8425	1.2	0.8784	0.8851	0.8890	0.8915	0.8969
25.0	0.8619	0·7911 0·7899	0-8117 0-8114	0.8283	0.8430	1.4	0.9042	0.9012	0.9040	0.9069	0.9103
30.0			11.8114	0.8280	0.8437	1.6	0.9185	0.9160	0.9181	0.9200	0.9232

SAXENA & JOSHI: THERMAL DIFFUSION F	FACTOR OF BIN.	ARY GAS MIXTURES
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T_{ij}^{*}	L-J(12-6) potential	Modified	Buckingha	am (Exp-6	potential	T_{ij}^{*}	L- $J(12-6)$ potential		Buckingha		
	porentiai	$\alpha = 12$	$\alpha = 13$	a=14	$\alpha = 15$		potential	x=12	x=13	x = 14	x=15
		$L_{ij}^* = \Omega_{ij}^{(2)}$	$^{4)*}/\Omega_{ij}^{(1,1)*}$					$L_{ij}^* = \Omega_{ij}^{(2,4)}$	$)^{*} / \Omega_{ij}^{(1,1)^{*}}$		
1.8	0.9303	0.9292	0.9309	0.9315	0.9335	16.0		1.0601	1.0562	1.0543	1.0503
2.0	0.9414	0.9410	0.9426	0.9421	0.9458	18.0		1.0638	1.0598	1.0561	1.0524
2.5	0.9632	0.9647	0.9658	0.9636	0.9674	20.0	1.0466	1.0670	1.0624	1.0583	1.0546
3.0	0.9792	0.9826	0.9826	0.9800	0.9831	25.0		1.0754	1.0727	1.0627	1.0586
3.5	0.9913	0.9956	0.9956	0.9924	0.9951	30.0	1.0518	1.0828	1.0774	1.0660	1.0623
4.0	1.0005	1.0055	1.0051	1.0023	1.0091	35.0		1.0901	1.0815	1.0698	1.0658
5.0	1.0139	1.0196	1.0184	1.0169	1.0175	40.0	1.0544	1.0971	1.0906	1.0731	1.0694
6.0	1.0210	1.0282	1.0262	1.0265	1.0259	45.0		1.1034	1.0966	1.0763	1.0727
7.0	1.0265	1.0349	1.0331	1.0281	1.0320	50.0	1.0571	1.1097	1.1028	1.0793	1.0758
8.0	1.0302	1.0397	1.0373	1.0384	1.0363	60.0	1.0597	1.1211	1.1130	1.0851	1.0811
9.0	1.0336	1.0435	1.0409	1.0416	1.0389	70.0	1.0606	1.1321	1.1226	1.0878	1.0860
10.0	1.0358	1.0466	1.0436	1.0444	1.0413	80.0	1.0622	1.1418	1.1317	1.0954	1.0883
12.0		1.0520	1.0483	1.0483	1.0451	90.0	1.0635	1.1505	1.1399	1.0974	1.0953
14.0		1.0562	1.0527	1.0518	1.0483	100.0	1.0731	1.1595	1.1473	1.1036	1.0991

TABLE 1 VALUES OF RATIOS OF COLLISION	INTEGRALS WHICH	OCCUR IN HIGHER	Approximations	TO ar - contd
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The expressions for the various h_k are given in Appendix II in terms of C_{ij} which are defined somewhat differently than by Mason⁵⁴. Following Mason⁵⁴, all the α_T expressions according to Kihara-Mason approximation scheme have been primed to distinguish them from those obtained on Chapman-Cowling procedure which have been left unprimed.

For those binary mixtures in which the heavier component is in trace the above expressions assume the following simpler forms⁵⁷:

$$[\alpha_{T+1}^{\prime \gamma}(X_1 \rightarrow 0) = (6C_{12}^* - 5)(-S_2/Q_2') \quad \dots (19)$$

and $[\mathbf{z}'_{T}]_{2}(X_{1} \rightarrow 0)$ is again given by Eq. (16) except K_{1} and K_{2} are now given by

$$K_1(X_1 \to 0) = \frac{C_{-1-2}''}{C_{-1-1}'' C_{-2-2}''} + \frac{C_{12}'^2}{C_{11}' C_{22}'} \qquad \dots (20)$$

and

$$\begin{split} K_{2}(X_{1} \rightarrow 0) &= \frac{5}{2} \left(\frac{M_{1} + M_{2}}{2M_{2}} \right)^{4} \left[\frac{a_{10}C_{-12}C_{12}'}{C_{11}'C_{22}'C_{-1-1}''} - \frac{a_{-10}C_{12}'^{2}}{C_{11}'C_{22}'C_{-1-1}''} \right] \\ &+ \frac{a_{10}C_{1-2}C_{-1}''}{C_{-2-2}'C_{-1-1}'C_{11}'} - \frac{a_{10}C_{-22}C_{12}'C_{-1-2}'}{C_{11}'C_{22}'C_{-1-1}''} - \frac{a_{20}C_{-12}}{C_{22}'C_{-1-1}''} \\ &+ \frac{a_{20}C_{-11}C_{12}'}{C_{11}'C_{22}'C_{-1-1}''} - \frac{a_{0-2}C_{-1-2}''}{C_{-1-1}''C_{-2-2}''} + \frac{a_{02}C_{-22}C_{-1-2}''}{C_{-1-1}''C_{22}'C_{-2-2}''} \right] \\ &- \frac{5}{2} \left(\frac{M_{1} + M_{2}}{2M_{1}} \right)^{4} \left[\frac{a_{10}C_{-12}''}{C_{-1-1}''C_{11}'C_{-2-2}''} + \frac{a_{20}C_{12}''}{C_{11}'C_{22}''} \right] \quad \dots (21) \end{split}$$

The corresponding expressions for the case of the lighter component in trace ${\rm are}^{\delta 8}$

$$\alpha'_{T_1}(X_2 \to 0) = (6C_{12}^* - 5)(S_1/Q_1') \qquad \dots (22)$$

$$K_1(X_2 \to 0) = \frac{C_{-1/2}'}{C_{-1/1}'} C_{-2-2}' + \frac{C_{12}''}{C_{11}'} C_{22}'' \qquad \dots (23)$$

and

$$\begin{split} K_{2}(X_{2} \rightarrow 0) &= \frac{5}{2} \left(\frac{M_{1} + M_{2}}{2M_{1}} \right)^{\frac{1}{2}} \left[\frac{a_{-10}C_{1-2}C_{-1-2}'}{C_{-1-1}'C_{11}'C_{-2-2}'} \\ &- \frac{a_{10}C_{-1-2}'}{C_{11}'C_{-1-1}'C_{-2-2}'} + \frac{a_{0-1}C_{-12}C_{12}''}{C_{22}'C_{-1-1}'C_{11}''} - \frac{a_{0-1}C_{2-2}C_{-2}'}{C_{22}''C_{-2-2}'C_{-1-1}''} \\ &- \frac{a_{0-2}C_{1-2}}{C_{11}'C_{-2-2}'} + \frac{a_{0-2}C_{1-1}C_{-1-2}'}{C_{11}'C_{-1-2}'} - \frac{a_{20}C_{12}''}{C_{11}'C_{22}'} + \frac{a_{-20}C_{2-2}C_{12}''}{C_{11}'C_{-2-2}''} \\ &- \frac{5}{2} \left(\frac{M_{1} + M_{2}}{2M_{2}} \right)^{\frac{1}{2}} \left[\frac{a_{0-2}C_{-1-2}'}{C_{-1-1}'C_{-2-2}''} + \frac{a_{0-1}C_{12}''}{C_{11}'C_{22}'C_{-1-1}'} \right] \quad \dots (24) \end{split}$$

In the above formulae certain combinations of C''_{ij} can be cast in the following simplified form:

$$\frac{C_{12}^{"'}}{C_{-1-1}^{"}C_{2-2}^{"'}} = \frac{1}{42} [7 - 8E_{22}^{*'}]^2 \qquad \dots (25)$$

and

$$\frac{C_{12}^{"2}}{C_{11}^{"}C_{22}^{"2}} = \frac{1}{42} 7 - 8E_{11}^{\bullet}]^2 \qquad \dots (26)$$

The above rigorous expressions are tedious for numerical calculation and any simplification without impairing the accuracy will be highly desirable. Saxena *et al.*⁵⁹ have suggested expansion of the various determinants in powers of $M = (M_2/M_1)$ neglecting those terms which explicitly contain the power of M higher than two. This method of simplification will be referred to as 'explicit mass approximation' and yields the following expressions for the three determinants which occur in $[\alpha_T]_2$ [Eq. (3)]:

$$\begin{split} A_{00}^{(2)} &= (T_{11}T_{22} - T_{12}^2)(T_{-1-1}T_{-2-2} - T_{-1-2}^2) \qquad \dots (27) \\ A_{01}^{(2)} &= M^{3/2}(1+M) \stackrel{2}{\to} T_{01}T_{22}(T_{-1-1}T_{-2-2} - T_{-1-2}^2) \\ &+ (1+M) \stackrel{-5/2}{\to} T_{01}T_{22}(T_{-11}T_{-2-2} - (1+M)^{-1}T_{1-2}T_{-1-2}) \\ &- (1+M) \stackrel{-7/2}{\to} T_{02}T_{22}(T_{-11}T_{-1-2} - (1+M)^{-1}T_{-1-1}T_{1-2}) \\ &\dots (28) \end{split}$$

and

The defining relations for the various T_{ij} occurring in Eqs. (27)-(29) are given in Appendix I. The T_{ij} like a_{ij} are functions of M_i , X_i , $\Omega_{ij}^{(l,n)*}$ and r_m or r_0 .

For the two limiting cases, the simplifying criterion of Saxena *et al.*⁵⁹ yields the following expressions corresponding to Eqs. (10) and (12):

$$\begin{aligned} (x_1)_2(X_1 \to 0) &= \frac{5(1+M)^4}{2\sqrt{2}} |a_{10}a'_{22}(a'_{11}a'_{22} - a'_{12})^{-1} \\ &+ \{M^{-\frac{4}{2}}(a'_{11}a'_{22} - a'_{12})(a_{-10}a''_{-2-2} - a_{-20}a''_{-1-2}) \\ &+ a_{10}a'_{22}(a_{1-2}a''_{-1-2} - a''_{-2-2}a_{-11})\}\{(a'_{11}a'_{22} - a'_{12}^2) \\ &\times (a''_{-2-2}a''_{-1-1} - a''_{-1-2})\}^{-1}] \quad \dots (30) \end{aligned}$$

and

$$\begin{aligned} \mathbf{z}_{T-2}(X_{2} \rightarrow 0) &= \frac{5(1+M)^{\frac{3}{2}}}{2\sqrt{2}} ||_{2}a_{10}a_{22}''(a_{1-1}'a_{2-2}'-a_{1-2}'^{\frac{2}{2}}) \\ &+ a_{1-1}a_{22}''(a_{-20}a_{1-2}'-a_{-10}a_{2-2}') + a_{1-2}a_{22}''(a_{-10}a_{1-2}'-a_{-20}a_{1-1}')|_{2} ||_{2}a_{1-1}'a_{2-2}'-a_{1-2}''(a_{1-1}'a_{2-2}'-a_{1-2}'')|_{2}a_{1-1}''(a_{1-1}'a_{2-2}'-a_{1-2}'')|_{2}a_{1-1}''(a_{1-1}'a_{2-2}'-a_{1-2}'')|_{2}a_{1-1}''(a_{1-1}'a_{2-2}'-a_{1-2}'')|_{2}a_{1-1}''(a_{1-1}'a_{2-2}'-a_{1-2}'')|_{2}a_{1-1}''(a_{1-1}'a_{2-2}'-a_{1-2}'')|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}''|_{2}a_{1-1}$$

If we try to derive Eqs. (30) and (31) from Eqs. (3) and (27)-(29) by going to the limiting cases we find that for the lighter component in trace we get the same result as Eq. (31) while for the case when the heavier component is in trace we get instead of Eq. (30) the following expression:

$$\begin{aligned} |z_{T_{2}}(X_{1} \rightarrow 0) &= \frac{5(1+M)^{4}}{2\sqrt{2}} \begin{bmatrix} a_{10}a_{22}' \\ (a_{11}'a_{22}' - a_{12}') \\ (a_{11}'a_{22}' - a_{20}'' - a_{12}') \\ &+ M^{-\frac{1}{4}} \begin{pmatrix} a_{10}a_{22}' - a_{20}a_{12}'' \\ (a_{22}' - a_{11}'' - a_{12}'') \\ (a_{22}' - a_{11}'' - a_{12}'') \end{bmatrix} \dots (30a) \end{aligned}$$

Thus, these two operations do not always commute. The reason is that when the explicit mass approximation is applied to the general case what matters is the explicit power of M in a_{ij} while in the case of trace the explicit powers of M associated with a'_{ij} and a''_{ij} are important.

In the case of binary mixtures with very small values of M, we can further simplify the expressions for the three determinants [Eqs. (27)-(29)] by expressing the various T_{ij} products also in powers of M and neglecting all those terms which involve the power of M higher than a certain value. This simplifying procedure will be referred to as ' implicit mass approximation'. The resulting expression for $|\alpha_{T_2}|$ can be finally expressed in the following simple form:

$$\alpha_{T,2} = 5(6C_{12}^* - 5)(1 + M)^{-3/2} \begin{bmatrix} Z_2 & M^{3/2}Z_1 \\ X_1 Z_3'' - X_2 Z_3' Z_3'' \end{bmatrix} \dots (32)$$

The expressions for Z_1 , Z_2 , Z_3' and Z_3'' depend upon the power of M up to which the terms are considered. Fairly accurate expressions are obtained by retaining terms up to M^2 . The only exception is Z_1 in which we retain terms up to $M^{\frac{1}{2}}$ only as it is explicitly multiplied by $M^{3/2}$. These expressions are given in Appendix III.

For systems which have comparatively smaller values of M, Eq. (32) can be further simplified by neglecting the second term within square brackets. Consequently, we have

$$[\alpha_T]_2 = 5(6C_{12}^* - 5)(1 + M)^{-3/2} [Z_2/X_1 Z_3''] \quad \dots (32a)$$

Mostly for such systems the defining relations for Z_2 and Z''_3 given in Appendix III can be used in much simpler forms by retaining terms up to M only.

Saxena and Dave⁵⁷ have earlier applied this implicit mass approximation to the rigorous expressions corresponding to the two limiting cases. They expressed all the a_{ij} in powers of M and gave the final expressions by neglecting all those terms in the α_T expression which contained powers of Mhigher than a certain value. For mixtures in which the heavier component is in traces, they gave three different sets of approximate formulae which correspond to retaining terms containing zero, first and second powers of M. These three formulae are distinguished from one another by assigning superscripts a, b and c respectively. Thus, we have⁵⁷

$$[\alpha_T]_1^a(X_1 \to 0) = 5(6C_{12}^* - 5)/4\sqrt{2}Z_{22} \qquad \dots(33) [\alpha_T]_1^b(X_1 \to 0) = [\alpha_T]_1^a(X_1 \to 0) \left[1 - M \left(\frac{3}{2} + \frac{2\sqrt{2}}{15} Z_{22} \right) \right]$$

$$\begin{aligned} [\alpha_T]_1^c(X_1 \to 0) &= [\alpha_T]_1^a(X_1 \to 0) \bigg[1 - M \bigg(\frac{3}{2} + \frac{2\sqrt{2}}{15} Z_{22} \bigg) \\ &+ M^2 \bigg\{ \frac{1}{24} - \frac{2\sqrt{2}}{15} Z_{22} + \frac{2}{5} B_{12}^* \\ &+ \frac{8}{15} A_{12}^* \bigg(1 + \frac{2\sqrt{2}}{15} Z_{22} \bigg) \bigg\} \bigg] \qquad \dots (35) \end{aligned}$$

$$[\alpha_T]_2^a(X_1 \rightarrow 0) = [\alpha_T]_1^a(X_1 \rightarrow 0) \left\lfloor \frac{b + 4cd}{(b - c^2)} \right\rfloor \qquad \dots (36)$$

$$[\alpha_T]_2^b(X_1 \to 0) = [\alpha_T]_1^a(X_1 \to 0) \frac{1}{120(b-c^2)} [120(b+4cd) - M\{16\sqrt{2Z_{22}(b-c^2)} + 180b + 1200cd\}] \dots (37)$$

and

$$[\alpha_T]_2^o(X_1 \rightarrow 0) = [\alpha_T]_1^a(X_1 \rightarrow 0) \frac{1}{120(b-c^2)} [120(b+4cd)]$$

$$-M\{16\sqrt{2Z_{22}}(b-c^2)+180b+1200cd\}-M^2\{16\sqrt{2}gZ_{22}\times(b-c^2)-2100cd-225b+4be+128fc\}\} \qquad \dots (38)$$

The defining relations for the various quantities occurring in Eqs. (33)-(38) are given in Appendix IV.

For mixtures containing the lighter component in trace we have⁵⁸

$$\begin{aligned} [\alpha_T]_1(X_2 \to 0) &= \frac{(6C_{12}^* - 5)}{2Y} \left[1 - M \binom{8A_{12}^*}{5Y} - 1 \right] + \frac{15M^{3/2}}{2\sqrt{2}Z_{11}} \\ \times \left(1 - \frac{8A_{12}^*}{15} \right) - \frac{3M^2}{Y} \left\{ 1 - \frac{8}{15} A_{12}^* \binom{8A_{12}^*}{5Y} - 1 \right\} + \dots \end{aligned}$$

$$(39)$$

and

$$\begin{split} &[\alpha_T]_2(X_2 \rightarrow 0) = [\alpha_T]_1^*(X_2 \rightarrow 0)(1 + MB_1 + M^2B_2) \\ &\times [(1 - B_{13})^{-1} \{1 - MB_{13}(B_3 + B_5)(1 - B_{13})^{-1} + M^2B_{13} \\ &\times (1 - B_{13})^{-1}(B_{13}(B_3 + B_5)^2(1 - B_{13})^{-1} + B_4 + B_6 + B_3B_5)\}| \\ &\times [1 - (1 + MB_5 + M^2B_6)(B_9d/B_{10})] - \frac{5\sqrt{2}M^{3/2}}{16Z_{11}}(6C_{12}^{\star} - 5) \\ &\times (1 - B)^{-1}(5B_{10}Y - 4B_9^2)^{-1}[10YB_{10} - BB_9^2] \\ &- B_{11}(B_{10} - B_9d) - B_{12}(10Yd - 8B_9)] + \dots \dots \dots (40) \\ &\text{where} \end{split}$$

$$[\alpha_T]_1^a(X_2 \to 0) = (6C_{12}^* - 5)/2Y \qquad \dots (41)$$

Here Y, B and B_i are functions of the reduced collision integrals and their expressions are given in Appendix IV.

Similar formulae have also been derived starting from the rigorous expressions for α_T obtained on Kihara-Mason approximation scheme^{54,65}. the Saxena et al.59 applied the explicit mass approximation and simplified Eqs. (17) and (18) by expanding $h_i h_k$ in powers of M and retaining terms which explicitly involved the power of M up to a certain definite value. Thus they found after some lengthy algebraic manipulations that the leading terms in h_3h_5 , h_4h_{-6} , $h_{-3}h_{-5}$ and $h_{-4}h_6$ possess the explicit power of M as 0, 7/2, 0 and 5/2 respectively. If all the terms with powers of M as 5/2 and higher are neglected one gets the following simple expression for K_1 :

$$K_1' = h_3 h_5 + h_{-3} h_{-5} \qquad \dots (42)$$

Similarly, the leading powers of M in the various terms of K_2 are 1/2 for $h_{-1}h_{-5}$, $h_{-2}h_3$; 3/2 for h_1h_5 , $h_{-2}h_4$; 5/2 for $h_{-1}h_{-6}$, h_2h_{-3} ; 3 for h_1h_6 ; and 7/2 for h_2h_4 . Again if the terms with powers of M as 5/2 and higher are neglected, one gets the following simple expression for K_2 :

$$K_{2}' = \frac{5}{2\sqrt{2}X_{1}} \left(\frac{1+M}{M}\right)^{\frac{1}{2}} (h_{-1}h_{-5} + h_{-2}h_{3}) - \frac{5}{2\sqrt{2}X_{2}} (1+M)^{\frac{1}{2}} (h_{1}h_{5} - h_{-2}h_{-4}) \qquad \dots (43)$$

Thus the new simplified expression for $[\alpha_T]_2$ is

$$[\alpha_T']_2 = [\alpha_T]_1[1 + K_1'] + K_2' \qquad \dots (44)$$

The two particular cases of Eq. (42) are same as Eqs. (20) and (23) while for K_2 [Eq. (43)] we get

$$\begin{split} K_{2}'(X_{1} \rightarrow 0) &= -\frac{5}{2\sqrt{2}}(1+M)^{4} \begin{bmatrix} a_{10}C_{1-2}''^{2} \\ C_{11}'C_{1-1}'C_{2-2}'^{2} \end{bmatrix} \\ &+ \frac{5}{2\sqrt{2}} \left(\frac{1+M}{M}\right)^{4} \begin{bmatrix} a_{10}C_{12}'C_{-12} \\ C_{11}'C_{22}'C_{-1-1}'' \\ -\frac{a_{20}C_{2}}{C_{1-2}'}C_{1-1}''C_{2-2}'' \end{bmatrix} \qquad \dots (45)$$

and

$$K_{2}(X_{2} \rightarrow 0) = \frac{5}{2\sqrt{2}}(1+M)^{\frac{1}{2}} \\ \times \left[\frac{a_{-10}C_{1-2}C_{-1-2}'}{C_{11}''C_{-1-2}'} - \frac{a_{10}C_{1-2}'^{2}}{C_{11}''C_{-1-1}C_{-2-2}'} \right] \\ + \frac{a_{20}C_{-11}C_{-2-2}'}{C_{11}''C_{-1-2}'} - \frac{a_{20}C_{1-2}}{C_{11}''C_{-2-2}'} - \frac{5}{2\sqrt{2}} \left(\frac{1+M}{M} \right)^{\frac{1}{2}} \\ \times \left[\frac{a_{-10}C_{12}''^{2}}{C_{11}''C_{-2}''C_{-1-1}'} + \frac{a_{20}C_{1-2}'}{C_{-1-1}''C_{-2-2}'} \right] \qquad \dots (46)$$

If the explicit mass approximation is applied to the rigorous expressions for the two limiting cases we get the same results as above except in the case corresponding to Eq. (45) for which we get

$$K'_{2}(X_{1} \rightarrow 0) = -\frac{5}{2\sqrt{2}}(1+M)^{\frac{1}{2}} \begin{bmatrix} a_{10}C''_{1-2} \\ C'_{11}C''_{-1-1}C''_{2-2} \end{bmatrix} + \frac{5}{2\sqrt{2}} \begin{bmatrix} 1+M \\ -M \end{bmatrix}^{\frac{1}{2}} \begin{bmatrix} a_{10}C_{1-2}C''_{-1-2} \\ C''_{-2-2}C''_{-1-1}C'_{11} \\ -\frac{a_{0-2}C''_{-1-2}}{C''_{-1-1}C'_{2-2}} \end{bmatrix} \dots (45a)$$

Here again we find that these two operations do not commute and, therefore, their order of application is important.

The implicit mass expansion technique can also be applied to the rigorous expressions for K_1 and K_2 [Eqs. (17) and (18)]. In actual practice, after this lengthy and tedious operation is completed, numerical calculations revealed that the expressions for K_1 and K_2 are not rapidly convergent. It was realized that the contribution of the second term in the expression for K_2 as given by Eq. (43) is negligible. Hence as an alternative to Eq. (43) for systems with small value of M we have

$$K_{2}'' = \frac{5}{2\sqrt{2}X_{1}} \left(\frac{1+M}{M}\right)^{4} (h_{1}h_{5} + h_{2}h_{3}) \quad \dots (47)$$

and consequently

$$[\alpha_T']_2 = [\alpha_T]_1[1+K_1'] + K_2'' \qquad \dots (48)$$

This implicit mass expansion technique has, however, been applied by Saxena and Dave^{57,58} with success for the two limiting cases. The expressions given by them are

$$\begin{aligned} \| \alpha_T' \|_{1}^{a} (X_1 \to 0) &= \| \alpha_T \|_{1}^{a} (X_1 \to 0) & \dots (49) \\ \| \alpha_T' \|_{1}^{b} (X_1 \to 0) &= \| \alpha_T \|_{1}^{b} (X_1 \to 0) & \dots (50) \end{aligned}$$

$$\begin{bmatrix} \mathbf{z}_{T}^{\prime} \end{bmatrix}_{1}^{c} (X_{1} \rightarrow 0) = \begin{bmatrix} \mathbf{z}_{T} \end{bmatrix}_{1}^{a} \begin{bmatrix} 1 - M \begin{pmatrix} 3 \\ 2 \end{pmatrix} + \frac{2\sqrt{2}}{15} Z_{22} \end{pmatrix} \\ + M^{2} \begin{bmatrix} 13 \\ 24 \end{pmatrix} \begin{bmatrix} -\frac{2\sqrt{2}}{15} Z_{22} \end{bmatrix} + \frac{8}{15} A_{12}^{*} \left(1 + \frac{2\sqrt{2}}{15} Z_{22} \right) \end{bmatrix} \qquad \dots (51)$$

and

$$\begin{bmatrix} \alpha_T' \ _2^a(X_1 \to 0) = \lceil \alpha_T \rceil_1(X_1 \to 0) \\ \times \left\{ 1 + \frac{(8E_{22}^* - 7)^2}{42} \right\} + \frac{2}{21} \lceil \alpha_T \rceil_1^a(X_1 \to 0) \\ \times (8E_{22}^* - 7) \left\{ 1 - \frac{3(5 - 4B_{12}^*)}{4(6C_{12}^* - 5)} \right\} \dots (52)$$

$$\begin{bmatrix} \alpha_T' \ _2^b(X_1 \to 0) = \| \alpha_T' \|_2^b(X_1 \to 0) + M \begin{bmatrix} (0 \ _{12} - 5)(8E_{22} - 7)^2 \\ -5 \ _{12}^b(X_1 \to 0) \begin{bmatrix} 5 \\ 21(8E_{22}^* - 7) \left(1 - \frac{3(5 - 4B_{12}^*)}{4(6C_{12}^* - 5)} \right) \end{bmatrix} \\ \dots (53)$$

$$[\mathbf{z}'_T; (X_1 \rightarrow 0)]$$

$$= \left| \mathbf{z}_{T}^{\prime} \, {}_{2}^{b} (X_{1} \rightarrow 0) + M^{2} \left[\frac{(6C_{12}^{\star} - 5)(8E_{22}^{\star} - 7)(1 - 8A_{12}^{\star}/15)}{252} + \mathbf{z}_{T} \right]_{1}^{a} (X_{1} \rightarrow 0) \right]$$

$$+ \left| \mathbf{z}_{T} \right]_{1}^{a} (X_{1} \rightarrow 0) \frac{21}{125} (6C_{12}^{\star} - 5)^{2} + \left| \mathbf{z}_{T} \right]_{1}^{a} (X_{1} \rightarrow 0) \right]$$

$$\times \left\{ \frac{5}{12} (8E_{22}^{\star} - 7) \left(1 - \frac{3(5 - 4B_{12}^{\star})}{4(6C_{12}^{\star} - 5)} \right) - \frac{21}{125} (6C_{12}^{\star} - 5)^{2} - \frac{4}{315} (8E_{22}^{\star} - 7) \left(16H_{12}^{\star} - 14A_{12}^{\star} - 7(6C_{12}^{\star} - 5) \right) \right\} \right] \dots (54)$$

If the lighter component is in trace Saxena and Dave⁵⁸ have shown that 1.1.

$$|z_{T_{1}}(X_{2})| = 1/2(6C_{12}^{*}-5)\left[1+M\left(1-\frac{8}{15}A_{12}^{*}\right)+M^{3/2}\frac{15}{2\sqrt{2Z_{11}}}\right] \times \left(1-\frac{8A_{12}^{*}}{15}\right)-3M^{2}\left\{1+\frac{8}{15}A_{12}^{*}\left(1-\frac{8}{15}A_{12}^{*}\right)\right\}+\dots\right]$$
...(55)

and

$$\begin{split} & [\mathbf{x}_{T}^{+}(X_{2} \rightarrow 0)] \\ &= |\mathbf{x}_{T}^{+}(X_{2} \rightarrow 0) \left\{ 1 + \frac{2}{5} (6C_{12}^{*} - 5)d + \frac{7}{25} (6C_{12}^{*} - 5)^{2} \right\} \\ &- M \left\{ |\mathbf{x}_{T}|(X_{2} \rightarrow 0) \left(8B_{14} + \frac{24}{5}A_{12}^{*} \right) \right. \end{split}$$

$$+ \frac{1}{84} (8E_{11}^{*} - 7)^{2} (6C_{12}^{*} - 5) \left(\frac{8}{5}A_{12}^{*} - 1\right)$$

$$- \frac{(6C_{12}^{*} - 5)^{2}d}{5} \left(4B_{14} + \frac{24}{5}A_{12}^{*} - 1\right) \right\}$$

$$+ M^{3/2} \frac{(6C_{12}^{*} - 5)^{2}}{5\sqrt{2}Z_{11}} \left\{\frac{7}{4} (6C_{12}^{*} - 5)$$

$$- 7 (6C_{12}^{*} - 5)(1 + B_{11}) - 2d(2A_{12}^{*} + 5B_{14}) \right\}$$

$$- M^{2} \left[[\alpha_{T}]_{1} (X_{2} - >0) \left\{3 - \frac{448A_{12}^{*2}}{25} + \frac{192}{35}K_{12}^{*} \right]$$

$$- \frac{192}{5}A_{12}^{*}B_{14} - 16B_{14}^{2} \right\}$$

$$- \left\{\frac{1}{84} (8E_{11}^{*} - 7)^{2} (6C_{12}^{*} - 5) \left(3 + \frac{8A_{12}^{*}}{5} - \frac{64A_{12}^{*2}}{25}\right)$$

$$+ \frac{d}{5} (6C_{12}^{*} - 5)^{2} \left(6 + 4B_{14} + \frac{24}{5}A_{12}^{*} + \frac{192}{35}K_{12}^{*} \right)$$

$$- \frac{96}{5}A_{12}^{*}B_{14} - \frac{448}{25}A_{12}^{*2} \right\} + \dots \qquad \dots (56)$$

The expression for B_{14} is given in Appendix IV. Saxena and Joshi^{60,61} noticed that the accuracy of the formulae derived on Chapman-Cowling approximation scheme using explicit mass expansion technique gets considerably improved if all those discarded terms which contain the product of two or more diagonal terms of the determinant $A^{(m)}$ are also retained irrespective of their power of M while simplifying $A^{(m)}_{ij}$. The reason for this is that the magnitude of the diagonal terms67 is usually much larger than the non-diagonal terms. If this criterion is used for simplifying the determinants of Eq. (3) we get the following expressions⁶¹ instead of Eqs. (27)-(29):

$$\begin{aligned} A_{00}^{(2)} &= (T_{11}T_{22} - T_{12}^2)(T_{-1-1}T_{-2-2} - T_{-1-2}^2) - M^{5/2}(1+M)^{-5} \\ &\times \{T_{-11}^2T_{22}T_{-2-2} + M^2(1+M)^{-2}T_{-12}^2T_{11}T_{-2-2} \\ &+ (1+M)^{-2}T_{1-2}^2T_{-1-1}T_{22} \\ &+ M^2(1+M)^{-4}T_{-22}^2T_{11}T_{-1-1}\} \qquad \dots (57) \end{aligned}$$

$$\begin{split} A_{01}^{(2)} &= M^{3/2} (1+M)^{-2} (T_{10} T_{22} (T_{-1-1} T_{-2-2} - T_{-1-2}^{2}) \\ &+ (1+M)^{-5/2} T_{10} T_{22} (T_{-11} T_{-2-2} - (1+M)^{-1} T_{1-2} T_{-1-1} \} \\ &- M (1+M)^{-1} T_{20} T_{-1-1} T_{12} T_{-2-2} \\ &- (1+M)^{-7/2} T_{-20} T_{22} (T_{-11} T_{-1-2} \\ &- (1+M)^{-1} T_{1-2} T_{-1-1} \} \end{bmatrix} \qquad \dots (58)$$

and

$$\begin{split} A_{0^{-1}1}^{(2)} &= M^4 (1+M)^{-2} [(T_{11}T_{22} - T_{12}^2) \{ (1+M)^{-1}T_{-20}T_{-1-2} \\ &- T_{-10}T_{-2-2} \} - M^{5/2} (1+M)^{-5/2} \{ T_{-11}T_{10}T_{22}T_{-2-2} \\ &+ M^2 (1+M)^{-2}T_{20}T_{-12}T_{11}T_{-2-2} \}] \qquad \dots (59) \end{split}$$

The expressions for T_{ij} are given in Appendix I.

Saxena and Joshi⁶⁰ also derived the following expressions for $[\alpha_T]_2$ in the two limiting cases:

$$\begin{split} &[\alpha_{T_{-}^{1}2}(X_{1} \rightarrow 0) \\ &= \frac{5}{2\sqrt{2}}(1+M)^{\frac{1}{2}}(a_{10}/a_{11}') + \{a_{10}a_{22}'(a_{-1-2}'a_{-21} \\ &-a_{-2-2}'a_{-11}) - a_{-2-2}'a_{02}a_{-12}a_{11}' + (a_{11}'a_{22}' - a_{12}'^{2})(a_{-10}'a_{-2-2}'' \\ &-a_{-20}'a_{-1-2}'')\}M^{-\frac{1}{2}}\{(a_{11}'a_{22}' - a_{12}'^{2})(a_{-2-2}'a_{-1-1}' - a_{-1-2}'')\}^{-1}\} \\ &\dots (60) \end{split}$$

and

$$\begin{split} [a_{T}]_{2}^{\dagger}(X_{2}\rightarrow 0) &= \frac{5}{2\sqrt{2}}(1+M)^{\frac{1}{2}} [a_{10}a_{22}''(a_{11}''a_{22}''-a_{12}'')^{-1} \\ &+ \{a_{1-1}a_{22}''(a_{-20}a_{1-2}'-a_{-10}a_{-2-2}') + a_{1-2}a_{22}''(a_{-10}a_{1-2}'-a_{-20}'a_{-1-2}') \} \{a_{1-1}'a_{2-2}'-a_{-22}''a_{-1-2}'')^{-1}\} \\ &- a_{-20}a_{-1-1}\} \{(a_{-1-1}'a_{-2-2}'-a_{-2-2}'a_{-1-2}')(a_{11}'a_{22}'-a_{12}'')^{-1}\} \\ &+ M^{-\frac{1}{2}}(a_{-10}a_{-2-2}'-a_{-20}a_{-1-2}')(a_{-1-1}'a_{-2-2}'-a_{-1-2}')^{-1}\} \\ &\dots (61) \end{split}$$

Numerical calculations based on the above equations showed considerable refinement in respect of the accuracy of the computed values and this led Saxena and Joshi^{62,63} to exploit this as an additional independent criterion for simplifying the rigorous α_T expressions. This procedure of simplification, which will be called hereafter 'diagonal approximation', thus consists in retaining only those terms which contain the product of diagonal terms of the determinant $A^{(m)}$, i.e. elements a_{ii} or their residuals C_{ii} in the case of Kihara-Mason approximation procedure.

The Chapman-Cowling $[\alpha_T]_m$ expression gets considerably simplified if one retains in the expansion of the determinants $A_{ij}^{(m)}$ only those terms which contain the product of two or more diagonal elements of the determinant $A^{(m)}$. The simplified expressions for the determinants which occur in $[\alpha_T]_2$ are⁶³

$$\begin{aligned} A_{00}^{(2)} &= a_{11}a_{-2-2}(a_{-1-1}a_{22}-a_{-12}^2) - a_{-2-2}(a_{-1-1}a_{12}^2+a_{22}a_{-11}^2) \\ &- a_{11}(a_{22}a_{-1-2}^2+a_{-22}^2a_{-1-1}) - a_{-1-1}a_{22}a_{1-2}^2 \qquad \dots (62) \end{aligned}$$

$$A_{01}^{(2)} = a_{-2-2}a_{-1-1}(a_{10}a_{22} - a_{20}a_{12}) -a_{22}(a_{-2-2}a_{-10}a_{1-1} + a_{-20}a_{-1-1}a_{-21}) \qquad \dots (63)$$

and

$$A_{0-1}^{(2)} = a_{-2-2}a_{22}(a_{-10}a_{11} - a_{-11}a_{10}) -a_{11}(a_{-2-2}a_{-12}a_{20} + a_{-20}a_{-1-2}a_{22}) \qquad \dots (64)$$

The expressions for the two limiting cases can also be derived by applying the diagonal approximation procedure to Eqs. (10) and (12). This leads to the following expressions:

$$\begin{aligned} & [\alpha_T]_2(X_1 \to 0) = \frac{5}{2\sqrt{2}} [a_{-2-2}'a_{-1-1}'(a_{11}'a_{22}' - a_{12}') \\ & -a_{11}'a_{22}'a_{-1-2}'']^{-1} \left[\left(\frac{M_1 + M_2}{M_1}\right)^{\frac{1}{2}} \{a_{-2-2}'a_{-1-1}'(a_{10}'a_{22}') \right] \end{aligned}$$

$$= a_{20}a'_{12} \left\{ + \left(\frac{M_1 + M_2}{M_2} \right)^{\frac{1}{2}} \left\{ a'_{11}a'_{22}(a''_{2-2}a_{-10} - a_{-20}a''_{-1-2}) - a''_{-2-2}(a_{-11}a_{10}a'_{22} + a_{-12}a_{02}a'_{11}) \right\} \right] \qquad \dots (65)$$

and

$$\begin{aligned} \left[\alpha_{T_{-2}}^{1}(X_{2} > 0) &= \frac{5}{2\sqrt{2}} \left[a_{22}^{''}a_{11}^{''}(a_{1-1}^{'}a_{-2-2}^{'} - a_{1-2}^{'2}) \right. \\ &- a_{-1-1}^{'}a_{-2-2}^{''}a_{2}^{''2} \right]^{-1} \left[\left(\frac{M_{1} + M_{2}}{M_{1}} \right)^{\frac{1}{2}} \left\{ a_{-1-1}^{'}a_{-2-2}^{'}(a_{-2}^{''}a_{10}) - a_{20}a_{12}^{''} - a_{22}^{''}(a_{-11}a_{-10}a_{-2-2}^{'} + a_{1-2}a_{0-2}a_{-1-1}^{''}) \right\} \\ &+ \left(\frac{M_{1} + M_{2}}{M_{2}} \right)^{\frac{1}{2}} \left\{ a_{22}^{''}a_{11}^{''}(a_{-10}a_{-2-2}^{'} - a_{-20}a_{-1-2}^{''}) \right\} \quad \dots (66) \end{aligned}$$

Eqs. (65) and (66) can also be derived from Eqs. (3) and (62)-(64) by going to the two limiting cases $X_1 \rightarrow 0$ and $X_2 \rightarrow 0$ respectively.

All these formulae are further simplified by applying the explicit mass expansion procedure in which we neglect those terms that contain explicitly the power of M greater than two. Eqs. (62)-(66) then assume the following simpler forms respectively:

$$\begin{split} A_{00}^{(2)} &= T_{-2-2}T_{-1-1}(T_{11}T_{22} - T_{12}^2) - T_{-1-2}^2T_{11}T_{22} & \dots (67) \\ A_{01}^{(2)} &= M^{3/2}(1+M)^{-2} T_{-2-2}T_{-1-1}T_{10}T_{22} \\ &+ (1+M)^{-5/2}T_{-2-2}T_{-10}T_{-11}T_{22} \\ &+ (1+M)^{-9/2}T_{-20}T_{-21}T_{-1-1}T_{22} \end{bmatrix} & \dots (68) \end{split}$$

$$\begin{array}{l} A_{0-1}^{(2)} = M^{\frac{1}{2}} (1+M)^{-2} |T_{11}T_{22} \{ (1+M)^{-1}T_{-20}T_{-1-2} \\ -T_{-2-2}T_{-10} \} | & \dots (69) \end{array}$$

$$\begin{split} [\alpha_{T}]_{2}(X_{1} \rightarrow 0) &= \frac{5}{2\sqrt{2}} [T_{11}' T_{22}' (T_{-2-2}' T_{-1-1}'' - T_{-2-1}'''_{2-1}) \\ &- M^{2} T_{-2-2}' T_{-1-1}' T_{12}'^{2-1} M (1+M) T_{-2-2}' T_{-1-1}' T_{10} T_{22}' \\ &+ (1+M)^{-3/2} \{ (1+M)^{-1} T_{-20} T_{-2-1}' T_{11}' T_{22}' \\ &- T_{-2-2}' T_{-10} T_{11}' T_{22}' - M^{2} T_{-2-2}'' T_{-11} T_{10} T_{22}' \} | \qquad \dots (70) \end{split}$$

and

$$\begin{split} [\mathfrak{a}_{T}]_{2}(X_{2}\rightarrow 0) &= \frac{5}{2\sqrt{2}} T'_{-2-2}T'_{-1-1}(T''_{11}T''_{22} - T''_{12}) \\ &- T'^{2}_{-1-2}T''_{11}T''_{22}\}^{-1}[M^{3/2}(1+M)^{-3/2}\{T'_{-2-2}T'_{-1-1}T_{10}T''_{22}] \\ &+ T'_{-2-2}T_{-10}T_{-11}T''_{22} + T_{-20}T'_{-1-1}T_{1-2}T''_{22}\} \\ &+ (1+M)T''_{11}T''_{22}(T_{-20}T'_{-1-2} - T'_{-2-2}T_{-10})] \qquad \dots (71) \end{split}$$

The order of applying these two approximations is immaterial and the final results obtained are the same in either case.

Similarly, the expressions for K_1 [Eq. (17)] and K_2 [Eq. (18)] are considerably simplified by applying the diagonal approximation, i.e. all the products h_jh_l are expressed in terms of C_{ij} and only the leading product terms of C_{ij} are retained⁶². We then get

$$K_{1} = \frac{C_{12}^{2}}{C_{11}C_{22}} + \frac{C_{-12}^{2}}{C_{-1-1}C_{22}} + \frac{C_{-21}^{2}}{C_{-2-2}C_{11}} + \frac{C_{-1-2}^{2}}{C_{-1-1}C_{-2-2}} \dots (72)$$

[†]This expression is slightly different from that given in ref. 60 where a few terms with the explicit power of M as 5/2 were also retained.

and

$$K_{2} = -\frac{5}{2\sqrt{2}X_{1}} \left[\frac{1+M}{M}\right]^{\frac{4}{2}} \left[\frac{a_{0}}{C_{-1}}\frac{2C_{-1}}{2} + \frac{a_{02}C_{-12}}{C_{-1}}\right] -\frac{5}{2\sqrt{2}X_{2}} (1+M)^{\frac{4}{2}} \left[\frac{a_{0}}{C_{1}}\frac{2C_{-1}}{2} + \frac{a_{02}C_{12}}{C_{11}C_{22}}\right] \dots (73)$$

For the two limiting cases Eqs. (72) and (73) can be further simplified. The expressions for K_1 in the two cases are the same as Eqs. (20) and (23) while for K_2 we get

$$K_{2}(X_{1} \rightarrow 0) = -\frac{5}{2\sqrt{2}}(1+M)^{\frac{1}{2}} \binom{a_{20}C_{12}}{C_{11}'C_{22}'} -\frac{5}{2\sqrt{2}} \left[\frac{1+M}{M}\right]^{\frac{1}{2}} \left[\frac{a_{20}C_{12}}{C_{22}'C_{-1-1}''} + \frac{a_{0-2}C_{-1-2}''}{C_{-1-1}''C_{-2-2}''}\right] \dots (74)$$

and

$$K_{2}(X_{2} \rightarrow 0) = -\frac{5}{2\sqrt{2}} (1+M)^{\frac{1}{2}} \begin{bmatrix} a_{-20}C_{1-2} + a_{20}C_{12}^{"} \\ C_{11}^{"}C_{-2-2}^{'} + c_{11}^{"}C_{-22}^{"} \end{bmatrix} \\ -\frac{5}{2\sqrt{2}} \begin{bmatrix} 1+M \\ M \end{bmatrix}^{\frac{1}{2}} \begin{bmatrix} a_{-20}C_{1-2}^{'} \\ C_{-1-1}^{'}C_{-2-2}^{'} \end{bmatrix} \dots (75)$$

Eqs. (74) and (75) can also be obtained by applying the diagonal approximation to Eqs. (21) and (24) respectively. If the explicit mass approximation is applied to the expressions for K_1 [Eq. (72)] and K_2 [Eq. (73)], we get

$$K'_{1} = \frac{C_{12}^{2}}{C_{11}C_{22}} + \frac{C_{-1-2}^{2}}{C_{-1-1}C_{-2-2}} \qquad \dots (76)$$

and

$$K_{2}' = -\frac{5}{2\sqrt{2X_{1}}} \left[\frac{1+M}{M}\right]^{\frac{1}{2}} \left[\frac{a_{0-2}C_{-1-2}}{C_{-1-1}C_{-2-2}}\right] \\ -\frac{5}{2\sqrt{2X_{2}}} (1+M)^{\frac{1}{2}} \left[\frac{a_{0-2}C_{1-2}}{C_{-1}C_{-2-2}}\right] \dots (77)$$

If we simplify the expressions for K_1 and K_2 as given by Eqs. (42) and (43) respectively by applying the diagonal approximation we again get Eqs. (76) and (77) respectively. This again illustrates that the order of applying these two approximations is immaterial.

The expression for K'_1 [Eq. (76)] yields for the two limiting cases results which are same as Eqs. (20) and (23); however, for K'_2 [Eq. (77)] the following expressions are obtained:

$$K_{2}'(X_{1} \rightarrow 0) = \frac{5}{2\sqrt{2}} \left(\frac{1+M}{M}\right)^{4} \left[-\frac{a_{0}}{C_{-1-1}'} \frac{2C_{-1-2}''}{C_{-2-2}''}\right] \dots (78)$$

and

$$K'_{2}(X_{2} \rightarrow 0) = \frac{5}{2\sqrt{2}} (1+M)^{\frac{1}{2}} \left[-\frac{a_{0} \cdot 2C_{1-2}}{C''_{11}C'_{-2-2}} \right] + \frac{5}{2\sqrt{2}} \left(\frac{1+M}{M} \right)^{\frac{1}{2}} \left[-\frac{a_{0} \cdot 2C'_{1-2}}{C'_{-1-1}C'_{-2-2}} \right] \dots (79)$$

These results for the two limiting cases can also be derived from Eqs. (20), (23), (74) and (75) by applying the explicit mass approximation.

Relative Appropriateness of Various Formulae

The relative accuracies of the various formulae for α_T have been investigated by performing numerical calculations on specific systems as a function of temperature and composition with a view to choosing a particular formula for a definite gas mixture. The two systems chosen are He-Xe and Ar-Xe. The calculations have been performed according to the Lennard-Jones (12-6) potential parameters listed in Table 2.

Values of α_T computed by both the approximation procedures, viz. Chapman-Cowling and Kihara, and based on rigorous as well as simpler expressions obtained on the basis of various simplifying criteria discussed in the previous section are given for the Ar-Xe system as a function of temperature in Table 3 (Xe in trace) and in Table 4 (Ar in trace), Similar data are given for the He-Xe system in Table 5 (He in trace). Various calculated α_T values for both these systems as a function of temperature around the middle composition and as a function of composition at a fixed temperature are recorded in Tables 6-9.

These calculations indicate that it is essential to consider the contribution of the second, and sometimes of still higher approximations, for a precise knowledge of α_T . From the data presented in Tables 3 and 4, which refer to the Ar-Xe system when one of the components is in trace, we find that the rate of convergence is nearly the same for both the approximation schemes. For this system around the middle composition (Table 6), however, the Chapman-Cowling procedure seems to be pre-ferable to that of Kihara. This inference is also substantiated by the calculation of α_T as a function of composition for this system (Table 8). Thus, on the whole, the Chapman-Cowling formulae should be preferred for this system. A critical examination of these tables further suggests that the contribution of second approximation is small when the heavier component is in trace and increases rather slowly but does assume an appreciable magnitude for the other end of the composition when Ar is in trace. To be specific we find that the difference between the first two approximations increases from an average value of 1.7 per cent when Xe is in trace to 5 per cent when Ar is in trace in the temperature range 500-900°K. On the other hand, at 300°K. this difference remains

TABLE	2 — Lennai for G		(12-6) Poter Gas Mixtu		AMETERS
Gas	$\frac{\epsilon/k}{(^{\circ}K.)}$	σ (Λ.)	Gas mixture	$\epsilon_{12}{}^{/k}({}^{^c}\mathrm{K.})$	σ ₁₂ (A.)
He Ar	10·22 119·8	2.556 3.405	He-Xe Ar-Xe	48·46 165·9	3·247 3·671
Xe	229.8	3.937			

*Parameters for pure gases are those given by R. J. Lunbcck, Thesis, Amsterdam, 1951. Parameters for the gas mixtures are derived from the corresponding pure gas values by adopting the geometric mean rule for ϵ_{12} and arithmetic mean rule for σ_{12} .

TABLE 3 - C	OMPUTED VALUES O	F α_T and α'_T for	THE Ar-Xe Syste	м (Xe→0) as a Fu	NCTION OF TE	MPERATURE
Formula	100°K.	300°K.	500°K.	700°K.	900 K.	Simplifying criterion*
$[\alpha_{T}]_{1}$, Eq. (9)	- 0.0416	0.155	0.272	0.317	0.346	R
$[\alpha_T]_1^a$, Eq. (33)	-0.0291	0.268	0.472	0.530	0.596	1 Mº
$[\alpha_T]_1^b$, Eq. (34)	-0.0328	0.133	0.233	0.260	0.293	1 M ¹
$[\alpha_T]_1^c$, Eq. (35)	-0.0429	0.158	0.252	0.309	0.348	$1 M^2$
$[\alpha_T]_2$, Eq. (10)	-0.0378	0.153	0.275	0.320	0.356	R
$[\alpha_T]_2^a$, Eq. (36)	-0.0777	0.270	0.476	0.540	0.388	I M ^o
$[\alpha_T]_2^b$, Eq. (37)	-0.0392	0.132	0.235	0.265	0.300	$1 M^1$
$[\alpha_T]_2^c$, Eq. (38)	-0.0463	0.156	0.280	0.317	0.359	$1 M^2$
$[\alpha_T]_2$, Eq. (30)	-0.0328	0.156	0.274	0.320	0.356	EM^2
$[\alpha_T]_2$, Eq. (60)	-0.0377	0.156	0.276	0.320	0.355	EM ² +DD
$[\alpha_T]_2$, Eq. (65)	-0.0378		0.275		0.356	DA
$[\alpha_T]_2$, Eq. (70)	-0.0379		0.274		0.356	DA & EM ²
$[\alpha_T]_1$, Eq. (13)	-0.0431	0.156	0.274	0.320	0.345	R
$[\alpha_T]_1^a$, Eq. (49)	-0.0719	0.268	0.472	0.530	0.596	1 110
$[\alpha_T^{\prime}]_1^b$, Eq. (50)	-0.0328	0.133	0.233	0.260	0.293	1 M ¹
$[\alpha'_T]_1^c$, Eq. (51)	-0.0429	0.159	0.254	0.312	0.349	$1 \mathrm{M}^2$
$[\alpha_T]_2$, Eq. (16)	-0.0416	0.154	0.275	0.323	0.355	R
$[\alpha_T]_2^a$, Eq. (52)	0.0412	0.151	0.275	0.325	0.358	I M ⁰
$[\alpha_T]_2^b$, Eq. (53)	-0.0424	0.155	0.275	0.321	0.352	$1 \mathrm{M}^1$
$[\alpha'_T]_2^c$, Eq. (54)	-0.0417	0.153	0.274	0.323	0.355	$1 M^2$
$[\alpha_T]_2$, Eq. (44)	-0.0416	0.154	0.274	0.323	0.355	EM^2
$[\alpha_T]_2$, Eqs. (16),	-0.0416	0.154	0.275	0.323	0.356	DA
(20) and (74)						
$[\alpha_T]_2$, Eqs. (44),	-0.0416	0.154	0.275	0.323	0.356	$DA \& EM^2$
(20) and (78)						

*R, rigorous; IM⁰, IM¹ and IM² represent implicit mass expansion up to M⁰, M¹ and M² respectively; EM², explicit mass expansion up to M²; DA, diagonal approximation; and DD, double diagonal discarded terms.

constant at 1 per cent. This explains the data presented in Table 8 which exhibit an almost uniform convergence in the composition range 30-70 per cent of Ar at $316\cdot4^{\circ}K$.

For the He-Xe system the data recorded in Tables 5, 7 and 9 show a definite superiority of the Kihara-Mason formulae. Further, the convergence of the formulae is slightly better when the proportion of Xe is less, and becomes comparatively inferior as the percentage of Xe is increased, though it never assumes a very objectionable magnitude.

The simplifying procedure of Saxena and Dave^{57,58} based on the expansion of the rigorous α_T formulae in powers of M works excellently for He-Xe system when either of the components is in trace. Even for Ar-Xe, a system for which M is not sufficiently small, we find the calculations to be satisfactory though these are distinctly superior for Kihara-Mason approximation. The approximation procedure of Saxena and Dave^{57,58} which does not

yield satisfactory results for systems having moderate value of M in the case of Chapman-Cowling scheme can be considerably improved if the explicit mass expansion technique of Saxena *et al.*⁵⁹ is used. The formulae so obtained are given by Eqs. (30) and (31) and the numerical calculations recorded in Tables 3 and 4 confirm this. The formulae derived by Saxena and Joshi⁶⁰ for the two limiting cases on the Chapman-Cowling scheme [Eqs. (60) and (61)] also are equally satisfactory. We further feel that the simplified formulae for $[x_{I_{-1}}]$ should be used only for those systems which have a very small value of M, otherwise the rigorous expressions should be preferred.

For mixtures of arbitrary composition the explicit mass expansion technique of Saxena *et al.*⁵⁹ works excellently well for He-Xe system and for both the approximation procedures as may be seen from the calculations. This is clear from Tables 7 and 9. For the Ar-Xe system also this procedure yields only satisfactory results in the case of formulae

TABLE 4 Com	puted Values o	$F \alpha_T \text{ and } \alpha'_T$	FOR THE AI	-Xe System	$(Ar \rightarrow 0)$ as a	FUNCTION C	OF TEMPER.	ATURE
" Formula	100 K.	200° K.	300°K.	400°K.	500°K.	700°K.	900°K.	Simplifying criterion
z_{T-1} . Eq. (11)	-0.0250	0.0309	0.0896	0.131	0.159	0.189	0.206	R
$[z_{T_{1}}]^{c}$. Eq. (39)	0.0287			-	0.188		0.235	IM^2
$\alpha_{I^{-2}}$. Eq. (12)	0.0231		0.0894		0.165	0.202	0-212	R
$\alpha_{T^{-2}}$, Eq. (40)	-0.0181		0.0977		0.200	0.238	0.248	IM
$[\alpha_T]_2$, Eq. (31)	-0.0230		1		0.165	12112	0.212	EM ²
$\alpha_{T^{2}}$, Eq. (61)	- 0.0234	-	0.0894	_	0.165	0.202	0.212	$\rm EM^2 + DD$
7 _{7 2} , Eq. (66)	- 0.0231	_	0.0899				0.215	DA
$\alpha_{T_{2}}$, Eq. (71)	-0.0231		0.0899				0.215	DA & EM ²
x_{T-1} , Eq. (22)	-0.0248	0.0326	0.0969	0.143	0.171	0.209	0.229	R
$\left[\alpha_{T}^{\prime}\right]_{1}^{c}$, Eq. (55)	-0.0588	-			0.206		0.268	I M ²
$[\alpha_{T}']_{2}$, Eqs. (16),	-0.0220	0.0305	0.0879	0.133	0.165	0.199	0.223	R
(23) and (24)								
$\alpha_T^{-a}_{2}$, Eq. (56)	-0.0245	0.0282	0.0855	0.133	0.170	0.214	0.242	IM ⁰
$\left[\alpha_{T_{2}}^{\prime}, \text{ Eq. }(56)\right]$	0.0251	0.0312	0.0870	0.132	0.160	0.193	0.212	IM ¹
$\left[x_T' \right]_2^c$, Eq. (56)	-0.0247	0.0296	0.0867	0.131	0.160	0.199	0.222	I M ²
$[\alpha'_{T-2}, \text{ Eqs. (44)},$	-0.0220	_	0.0881	0.131	0.164	0.199	0.223	EM ²
(23) and (46)								
$[\alpha_T]_2$, Eqs. (16),	0.0220		0.0886	0.132	0.165	0.200	0.224	DA
(23) and (75)				ter terterer				
$[\alpha_{T_{2}}, \text{Eqs. (44)},$	-0.0220		0.0888	0.132	0.165	0.200	0.224	DA & EM ²
(23) and (79)								

Table 5 — Computed Values of α_T and α_T' for the He-Xe System (He->0) as a Function of Temperature

Formula	200°K.	300° K.	500°K.	700°K.	900°K.	Simplifying criterion
$[\alpha_{T_{1}}]$, Eq. (11)	_	0.260	0.283	0.288	0.285	R
$\begin{bmatrix} \alpha_T \end{bmatrix}_{1}^{c}$, Eq. (39)	Canada	0.260		0.289	0.284	IM^2
$[\alpha_T]_2$, Eq. (12)	-	0.280	0.309	0.295	0.318	R
$[\alpha_T]_2$, Eq. (40)		0.279	0.308		0.313	IM
$[\alpha_T]_2$, Eq. (66)	_		0.310	0.297	0.320	DA
x_{T-2} , Eq. (71)			0.310	0.297	0.320	DA & EM ²
z'_{T-1} , Eq. (22)	0.270	0.307	0.329	0.332	0.335	R
$z'_{T_{-1}}^{c}$, Eq. (55)		0.307		0.332	0.335	IM^2
$[x'_{T,2}]$, Eqs. (16),	0.255	0.301	0.340	0.340	0.320	R
(23) and (24)						
$z'_{T=2}^{a}$, Eq. (56)	0.227	0.302	0.346	0.32	0.322	IM ⁰
$[\sigma'_T]_2^{\prime}$, Eq. (56)	0.254	0.303	0.341	0.348	0.349	IM^1
$\alpha'_{T=2}$, Eq. (56)	0.255	0.303	0.341	0.350	0.349	$I M^2$
$[a'_{T_{2}}]_{2}$, Eqs. (44),	0.255	0.301	0.340	0.340	0.350	EM^2
(23) and (46)						
$[x_{T_{-2}}^{\prime}, \text{ Eqs. (16)},$	0.256	0.301	0.341	0.340	0.353	\mathbf{DA}
(23) and (75) $[\alpha'_T]_2$, Eqs. (44),	0.255	0 201	0.341	0.340	0.252	DA & EM ²
(23) and (79)	0.255	0.301	0.341	0.340	0.353	DA & EMª
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Formula	185°K.	233°K.	293°K.	369°K.	464° K.	585°K.	Simplifying criterion	
$[\alpha_T]_1$, Eq. (4)	0.0272	0.0652	0.110	0.154	0.194	0.226	R	
$[\alpha_T]_2$, Eq. (3)	0.0258		0.108	0.154	-	0.232	R	
$[\alpha_T]_2$. Eqs. (3), (27)	0.0261	—	0.109	0.156		0.234	EM ²	
to (29)								
$[\alpha_T]_2$, Eqs. (3), (57)	0.0259	-	0.109	0.155	_	0.233	$\rm EM^2 + DD$	
to (59)								
$[\alpha_T]_2$, Eqs. (3), (62)	0.0260		0.108	0.155	—	0.232	$\mathbf{D}\mathbf{A}$	
to (64)								
$[\alpha_T]_2$, Eqs. (3), (67)	0.0262		0.110	0.156		0.235	DA & EM ²	
to (69)								
$[\alpha'_T]_1$, Eq. (13)	0.0280	0.0673	0.115	0.162	0.206	0.240	R	
$[\alpha'_T]_2$, Eqs. (16)-(18)	0.0263	0.0636	0.108	0.154	0.197	0.233	R	
$[\alpha'_{T}]_{a}$, Eqs. (44), (42)	0.0263	0.0633	0.108	0.155	0.197	0.233	EM ²	
and (43)								
$[\alpha'_T]_2$, Eqs. (16), (72)	0.0266	0.0635	0.108	0.155	0.196	0.233	DA	
and (73)								
$[\alpha'_T]_2$, Eqs. (44), (76)	0.0263	0.0635	0.108	0.155	0.198	0.234	DA & EM ²	
and (77)								

Table 7 — Computed Values of α_T and α'_T for the He-Xe System (46.4 per cent Xc) as a Function of Temperature

Formula	185°K.	233°K.	293°K.	369°K.	464°K.	585°K.	Simplifying criterion
$[\alpha_T]_1$, Eq. (4)	0.365	0.404	0.424	0.440	0.454	0.465	R
$[\alpha_T]_2$, Eq. (3)	0.379	0.425	0.448	0.468	-	0.512	R
$[\alpha_T]_2$, Eqs. (3), (27)	0.379	0.425	0.448	0.468		0.512	EM ²
to (29)							
$[\alpha_T]_2$, Eqs. (3), (62)	—	0.425	0.448	0.468	-	0.513	DA
to (64)							
$[\alpha_T]_2$, Eqs. (3), (67)		0.425	0.448	0.468		0.512	DA & EM ²
to (69)							
$[\alpha_T]_2$, Eq. (32)	0.380	0.427	0.449	0.469		-	IM
$[\alpha_T]_2$, Eq. (32a)	0-378	0.425	0.447	0.467		—	IM
$[\alpha_T]_2$, Eq. (32a)	0.379	0.426	0.450	0.468			*
$[\alpha'_T]_1$, Eq. (13)	0.414	0.456	0.480	0.498	0.513	0.524	R
$[\alpha'_T]_2$, Eqs. (16)-(18)	0.390	0.442	0.469	0.492	0.513	0.531	R
$[\alpha'_T]_2$, Eqs. (44), (42)	0.390	0.442	0.469	0.492	0.512	0.531	EM ²
and (43)							
$[\alpha'_T]_2$, Eqs. (16), (72)	0.390	0.442		0.492		0.531	DA
and (73)							
$[\alpha'_T]_2$, Eqs. (44), (76)	0.390	0.442	0.469	0.492	0.513	0.532	DA & EM ²
and (77)							
$[\alpha'_T]_2$, Eqs. (48), (42)	0.390		0.469	0.492	0.513	0.532	EM
and (47)							

*In the expressions of Z_2 and Z''_3 all terms involving the power of M as 2 and higher have been neglected.

Formula	Argon, %							Simplifying
	10	30	40	50	60	70	90	criterion
$[\alpha_T]_1$, Eq. (4)		0.111	0.117	0.123	0.130	0.138	_	R
$[\alpha_T]_2$, Eq. (3)	_	0.111		0.123	—	0.137	-	R
$[\alpha_{T_{-2}}]$, Eqs. (3), (27) to (29)	—	0.111	—	0.123	_	0.140	-	EM ²
$[\alpha_T]_2$, Eqs. (3), (57) to (59)	-	0.111	-	0.123	-	0.138	_	EM ² +DD
$[x_T]_2$, Eqs. (3), (62) to (64)	-	0.111	-	0.123	-	0.138	-	DA
$[\alpha_T]_2$, Eqs. (3), (67) to (69)	-	0.111	_	0.124	-	0.141	-	DA & EM ²
$[x'_T]_1$, Eq. (13)	0.110	0.118	0.124	0.129	0.136	0.141	0.173	R
$[\alpha'_T]_2$, Eqs. (16)-(18)	0.101	0.110	0.116	0.122	0.129	0.137	0.169	R
$[\alpha'_T]_2$, Eqs. (44), (42) and (43)	0.101	0.111	0.116	0.122	0.129	0.137	0.169	EM ²
$[\alpha'_T]_2$, Eqs. (16), (72) and (73)	0.102	0.111	0.117	0.123	0.129	-	0.170	DA
$[\alpha'_T]_2$, Eqs. (44), (76) and (77)	0.102	0.111	0.117	0.123	0.129	0.137	0.170	DA & EM ²

Table 9 — Computed Values of α_T and α'_T for the He-Xe System at 316.4°K. As a Function of Composition

Formula	Helium, %							Simplifying
	10	30	40	50	60	70	90	criterion
$[x_T]_1$, Eq. (4)	0.282	0.335	0.370	0.413	0.467	0.537	0.769	R
$[\alpha_T]_2$, Eq. (3)		0.358		0.438	-	0.565		R
$[\alpha_T]_2$, Eqs. (3), (27) to (29)	-	0.358	-	0.438	-	0.565	~	EM ²
$[x_T]_2$, Eqs. (3), (62) to (64)	~	0.358	-	0.438	-	0.565	-	DA
$[\alpha_T]_2$, Eqs. (3), (67) to (69)	-	0.358		0.438		0.565	~	DA & EM ²
$[\alpha_T]_2$, Eq. (32)	~	0.359	-	0.440		0.566		IM
$\left[\alpha_{T}\right]_{2}$, Eq. (32a)	-	0.357	-	0-437		0.565	~	1 M
$[x_T]_2$, Eq. (32a)		0.357		0.439		0.566	~	*
$[x'_T]_1$, Eq. (13)	0.331	0.388	0.418	0.469	0.524	0.593	0.802	R
$[\alpha'_T]_2$, Eqs. (16)-(18)	0-327	0.382	0.418	0.461	0.515	0.584	0.807	R
$[\alpha'_{T}]_{2}$, Eqs. (44), (42) and (43)	0.327	0.382	0-418	0.461	0.515	0.584	0.807	EM^2
$[\alpha'_{T}]_{2}$, Eqs. (16), (72) and (73)	0.327	0.381		0.461	-	0.584	0.807	DA
$[\alpha'_T]_2$, Eqs. (44), (76) and (77)	0.327	0.383	0.418	0.461	0.515	0.583	0.807	DA & EM ²
$[\alpha_T]_2$, Eqs. (48), (42) and (47)		0.382	0.418	0.461	_	0.584	0.807	EM

*In the expressions of Z_2 and Z_3'' all terms involving the power of M as 2 and higher have been neglected.

derived on Chapman-Cowling scheme while for the Kihara-Mason scheme it works excellently well, as may be seen from Tables 6 and 8. For this system, however, a significant improvement is obtained for the Chapman-Cowling approximation formulae if some additional terms are added following Saxena and Joshi⁶¹. We, therefore, suggest that for systems having moderate values of M in the case of Chapman-Cowling approximation the formulae given by Eqs. (3) and (57)-(59) should be preferred to those given by Eqs. (3) and (27)-(29).

The mass expansion procedure employed by Saxena et al.59 for a general mixture is slightly different from that employed by Saxena and Dave^{57,58} for the two limiting cases. In the former procedure terms have been discarded only on the consideration of the explicit power of M while in the latter procedure the implicit power of M of each term occurring in a_{ij} and C_{ij} is also considered. The latter procedure thus makes the approximation more stringent and, therefore, for systems having moderate values of M the procedure based on explicit mass expansion is preferable. This, of course, is confirmed by the calculations on these two systems. For systems with small value of M, like He-Xe implicit mass expansion is justified. This encouraged us to simplify the expressions of Saxena et al.⁵⁹ [Eqs. (27)-(29)] by applying the implicit mass expansion criterion of Saxena and Dave^{57,58}. This yields an expression for $[\alpha_T]_2$ given by Eq. (32). If the term containing $M^{3/2}$ is also neglected in Eq. (32) we get a still simpler formula given by Eq. (32a). Calculations according to these formulae have been performed for the He-Xe system with excellent success, and are recorded in Tables 7 and 9. For such low values of M equations for Z_2 and Z'_3 occurring in Eq. (32a) can be further simplified by neglecting all terms with powers of M greater than one. This is confirmed by the numerical calculations on this system recorded in Tables 7 and 9.

The simpler expression derived on Kihara-Mason approximation by Saxena *et al.*⁵⁹ may be further simplified by neglecting terms in K'_2 which contain explicitly the power of M as 3/2. This formula [Eqs. (48), (42) and (47)] is also accurate and reliable for the He-Xe system as confirmed by the calculated values recorded in Tables 7 and 9.

The formulae derived on applying the diagonal approximation to the rigorous α_T expressions are very reliable in all cases and for both the approximation procedures. Even for the Ar-Xe system the data so obtained (Tables 3, 4, 6 and 8) are in excellent agreement with the computed rigorous values. This conclusion is very useful specially because for such systems, which have appreciable M value, the formulae derived on the criterion of mass expansion tend to be of uncertain accuracy. We, however, feel that the Kihara-Mason approximation formulae should be preferred to Chapman-Cowling because these are simpler for computational purposes and are also liable to yield accurate results as indicated by the calculations.

The doubly approximated formulae, i.e. formulae obtained from rigorous expressions, by applying both the diagonal and explicit mass approximations, are extremely satisfactory for the He-Xe system both as a function of temperature and composition. This, of course, is expected on the consideration of its low M value. In the case of the Ar-Xe system some accuracy is lost obviously because M is not quite small for this system and consequently the explicit mass approximation is less justified. However, we find from Tables 6 and 8 that the Kihara-Mason doubly approximated formulae should be preferred to those of Chapman-Cowling in view of their simplicity and accuracy. In the two limiting cases also the same qualitative picture holds except that here the results are accurate even for the Ar-Xe system. Further, these formulae for both the systems yield results of reasonable accuracy which are comparable to that obtained by using any other formula and, therefore, should be preferred.

Concluding Remarks

Thus in view of the detailed calculations on these two systems and on the basis of the particular inferences derived, it is possible to make the following general remarks regarding the appropriateness and applicability of the various formulae for the thermal diffusion factor given in the previous section.

(1) The simplification based on the consideration of the power of M is a well-defined approximation and the numerical calculations reveal that the much simpler formulae so obtained are capable of giving very accurate results provided the value of M is small.

(2) The accuracies of the formulae mentioned in (1) can be considerably improved for those systems also for which M is not quite small, by adding the additional terms in the simplified formulae which contain products of two diagonal elements.

(3) The criterion of simplifying the rigorous formulae on the basis that the diagonal elements are much larger than the non-diagonal elements of the Chapman-Cowling determinants, though not so well defined, yet has a distinct utility for systems having moderately small values of M.

(4) The doubly approximated formulae are simpler than either set of formulae obtained on the criterion of any other approximation and the numerical calculations reveal that these formulae are also capable of giving accurate results.

It will be interesting to point out here that some of the α_T formulae derived and discussed in this paper have already been utilized by Saxena and Mathur⁶⁸ for interpreting the data of binary thermal diffusion factor for a large number of systems as a function of temperature and composition. Recently, a Morse type potential⁶⁹ has been employed by Konowalow *et al.*⁷⁰ for discussing the gas properties⁷¹. Lovell and Hirschfelder⁷² have computed the various transport properties collision integrals. Saxena and Gambhir⁷³ have extended this potential to gaseous mixtures and since then it has been widely applied⁷⁴⁻⁷⁷ to gases and gaseous mixtures. Unfortunately, these investigations do not encourage one to anticipate any distinctive merit for this potential over what has already been achieved by the exp-six potential.

Summary

The various simpler versions of the expressions for the binary gaseous thermal diffusion factor, α_T , have been discussed. Their relative appropriateness has been investigated on the basis of numerical computations for a few gas mixtures. New formulae have been derived and alternative forms of the older formulae, which are more convenient for computational purposes, are given. Tabulations of certain quantities, in terms of which α_T is expressed, are presented to facilitate numerical work. Some general recommendations are given for the selection of a suitable formula while dealing with a particular gas system. The survey is intended not only to cater to the needs of the practical or applied scientist but also to those of pure theoretical physicists.

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APPENDIX I

The expressions for the a_{ij} which are required for the calculation of the first two approximations to α_T on the Chapman-Cowling approximation scheme are given below. The remaining a_{ij} can be generated from the following a_{ij} using the symmetry properties, viz. in general $a_{ij} = a_{ji}$, and if *i* and *j* are not equal to zero then a_{-i-j} can be obtained from a_{ij} by interchanging the subscripts *i* and *j* which refer to the molecular species.

$$\begin{split} a_{10} &= a_{01} = M^2 (1+M)^{-5/2} T_{01} \\ a_{-10} &= a_{0-1} = -M^{3/2} a_{01} \\ a_{20} &= a_{02} = M^3 (1+M)^{-7/2} T_{20} \\ a_{-20} &= a_{0-2} = -M^{5/2} a_{02} \\ a_{11} &= a_{11}' + (X_1 | X_2) a_{11}'' \\ a_{11}'' &= M (1+M)^{-3} T_{11}'' \\ a_{11}'' &= M^{\frac{1}{2}} (1+M)^{-\frac{1}{2}} T_{11}'' \\ a_{1-1} &= a_{-11} = M^{3/2} (1+M)^{-3} T_{1-1} \\ a_{12} &= a_{12}' + (X_1 | X_2) a_{12}'' \\ a_{12}' &= M^2 (1+M)^{-4} T_{12}'' \\ a_{21}'' &= M^{\frac{1}{2}} (1+M)^{-\frac{1}{2}} T_{12}'' \\ a_{-21} &= a_{1-2} = M^{3/2} (1+M)^{-4} T_{1-2} \\ a_{22} &= a_{22}' + (X_1 | X_2) a_{22}'' \\ a_{22}'' &= M (1+M)^{-5} T_{22}'' \\ a_{22}'' &= M^{\frac{1}{2}} (1+M)^{-\frac{1}{2}} T_{22}'' \\ a_{-22} &= M^{5/2} (1+M)^{-5} T_{-22}'' \\ \end{split}$$

Here $M = M_2/M_1$ and the various T_{ij} occurring in the above expressions are defined as follows:

$$\begin{split} T_{01} &= T_{0-1} = -2\sqrt{2}(6C_{12}^*-5) \\ T_{02} &= T_{0-2} = (1/\sqrt{2})[35-12B_{12}^*-24C_{12}^*] \\ T_{11}' &= 5(6+5M^2) + 16MA_{12}^*-12M^2B_{12}^* \\ T_{11}'' &= 4\sqrt{2}Z_{11} \\ T_{1-1} &= T_{-11} = 16A_{12}^*+12B_{12}^*-55 \\ T_{12}' &= 8M(7A_{12}^*-8H_{12}^*) - 3M^2(19B_{12}^*-40G_{12}^*) \\ &\quad -(3/2)(84-85M^2)C_{12}^*+(35/4)(12+5M^2) \\ T_{12}'' &= \sqrt{2}(7-8E_{11}^*)Z_{11} \\ T_{1-2} &= T_{-12} = 8(7A_{12}^*-8H_{12}^*) + 3(19B_{12}^*+40G_{12}^*) \\ &\quad -(3/2)C_{12}^*-(595/4) \\ T_{22}'' &= (35/16)(40+168M^2+35M^4) \\ &\quad +28M(4+7M^2)A_{12}^*-(3/2)M^2(108+133M^2)B_{12}^* \\ &\quad +18M^2(35M^2-4)C_{12}^*-448M^3H_{12}^* \\ &\quad -120M^4(7G_{12}^*-3J_{12}^*) + 320M^2L_{12}^*+96M^2K_{12}^* \end{split}$$

The expressions for the various h_k and C_{ij} to be used in connection with the thermal diffusion formulae on Kihara-Mason approximation scheme are

$$\begin{split} h_1 &= \frac{a_{10}C_{-1-2} - a_{-10}C_{1-2}}{C_{11}C_{-1-1} - C_{-11}^2} \qquad h_2 &= \frac{a_{20}C_{-2-2} - a_{-20}C_{2-2}}{C_{22}C_{-2-2} - C_{-22}^2} \\ h_3 &= \frac{C_{11}C_{-1-2} - C_{-11}C_{1-2}}{C_{11}C_{-1-1} - C_{-11}^2} \qquad h_4 &= \frac{C_{11}C_{-12} - C_{-11}C_{12}}{C_{11}C_{-1-1} - C_{-11}^2} \\ h_5 &= \frac{C_{22}C_{-1-2} - C_{-22}C_{-12}}{C_{22}C_{-2-2} - C_{-22}^2} \qquad h_6 &= \frac{C_{22}C_{1-2} - C_{-22}C_{12}}{C_{22}C_{-2-2} - C_{-22}^2} \end{split}$$

$$T_{22}'' = \sqrt{2[(77/4) - 28E_{11}^* + 20F_{11}^*]Z_{11}}$$

$$T_{2-2} = T_{-22} = 308A_{12}^* + (723/2)B_{12}^* - 558C_{12}^*$$

$$+ 840G_{12}^* - 448H_{12}^* - 360J_{12}^* + 320L_{12}^*$$

$$- 96K_{12}^* - (8505/16)$$

where

$$\begin{split} E_{ii}^{*} &= \Omega_{ii}^{(2,3)*} / \Omega_{ii}^{(2,2)*} \\ F_{ii}^{*} &= \Omega_{ii}^{(2,4)*} / \Omega_{ii}^{(2,2)*} \\ G_{ij}^{*} &= \Omega_{ij}^{(1,4)*} / \Omega_{ij}^{(1,1)*} \\ H_{ij}^{*} &= \Omega_{ij}^{(2,3)*} / \Omega_{ij}^{(1,1)*} \\ J_{ij}^{*} &= \Omega_{ij}^{(2,3)*} / \Omega_{ij}^{(1,1)*} \\ K_{ij}^{*} &= \Omega_{ij}^{(3,3)*} / \Omega_{ij}^{(1,1)*} \\ L_{ij}^{*} &= \Omega_{ij}^{(2,4)*} / \Omega_{ij}^{(1,1)*} \end{split}$$

In addition the following T_{ij} are required in connection with the various simplified formulae:

$$\begin{split} T_{11} &= M^{\frac{1}{2}}(1\!+\!M)^{-5/2}T'_{11}\!+\!(X_1/X_2)T''_{11} \\ T_{12} &= M^{3/2}(1\!+\!M)^{-7/2}T'_{12}\!+\!(X_1/X_2)T''_{12} \\ T_{22} &= M^{\frac{1}{2}}(1\!+\!M)^{-9/2}T'_{22}\!+\!(X_1/X_2)T''_{22} \end{split}$$

These T_{ij} , which are slightly different from those earlier given by Joshi and Saxena⁶³, also follow the two symmetry rules of a_{ij} , i.e. $T_{ij} = T_{ji}$, and $T_{-i \ j}$ is obtained from T_{ij} by interchanging the subscripts referring to the molecular species.

In the formulae for the limiting cases quantities like T'_{i-j} and T''_{-i-j} also occur and their explicit expressions are

$$\begin{split} I_{-1-1} &= 5(6M^2+5) + 16MA_{12}^2 - 12B_{12}^2 \\ T_{-1-1}' &= 4\sqrt{2}Z_{22} \\ T_{-1-2}' &= (35/4)(5+12M^2) + 8M(7A_{12}^* - 8H_{12}^*) \\ &\quad -57B_{12} + [(255/2) - 126M^2]C_{12}^* - 120G_{12}^* \\ T_{-1-2}'' &= \sqrt{2} (7 - 8E_{22}^*)Z_{22} \\ T_{-2-2}' &= (35/16)(35+168M^2 + 40M^4) \\ &\quad + 28M(7 + 4M^2)A_{12}^* - (3/2)(133 + 108M^2)B_{12}^* \\ &\quad -(630 + 72M^2)C_{12}^* - 840G_{12}^* - 448MH_{12}^* \\ &\quad + 360J_{12}^* + 96M^2K_{12}^* + 320ML_{12}^* \\ T_{-2-2}'' &= \sqrt{2}[(77/4) - 28E_{22}^* + 20F_{22}^*]Z_{22} \end{split}$$

APPENDIX II

$$\begin{split} C_{11} &= C_{11}' + (X_1/X_2) C_{11}'' \\ C_{11}' &= \frac{8M}{(1+M)^3} [(5/4)(3+M^2) + 2MA_{12}^*] \\ C_{11}'' &= 4 \left[\frac{2M}{1+M} \right]^{\frac{1}{2}} Z_{11} \\ C_{-11} &= C_{1-1} = -\frac{8M^{3/2}}{(1+M)^3} [5-2A_{12}^*] \\ C_{12} &= C_{21} = C_{12}' + (X_1/X_2) C_{12}'' \end{split}$$

$$\begin{split} C_{12}' &= \frac{8M^3}{(1+M)^4} \left(7A_{12}^* - 8H_{12}^*\right) \\ &\quad - \frac{7M^2(3+M^2)}{(1+M)^4} \left(6C_{12}^* - 5\right) \\ C_{12}'' &= \left[\frac{2M}{1+M}\right]^{\frac{1}{2}} \left[7 - 8E_{11}^*\right] Z_{11} \\ C_{-12} &= C_{2-1} = \frac{28M^{5/2}}{(1+M)^4} \left(6C_{12}^* - 5\right) \\ &\quad + \frac{8M^{5/2}}{(1+M)^4} \left(7A_{12}^* - 8H_{12}^*\right) \\ C_{22} &= C_{22}' + (X_1/X_2)C_{22}'' \end{split}$$

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$$\begin{split} &Z_1 = [\sqrt{2}Z_{11}A_5 + (175X_2/2X_1)M^4] \\ &\times [\sqrt{2}Z_{22}\alpha + (X_1/X_2)\beta + 2(X_2/X_1)Z_{22}^2\gamma] \\ &Z_2 = [(A_6 - A_2d) + (\sqrt{2}X_2/X_1)Z_{22}(A_8 + cd)] \\ &+ M[A_7 - 8ld - (9/2)(A_6 - A_2d) - (\sqrt{2}X_2/X_1)Z_{22}cd] \\ &+ M^2[(99/8)(A_6 - A_2d) - (9/2)(A_7 - 8ld) \\ &+ A_4 + 21d(6C_{12}^* - 5) + (\sqrt{2}X_2/X_1)Z_{22}cd] \\ &Z_3' = (\sqrt{2}X_1/X_2)^2Z_{11}^2(A_5 - n^2) \\ &+ 2625M + (\sqrt{2}X_1/X_2)Z_{11}M^4[350 + 30A_5 \\ &+ M[448A_{12}^* - 1575 + 16A_{12}^*A_5 - 75A_5 \\ &- 42n(6C_{12}^* - 5)]] + M^2(4760A_{12}^* - 18375) \\ &Z_3'' = (A_1A_6 - A_2^2) + (\sqrt{2}X_2/X_1)Z_{22}(4A_6 + A_1A_8 + 2cA_2) \\ &+ (\sqrt{2}X_2/X_1)^2Z_{22}^2(4A_8 - c^2) + M[16A_6A_{12}^* + A_1A_7 \\ &- 16lA_2 - 7A_1A_6 + 7A_2^2 + (\sqrt{2}X_2/X_1)Z_{22}[4A_7 \\ &- 18A_6 + 16A_8A_{12}^* - (5/2)A_1A_8 + 16cl - 7cA_2]] \\ &+ M^2[30A_6 + 16A_7A_{12}^* + A_1A_4 - 64l^2 + 42(6C_{12}^* - 5)A_2 \\ &- 112A_6A_{12}^* - 7A_1A_7 + 112lA_2 + 28A_1A_6 - 28A_2^2 \\ \end{split}$$

$$\begin{split} C_{22}' &= \frac{8M}{(1+M)^5} \left[(35/16)(1+M^2)(5+M^2) \right. \\ &\qquad +7M(2+M^2)A_{12}^* + 12M^2K_{12}^* \right] \\ C_{22}'' &= \frac{21}{2} \left[\frac{2M}{1+M} \right]^{\frac{1}{2}} Z_{11} \\ C_{-22} &= C_{2-2} = - \frac{8M^{5/2}}{(1+M)^5} \left[(105/4) - 21A_{12}^* + 12K_{12}^* \right] \end{split}$$

The quantities h_{-k} and C_{-i-j} can be obtained from the corresponding expressions for h_k and C_{ij} by an interchange of the subscripts *i* and *j* characterizing the two molecular species.

APPENDIX III

+
$$(\sqrt{2}X_2/X_1)Z_{22}[(99/2)A_6-18A_7+4A_4 + (35/8)A_1A_8-40A_8A_{12}^*+30A_8+(63/4)A_2c - 56cl-42c(6C_{12}^*-5)]$$

where

$$\begin{aligned} \alpha &= 4A_{6} + A_{1}A_{8} - eA_{8} + 2cA_{2} + cA_{3} - cde + 4A_{3}d \\ \beta &= A_{1}A_{6} - eA_{6} - A_{2}^{2} - A_{2}A_{3} + deA_{2} + dA_{1}A_{3} \\ \gamma &= 4A_{8} - c^{2} \\ A_{1} &= 25 - 12B_{12}^{*} \\ A_{2} &= (175/4) + (255/2)C_{12}^{*} - 57B_{12}^{*} - 120G_{12}^{*} \\ A_{3} &= 8l + 57B_{12}^{*} + 120G_{12}^{*} - (1/4)(6C_{13}^{*} - 5) - 150 \\ A_{4} &= (735/2) - 72C_{12}^{*} - 162B_{12}^{*} + 96K_{12}^{*} \\ A_{5} &= (77/4) - 28E_{11}^{*} + 20F_{11}^{*} \\ A_{6} &= (1225/16) + 630C_{12}^{*} - (399/2)B_{12}^{*} - 840G_{12}^{*} + 360J_{12}^{*} \\ A_{7} &= 196A_{12}^{*} - 448H_{12}^{*} + 320L_{12}^{*} \\ A_{8} &= (77/4) - 28E_{22}^{*} + 20F_{22}^{*} \\ A_{9} &= (723/2)B_{12}^{*} + 840G_{12}^{*} + 308A_{12}^{*} + 320L_{12}^{*} - 360J_{12}^{*} \\ &- 558C_{12}^{*} - 448H_{12}^{*} - 96K_{12}^{*} - (8505/16) \\ h &= (5 - 2A_{*}^{*}); \ l = (7A_{*9}^{*} - 8H_{*9}^{*}); \ \text{and} \ n = (8E_{*1}^{*} - 7) \end{aligned}$$

APPENDIX IV

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The defining relations for quantities which occur in formulae for the limiting cases on implicit mass approximation procedure are

$$\begin{split} b &= 77 - 112E_{22}^* + 80F_{22}^* = 4A_8 \\ c &= 8E_{22}^* - 7 \\ d &= 1 - \frac{3(5 - 4B_{12}^*)}{4(6C_{12}^* - 5)} \\ c &= 55 - 12B_{12}^* - 16A_{12}^* \\ f &= (595/32) + (3/16)C_{12}^* - (57/8)B_{12}^* - 15G_{12}^* \\ -7A_{12}^* + 8H_{12}^* \\ g &= (1 - 8A_{12}^*/15) \\ Y &= (1/10)(25 - 12B_{12}^*) \\ B &= n^2/4A_5 \\ B_1 &= 1 - (8A_{12}^*/5Y) \\ B_2 &= (8A_{12}^*/5Y)^2 - (15 + 8A_{12}^*)/5Y \\ B_3 &= (l/B_9) - (8A_{12}^*/5Y) \end{split}$$

$$\begin{split} B_4 &= -\frac{21(6C_{12}^*-5)}{8B_9} - \frac{3}{Y} - \frac{8A_{12}^*l}{5YB_9} + \frac{64A_{12}^{*2}}{25Y^2} \\ B_5 &= (l/B_9) - (B_7/B_{10}) \\ B_6 &= -\frac{21(6C_{12}^*-5)}{8B_9} + \frac{lB_7}{B_9B_{10}} + \frac{B_7^2}{B_{10}^2} - \frac{B_8}{B_{10}} \\ B_7 &= (49/2)A_{12}^*-56H_{12}^*-40F_{12}^*A_{12}^* \\ B_8 &= (735/16) + 12K_{12}^*-9C_{12}^* - (81/4)B_{12}^* \\ B_9 &= (175/32) + (255/16)C_{12}^* - 15G_{12}^* - (57/8)B_{12}^* \\ B_{10} &= (1225/128) + (315/4)C_{12}^* - (399/16)B_{12}^* \\ &\quad +45f_{12}^* - 105G_{12}^* \\ B_{11} &= 55 - 12B_{12}^* - 16A_{12}^* \\ B_{12} &= (595/32) + (3/16)C_{12}^* - (57/8)B_{12}^* - 15G_{12}^* - l \\ B_{13} &= 4B_9^2/5B_{10}Y \\ B_{14} &= 2l/7(6C_{12}^*-5) \end{split}$$

Oxidimetric Determination of Thiourea & Its Organic Derivatives

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THIOUREA possesses several industrial, medicinal and analytical applications. Consequently, its estimation has received considerable attention. The various methods used for the determination of thiourea are based either on its tendency to react with metals to undergo desulphurization or complex formation or its quantitative oxidation to different products by various oxidants in acidic and alkaline media.

Complex Formation and Desulphurization Methods

The earliest method for the determination of thiourea is by Volhard¹ who titrated its hot ammoniacal solution with standard silver nitrate using an external end-point method. Cuthill and Atkins2, finding no precise location of the endpoint by this method, developed a modified procedure by treating thiourea with an excess of strongly ammoniacal silver nitrate solution and titrating excess reagent, after acidification of the solution with nitric acid and removal of the precipitated silver sulphide, against standard thio-cyanate using ferric alum as an indicator. Landa and Soukenik3 proposed a gravimetric method for determining thiourea by precipitating it with ammoniacal silver nitrate in the presence of potassium cyanide, igniting the precipitate and weighing the silver formed. Nakanishi and Kobayashi4 used coulometric method with a constant current for the argentometric titration of thiourea.

Korinfskii⁵ estimated thiourea by treating it with cadmium acetate and determining the cadmium sulphide formed iodimetrically. Gupta⁶ desulphurized the liquid containing thiourea with alkaline solution of lead acetate and the resulting lead sulphide converted to lead sulphate which was determined gravimetrically. Rulfs and Mackela⁷ determined thiourea by digesting it with lead nitrate in Carius tube, dissolving the lead sulphate formed in acetate buffer and titrating the resulting solution of lead ions with standard dichromate amperometrically.

Gutierrez⁸ developed a method for estimating thiourea, based on its tendency to form a complex with alkaline mercuric iodide. Brada⁹ titrated thiourea with copper sulphate at 30°C. using bismuth nitrate as an indicator. Based on the property of thiourea to form a complex with mercury, Kies^{10,11} developed a 'dead-stop end-point' method with two mercury electrodes for its estimation. Kies and van Weezel¹² also developed a coulometric method for the estimation of thiourea. Kies et al.13 further extended the coulometric method for the determination of some derivatives of thiourea. Wronski14 titrated thiourea and some of its derivatives in aqueous or alcoholic solution with tris (acetoxy-mercuri) aniline solution in the presence of perchloric acid using p-dimethylaminobenzylidinerhodanine as an indicator.

Redox Methods

Maly¹⁵ found that when thiourea is oxidized with permanganate in neutral solutions, urea is formed and nearly all the sulphur is oxidized to sulphuric acid. Thiourea was quantitatively oxidized to urea by permanganate in neutral medium by Schmidt¹⁶. Werner¹⁷ studied this reaction and observed that although 98·7 per cent of sulphur is oxidized to sulphuric acid, only 44 per cent of urea is obtained, in addition to ammonia, carbon dioxide, and a substance $C_3H_7N_5$.

Cuthill and Atkins² developed an indirect method for the estimation of thiourea with ceric sulphate or potassium dichromate in sulphuric acid medium by adding an excess of these reagents to the thiourea solution, boiling the solution under reflux condenser for 30 min. and titrating the excess of the reagents with standard ferrous ammonium sulphate. Kimoto¹⁸ also proposed an indirect method for the estimation of thiourea with ceric sulphate.

Szebelledy and Madis¹⁹ determined thiourea by titrating it with standard potassium bromate in hydrochloric acid medium at 40-50°C. in the presence of potassium bromide and a little of gold chloride. The end-point was marked by the appearance of yellow colour which persisted for 5-10 sec. Mahr²⁰ titrated thiourea with standard bromate-bromide solution in sulphuric acid medium at 35°C. in the presence of potassium iodide and a little of starch. The end-point was marked by the appearance of blue colour when thiourea was oxidized to formamidine disulphide. Banerjee21 determined thiourea in the presence of varying amounts of mercuric chloride by using Mahr's method in a modified form. Rao et al.22 found the Mahr's method to be erratic and developed a method replacing potassium bromate by potassium permanganate. Rosenthaler23 estimated thiourea by oxidizing it with bromine and titrating the acid formed with sodium hydroxide. Berka and Zvka²⁴ determined thiourea with N-bromo-succinimide in sodium bicarbonate medium.

Afanas'ev²⁵ titrated thiourea with chloramine-T in hot dilute sulphuric acid using methyl red or indigo carmine as an indicator. Singh *et al.*²⁶ carried out a potentiometric titration of thiourea with chloramine-T in sulphuric acid at 80° C, when thiourea was oxidized to carbon dioxide, sulphur trioxide and nitrogen. Berka and Zyka²⁷ found that the direct potentiometric determination of thiourea with chloramine-T in the presence of potassium bromide in acid medium is possible. Aravamudan and Rao²⁸ determined thiourea indirectly with chloramine-T. Grover and Mehrotra²⁹ reported that thiourea is oxidized to urea and sulphate by hypoiodite and to sulphate, carbonate and nitrogen by hypobromite in alkaline solutions. Claeys *et al.*³⁰ determined thiourea by oxidizing it with an excess of sodium hypobromite in alkaline medium and estimating excess reagent iodometrically. Berka and Zyka³¹ titrated thiourea potentiometrically with potassium metaperiodate in hydrochloric acid medium. Bapat and Sharma³² developed direct and indirect amperometric procedures, while Bapat and Tatwawadi³³ performed colorimetric titrations for the estimation of thiourea with alkaline ferricyanide using osmium tetroxide as a catalyst.

Joshi³⁴ determined thiourea by treating it with an excess of selenious acid in hydrochloric acid medium, heating the mixture under reflux for 20-30 min. and determining the unreacted excess reagent iodometrically. Werner³⁵ developed · another indirect method involving the oxidation of thiourea to formamidine disulphide in sulphuric acid medium by selenious acid. The excess of selenious acid was determined iodometrically or by direct titration with standard sodium hydroxide. Bapat and Sharma³⁶ determined thiourea by adding an excess of potassium iodate and determining the excess reagent by titration with arsenious oxide in the presence of saturated mercuric chloride solution using 'dead-stop end-point ' with 0.1 V. applied potential. Deshmukh and Bapat³⁷ found that the oxidation of thiourea with potassium iodate, using iodine monochloride end-point, is not quantitative. Recently Bagbanly and Guseinov38 developed a method based on the oxidation of thiourea with potassium iodate at 60°C.

¹ Preisler and Berger³⁹ found the oxidation-reduction potential of thiourea-formamidine disulphide system (Eq. 1)



to be 0.420 V. in 0.05-1.00N hydrochloric acid. Reynolds and Werner⁴⁰ developed a method for the estimation of thiourea by oxidizing it quantitatively to formamidine disulphide by iodine in aqueous medium. Werner⁴¹ later found that this method gives low results if the concentration of thiourea exceeds 0.02 g. per 100 ml. of the titration mixture. Gilfillan⁴², however, in an attempt to analyse a mixture of thiourea and ammonium thiocyanate reported that this method did not give accurate results if more than 5 mg. of thiourea per 100 ml. of the reaction mixture is titrated. Cuthill and Atkins² estimated thiourea by oxidizing it quantitatively to urea and sulphate in alkaline medium with iodine. Skramovsky⁴³ adopted a similar procedure but noted the appearance of turbidity due to the formation of sulphur in solution. Protopopescu and Nedioglu⁴⁴ suggested that accurate results in the iodometric determination of thiourea could be obtained provided the determination was carried out at a low thiourea concentration in the absence of excess of potassium iodide and other alkali halides. Joshi 45 presented a modified procedure for the estimation of thiourea and tetramethyl thiourea, by treating them with an excess of iodine in alkaline medium and determining

excess iodine by titration with standard arsenious oxide using borax and boric acid as buffer. Gupta⁴⁶ estimated thiourea with standard iodine in the presence of sodium bicarbonate buffer and extended the use of this method to the determination of N-methyl derivatives of thiourea. Wojahn⁴⁷ titrated thiourea and a few of its derivatives with standard iodine and silver nitrate solutions. Cihalik and Ruzicka⁴⁸ titrated thiourea at ρ H 4-7 with iodine monochloride potentiometrically; the thiourea was oxidized to formamidine disulphide.

Acidimetric Methods

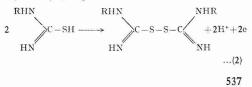
Bayer and $Posgay^{49}$ determined thiourea and allyl thiourea by titrating their acetic acid solutions with 0·1N perchloric acid (in anhydrous glacial acetic acid) in the presence of mercuric acetate using gentian violet as an indicator. Alicino⁵⁰ used acetic acid solutions of crystal violet and quinaldine red as indicators in the above titration.

Oxidimetric Study of Thiourea and Its Derivatives

The various oxidimetric methods proposed for the determination of thiourea are based either on its oxidation to urea and sulphate, or to sulphate, carbonate and nitrogen or to formamidine disulphide under various conditions. Oxidation of thiourea to sulphate and cyanamide, and to urea, sulphate and formamidine sulphonic acid is also reported. Prior to the work of Singh and coworkers⁵¹⁻⁵⁸, no systematic study on the oxidimetric determination of thiourea and its organic derivatives was reported. In our investigations potassium iodate⁵¹, iodine halides (monochloride⁵², trichloride⁵³ and monobromide⁵⁴), potassium dichromate⁵⁵, diethylene tetra-ammonium sulphatocerate⁵⁶ (DTS), potassium bromate (unpublished work), chloramine-T⁵⁷ and potassium ferricyanide58 have been used as oxidants for the direct visual and potentiometric determination of thiourea in sulphuric acid medium. Thiourea has also been determined indirectly by using sodium vanadate and diethylene tetra-ammonium sulphatocerate (DTS) as oxidants in acid medium (unpublished work).

As no visual or potentiometric method with these oxidants seem to have been developed for the determination of organic derivatives of thiourea, we therefore, extended our work to the determinations of thiourea derivatives, viz. methyl thiourea, ethyl thiourea, isopropyl thiourea, *n*-butyl thiourea, *p*-tolyl thiourea, *n*-amyl thiourea, *o*-tolyl thiourea, *p*-tolyl thiourea, *o*-ethoxyphenyl thiourea, *p*-ethoxyphenyl thiourea, *p*-carbethoxyphenyl thiourea and phenyl thiourea.

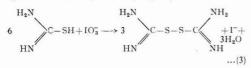
Thiourea and its derivatives are oxidized by these oxidants to the corresponding disulphides with a single-electron change (Eq. 2). In Eq. (2) R=H, alkyl or aryl group.



For convenience the discussion regarding the work done with these oxidants has been classified as follows: (i) potassium iodate and iodine halides; (ii) potassium dichromate; (iii) diethylene tetraammonium sulphatocerate (DTS); (iv) potassium bromate, chloramine-T and potassium ferricyanide; and (v) sodium vanadate.

Potassium Iodate and Iodine Halides as Oxidants

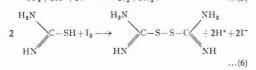
It has been found that one molecule of iodate quantitatively oxidizes six molecules of thiourea to three molecules of formamidine disulphide [Eq. (3)] in sulphuric acid medium at room temperature. R represents H, alkyl or aryl group.



The overall reaction may be represented as shown in Eqs. (4)-(6).

 $IO_3^- + 6H^+ + 6e \longrightarrow I^- + 3H_2O$...(4)

$$IO_3^- + 6H^+ + 5I^- \longrightarrow 3I_2 + 3H_2O$$
 ...(5)



The end-point has been detected visually and potentiometrically. In visual titrations amylose (or chloroform) is used as an indicator. In the potentiometric titrations, change in potential at the equivalence point has been found to be of the order of 40-60 mV. with the addition of 0.05 ml. of 0.05N iodate. The method has been found to be applicable over wide range of acidity, i.e. 0.05-4.00N sulphuric acid. This study has been extended to the determination of various alkyl and aryl derivatives of thiourea. The estimation of thiourea derivatives is direct, simple, accurate, instantaneous and can be carried out at room temperature. As potassium iodate is a primary standard in volumetric analysis, this method is and shall be widely applicable for the analysis of such compounds.

The effect of various organic compounds in the titration of thiourea with potassium iodate using amylose as an indicator was also studied. It has been found that there is no interference due to the presence of sugars (sucrose, maltose, lactose or D-glucose), amines (methylamine hydrochloride, isopropylamine, *n*-butylamine or aniline hydrochloride), amides (formamide, acetamide or urea), acids (oxalic, succinic, adipic, mandelic, tartaric, citric or lactic acid) or carbo-xylic acid salts (sodium formate, sodium acetate, sodium salicylate or potassium hydrogen phthalate).

With the exception of a few potentiometric titrations of thiourea carried out with iodine monochloride⁴⁸, no further work on the estimation of thiourea or its derivatives seems to have been done with iodine halides. During the course of this investigation, the thiourea derivatives have been successfully titrated visually and potentiometrically with iodine monochloride, iodine trichloride and iodine monobromide in sulphuric acid medium. Thiourea derivatives are quantitatively oxidized to their corresponding disulphides and the oxidation follows the same course as discussed above. The determinations with iodine halides are simple, rapid and accurate but the reagents are not sufficiently stable to be recommended in place of iodate.

Potassium Dichromate

Cuthill and Atkins² proposed a method which besides being indirect requires refluxing of the reagents for 30 min. to ensure complete oxidation of thiourea to urea and sulphate. No direct method has so far been developed to determine thiourea or its organic derivatives with potassium dichromate as an oxidant.

During the course of work on this problem it was found that thiourea and its organic derivatives are quantitatively oxidized rapidly to their corresponding disulphides with dichromate at room temperature in sulphuric acid medium using diphenylamine or diphenylbenzidine as an indicator. In potentiometric titrations, the potential shows a drift and takes time to attain a steady value at room temperature. When the titrations are performed with hot solutions, potential attains a steady value immediately on addition of the oxidant. In these titrations, the change in potential at the equivalence point per 0.05 ml. of 0.05N dichromate is 70-120 mV.

The determination of thiourea and its derivatives with potassium dichromate in the presence of potassium iodide in sulphuric acid medium, using amylose (or chloroform) as an indicator, was also found to be successful. With dichromate the course of oxidation can be represented as given in Eqs. (7) and (8). In Eq. (8) R = H, alkyl or aryl group.

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 6\operatorname{I}^{-} + 14\operatorname{II}^{+} \longrightarrow 2\operatorname{Cr}^{3+} + 3\operatorname{I}_{2} + 7\operatorname{II}_{2}\operatorname{O} \qquad \dots (7)$$



All the direct methods worked out for the determination of thiourea and its derivatives with dichromate are simple, accurate and rapid under the specified conditions. Since potassium dichromate is a primary standard, the methods are and shall be of wide application for the determination of such compounds.

It has been found that various organic compounds such as sugars (sucrose, lactose, maltose or D-glucose), amines (methylamine hydrochloride, ethylamine hydrochloride, isopropylamine, *n*-butylamine or aniline hydrochloride), amides (formamide, acetamide or urea), carboxylic acids (succinic or adipic) or carboxylic acid salts (sodium formate, sodium acetate, sodium salicylate or potassium hydrogen phthalate) do not affect the course of titration of thiourea with potassium dichromate in sulphuric acid medium using diphenylamine or diphenylbenzidine as an indicator.

Diethylene Tetra-ammonium Sulphatocerate (DTS)

Cuthill and Atkins² oxidized thiourea to urea and sulphate with ceric sulphate and developed an indirect method for the determination of thiourea by refluxing it with an excess of ceric sulphate for 30 min. and determining excess of ceric sulphate ferrometrically. Kimoto¹⁸ also proposed an indirect method for the determination of thiourea. Diethylene tetra-ammonium sulphatocerate was used by Singh and coworkers as an oxidant in the visual and potentiometric methods for the direct determination of thiourea and its derivatives in sulphuric acid medium.

The reaction between thiourea and Ce (IV) is rapid in the initial stages but becomes slow as the titration proceeds. The reaction has been accelerated by using a few drops of potassium iodate (0.00166M) as a catalyst. Ferroin (or ferrous 2.2'-dipyridyl sulphate) has been used as an indicator in the visual titrations of thiourea and its organic derivatives with DTS. In the potentiometric titrations of thiourea and its organic derivatives with this oxidant, the potential shows a drift in neighbourhood of the equivalence point but the addition of 2-3 drops of ferrous sulphate (0.005N) solution helps to stabilize the potential jump. A sharp jump in potential, i.e. 250-350 mV./(0.05 ml. of 0.02N DTS, has been found at the equivalence point in these titrations. Ferrous salt has already been used by Fisher and Lyubimtsev⁵⁹ for the establishment of steady potential in redox titrations. Visual titrations have also been done indirectly by adding an excess of the standard DTS solution to the thioureas and immediately titrating the excess reagent ferrometrically.

Another direct method of visual and potentiometric determination of thiourea and its organic derivatives with DTS in sulpluric acid medium in the presence of potassium iodide has also been worked out. In visual titrations amylose (or chloroform) has been used as an indicator which turns blue at the end-point. The overall reaction between thiourea and DTS can be represented as shown in Eqs. (9) and (10). In Eq. (10) R = H, alkyl or aryl group.



All the methods, directly or indirectly developed using DTS as oxidant, are simple, accurate and rapid under the specified conditions. Organic compounds such as sugars (sucrose, lactose, maltose or p-glucose), amines (methylamine hydrochloride, ethylamine hydrochloride, isopropylamine, *n*-butylamine or aniline hydrochloride), amides (formamide, acetamide or urea), carboxylic acids (succinic, adipic, tartaric, citric or lactic) or carboxylic acid salts (sodium formate, sodium acetate, sodium salicylate or potassium hydrogen phthalate) do not affect the titration of thiourea with DTS in sulphuric acid medium using ferroin as an indicator.

Potassium Bromate, Chloramine-T and Potassium Ferricyanide

Szebelledy and Madis¹⁹ carried the titration of thiourea with potassium bromate in hydrochloric acid medium at 40-50°C. in the presence of potassium bromide and a little of gold chloride. The end-point which was marked by the appearance of a yellow colour persisted only for 5-10 sec. Mahr²⁰ titrated thiourea with standard bromate-bromide solution in sulphuric acid (6.8*N*) medium at 35° in the presence of potassium iodide and a little of starch. Blue colour appeared at the end-point, when thiourea was oxidized to formamidine disulphide. Rao *et al.*²² found the Mahr's method to be erratic and unsatisfactory.

Singh *et al.*²⁶ carried out potentiometric titration of thiourea by oxidizing it to carbonate, sulphate and nitrogen by chloramine-T in sulphuric acid medium at 80°C. Afanas'ev²⁵ used methyl red or indigo carmine as an indicator in the titration of thiourea with chloramine-T in hot sulphuric acid. Berka and Zyka²⁷ reported that the potentiometric titration of thiourea with chloramine-T in the presence of potassium bromide is possible.

Bapat and Sharma³² developed an indirect method for the estimation of thiourea with potassium ferricyanide using osmium tetroxide as a catalyst. They also reported that ferricyanide could be titrated with dilute thiourea solution with amperometric 'dead-stop end-point' indication but the reverse method of operation was not possible. Bapat and Tatwawadi³³ performed the colorimetric titration of thiourea with alkaline ferricyanide in the presence of osmium tetroxide as a catalyst. All the methods adopted for the estimation of thiourea with this oxidant have been carried out in alkaline medium.

With a view to developing an accurate and quick method which could be carried out at room temperature in acidic medium, Singh and coworkers developed an oxidimetric method, using potassium bromate, chloramine-T or potassium ferricyanide as oxidants, for determining thiourea and its organic derivatives. In this method potassium iodide is used as a catalyst in the visual as well as potentiometric titrations in acidic medium. In visual titrations amylose (or chloroform except in titrations with ferricyanide) is used as an indicator. In titrations with potassium ferricyanide, zinc sulphate is added to precipitate ferrocyanide formed during the reaction as sparingly soluble zinc ferrocyanide. Iodine liberated from potassium iodide by all the three reagents oxidizes thiourea and its derivatives to their corresponding disulphides.

These direct methods are simple and accurate and are carried out at room temperature in acidic medium.

Sodium Vanadate

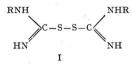
No attempt has so far been made to estimate thiourea or its organic derivatives using sodium vanadate.

Preliminary experiments carried out by Singh and coworkers showed that the reaction between vanadate and thiourea is slow in sulphuric acid medium. The speed of the reaction, however, increases with the concentration of sulphuric acid. Iodine monochloride has also been found to catalyse the reaction. From a number of trial experiments utilizing the high acidity of the solution with respect to sulphuric acid and catalytic effect of iodine monochloride, it was found possible to quantitatively oxidize thiourea and its organic derivatives to their corresponding disulphides.

In this method thiourea and its alkyl and aryl derivatives have been determined by oxidizing them to their corresponding disulphides by an excess of vanadate in sulphuric acid medium and determining the unreacted excess of the oxidant by titration with standard ferrous ethylenediamine sulphate solution using diphenylbenzidine as an (FES) indicator.

Conclusion

All the oxidants described above quantitatively oxidize thiourea and its derivatives to salts of their corresponding disulphides (I)



which are the products of oxidation in acidic medium of compounds containing the thiol (-SH) group. This suggests that thiourea in the presence of acids is a cation (II),



which is derived from the zwitterion structure of thiourea (III)



This is in conformity with its property of being a neutral substance but reacting with acids as a monoacid base forming stable salts.

All the methods developed with the various reagents for the oxidimetric determination of thiourea and its alkyl and aryl derivatives are simple, accurate and rapid under the specified conditions. Particular mention may be made of primary standards, potassium iodate, potassium dichromate, potassium bromate and diethylene tetra-ammonium sulphatocerate (DTS) which have been used for the direct oxidimetric determination of thioureas. All these reagents form stable solutions which do not deteriorate even on long standing. These reagents, therefore, can be recommended for this work.

As the solubility of DTS is limited, it can be used for the determination of small quantities of thiourea and its organic derivatives.

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Biochemical Effects of Trace Element Toxicities

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VER since the middle of the nineteenth century, many elements such as iron, copper, cobalt, zinc, molybdenum, iodine, etc., have been shown to occur in various organisms in minute amounts. The presence of these elements as an integral part of various important cell constituents, such as haemoglobin, haemocyanin, carbonic anhydrase, nitrate reductase, vitamin B12 and thyroxine, indicates the important role played by them in the metabolism of living organisms. The significant part which they play in the harmonious well-being of plants and animals is underlined by the fact that many nutritional disorders of both the phyla can be ascribed to trace element deficiencies or toxicities. To mention only a few examples, iodine deficiency has been shown to be the cause of endemic goiter1, while avian ' perosis' has been demonstrated to be due to manganese deficiency². Further, ' teart', the scouring disease of cattle, is the result of intake of excess molybdenum3, and chlorosis in plants is caused by toxic amounts of cobalt, nickel, copper, manganese and cadmium⁴.

Subsequent to the classical work of Hart et al.5, who unequivocally proved the involvement of copper, besides iron, in haemoglobin formation, many aspects of trace element metabolism have been extensively studied. Thus Vallee⁶ and Lehninger⁷ have discussed the dependence of enzymes on trace elements for their activity. Marston⁸ and Hewitt^{4,9} have described the general metabolism of trace elements in animals and plants, while Vallee¹⁰, Cotzias¹¹ and Coons¹² have reviewed the work done on various aspects of the metabolism of individual trace elements. The treatise by Underwood13 contains a detailed account of the researches on the nutritional aspects of all the important trace elements.

For a study of the role of trace elements, two different lines of approach have been adopted. The first is an investigation of various naturally occurring diseases of man and cattle caused by deficiency or toxicity of a single trace element, while the second consists of an investigation of the effects of either a deficiency or an extremely high amount

of a single trace element present in an otherwise adequate diet for animals, or in the media for microorganisms. As an example of the former, the influence of copper on 'teart' can be quoted¹⁴. The present review summarizes the work carried out for several years adopting the latter approach, primarily with a view to elucidating the toxicological mode of action of heavy metals in their cationic (Co2+, Ni2+ and Zn2+) or anionic (molybdate) forms, and the possible interference of these heavy metals in the function of essential metals, particularly with respect to iron and magnesium.

Zinc Toxicity and Purine Metabolism in the Lepidopterous Insect, Corcyra cephalonica St.

Smith and Larson¹⁵ demonstrated that the growth inhibition and anaemia induced by zinc toxicity in rats were quite unrelated processes. Liver extract partially reversed the growth inhibition without correcting the anaemia. Copper was also able to restore to normal, the levels of the iron containing enzymes, cytochrome oxidase and catalase^{16,17} though it was suggested that disturbance in the normal enzyme make-up did not explain the toxic action of zinc17. To investigate the universality of the above phenomenon, zinc toxicity was studied in Corcyra cephalonica St. which has been shown to resemble the rat in its nutritional requirements and metabolism¹⁸.

Similar to the phenomenon observed in the rat, small amounts of copper sulphate (0.01 per cent of the basal diet) restored to normal the decrease in catalase levels, caused by 0.4 per cent zinc sulphate in the basal diet, without affecting the growth inhibition¹⁹. A zinc-copper antagonism, manifesting itself both at the level of absorption in the gut, and the cellular level as implicated in the rat²⁰, may also play a role in the larva of Corcyra. When the effects of liver extract and vitamin B12 were studied, it was found that both these reduced the high incidence of mortality induced by 1 per cent zinc in the diet without affecting the growth inhibition. However, the partial growth inhibition caused by only 0.4 per cent zinc sulphate in the

diet was found to be completely reversed, and on weight basis liver extract was found more effective than vitamin B12. Hence, factors other than vitamin B₁₂ in the liver extract were looked for. An alkali stable fraction of the liver extract resembled the parent material in restoring to normal the observed inhibition in growth. Other vitamins of the B group were also screened for their ameliorating effect, but were found to be comparatively ineffective. To test whether the beneficial activity of the alkali stable factor was due to its content of nucleic acids, the influences of DNA and RNA were next studied. Both the nucleic acids were as potent as the alkali stable fraction. Since the uptake of zinc was not affected, the possibility of the nucleic acids chelating with zinc to make it unavailable was considered a remote possibility. An imbalance in nucleic acid metabolism involving the enhancement of the requirement of nucleic acid per se, or some of their structural constituents, due to zinc toxicity to Corcyra, was, therefore, indicated²¹.

As a natural corollary to the above findings, the ability of the constituents of DNA and RNA to overcome zinc toxicity in this insect larva was studied, since nucleic acids are known to be degraded to their structural constituents in the gut²². Among the purine bases tested, only adenine and guanine at 0.5 per cent levels annulled the growth depressing effect of excess zinc, while neither the precursor of pyrimidines such as orotic acid nor a typical pyrimidine base like cytosine had a beneficial influence. RNA nucleotides obtained by alkali hydrolysis according to the method of Herbert et al.23 and the purine nucleotides, adenosine and guanosine, resembled the free purine bases in their action^{24,25}. Since the capacity of adenosine to form chelate compounds with metals was reported to be poor26, a disturbance in purine metabolism, due either to an inhibited de novo synthesis or to an accelerated catabolism of purine bases consequent on the intake of excess zinc, was suggested. The salutary influence of vitamin B12, a deficiency of which depresses purine synthesis in the rat27, on zinc toxicity in the lepidopterous insect could also be explained on this basis. All these data indicate that the primary lesion due to zinc toxicity in Corcyra is an impairment in purine metabolism.

Zinc Toxicity and Ascorbic Acid Metabolism in Rat

Earlier observations of Sadasivan²⁸ that intake of excess zinc by the rat affected the levels of liver alkaline phosphatase were confirmed. In view of the reported correlation between ascorbic acid levels and alkaline phosphatase activity²⁹, the effect of zinc toxicity on tissue ascorbic acid content was studied. A depletion of the vitamin C content of the liver was observed. Liver extract partially restored the depressed growth, concomitantly correcting the levels of alkaline phosphatase and vitamin C. Vitamin B₁₂ resembled liver extract in its effect on the inhibited growth and enhanced enzyme level, but it did not alter the ascorbic acid content. The alkali stable fraction of the liver extract partially counteracted only the growth inhibition. DNA was ineffective unlike in *Corcyra ccphalonica* St. The ability of vitamin B_{12} to bring alkaline phosphatase levels to normal without restoring the growth inhibition was similar to the effect of copper on zinc toxicosis^{16,19}. The fall in ascorbic acid content of the liver, considered in conjunction with the observation that the mammalian cell contains the full complement of enzyme for ascorbic acid biosynthesis³⁰, pointed to a decreased ascorbic acid synthesis in zinc toxicosis³¹.

Heavy Metal Toxicities and Ascorbic Acid Metabolism in Phaseolus radiatus

Evidence in literature, though equivocal, indicates that ascorbic acid synthesis by plants is governed by their trace element nutrition. For instance, the observations of Hewitt ct al.32 that, under conditions of molybdenum deficiency, ascorbic acid content was low in plant tissue has not been confirmed by others³³. The prevalence of trace element interrelationships further complicates the situation. This aspect of trace element metabolism was studied with a view to elucidating the role of trace elements on ascorbic acid biosynthesis by P. radiatus during germination. None of the trace elements studied was inhibitory either to growth or to accumulation of ascorbic acid up to a concentration of $5 \times 10^{-3}M$; both the parameters were, however, affected when the amount of trace elements was increased to $1 \times 10^{-2}M$. The trace elements were supplied as their organic acid salts to circumvent the inhibitory effect of anions³⁴⁻³⁶. Zinc, magnesium and iron depressed the growth and synthesis of ascorbic acid, while manganese and copper suppressed the growth without affecting the vitamin production. Iron counteracted the effect of zinc in inhibiting ascorbic acid synthesis without restoring the suppressed growth to normal. In the light of the observations of Hewitt⁴, that zinc toxicity induced iron deficiency chlorosis, these findings might indicate an interference by zinc in iron utilization by the seedlings. Accordingly, the reversal by iron was possibly indicative of a role for iron in the biosynthesis of ascorbic acid by P. radiatus. Moreover, the inhibitory effect of excess iron on ascorbic acid synthesis was annulled by manganese. Somers and Shive³⁷ had shown that if the optimal ratio of 2 between iron and manganese was altered, one metal became toxic, inducing a deficiency of the other. A similar relationship might hold good for ascorbic acid synthesis as well³¹.

Molybdenum Toxicity and Sulphur Amino Acid Metabolism

The ability of toxic amounts of molybdenum to induce copper deficiency in ruminants³⁸ had been demonstrated to be governed by the nutrient status of inorganic sulphate³⁹. Intake of excess molybdenum in rats enhanced the activities of liver and kidney alkaline phosphatases⁴⁰, which could be corrected by feeding sulphate, thiosulphate, cysteine and methionine⁴¹. In animals, these experimental data could not be explained on the basis of any relationship between molybdenum and sulphur amino acid metabolism.

The presence of excess molybdenum in the medium was found to inhibit the growth of a wild strain of Neurospora crassa Em 5297a. This effect of molybdenum was annulled by small amounts of sulphate, sulphite, thiosulphate, cysteine, cysta-thionine, homocysteine and methionine⁴². In_view of the well-known biosynthetic relationship of these sulphur compounds in this organism43, it was apparent that toxic amounts of molybdenum caused an impairment in methionine biosynthesis. As thiosulphate was more efficient than sulphate, it appeared that the conversion of sulphate to thiosulphate was affected. All the sulphur compounds tested had no influence on molybdenum uptake, when the metal was present in the culture fluid in such concentration as to cause inhibition of growth. The extent of inhibition of growth due to molyb-denum toxicity was inversely related to the concentration of sulphate or thiosulphate in the medium.

Molybdenum did not influence the uptake of labelled sulphate by growing cultures of the microorganism, while the uptake by preformed mycelia and subsequent incorporation into protein were inhibited. The decrease of the label in mycelial protein was due to low content of cysteine and methionine. These results led to the conclusion that molybdenum toxicity in *N. crassa* interfered with the biosynthesis of the essential amino acid, methionine, possibly at the stage of sulphate activation⁴⁴. When the metal was present in the medium at a concentration which did not inhibit growth, sulphate, sulphite, thiosulphate, cysteine and methionine depressed the accumulation of the metal by the mycelium⁴⁵.

The mechanism by which molybdenum toxicity was manifested in *Aspergillus niger* appeared to be different from that in *N. crassa*. The amounts of methionine required to overcome the growth inhibition was 5 μ g. per ml. culture fluid in the case of *N. crassa*, while it was 20 mg. per ml. basal medium in the case of *A. niger*. With the restoration of growth to normal, a concomitant decrease in the toxic metal accumulation by *A. niger* was observed⁴⁶.

Molybdenum toxicity appeared to differ from other heavy metal toxicities in A. niger. Magnesium had no influence either on the growth inhibition due to molvbdenum toxicosis or on the uptake of the toxic metal. This was in contrast to its influence on cobalt, nickel and zinc toxicities in this mold. The beneficial influence of iron was found to be dependent on the amount of molybdenum in the medium. When the amount of molybdenum in the culture fluid was increased twofold, from 5 mg. to 10 mg. per 10 ml. basal medium, the amount of iron required to counteract the growth inhibition was found to increase nearly a thousandfold from 5 µg. to 4 mg. per 10 ml. culture fluid. With the restoration of growth to normal, the uptake of the toxic metal was also suppressed (Raman, N. & Sarma, P. S., unpublished data). This is in contrast to the effect of iron on cobalt toxicity in A. niger.

Trace Element Interrelationships in Cobalt, Nickel and Zinc Toxicities

In plants, iron deficiency chlorosis could be induced by extraphysiological concentrations of heavy metals like cobalt, nickel, zinc, etc.⁴. Abelson and Aldous⁴⁷ observed that the deleterious effect produced by excessive amounts of cobalt, nickel, zinc and cadmium in *Torulopsis utilis*, *Aerobacter aerogenes*, *Escherichia coli* and *A. niger* could be counteracted by magnesium, indicating that the toxicity of these heavy metals interfered with magnesium metabolism. In *N. crassa*, cobalt toxicity induced a decrease in the activities of iron dependent enzymes. This decrease could be restored to normal, without affecting the inhibited growth, by small amounts of iron⁴⁸. The toxicities of the heavy metals cobalt, nickel and zinc were extensively investigated in various organisms to determine their universality⁴⁹.

Studies with A. niger

To study the detailed mechanism by which cobalt, nickel and zinc induced their toxicities in *A. niger*, three parameters of comparison were chosen, viz. growth, acid production and glucose utilization. Nickel was found to be the most toxic followed by cobalt and zinc in that order. The organism tolerated a fairly large amount of zinc, unlike cobalt and nickel. Concomitant with the suppression of growth, the acid production and glucose utilization were also depressed.

Since the earlier studies^{4,47,48} indicated that excessive amounts of heavy metals probably interfered with the metabolism of iron and magnesium. the influence of the latter two metals on heavy metal toxicosis was investigated. Though magnesium counteracted the growth inhibiting effect of all the three heavy metals, it was most effective in zinc toxicity. The decreased acid production caused by excessive amounts of nickel or zinc in the medium was restored to normal by magnesium, while that caused by cobalt toxicity was unaffected. A similar beneficial effect was observed on the impaired glucose utilization. The amounts of magnesium required to correct the deranged acid production and glucose utilization were comparatively higher than that required to restore the depressed growth to normal. These data indicated that the three parameters were probably indepen-dent effects of different levels of heavy metal ions. Complete annulment of zinc toxicity by magnesium was indicative of a conditioned deficiency of magnesium due to zinc toxicosis. Iron had a salutary effect on the depressed growth caused by excess cobalt, nickel and zinc in the medium. However, greater amounts of iron than magnesium were required for manifestation of this effect. Iron restored the impaired glucose utilization to normal only in cobalt toxicosis. It was without effect on the decreased acid production, due to all the three heavy metal toxicities, probably because iron by itself has been reported to repress acid production by this fungus⁵⁰. These data also suggested that cobalt toxicity was a conditioned iron deficiency. Sporulation was restored in this mold only when magnesium annulled the heavy metal toxicities, while iron was ineffective. From the above findings it was apparent that the three heavy metals differed in their possible modes of action though their gross overall effects were similar⁵¹.

A study of the influence of magnesium on toxic metal uptake by the mold revealed that only the uptake of zinc and nickel was suppressed, but not that of cobalt. The uptake of the toxic metals was only partially suppressed by magnesium, with restoration of growth to normal, whereas a greater inhibition of the heavy metal accumulation by the fungus was observed when the other two disturbed parameters were corrected. It is quite probable that low levels of magnesium controlled the uptake of the toxic metal at sites associated with overall growth, while the binding of the toxic metals at other loci was strong, thereby making the presence of higher amounts of magnesium obligatory. A mathematical analysis revealed that the antagonism between zinc or nickel and magnesium was similar even quantitatively. Unlike magnesium, iron had no repressive effect on the uptake of the heavy metals concomitant with the annulment of toxicity. This is probably due to a redistribution of the toxic metal to innocuous binding sites within the cell⁵².

Studies with N. crassa

Abelson and Aldous⁴⁷ had conclusively proved that the status of magnesium nutrition governed the induction of heavy metal toxicities in many microorganisms. The existence of such a phenomenon had not been investigated in N. crassa. The growth of the fungus was found to be directly proportional to the concentration of magnesium. up to a level of 50 µg, magnesium per 10 ml, basal medium. Further increase in magnesium levels did not result in enhanced growth. But the conventional normal medium employed actually contained 493.7 μ g. magnesium per 10 ml. culture fluid. However, it was found that the amount of the heavy metals cobalt, nickel and zinc required to induce toxicity in the former minimal magnesium medium was one-tenth of those required to induce similar effect in normal magnesium medium. Enhancing the magnesium contents of both the minimal magnesium and normal magnesium media, under conditions of these heavy metal toxicities, counteracted the growth inhibitory effects. The beneficial effect of iron was found to be dependent on the magnesium content of the medium. More iron was required to overcome heavy metal toxicities in minimal magnesium medium and less iron in normal magnesium medium.

As was the case with A. niger, magnesium was found to counteract by inhibiting the toxic metal uptake by N. crassa while iron had no such effect, though it restored the inhibited growth to normal⁵³.

Investigations with Phaseolus radiatus

When the seeds were germinated for 72 hr in the presence of toxic amounts of cobalt or zinc, a decrease in the growth of the hypocotyl and a parallel increase in the weight of cotyledons were observed. Magnesium restored the weights of the tissues to control values while iron had no such effect. The changes were more pronounced when the weights of the individual parts of the seedlings were considered, indicative of a disturbed utilization of food reserves. The control of the toxic metal uptake by magnesium was pronounced in leaves and cotyledons than in the whole seedlings. Further, these studies were not strictly comparable with growth experiments spread over a longer period, since in short time studies the amount of reserve supplies was restricted⁵⁴.

Studies with Corcyra cephalonica St.

This insect larva resembled the fungi, A. niger and N. crassa, in that cobalt and nickel were more toxic than zinc. Iron counteracted the growth inhibition due to all the three heavy metals, being most effective in nickel toxicity. In contrast to the microorganisms, magnesium annulled cobalt and nickel toxicities, but not that due to $zinc^{55}$.

Heavy Metal Toxicities and Metabolism of Carbohydrates

One of the lesions induced by heavy metal toxicities appeared to be a derangement in the metabolism of the citric acid cycle intermediates, since concomitant with growth, glucose utilization and acid production were also inhibited. To explore this possibility, the influences of citrate, succinate, fumarate, malate and pyruvate on cobalt, nickel and zinc toxicities in A. niger were investigated. Malate and pyruvate were the most effective in restoring both the repressed growth and acid production to normal. Additional inhibition by succinate and the insignificant alleviating effect of citrate on cobalt toxicity indicated the mechanism of manifestation of cobalt toxicity was different from those of the other two metal toxicities. Generally, the acids had little influence on the uptake of the toxic metal, except pyruvate and malate. Concomitant with the annullment of toxicosis, pyruvate in all the metal toxicities and malate in zinc toxicosis suppressed the uptake of the heavy metals. The primary lesion of the disturbed organic acids metabolism appeared to be at the level of the formation of pyruvic and malic acids⁵⁶.

Control Mechanisms in Iron Metabolism in N. crassa

The capacity of microorganisms to survive under adverse conditions had been well established. A striking example of the above could be seen in the case of heavy metal toxicities. It was found that under conditions of cobalt toxicity, an iron binding compound was secreted into the culture fluid by N. crassa⁵⁷. The compound had been found to exhibit a specific affinity for binding iron. This compound was also secreted under conditions of straight iron deficiency. This has been shown to be related to ferrichrome type of compounds, which are secreted by various microorganisms under conditions of iron deficiency. The role of these compounds in iron metabolism have been extensively reviewed58,59. Such iron binding compounds could not be detected in the culture fluid under conditions of nickel and zinc toxicities. This would indicate a direct antagonism between cobalt and iron, and also the fact that the organism developed a mechanism to bind and make available any iron, under conditions of stress caused by the unavailability of this essential metal. The survival value of this

phenomenon was evident from the metabolic potency of iron, chelated in this manner.

Conclusion

On the basis of the studies carried out so far, it may be concluded that heavy metals like cobalt, nickel and zinc induce a gross effect which can be finally traced to a derangement in iron and/or magnesium metabolism. A parallel situation exists in plants, where different heavy metals ultimately induce an iron deficiency resulting in chlorosis⁴. But subtler differences in the mode of action of heavy metals are evident. For example, only in the case of cobalt, a direct antagonism between cobalt and iron can be established, but not in the case of the other heavy metals. Zinc toxicity primarily interferes with the metabolism of nucleic acid intermediates in rice moth larva and magnesium metabolism in microorganisms.

The toxic effects produced by any metal also vary with the test organism employed in the investigation. This has been very well indicated in the case of molybdenum toxicity. In N. crassa it impairs the biosynthesis of sulphur amino acids, while in A. niger its mechanism of action appears to be different. Molybdenum toxicity appears to be different from other heavy metal toxicities in that magnesium has no beneficial influence on the former, even though it does exert its effect on the latter.

The interference with iron and magnesium metabolism by heavy metals is substantiated by the general counteracting effects of the former two metals though subtler differences are apparent. There is also a basic difference in the modes of action of iron and magnesium. Magnesium generally exerts its beneficial effect by suppressing the uptake of the toxic metal, while iron counteracts the toxic effect without inhibiting the entry of the toxic metal into the cell.

The isolation of the iron binding compound under conditions of cobalt toxicity or direct iron deficiency in N. crassa and its metabolic potency in iron nutrition emphasize the role of such types of chelated iron compounds in iron transport. Thus, studies on heavy metal toxicities not only lead to an understanding of the mode of action of the toxic metal but also provide an insight into certain aspects of normal cell function.

Summary

Biochemical effects of trace element toxicities in different types of organisms have been reviewed. These include: (i) zinc toxicity and purine metabolism in Corcyra cephalonica St.; (ii) zinc toxicity and ascorbic acid metabolism in the rat; (iii) heavy metal toxicities and ascorbic acid metabolism in Phaseolus radiatus; (iv) molybdenum toxicity and sulphur amino acid metabolism in Neurospora crassa and Aspergillus niger; (v) trace element interrelationships in cobalt and zinc toxicities in A. niger, N. crassa, P. radiatus and C. cephalonica; (vi) heavy metal toxicities and metabolism of carbohydrates; and (vii) control mechanisms in iron metabolism in *N. crassa*. On the basis of the studies carried out so far, it has been concluded that trace element toxicity is dependent on the nature of the trace element as well as the organism investigated. It is also concluded that heavy metals like cobalt, nickel and zinc induce gross biochemical effects which can be finally traced to iron and/or magnesium metabolism. It is indicated that studies on heavy metal toxicities provide an insight into certain aspects of cell function.

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Symposium on Recent Advances in Development, Production & Utilization of Medicinal & Aromatic Plants in India

A Symposium on Recent Advances in Development, Production and Utilization of Medicinal and Aromatic Plants in India will be held at Lucknow during 12-14 January 1966 under the auspices of the Central Indian Medicinal Plants Organization. The symposium will confine itself to developments in the production and utilization of medicinal and aromatic plants in India since 1955. The main topics of discussion at the symposium will be: (i) Distribution, acclimatization, collection and cultivation of the plants; codes of practice for their storage, handling, processing, etc.; (ii) Improvement of the plants by methods of selection, hybridization, induced mutations, etc.; (iii) Pests and diseases of the plants and their control; (iv) Standardization of plant materials, process equipment, etc., with a view to upgrading the yield and quality of the products derived therefrom;

(v) Pharmacological and microbiological studies on products derived from medicinal and aromatic plants; (vi) Studies on insecticidal, insect-repellent, pesticidal and fungicidal properties of medicinal and aromatic plants and the products derived therefrom; (vii) Utilization of medicinal and aromatic plants based on their chemical and phytochemical characteristics; (viii) Subjects of vital interest such as Nematode problem in patchouli, Spike disease of sandalwood, utilization of non-citral portion of lemongrass oil, etc.; and (ix) Survey and availability of medicinal and aromatic plant materials and products made therefrom, their import and export.

Details regarding contribution of papers and other information can be had from Dr S. C. Datta, Central Indian Medicinal Plants Organization, 4 Sapru Marg, Lucknow.

VARIATIONAL TECHNIQUES IN ELECTROMAGNETISM by Laurent Cairo & Théo Kahan (Blackie & Son

Ltd, London), 1965. Pp. xv+152. Price 27s. 6d. Variational techniques have been widely employed in the solution of quantum mechanical and other problems in the last 15 years. This book contains a useful introductory account of these techniques and their application to the electromagnetic theory. The first chapter describes some concepts of vector space and introduces the delta function; the second chapter introduces dyads; Green's functions are described in the third chapter; a survey of the variational principles is given in the fourth and the fifth chapters, and the applications of variational principles to the solution of diffraction, scattering and waveguide propagation problems are given in the next six chapters. There are two appendices, one on the axiomatic definition of a vector space and the other describing the bra and ket notation of Dirac.

The book does not describe the physical significance of the results; it is concerned only with the mathematical techniques. Even the electromagnetic equations or the significance of the boundary conditions imposed on the electric and the magnetic fields are not explained adequately anywhere. The book is, therefore, not meant for a beginner or a general physicist; it is valuable only to the specialist who wants to use these techniques in his own work.

There are some statements in the book which need to be corrected or elaborated. For example, the statement 3(a) on p. 26 about the symmetry of Green's function is not true for the explicit expression (3.15). The addition theorem for spherical harmonics mentioned on p. 28 should be stated. The introduction of the operator f(u) on p. 30 is unnecessary and the difference of minus sign between the P used in Eq. (3.29) and the **P** used earlier should be avoided, or, at least, stated. The employment of variations on p. 43 that vanish at the boundaries needs further explanation, and the condition $\Psi' = \Psi$ should be more precisely stated to be true only at the limits or to first order in α elsewhere. The use of Δ for denoting variations on p. 43 is confusing in view of its earlier definition in Eq. (4.3) as the Laplacian operator. The statement about the definition of electromagnetic coupling on p. 61 should be further elaborated. Lastly, the reviewer would suggest the use of tensor notation which is clearer and much more powerful than the dyad notation employed in the book.

The book is very well printed, though there are some minor errors left. To mention a few, the left-hand side of Eq. (3.21) should be $f(r, \theta, \phi)$ instead of (r, θ, ϕ) ; the sign in one of the identities on p. 30 should be plus instead of minus; the second expression for [λ] in Eq. (4.24) ought to have been $\tilde{\chi}$ and not f. On p. 79, N should be defined as $\partial \Psi / \partial n$ and not $\partial \Psi / \partial n'$.

The book is recommended to the theoretical physicists intersted in finding approximate solutions of quantum mechanical or electromagnetic problems. VACHASPATI

ELECTROMAGNETIC ASPECTS OF HYPERSONIC FLOW edited by Walter Rotman, Howard K. Moore & Robert Papa (Spartan Books Inc., Baltimore), 1964. Pp. ix+369. Price Rs 75.00

When an aerospace vehicle re-enters the earth's atmosphere, it is surrounded by a plasma sheath and further trailed by a wake of ionized gas. Ionization of the flow around the vehicle arises due to several causes, such as the shock heating of the atmospheric gases during re-entry, the plume exhausts of both chemical rockets and electrical propulsion engines, and solar radiation. In recent years, interest around the nature and properties of the plasma sheath surrounding the space vehicle has grown enormously consequent to the discovery that the sheath is able to black out radio communication and distort radar signals. The volume under review is a collection of papers presented at the second sym-posium on 'Plasma sheath — Its effect upon re-entry communication' held in Boston in 1962, and provides the radar with the very recent advances in several topics of technological importance in re-entry communications and diagnostic techniques.

The first few papers in the book deal with the electrical properties of ionized flow fields and the effects of contaminants in changing plasma parameters. A second and more important topic treated in several of the papers relates to the radiation characteristics of plasma covered antennas. Although estimates of signal attenuation during reentry have usually been based upon the idealized assumption of a plane wave incident on a semiinfinite slab of plasma, this does not adequately describe the changes in the radiation patterns of a small aperture antenna in a complex aerospace vehicle. For example, the radiation patterns of a slot radiator on a cylinder are drastically modified by the presence of the plasma sheath even when the plasma frequency is substantially below that of the radio signal. The most direct method of improving communications and radar system reliability is to increase the propagation frequency well beyond the peak plasma frequency in the shock wave. Other suggested solutions include the aerodynamic modifications to the airframe and its radiating systems, chemical additives for the reduction of electron densities in the flow fields, and static magnetic fields which can open radio frequency 'windows' in the plasma.

A third group of papers in the book deal with diagnostic techniques for flow field studies, re-entry radar cross-section, effects of static magnetic fields and voltage breakdown of antennas at high altitudes. The diagnostic techniques include instrumentation for hypersonic shocks and wind tunnels, for ballistic ranges, and for missile flight tests.

It needs hardly to be mentioned that this book will be warmly welcomed by all workers in hypersonic flow and re-entry physics.

K. S. VISWANATHAN

ELEMENTARY PLASMA PHYSICS by Lev A. Arozimovich (Blaisdell Publishing Co., New York), 1965. Pp. 188. Price \$ 2.25

Recently a number of books have appeared on plasma physics, but they are meant for persons familiar with physics usually taught at the postgraduate level. The volume under review is a remarkable book in which the principles of plasma physics are discussed from the point of view of a reader familiar with higher secondary school physics and mathematics. The author has succeeded in this job. Starting from the properties of charged particles in electric and magnetic fields, he discusses the fundamental properties of plasma, and describes experimental techniques for determining the parameters characterizing a plasma. The subject is developed to the point when the reader is able to appreciate the technological applications of plasma to thermonuclear reactions and plasma engines.

¹ The book makes a very interesting reading and can be recommended to any general reader interested in plasma physics and its applications.

F. C. Auluck

PROGRESS IN DIELECTRICS: Vol. 6, edited by J. B. Birks & J. Hart (Heywood & Co., London), 1965. Pp. vii+334. Price 84s.

The book consists of 4 critical reviews on electric force effects that occur in dielectric liquids, polymeric semiconductors, space charges in dielectrics and the theory of ionic and electronic mobility in liquids. Each of these review articles and an extensive bibliography on energy transfer in polyacene solid solutions are written by the authors who are experts in their fields.

The polymeric semiconductors is a new class of materials and these materials are becoming increasingly important. The authors of this article have given a full and up-to-date account of the composition and properties of polyacene quinone radical polymers, polymeric donor-acceptor complexes and biological polymers. Special attention is given to experimental techniques. The electrical behaviour of these materials is related to that of organic crystals and hence the inclusion of bibliography on energy transfer in solid polyacene solutions is very appropriate. The article on space changes in dielectrics is devoted to the theoretical as well as experimental studies of the topic and is very lucid. Similarly, the articles on the theory of ionic and electronic mobility in liquids and on electrical force effects in dielectric liquids are very detailed descriptions of the progress that we have made in understanding these subjects. An extensive bibliography is given at the end of each of the four review articles. Subject index and author index are given at the end of the book.

The book certainly fulfils the aim of the series (of which it is the sixth volume) "to provide a common meeting point for all interested in dielectrics — the electrical engineer, the physicist, the electronic engineer, the molecular chemist, the biologist and the technologist in the whole range of newer dielectric materials". It will be warmly received by scientists interested in many different disciplines.

S. C. JAIN

POLYMERS: STRUCTURE AND BULK PROPERTIES by P. Meares (D. Van Nostrand Co. Inc., New York), 1965. Pp. xii+189. Price 27.6s.

In recent years great advances have been made in the control exercised in the syntheses of large number of polymers. The enormous variability of polymer technology has provided a whole spectrum of substances that can be made depending on the ratio of the three phases, liquid, solid and rubber, put into the system. With such a wide spectrum of materials possessing a wide range of physical properties, information on the structure and bulk properties becomes valuable for successful utilization of the materials in industries and in well-known popular usages. This book on polymers - their structure and bulk properties provides an excellent account of current knowledge of the physical properties of polymers in bulk in relation to their molecular structures. The first three chapters on chemical basis of polymers, the microstructure of chain molecules and molecular weight and branching give wellunderstood knowledge and information on the control and characterization of the molecular structure relevant to the bulk properties of the polymers. Chapters 4 and 5 deal with crystalline polymers, principles of crystalline structure, morphology of crystalline polymers, general kinetic features of crystallization among other related topics.

The remaining eight chapters are devoted mostly to amorphous polymers, developing the thermodynamics of rubber-like elasticity, the statistical thermodynamic theory of high elasticity, practical aspects of elasticity theory, the nature of viscoelasticity, retarded high elasticity and irreversible deformations. Mechanical properties of polymeric glasses, theories of glass transition are described in some detail. Diffusion of gases and vapours in polymers and irreversible deformations, theoretical treatment of bulk viscosity, effect of temperature and molecular weight on viscosity and related topics are covered in the last two chapters in the book.

The book is well written and well indexed. It will be very useful to advanced students and research workers in polymer science. To the technologists in industry who need to understand bulk properties of polymers to select wisely their materials for specific end uses, the book will also be useful.

M. S. MUTHANA

CLASSICS OF SCIENCE: Vol. 2 — THE DISCOVERY OF RADIOACTIVITY AND TRANSMUTATION edited by Alfred Romer (Dover Publications Inc., New York), 1964. Pp. xi+233. Price \$1.65

This book is Vol. 2 of the Classics of Science series and is a collection of articles by Becquerel, Rutherford, Crookes, Soddy, P. Curie, M. S. Curie, Laborde and Ramsay — pioneers in the fields of radioactivity and transmutation — with editorial comments.

The first chapter deals with the discovery of the uranium radiation which was mistaken to be phosphorescence. Rutherford's discovery of similar radiation emitted by thorium forms the second chapter. The chemical investigations of Sir William Crookes on the radioactivity of uranium and the separation of uranium-X are included in Chapter 3. Chapter 4 deals with investigations on the nature of changes occurring as a consequence of these radiations, while Chapter 5 outlines the estimates of the energy involved in the radioactive change. Chapter 6 contains an article by Ramsay and Soddy, establishing the transmutations beyond doubt. The Bakerian lecture of Rutherford forms Chapter 7 giving a detailed disposition of the subject.

Some of these articles are translated versions of the originals. The articles themselves are highly interesting and are well selected to form a coherent picture of the history of the field. A reader never fails to see the systematic approach in the development of the time-consuming investigations with the then available equipment. The editor has carefully selected the papers and divided them into chapters to deal with the progressive development under separate heads and connected the articles as well as the chapters with his commentary.

On the whole, the book makes an interesting reading even to a layman and can be recommended to every student concerned with the history of science, in general, and history of radioactivity, in particular.

V. LAKSHMINARAYANA

MILLING METHODS IN THE AMERICAS edited by Nathaniel Arbiter (Gordon & Breach Science Publishers, New York), 1964. Pp. viii+486. Price \$ 7.50 (paper); \$ 11.50 (cloth)

This publication issued on the occasion of the Seventh International Mineral Processing Congress, 1964 and the Centennial Celebrations of the School of Mines, Columbia University, surveys, as the title indicates, the mineral processing operations in the Americas.

There are 20 chapters in the publication. Two are of general interest and the remainder covering processing of mineral commodities in Chile (1), Canada (5) and USA (12) truly represent the milling methods in the Americas. The editor has to be congratulated for securing contributions on representative milling operations, covering, in general, 'the larger and newer plants producing the more important minerals'. All the chapters are contributed by experts in the field and deserve study by scientists, technologists, mill operators and businessmen interested in the processing of minerals.

Special mention must be made of the second chapter on 'Present trends in mill design', wherein attempts have been made to correlate major trends in mill design with important technological developments of the last decade involving the use of (i) hydrocyclone particularly in fine grinding circuit, (ii) instrumentation and automatic control, and (iii) the employment of new techniques, tools and materials. This chapter containing many useful facts, personal observations and conclusions of the authors on their experience will be of special interest to metallurgists designing new plants.

The publication covers information on a number of minerals, both metallic and non-metallic, and also a variety of methods employed for their processing. The commodities covered include iron ores, including taconite (3), copper (3), copper-nickel (1), lead (1), zinc (1), lead-zinc (1), uranium (1), gold (1), columbium (1), beach sands (1), ilmenite (1), asbestos (1), phosphates (1) and potash (1). It is not possible to give all the details in this short review. However, it may be said that most of the milling methods have been comprehensively described and profusely illustrated with flowsheets, diagrams and photographs.

Chapters 5, 7 and 10 on processing of iron ores after beneficiation to pellets are of special significance to India with large reserves of iron ore. Similarly, Chapters 15 and 16 on the recovery of nickel and molybdenum as byproducts from copper ores are equally important. These chapters could have been more useful, if data on flotation, reagent additions and chemical analyses of products at various stages of processing had been made available. Another interesting fact is the recovery of nickel sulphide from Bessemer matte at Copper Cliff (by flotation).

Although the details of many of the plants described are available scattered in the technical literature, Prof. Arbiter has to be complimented for making them available together in a single volume.

G. V. SUBRAMANYA

SOLUBILITIES OF INORGANIC AND ORGANIC COM-POUNDS: Vol. II — TERNARY AND MULTICOMPO-NENT SYSTEMS, Part 2, edited by H. Stephen & T. Stephen (Pergamon Press Ltd, Oxford), 1964. Pp. 947-2053. Price £ 12.10s.

This volume (comprising Parts 1 and 2) is part of the two-volume extensive work of reference originally compiled in Russian — by a panel of scientists specially appointed by the USSR Academy of Sciences and subsequently brought out in English.

Carefully selected data from the international chemical literature on the solubility of elements, inorganic compounds, metallo-organic compounds and organic compounds in ternary and multicomponent systems are presented in this volume, while Vol. I dealt with their solubility in binary system only.

To obviate ambiguity as to the exact structure of a compound and also any possibility of misinterpretation resulting from various types of nomenclature, the editors have ensured that all the compounds have been named in accordance with the recommendation of the Commission on Nomenclature of Organic and Inorganic Compounds of the IUPAC. This enables the user to combine, compare and evaluate without difficulty the data obtained from a variety of sources on the same or closely related compounds.

The extensive solubility data are presented in a special tabular form (Tables 1-4955) dealing with ternary systems and Table 4956 *et seq.* devoted to multicomponent systems. Tables are numbered consecutively; the number on top left-hand corner enables the location of any required compound in the index published at the end of Vol. II, Part 2 (pp. 1796 *et seq.*), while numbers on the top right-hand corner refer to the original literature reference from which the data have been selected and these references are arranged numerically on pp. 1762-95 in Vol. II, Part 2.

The arrangement of the data in both ternary and multicomponent systems is the same, namely the first tables are systems in which an element is a component. These are followed by data for systems containing inorganic compounds, then metallo-organic compounds. Next in order are systems in which water is one component, the remaining components being organic, followed finally in the ternary section only by systems all the components of which are organic substances.

The sequence of tables containing elements, inorganic compounds and metallic salts of organic acids are determined by the position of the element of the cation corresponding to the element in the periodic classification of elements. The compounds of each element are arranged: first the oxides and their hydrates are given, and then salts of halogen acids, followed by salts of other acids.

Salts of organic bases with inorganic and organic substances are arranged within each group in numerical order by the number of C, H, N, O and other elements in the molecules of these compounds.

In the formula index, the formula of components A (the substances dissolved) are arranged in accordance with the systematization indicated above. The components B, C (and D in the case of multicomponent system) refer to the solvents in each case and are arranged in line with component A.

In the index of compounds, the names of component A are arranged alphabetically and conform to the IUPAC rules. Inorganic and metallcorganic compounds are listed under the elements in alphabetical order (except that acids, hydrazines, hydroxylamines, etc., have separate headings). The organic compounds are arranged within the same alphabet by the parent compound. The components B, C and D in the case of multicomponent systems are arranged alongside component A, also in alphabetical order.

Compilation of such data compressed into two volumes is a highly difficult task, though the results greatly benefit the research worker in saving time and energy which otherwise would have been wasted in searching out the various details from innumerable (and often inaccessible) sources.

For bringing out such a valuable reference work the Soviet scientists who brought out the original volumes should be highly commended and the Pergamon Press and the editors of the English edition congratulated in making these data available to the whole English-speaking world.

Needless to say, this volume (and its predecessor) will be highly useful as a reference work and as such should find a place in all libraries.

B. C. SUBBA RAO

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RARE EARTH RESEARCH: II — Proceedings of the Third Conference on Rare Earth Research, edited by Karl S. Vorres (Gordon & Breach Science Publishers, New York), 1964. Pp. xvi+621. Price \$ 29.50

This book covers the proceedings of an international conference on materials organized at the Carnegie Institute, Washington, by the financial support of the Buhl Foundation. The conference was obviously well attended by prominent workers as could be assessed from the list of contributors as well as from the names of participants appearing in the 'Discussion'. The papers, though they cover a narrow field, are of a high calibre and are comprehensive. The policy committee has done well in focusing its attention on some of the more important current problems in the field of solid state chemistry and physics of transition metal oxides. The ten papers presented at this conference cover the transport properties of transition metal compounds, with particular emphasis on the role of the magnetic structure. They deal both with experimental techniques now employed, such as the neutron diffraction and X-ray diffraction, as well as with the theoretical aspects based on the band picture of solids.

The arrangement and the scope of the papers give a fine review to the worker in the field, for whom the book will be extremely useful, especially the lively discussions which have been reproduced from the original tape-recordings.

Being the 'informal' proceedings, the book lacks an index and a list of all the participants and their affiliations; even the affiliations and addresses of the authors of the papers are not given. Nevertheless, the book will be of interest to the specialized research worker in many disciplines.

JAGDISH SHANKAR

ACID BASE EQUILIBRIA by Edward J. King (Pergamon Press Ltd, Oxford), 1965. Pp. xi+341. Price £ 6

This is a volume in the series on the International Encyclopaedia of Physical Chemistry and Chemical Physics. The volume under review is intended as an introduction to experimental studies and theoretical interpretation of equilibria and represents a fairly thorough study of acidity functions under various conditions. The subject is covered in 12 chapters. A brief introduction to the subject is followed by a critical account of the different experimental techniques that have been adopted. A feature of the volume is the choice of data and the illustrative examples worked in detail taking data from original papers which a beginner in the field will find quite useful. The limitations of each method are clearly indicated. The experimental section is followed by one correlating acidity constants with molecular Grimm in evaluating proton affinity sounds the cautious note, " it is difficult to obtain reliable values for the proton affinities of complex bases" and "more limited information about the behaviour of complex acids in the gas phase can be obtained by standard methods of statistical mechanics". The role of structure of solvents as well as of electrostatic effects in proton transfers are clearly indicated. A chapter which will be of particular interest to many will be the one on temperature and pressure effects. The impact of more recent work on mixed solvent systems in electrochemical and kinetic studies is noticed in the inclusion possibly for the first time in such a monograph of sections on medium effects and non-aqueous solvent systems. A careful study of the volume will suggest many problems for further study, both experimental and theoretical, and the reviewer can strongly commend this to all workers in this field. As one might expect, while there is initial reference to Lewis acids, since only the Bronsted theory is capable of quantitative analysis, the volume treats acids and bases only in the Bronsted sense. A well-produced volume, it should find a place in all advanced libraries, but the prohibitive price will deter any college or individuals, at any rate in this country, from buying a copy.

S. V. ANANTAKRISHNAN

ADVANCES IN RADIATION BIOLOGY: Vol. 1, edited by Leroy G. Augenstein, Ronald Mason & Henry Quastler (Academic Press Inc., New York), 1964. Pp. x+285. Price \$ 11.00

This first volume in this series contains six essays on specific topics by authors distinguished for their personal researches in the respective areas.

Harold A. Schwarz reviews recent works bearing on the nature of the radicals produced in water by radiation and on the rates of some of the reactions of these radicals. Gordon Tollin attempts to delineate the essential features of the primary process of photosynthesis from considerations of light absorption and emission by plant pigments, electromagnetic energy transfer among and between pigment molecules and the transfer and migration of electric charge. D. E. Wimber considers various radiobiological effects that may be produced by intracellular tritium incorporation and cautions on the need to bear these in mind in the design of experiments in which this marvellously versatile tool is to be used as a tracer, although, admittedly, there may be variations within several orders of magnitude in the radiosensitivity to tritium beta-irradiation of different organisms. Arne Forssberg surveys known information on biological effects of small doses of ionizing radiations, the materials presented being chosen in a somewhat arbitrary manner. These include cytological lesions, cell deaths and growth rate changes, as well as biochemical and biophysical effects. The author has, in many cases, drawn attention to claims of radiation activity which may need further enquiry. J. Liebster and J. Kopoldova give a detailed picture of the present state of knowledge of the reactions of amino acids in aqueous solutions under the influence of ultraviolet and, more especially, ionizing radiations. L. G. Augenstein, Tor Brustad and Ronald Mason analyse extensively the nature of temperature effects on enzyme inactivation by various radiations vis-à-vis the development of radiobiological damage and conclude that non-ionizing excitations may play a prominent - and perhaps predominant - role in enzyme inactivation.

Radiation biology, like other emerging sciences, is an interdisciplinary subject where significant advances have resulted from the coordination of sophisticated concepts and methodologies associated with the more traditional areas of biology, chemistry and physics. Research has also changed in many ways from individual to team effort and from simple to more complex, in pattern and productivity. In an area of rapidly accumulating knowledge, therefore, this series will be of immense value to keep us in contact with branches of the subject other than our own, to follow, in summary, techniques of experimentation and developments, as well as, generally, to draw guidelines for future progress in the subject.

A. SREENIVASAN

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- NUCLEAR MAGNETIC RESONANCE IN A FLOWING LIQUID by A. N. Zhernovoi & G. D. Latyshev (Consultants Bureau Enterprises Inc., New York), 1965. Pp. 180. Price \$ 22.50

Wig-wag: An inexpensive device for measuring solar radiation

A new mechanical device for measuring solar radiation, having the advantages of low cost, high accuracy, dependable field performance, easy maintenance and simplicity of measurement, has been developed at the Experiment Station, Hawaiian Sugar Planters Association, Honolulu. The new instrument is made up of three basic components, viz. (i) a swinging pulse-glass made up of two spherical glass bulbs connected by a straight tube and mounted in a special way, (ii) a wooden housing, and (iii) a counter. The pulse-glass bulbs are filled with anhydrous methyl alcohol evacuating them and scaled and mounted at the midpoint of the assembly, on a shaft so inclined that the bulb exposed to the sun is at a slightly lower level. In operation, the exposed lower bulb gets warmer. The resulting increase in vapour pressure forces the liquid in the bulb to move up and hence causes the pulse-glass to tilt and thus bring the cooler bulb to the lower level. The action is now repeated as long as there is a sufficient temperature difference between the two bulbs, the rate being proportional to the incident energy. It is because of this swinging motion caused during its operation that the device is called the 'Wigwag'.

The wooden housing (made of plywood boards) has been designed (i) to permit the lower bulb of the pulse-glass to be exposed to the sun while the upper one is shaded, (ii) to allow for run-off rain and (iii) to present external radiation from entering the interior of the housing. With the present design, it is necessary to change the orientation of the housing of the unit twice a year (summer and winter). However, it is also possible to confine the unit to a permanent setting by changing the slope of the front of the housing. The mechanical counter is a gear-anddial mechanism of a watt-hour meter modified to move the unit · Zero-leakage pump dial by one division for every completed swing. The incident radiation can be expressed in terms of that received by a horizontal surface through the application of

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the Lambert's cosine law and a calibration curve can be drawn connecting the swing rates with the solar radiation received [Solar Energy, 9 (2) (1965), 277.

Laser-actuated anemometer

A laser-actuated anemometer, developed at the Sperry Rand Corp., Great Neck, NY, can measure the motion of matter in all its three states of aggregation at flow rates as low as 0.5 mile/hr for air and thousandth of a mile/hr for water. The new instrument, more sensitive and cheaper than the new sonic anemometers, is based on Fresnel's theory that light propagating through a moving transparent medium undergoes a change in velocity, that is, a dragging effect.

Two counter-rotating beams of light are made to whirl around a small square 'ring' by mirrors set at 45° at each corner of the ring. One of the mirrors is partially transparent and both the beams slip through it to strike a photocell. The photodevice can detect no appreciable difference between the two beams if they are tuned to a set frequency. If a moving transparent system is introduced in the optical path, the beam travelling in the same direction speeds up and the other moving in the opposite direction slows down. The frequency shift thus caused in both the beams is sensed by the photocell and converted into a precise rate measure. The faster the flow, greater will be the frequency difference. A Faraday bias applied to the optical path ensures accuracy of measurement. The laser flow meter has no moving parts, is quick to respond, does not interrupt the flow and can be built as a three-axis device to sense all possible flow directions [Chem. Engng, 72 (4) (1965), 116].

A zero-leakage canned motor pump for use with controlledcirculation boilers in electric utility power plants has been developed at the Atomic Motor Product Section of the General Electric, Schenectady, USA. The pump is an integral unit consisting of a polyphase induction motor and a centrifugal pump. Motor parts are arranged in a pressure vessel so that high pressure, high temperature boiler water can be circulated without using high pressure mechanical seals. An externally mounted integral heat exchanger cools the internal motor water and at the same time a small shaft-mounted pump circulates this internal water for motor cooling and bearing lubrication. Because the rotor shaft and the bearings are housed inside the pressure vessel, there is no rotating shaft seal between the motor and the pump. As a result, leakage, seal maintenance, and the need for high pressure injection water and complicated starting procedures are eliminated. Bolted and gasketed construction prohibits leakage at the top cover and at motor-pump joints; and motor windings are in a hermetically sealed cavity filled with inert gas. A heat resistant adapter between the motor and the pump ensures lower motor-cavity temperatures while the equipment is running or is on hot stand-by. Even if the circulation of cooling water is interrupted the internal temperature remains below safe operating limits for about 2 hr. As there is no leakage the pump can be used to circulate fluids that are corrosive, toxic, explosive or flammable [Mech. Engng, 87 (2) (1965), 547].

Mass spectrometers in geophysical and geochemical research

In analytical work, mass spectrometers using spark excitation of solid samples have many advantages over other analytical techniques, viz. emission spectroscopy, neutron activation, polarography, flame photometry and chemical methods in that they are capable of determining elements in geological materials with impurity concentrations of the order of 1 p.p.m. They are useful in general survey

analysis and in dating of rocks. Two mass spectrometers, MS7 and MS10, developed by the Associated Electrical Industries Ltd, UK, have been successfully employed in some laboratories for geophysical work and geochemical analysis.

Geochemical application of spark source spectrography - In this machine a vacuum spark is used to produce a beam of positive ions, largely because this provides roughly equal sensitivity for all elements. Ions produced in the spark discharge are accelerated through a series of slits by a potential difference of 20 kV. A double focusing system with both an electrostatic and a magnetic analyser is used. This design compensates for the wide spread of ion energies produced in the spark source and brings ions to focus in one plane, enabling a photographic plate to be used to detect them.

The rock samples are crushed into powder, mixed with an equal weight of high purity graphite powder and formed into a rod $20 \times 2 \times 2$ mm. in a small laboratory press. The sample is then trimmed in a lathe to remove possible surface contamination. Two of the rods are clamped in the electrode holders in the source. Since only a few mg. of the sample are consumed for the largest exposures, careful attention to mixing and sampling procedures is necessary. To achieve the requisite detection limits, pressures of the order of 10⁻⁸ mm. Hg (torr) are required in the analyser region. A spark voltage of 25 kV. has been applied and graded series of exposures recorded, the pulse length and repetition of the spark being increased for larger exposures. To minimize the effects of instability of the spark discharge, exposure is measured in terms of the total integrated ion content. Instantaneous ion current is of the order of 10⁻¹² amp. for short exposure conditions, rising to about 10-9 amp. when large exposures are recorded. Mass spectra are normally recorded in the range 7-240 mass units. enabling nearly all the elements to be recorded during a single exposure. When the plates are developed, the density of the mass lines is read using a microdensitometer. Densities are converted to intensities using a plate calibration curve.

Readily volatile and easily ionized elements such as the alkalis show increased sensitivity, other readily volatile elements, such as thallium, lead and antimony, which possess high ionization potentials, are less sensitive. The least sensitive appear to be the non-volatile elements such as titanium and zirconium. The instruments are well suited to the determination of the rarer elements in geological materials, particularly those with isotopes of mass greater than 90. The lighter, rarer elements, lithium and beryllium, suffer interference from multiple-charged silicon and aluminium, but boron can be determined using ¹¹B.

Potassium-argon method of dating — The mass spectrometer has been used successfully for the isotopic dilution determination of the minute amounts of ${}^{40}A$ (argon) generated in rocks by the radioactive decay of ${}^{40}K$ (potassium). It can identify components present at partial pressures below 10^{-10} mm. Hg. The instrument analyses gases according to the mass numbers of the constituents present; and covers mass numbers from 2 to 200.

Simplicity, consistent with the ability to separate hydrocarbon residuals from the argon peaks, has been the chief aim in its design and construction. MS10 mass analyser has been proved to be of value in isotopic dilution determination of minute amounts of ⁴⁰A generated in rocks by the radioactive decay of ⁴⁰K. Analysis of rocks from the oldest available down to those only 1 million years is possible. An extreme advantage has been the fact that there is no trace of the memory' effect from the previous analysis which has long been troublesome in other work and which has not been completely removed by baking. Isotope ratios may be measured with an accuracy of ± 0.5 per cent or better after calibration of the amplifier and recorder systems.

Microtechnique for cell electrophoresis

Micromethods have been applied to minimize the large quantities of materials and chambers involved during the electrophoretic study of cells. The following three approaches have been made to improve the conventional apparatus: (1) to decrease the total volume of the chamber; (2) to build the apparatus from several parts and fill only one of them with the cell suspension; and (3) to introduce the sample to the measuring place of a previously filled chamber. The first approach is complicated by the contamination of the electrodes. the second approach, the In problem has been resolved by constructing an apparatus containing 3 parts which can handle samples of the order of 1 ml. or even less. Only the microelectrophoresis tube is filled with sample while the electrode compartment remains free from cells | Blood, 18 (1961), 599. The third approach has been made possible with the construction of an apparatus that can handle minimum volumes of 0.1-0.2 ml., which has been further reduced to 0.01 ml. by modifying the apparatus described by Bangham et al. [Nature, Lond., 182 (1958), 642].

The modified apparatus has been tested and calibrated with human red blood cells whose electrophoretic mobility is known to be independent of age, sex and blood group of the donor and of the pHbetween 5.0 and 9.0. The apparatus permits one to work with cell volumes smaller than those allowed by earlier techniques. In problems involving small tissue fragments, this method is useful and even when large amounts of cells are involved, it is handy and rapid for repeated measurements [Nature, Lond., 205 (1965), 1105 ...

Specific cleavage of serine peptides

The first step in understanding the architecture of a complex protein molecule is the determination of the amino acid sequence, i.e. the primary structure. So far this has been achieved by the matching of the overlapping sequences of various peptides obtained by the proteolytic and at times by the chemical degradation. This method is known as the accounting method of the determination of the primary structure and the proteolytic enzymes generally employed in such cases for specific proteolytic cleavage are trypsin and chymotrypsin. In cases of proteins containing more than 100 amino acid residues, these enzymes usually

vield a large number of peptides, the quantitative separation and characterization of which is often difficult. In such cases it would be convenient to have the cleaving agent that splits a fewer number of peptide bonds selectively, possibly next to an amino acid other than lysine, arginine or the aromatic amino acids. There has been some progress in recent years in studies on the development of the nonenzymic methods for the cleavage of peptide bonds. The use of NBS for the hydrolysis of bonds adjacent to tryptophan and of CNBr for methionine peptides are probably the most successful procedures in specific peptide degradations. More recently, Hess from Cornell University, USA, has standardized the conditions needed for the specific cleavage of the peptide bonds adjacent to serine and threonine residues by making use of the well-known $N \rightarrow O$ acyl shift to impart specificity to the reaction.

A nitrogen to oxygen acyl migration in 3-hydroxy amino acids first investigated by Bergmann has been the basis of several attempts to cleave the serine and threonine peptide bonds. The shift in serine and threenine residue is induced by acid and reversed by alkaline solution; the subsequent hydrolysis of the ester bond results in the cleavage of the peptide bond. The $N \rightarrow O$ acyl shift depends on the steric relationship between the amide and the hydroxyl groups and proceeds via a cyclic intermediate. This shift is due to the acid catalysed breakdown of the cyclic hydroxyoxazolidone tautomer which is probably present in small microscopic equilibrium.

Attempts to effect such a cleavage in protein by the reagents such as concentrated sulphuric acid and phosphoric acid were generally unsuccessful because of the undesirable side reactions. It has been reported earlier that these side reactions could be avoided by the use of anhydrous hydrogen fluoride to induce the $N \rightarrow O$ acyl shift. This reagent was subsequently found to give satisfactory results in several synthetic dipeptides of serine and threonine. The peptides are first treated with 25 per cent methanolic hydrogen fluoride for 12 hr at 30°C. to effect the N acyl shift. The resulting product is then subjected to formylation with 98-100 per cent formic acid and a small amount of acetic anhydride for 20-30 min. By this procedure the reverse reaction of $N \rightarrow O$ shift is prevented and the conversion of the peptide bond to an ester bond is rendered quantitative. The ester bond is subsequently hydrolysed in a specific manner by the use of 11M aqueous piperidine [Hess *et al.*, J. biol. Chem., **239** (1964), 3275; Biochim. biophys. Res. Commun., **14** (1964), 4981.

The above procedure has now been applied by Hess to oxidized A-chain of insulin and α -MSH. The A-chain of insulin contains two serine residues and the cleavage gave the three expected peptides in 85-91 per cent yield. α -MSH with one susceptible bond yielded 90 per cent of the expected peptides. However, the method is applicable to only those peptides which do not contain tryptophan, as it is unstable towards these treatments.

Previously it has been shown that the methionyl peptide bonds of α -MSH and of the dipeptide L-methionyl glycine are cleaved on treatment with hydrogen fluoride. The cleavage reaction can be prevented by oxidation of methionine residue to sulphone or sulphoxide. For the specific cleavage of the peptide bonds adjacent to serine and threonine in peptides containing methionine, it is essential to oxidize the thioether prior to the treatment of the peptide with hydrogen fluoride.

Thus the two readily separable specific cleavages of the protein chain, namely one involving the methionine residue and the other involving the aliphatic hydroxy amino acids, have been demonstrated to result from the reactions taking place in the presence of hydregen fluoride. If the cleavage at the methionyl peptide is desired, the N -> O shift can be reversed by dissolving the protein in a neutral or basic solution after treatment with hydrogen fluoride. If $N \rightarrow O$ acyl shift is desired the methionine residue can be oxidized as a preliminary step.

A more universal application of this approach to the problem of structure determinations may require improvements in the methods of cleavage of ester bonds. The introductions of N-formv1 groups into peptides results in several difficulties. Firstly, the blocking of all the amino groups makes the peptide extremely acidic. This creates solubility problems and complicates the separation by ion-exchange chromatography. Secondly, the blocking of the α -amino groups prevents the use of the fluorodinitrobenzene and phenylisothiocyanate methods to determine the end groups which are essential in the sequence studies. — A. S. ACHARYA

Polarity and role of genetic message in polyribosome function

Polyribosomes consisting of aggregates of monomeric 80s ribosomes have been shown to be the site of protein synthesis in reticulocytes by Warner, Rich and Hall [Science, 138 (1962), 1399]. Williamson and Schweet [J. mol. Biol., 11 (1965), 358] have confirmed and extended the observations which support the concept of a dynamic equilibrium of attachment and detachment of 80s ribosomes from polyribosomes. during protein synthesis. The rate of attachment of polyribosome is probably the rate-limiting step in protein synthesis. They have demonstrated that a ribosome is capable of initiating a polypeptide chain at any point on the messenger RNA. Thus the N-terminal amino acid of a peptide chain is determined by the position of attachment of ribosome to the messenger when the chain is initiated. Earlier it was shown that the release of completed peptide chain is correlated with release of 80s ribosomes from polyribosomes. Since chains lacking C-terminal portions normally exist in polyribosomes without being released, it appears that it is both a sufficient and necessary criterion for chain release that the ribosomes reach the 'end' of the genetic message for a given protein.

Since the effects of puromycin on polyribosomes are not direct and require the continuance of peptide bond formation, they may be explained dynamically by an increased rate of travel of ribosome along the messenger RNA and thus an increased rate of detachment, thereby eliminating the rate-limiting steps in the translation process caused by a requirement for 'rare' s-RNA species. It has been demonstrated earlier that the mechanism of translation of the genetic message involves two enzymes, the binding enzyme and the peptide synthetase enzyme, which respectively mediate the binding of aminoacyl-s-RNA to the ribosomemessenger RNA complex and the transfer of the growing peptide chain from the s-RNA to which it is attached to the incoming aminoacyl-s-RNA. The alternation of these two reactions results in the movement of the ribosomes along the messenger RNA and the growth of the peptide chain. Puromycin does not inhibit the binding of aminoacyl-s-RNA to the ribosome-messenger RNA complex but releases the peptide chain by becoming coupled to the C-terminal end. Thus puromycin is a competitive substrate for peptide synthetase, and the frequency of puromycin action at a given codon will depend on the abundance of the s-RNA complementary to that codon. Puromycin will substitute for aminoacyl-s-RNA more often at a codon where a rare or modulator s-RNA is required, and so the modulating step will be bypassed, allowing the ribosome to move rapidly along the m-RNA.

The direction in which the ribosome moves along the messenger RNA, that is the polarity of the genetic message, remains unsettled. From the study of the action of specific exonucleotidases on the synthesis of haemoglobin in the cell-free system by Williamson and Schweet [Nature, Lond., 206 (1965), 29], 3'-terminal codeword is designated as the attachment site for ribosomes corresponding to the N-terminal amino acid of the polypeptide. Pretreatment of ribosomes with venom diesterase, which cleaves RNA sequentially from 2',3'-hydroxyl end, liberating a nucleoside-5'-phosphate and leaving a free 3'-hydroxyl, inhibited incorporation into N-terminal ¹⁴C-valine to a much greater extent than did spleen diesterase, which is complementary to venom diesterase, at equivalent levels of total inhibition. These results lead to the conclusion that the genetic message is read from 3'-terminal codon. A detachment site might consist of a special release codon, or it might be any C-terminal codon with a free 5'-hydroxyl, for the

absence of a 5'-phosphate group has been reported to reduce the ability of a codon to bind s-RNA. However, further work with purified exonucleotidases is needed before definite conclusions on the release mechanism can be reached. --- K. SANTHANAM

Metabolism of tryptophan

Earlier reports have established that 3-hydroxy anthranilic acid is an intermediate in the conversion of tryptophan to niacin, quinolinic acid and picolinic acid.

 $\begin{array}{rl} {\rm Tryptophan} & \rightarrow {\rm Kynurenine} \longrightarrow {\rm 3-Hydroxy} & {\rm kynurenine} \\ & & & \\ {\rm Quinolinic} & {\rm acid} \leftarrow {\rm -3-Hydroxy} & {\rm anthranilic} & {\rm acid} \\ & & & \\ {\rm Picolinic} & {\rm acid} \end{array}$

A fourth fate of 3-hydroxy anthranilic acid has been proposed, suggesting that tryptophan might be metabolized to carbon dioxide by way of acetate. It has also been shown earlier that 3-hydroxy anthranilic acid is converted to niacin ribonucleotide (NR) in the presence of 5-phosphoribosyl-1pyrophosphate (PRPP) by a soluble enzyme system present in both rat and cat liver. Amino-3-acroleylfumaric acid (2-AAF) and quinolinic acid were shown to be intermediates in this conversion. NR was further converted to deamido-NAD in the presence of ATP and then amidated in the presence of ATP and glutamine to give NAD.

In order to establish the role of niacin as a free intermediate, studies have been carried out using niacin and NR as co-substrates of quinolinic acid (metabolic traps) and a partially purified enzyme preparation from Esch. coli. Using quinolinic acid-14C, in the presence of NR, a significant increase in the accumulation of radioactive NR and a concomitant decrease in niacin has been observed. In contrast, the presence of niacin as a co-substrate does not decrease the level of NR-14C or 14CO₂. It is also evident that NR-14C is not formed to a significant extent from niacin-14C, either by exchange or in the presence of PRPP. No radioactive deamido-NAD or NAD is formed. In Esch. coli the conversion of niacin to NR is both PRPP and ATP dependent, while NR formation from quinolinic acid is ATP independent.

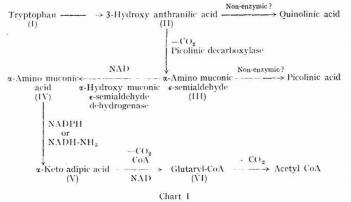
In order to elucidate the mechanism of this reaction, the precise nature of the enzyme involved from beef liver acetone powder has been studied earlier. This enzyme has been referred to as 'quinolinate transphosphorylase'. Attempts to isolate quinolinic acid-ribonucleotide have been so far unsuccessful. The results suggest that a single protein is responsible for both the condensation of quinolinic acid with PRPP and the subsequent decarboxylation to yield NR. The decarboxylation step could be nonenzymic since the formation of the

ribonucleotide makes the pyridine ring nitrogen quaternary nitrogen. This positively charged nitrogen would raise the electronegativity at position-2 and eliminate CO_2 from the molecule. It is noteworthy that this reaction does not require extra ATP, whereas the formation of NR from niacin and PRPP requires ATP as an essential co-factor.

All previous experiments *in vitro* indicated that picolinic acid and quinolinic acid are the only stable products formed from 3-hydroxy anthranilic acid in mammalian liver.

The discovery of the new metabolic sequence of reactions (glutarate pathway) which could account for the observed oxidation of the benzene ring of tryptophan was described by A. Ichiyama, S. Nakamura, H. Kawai, T. Hanjo, Y. Nishizuka, O. Haishi and S. Senoh [*J. biol. Chem.*, **240** (1965), 733, 740]. An enzyme system prepared from cat liver extracts converts 3-bydroxy anthranilic acid to glutaric acid and CO₂ and the preceding intermediates have been identified (Chart I).

Quinolinic acid has been shown to be formed from the primary oxidation product of the reaction catalysed by 3-hydroxy anthranilic acid oxygenase present in mammalian liver and kidney. The primary oxidation product is an unstable, acyclic compound having an absorption maximum at 360 mµ but has not been identified unequivocally. However, the structure has been assumed to be (III).



The enzyme picolinic carboxylase reacts with this giving rise to the stable product picolinic acid, which is metabolically inert and is excreted in the urine as a glycine conjugate. The primary product of this reaction catalysed by picolinic carboxylase (renamed by O. Haishi as a-amino B-carboxy muconic ϵ -semialdehyde decarboxylase) would be α -amino muconic ϵ -semialdehyde. This compound is very unstable and cyclizes to picolinic acid. A small shift of the absorption maxima at 360 mµ of compound (III) to 364 mu was observed during the carboxylase action suggesting the existence of this intermediate. This unstable intermediate is metabolized, in the presence of NAD-linked aldehyde dehydrogenase and NAD, to z-amino muconic acid rather than being cyclized to picolinic acid nonenzymically. Before cyclization the aldehyde group is oxidized by an NAD-linked specific aldehyde dehydrogenase resulting in the formation of compound (IV) which thus produced is then reduced and deaminated to a-keto adipic acid by an NADPH or NADH dependent reductase. This has been further confirmed by experiments using benzene ring labelled anthranilic acid. Tryptophan metabolism is thus convergent with the pathway of lysine degradation at the level of a-keto adipic acid. a-Keto adipic acid thus produced is shown to be oxidatively decarboxylated to produce glutaryl-CoA in the presence of NAD and CoA, and the reaction appears to be catalysed by a-ketoglutaric dehydrogenase. Carbon atoms 2, 1, 6, 5 and 4 of 3-hydroxy anthranilic acid directly

provide carbon atoms 1, 2, 3, 4 and 5 of glutaryl-CoA respectively. Further metabolism of glutaryl-CoA to acetate and CO₂ could account for the complete oxidation of the benzene ring of tryptophan observed in studies *in vivo.*— B. V. S. SHARMA

Puromycin: Effect on induced enzyme synthesis

The effect of antibiotics in the synthesis of proteins and nucleic acids in microorganisms has elicited considerable interest. Puromycin is a potent inhibitor of protein synthesis in microorganisms and mammalian cells. It is structurally similar to the functional end of an amino acid-transfer RNA complex. Studies of other workers indicate that puromycin prevents protein synthesis by interfering at a step in the transfer of amino acids from soluble RNA to the polypeptide chain.

In Esch. coli, it has been demonstrated that puromycin inhibits protein formation while allowing ribosomal and transfer RNA to accumulate. Investigations have been subsequently carried out on the effect of puromycin on induced synthesis of β-galactosidase, and to determine whether puromycin would also allow messenger RNA formation in its presence [Sells, B. H., Science, 148 (1965), 371]. Evidence is presented indicating that puromycin does not suppress synthesis of messenger RNA for B-galactosidase but inhibits the enzyme synthesis.

Cell crops of *Esch. coli* **15** T⁻ were grown in a basal salt medium containing glycerol. After harvesting

and resuspending the bacteria in fresh medium containing glycerol, two cultures, both containing puromycin, were prepared. To one leucine-14C was added and to the other thiomethyl galactoside, an inducer of β-galactosidase, was added. Puromycin was found to inhibit B-galactosidase formation to a greater extent than it inhibits protein synthesis, determined by measuring the incorporation of leucine-14C. The effect of puromycin on B-galactosidase formation and protein synthesis in Esch. coli 33.00, which produces this enzyme constitutively, was also studied. In this case also, enzyme synthesis was inhibited to a greater extent than leucine-14C incorporation, indicating that the effect of puromycin is not directly manifested in the process of induction. In order to obtain a greater insight into the selective effect of puromycin on β-galactosidase formation, the following experiment was performed. Suspensions of Esch. coli 15 T- were harvested, washed and resuspended in basal medium lacking Mg²⁺, which makes the cell more sensitive to puromycin. Thiomethylgalactoside was then added to cell suspensions and the incubation was continued. Puromycin was added at intervals thereafter and β-galactosidase formation was measured. The incorporation of tryptophan-14C was measured under the same conditions. The effect on *B*-galactosidase was found to be much greater than the effect on overall protein production. As an explanation of this result, it has been pointed out that the inhibition of production of B-galactosidase, which occurs after the addition of puromycin, results from cessation of messenger RNA synthesis specific for this enzyme.

To study the effect of the antibiotic on messenger RNA, experiments were performed to separate the protein synthesizing step from the formation of messen-RNA. Investigations were ger made on the effect of puromycin (in the presence and absence of glycerol) on the first stage of transcription during a time when protein synthesis is not inhibited. Suspensions of Esch. coli 15 T- were grown on basal medium, lacking Mg²⁺ in the presence and absence of glycerol. Each group of cells was

treated with puromycin. After the addition of thiomethylgalactoside, the cells were incubated for 2 min. and then the inducer and inhibitor were removed by washing. The filtered bacteria were resuspended in warmed media containing glycerol and the incubation was continued for 18 min. It was observed that the messenger expresses itself as the enzyme during the second incubation. After resuspension of the bacteria, no further messenger can be formed because of the absence of the inducer. Puromycin does not influence the production of messenger RNA in the first phase of transcription, in the absence of glycerol in the medium. If glycerol is added to the medium, suppression of messenger RNA formation is conspicuous in the presence of puromycin, although protein synthesis is only slightly affected.

The suppression of B-galactosidase synthesis in the puromycintreated cells is reported to be due to the inhibition of the first step in transcription, namely messenger RNA formation. It has been suggested that puromycin in the presence of glycerol is responsible for the accumulation of a substance which represses the synthesis of messenger RNA. It has been postulated earlier that the inducer stimulates the synthesis of an unstable messenger RNA specific for β-galactosidase. It has also been pointed out by some workers earlier that the repressor may affect the formation of this messenger RNA. The synthesis of B-galactosidase is repressed by catabolites in cells which are supplied with a source of energy but deprived of an amino acid required for growth. Earlier reports suggest that glycerol, presumably by virtue of the catabolites to which it gives rise, exerts a specific repression on the synthesis of β -galactosidase, in the threonine starved cells. Such a phenomenon has been termed catabolite repression'.

The possibility that catabolite repressor can determine the rate of synthesis of specific messenger RNA has also been indicated and it has been concluded that induction promotes and catabolite repression decreases the formation

of an unstable messenger RNA specific for β -galactosidase. Puromycin together with glycerol prevents the production of messenger RNA for β -galactosidase presumably as a result of ' catabolite repression',---C. KANDASWAMI

Progress Reports

Council of Scientific & Industrial Research, South Africa

The annual report of the Council of Scientific & Industrial Research, South Africa, for the year 1964 records the progress made at the various national laboratories, and the significant results obtained in medical and industrial research carried out with the Council's support.

An extremely sensitive calorimeter which can measure heat as low as 0.0005 cal. has been developed for use in dielectric heating. The new apparatus makes it possible to determine not only the dielectric characteristics but also the specific heat, transition heat and heat generated by external processes. A new principle of dynamic quotient calorimetry' has been applied, in terms of which measurement is made independently of changes in the heat conductivity and heat capacity of the materials used. Only 0.001-0.1 g. of the sample is necessary. Though primarily intended for the determination of heat characteristics in dielectric heating, this instrument can also be used in other fields, e.g. in the energization of chemical reactions, such as polymerization. A large window testing calorimeter for studying the problems associated with solar heat through windows has been designed and constructed.

Considerable progress has been made in desalting of brackish water by electrodialysis. A method for making new, inexpensive membranes has been developed. An installation has been set up in which 2-5 million gallons of brackish water pumped from gold mines are being desalted every day. Though not very economical, the system appears to be the

cheapest among the known desalting processes.

The National Institute of Telecommunications Research has developed parametric amplifiers for use at 600 Mc/s. with very low noise figure, using a semiconductor diode as the variable reactance element. This improved receiver sensitivity has resulted in a significant increase in the range of the transmitter equivalent to that obtained from a fourfold increase in transmitter power.

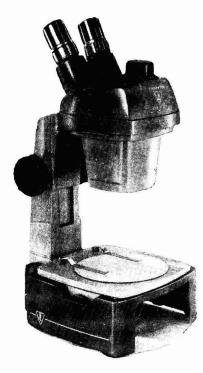
Attempts at improving the methods of spectrochemical analysis have resulted in a number of new spectrographic instruments, the latest of them being a sixchannel direct reading spectrograph head which increases the range of application of the medium prism spectrograph. Experiments conducted at the National Institute for Water Research have resulted in a new ' soft ' base for detergents which allows 8.5 per cent of the detergents to be digested in water as against 25 per cent in the case of commercial detergents.

Other achievements include: detection and measurement of double stars carried out for the first time with a stellar interferometer; development of a doublewalled plastic pipe for carrying sewage, industrial and other effluents; systematic survey and isolation of alkaloids from South African plants; and the development of a technique for accurate measurement of temperature using semiconductor thermistors.

Announcement

. The Indian Pharmaceutical Congress Association is holding its seventeenth session at Banaras Hindu University, Varanasi, during 27-30 December 1965. Separate sections will be devoted to: Industrial pharmacy. Professional pharmacy, Pharmacognosy and phytochemistry, Pharmacology and microbiology, Pharmaceutical education, and Indigenous pharmacy. Those intending to participate in the session or present papers should write to Dr Diptish Chakravarty, Hony General Secretary, 18 Convent Road, Calcutta 14.

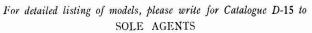
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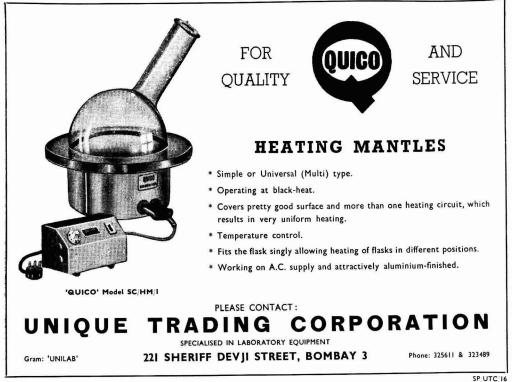
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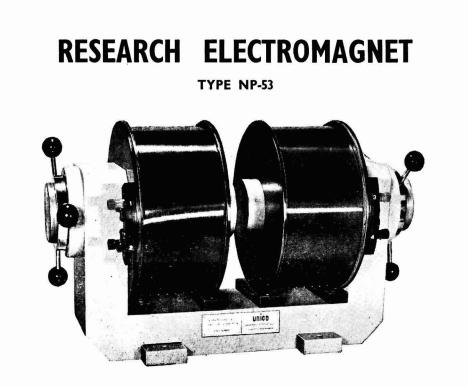
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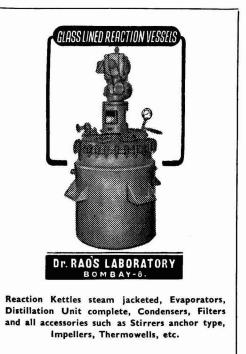
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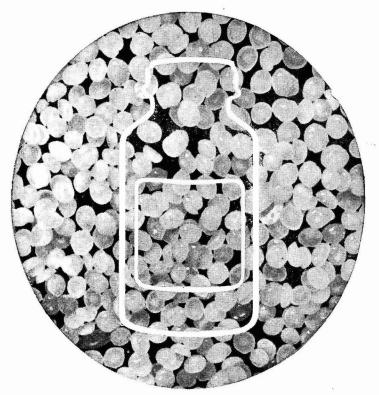
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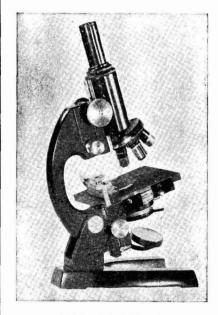
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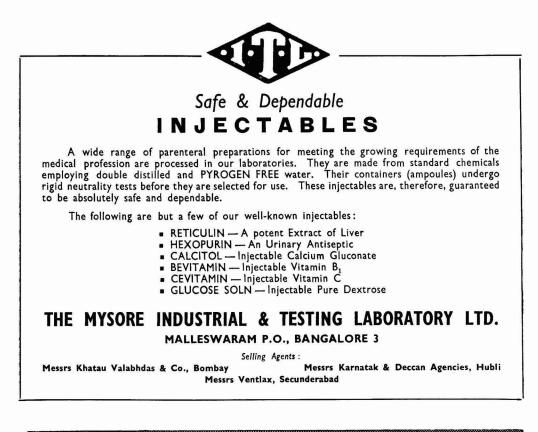
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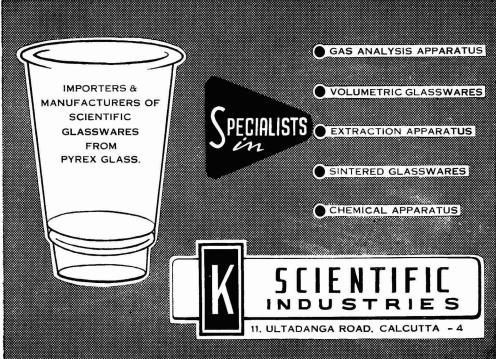
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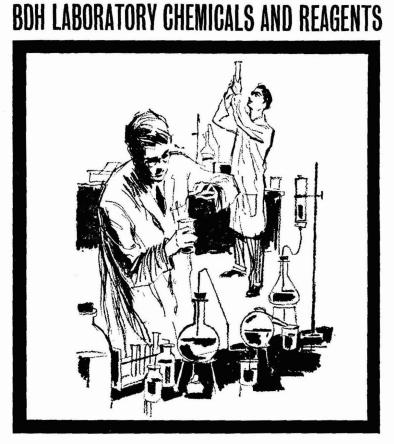
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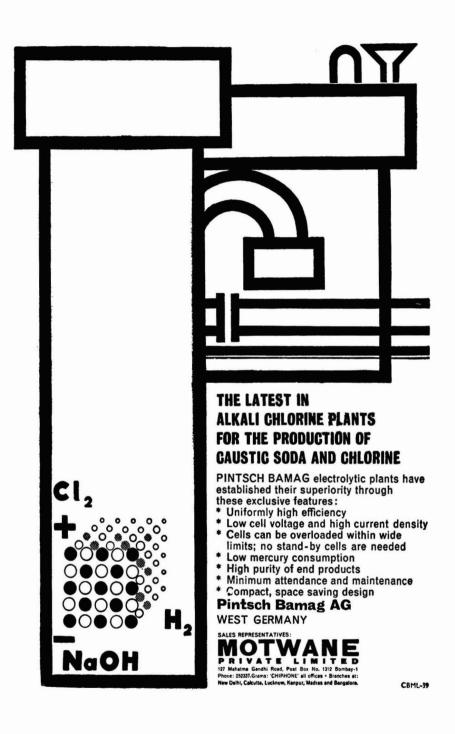
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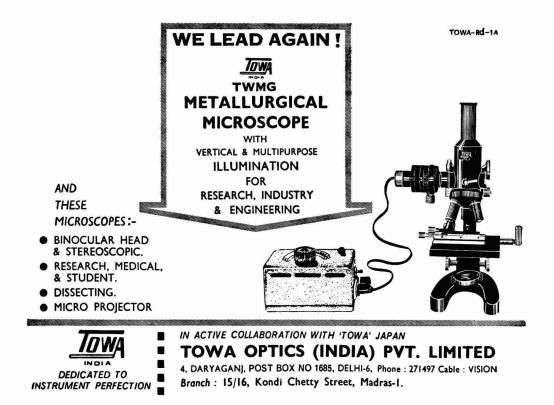
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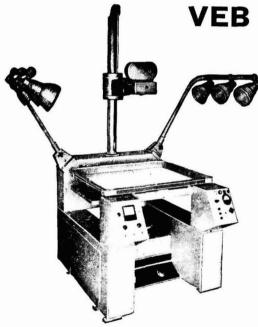
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Each Model 33 is individually calibrated in final test, and the calibration data for each range and function are recorded on certificates supplied with the instruction manual. Down scale tracking data for both standard instruments are also supplied. Calibrations are performed using measurement standards having a certified accuracy of \pm 0.06 per cent traceable to NBS.

The Model 33 meter calibrator may be used to calibrate instruments from effectively zero load, such as vacuum tube voltmeters, to high burden electrodynamometer type meters requiring as much as 50 volt-amperes.

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